PROGRAM AND ABSTRACTS BOOK

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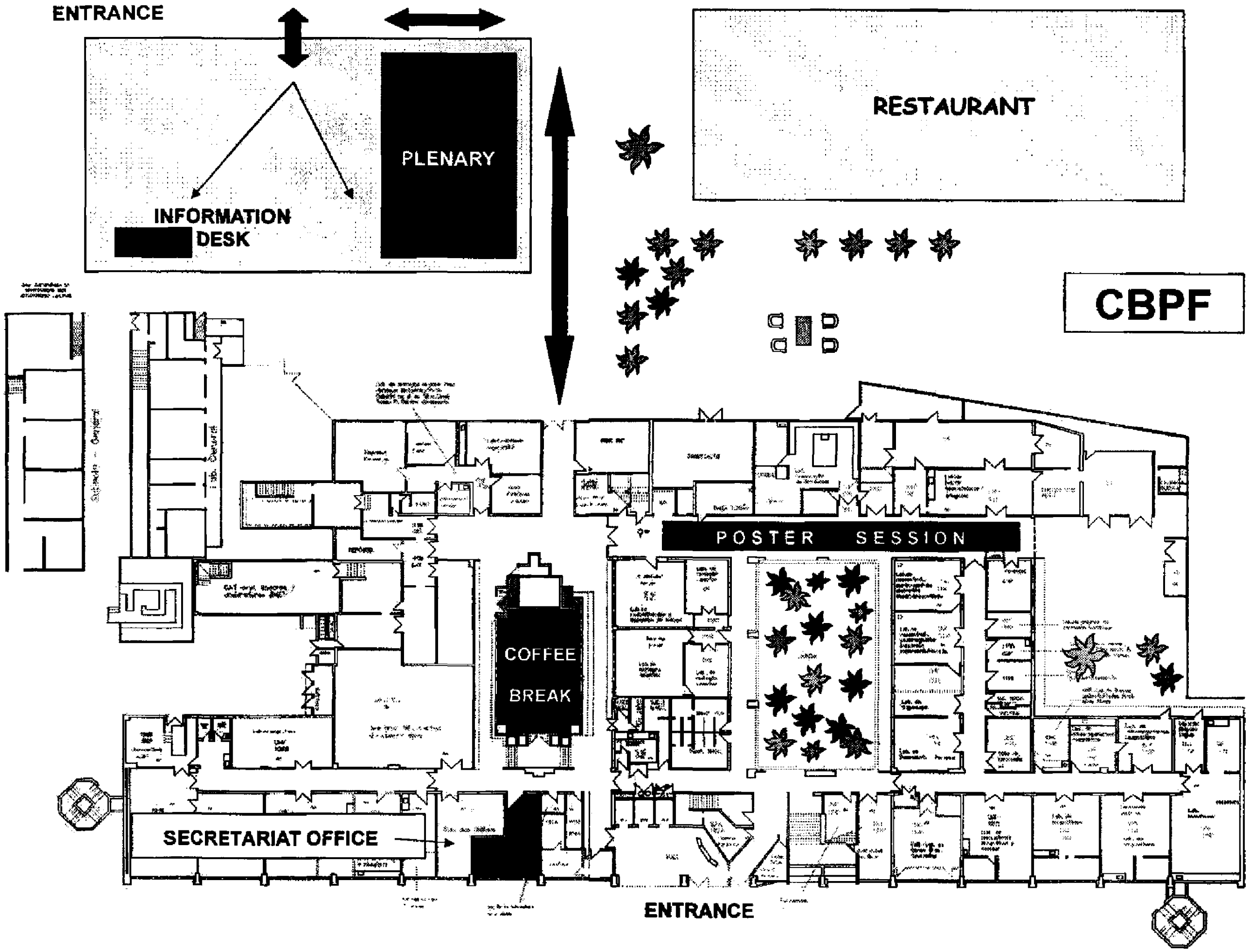
ENTRANCE
PLENARY
INFORMATION DESK
RESTAURANT
CBPF
POSTER SESSION
COFFEE BREAK
SECRETARIAT OFFICE
ENTRANCE

LACAME 2006 - PROGRAM

Sunday - 11/05	
19:00 - 21:00	**RECEPTION AND REGISTRATION**

Monday - 11/06	
08:00 - 09:00	**REGISTRATION**
09:00 - 09:30	**OPENING CERIMONY** Chair: **Elisa Saitovitch**, *Centro Brasileiro de Pesquisas Físicas, Brazil* Co-chair: Edson **Passamani**, Universidade Federal do Espírito Santo,Brazil
09:30 - 10:05	**INVITED TALK** Chair: **Elisa Saitovitch**, *Centro Brasileiro de Pesquisas Físicas, Brazil* **Roberto C. Villas-Bôas**, CETEM, Brazil - *Enviromental Issues and Minerals Extraction* **- T2**
10:05 - 10:20	**ORAL TALK** **F. Gonzalez**, UCV, Venezuela - *Mössbauer and Magnetic Measurements of Very Small Ferrihydrite Nanoparticles* **- T3**
10:20 - 10:35	**ORAL TALK** H. Rechenberg, USP, Brazil - *In-Field Mössbauer Study of Core-Shell Magnetic Structure In Ferrite Nanoparticles* **- T3**
10:35 - 10:50	**ORAL TALK** A. C. Saraiva, UEM, Brazil - *Structural and Hyperfine Characterization of Zinc Substituted Magnetites* **- T2**
10:50 - 11:20	**BREAK**
11:20 - 11:45	**INVITED TALK** Chair: ***Judith Desimoni***, *Universidad Nacional de La Plata, Argentina* **C. Partiti**, USP, Brazil - *Characterization of Marine Sediments of Casqueiro River, São Paulo, Brazil, by Mössbauer Spectroscopy, Pixe and Magnetic Susceptibility: A Study of Environmental Magnetism* **- T2**
11:45 - 12:00	**ORAL TALK** **E. M. Valenzuela**, UCHILE, Chile - *^{57}Fe Mössbauer Spectroscopy for Ordinary Chondrites of the Atacama Desert (Chile): Constraining the Weathering Processes on Desert Meteorites.* **- T2**
12:00 - 12:15	**ORAL TALK** **S. Medeiros**, UEM, Brazil*Fabrication and Mössbauer Studies of Al-Cu-Fe alloys* **- T8**
12:15 - 12:40	**INVITED TALK** **R. Mercarder**, UNLP, Argentina - Hyperfine and Magnetic Characterization of Recent Soils Around 3° South in the Province of *Buenos Aires, Argentina* **- T2**
12:40 - 14:25	**LUNCH**
14:25 - 15:00	**INVITED TALK** Chair: **Hans Micklitz**, *Universitaet Koeln, Germany* **M. Pasternak**, TAU, Israel - *The Outstanding Contribution of Mössbauer Spectroscopy to the Elucidation of Properties Matter at Very High-Pressures* **- T9**
15:00 - 15:15	**ORAL TALK** **J. F. Litterst**, TU Braunschweig, Germany - *Magnetic Properties of Molecular Magnets and Spin Chains Studied by Mössbauer Spectroscopy* **- T7**
15:15 - 15:30	**ORAL TALK** **P. Sharma**, UEM, Brazil - *Structural, Mössbauer and Magnetic Studies on Mn-substituted Barium Hexaferrite Prepared by High Energy Ball Milling* **- T7**
15:30 - 16:00	**COFFEE-BREAK**
16:00 - 16:15	**ORAL TALK** Chair: **Angel G. Bustamante Dominguez** *Universidade Nacional Mayor de San Marcos, Peru* **D. Sanchez**, CBPF, Peru - *Pair-Breaking Field and Structural Effects in the Magnetically Diluted*
	Antiferromagnetic Superconductor DyNi$_2$B$_2$C **- T7**
16:15 - 16:30	**ORAL TALK** **F. R. Pérez**, UDEA, Colombia - *Composition of Rust Layers Formed on Low Carbon Steels Exposed to Total Immersion Tests for Different NaCl Concentrations* **- T5**
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10:05 - 10:20	**ORAL TALK** **F. Ivashita**, UEM, Brazil - *Mössbauer Study and Structural Characterization of Compounds* UO_2-TR_2O_3 *(TR=Gd and Eu)* - **T9**
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10:35 - 10:50	**ORAL TALK** **C. Casagrande**, CVRD, Brazil - *Mössbauer Analysis of Gas-Metallized Iron Ore Pellets* - **T9**
10:50 - 11:20	**BREAK**
11:20 - 11:45	**INVITED TALK** Chair: **Mohammad Ghafari**, *Technical University Darmstadt, Germany* **A. P. Alvarenga**, INMETRO, Brazil - *XMCD Applied to Magnetic Thin Films Investigations* - **T7**
11:45 - 12:00	**ORAL TALK** **V. P. Nascimento**, CBPF, Brazil - *Interfacial Magnetic Properties of NiFe/FeMn/NiFe Exchange-Biased Trilayers* - **T7**
12:00 - 12:15	**ORAL TALK** **B. Segatto**, UFES, Brazil - *Bcc-Mn Magnetism and Magnetic Couplings in Fe/Mn/Fe Trilayers Grown by Molecular Beam Epitaxy on MgO(001) Substrate* - **T7**
12:15 - 12:40	**INVITED TALK** **C. Larica**, UFES, Brazil - *Magnetoelastic Effect in Al/Amorphous Ribbons/Al Trilayers Observed by Mössbauer Spectroscopy* - **T7**
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14:25 - 15:00	**INVITED TALK** Chair: **José Ramón Gancedo**, *Instituto Rocasolano,Spain* **M. Schmal**, COOPE - UFRJ, Brazil - *Nano Science in Catalysis-Brigde of Conventional to Surface Experiences* - **T1**
15:00 - 15:15	**ORAL TALK** **C. I. Wynter**, SUNYNASSAU, USA - *Mössbauer Effect of* ^{151}Eu *Carboxylic Acid Salts* - **T1**
15:15 - 15:30	**ORAL TALK** **S. Zanatta**, UEM, Brazil - *Mössbauer Studies of Non-Cubic Garnets* - **T7**
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16:00 - 16:15	**ORAL TALK** Chair: **Andrea Paesano Júnior**, *Universidade Estadual de Maringá, Brazil* **R. D. Pereira**, UFES, Brazil - *Nanocrystalline and Amorphous Nanoperm Phases Prepared by Mechanosynthesis* - **T3**
16:15 - 16:40	**INVITED TALK** **J. G. Stevens**, NCSU, USA - *The Next Generation of Mössbauer Researchers* - **T9**
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Wednesday - 11/08	
09:30 - 10:05	**INVITED TALK** Chair: **Izabel de Souza Azevedo**, *Centro Brasileiro de Pesquisas Físicas, Brazil* **U. Wagner**, TU-Muenchen, Germany - *Systematic Approach to Mössbauer Spectroscopy in Archaeology* - **T9**
10:05 - 10:50	**LESS USED MÖSSBAUER ISOTOPES: A ROUND TABLE**
10:50 - 11:20	**BREAK**
11:20 - 11:45	**INVITED TALK** Chair: **Francisco Sánchez**, *Universidad Nacional de La Plata, Argentina* **A. E. Rivas Mendonza**, UC, Venezuela - *Spin Density Waves in the Layered Compound* $CuFeTe_2$*: Direct Evidence of the Coexistence of the Normal and Condensate States* - **T7**
11:45 - 12:00	**ORAL TALK** **J. Larrea**, CBPF, Peru - *Evidence for Kondo effect in Zn:Fe films: A* ^{57}Fe *Mössbauer effect study* - **T7**
12:00 - 12:15	**ORAL TALK** **J. A. Tabares**, UNIVALLE, *Colombia - Effect of Mn and Cu in Fe-Mn-Cu-Al Alloys Study by ICEMS and XRD* - **T8**
12:15 - 12:40	**INVITED TALK** **J. Restrepo**, UDEA, Colombia - *Structural and hyperfine Properties in Nanocrystalline Ball-milled Iron* - **T7**
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10:50 - 11:20	**BREAK**
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11:45 - 12:00	**ORAL TALK** **J. Pechousek**, UPOL, Czech Republic *Improving Detector Signal Processing with Pulse Height Analysis in Mössbauer Spectrometers* - T8
12:00 - 12:15	**ORAL TALK** S. Irkaev, , Russia - Mössbauer Spectrometer. The Past. The State of the Art. Quo Vadis? T6
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14:25 - 15:00	**INVITED TALK** Chair: **Edson Passamani Caetano**, *Universidade Federal do Espírito Santo, Brazil* **J. D. Fabris**, UFMG, Brazil - *Mössbauer Spectroscopy As A Key Technique To Characterize Iron Oxides And Trace Their Transformations in*
	in Natural System - T2
15:00 - 15:35	**INVITED TALK** **P. C. Morais**, UNB, Brazil - *Using Mössbauer Spectroscopy as a Key Technique in the Investigation of Nanosized Magnetic Particles* - T3
15:35 - 16:00	**CLOSING REMARKS**
16:00 - 16:30	**TEA**
16:30 - 17:30	**CBPF COLLOQUIUM**

Session 1 - 06/11/2006

Poster Session - 06 and 09/11/2006

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T3-Amorphous, nanocrystals and small particles

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T4-Chemical applications: electronic structures, bounds, etc

T5-Corrosion and environments

T6-Experimental techniques and data analysis

T7-Magnetism and magnetic materials

T8-Physical metallurgy and materials science

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12:15 Structural and hyperfine properties in nanocrystalline ball-milled iron
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Session 4 - 09/11/2006

Session 1

[06/11/06 - 09:30h]
Environmental Issues and Minerals Extraction, Roberto C. Villas-Bôas, *CETEM/MCT* ■It is presented some environmental issues originated from industrial mining activities as well as from informal mining where Mossbauer analysis May play a significant role in determing causes and eventually indicating ways to minimize such environmental hazards.

[06/11/06 - 10:05h]
Mössbauer and Magnetic Measurements of Very Small Ferrihydrite Nanoparticles, F. Gonzalez-Jimenez, L. D'Onofrio, *Laboratorio de Magnetismo, Fac. Ciencias, Escuela de Fisica, UCV, Paseo los Ilustres,Los Chaguaramos, Caracas-1040, Venezuela.*, Y. Henriquez, O. Dominguez-Quintero, L. D'Ornelas, *Laboratorio de Síntesis Organometálica, Fac. Ciencias, Escuela de Química, UCV*, S. Martínez, *PDVSA-INTEVEP, apartado76343, Caracas-1070, Venezuela.*, M.J. Casanove, P. Lecante, *CEMES-CNRS, 31055Toulouse-CEDEX, Francia*, P. Bonville, *DRECAM/SPEC, CEA-Centre d'Etudes de Saclay,91191Gif-Sur-Yvette, Francia* ■Ferrihydrite (Fh, 5Fe2O3,9H2O), is an antiferromagnetic iron oxyhydroxide, which have been found in natural systems in the form of nanoparticles(NP). For example, in stalactites of some type of mines, some of us found crystals of aggregated Fh NPs with 3 nm diameter. Also (Bonville et al.))found in ferritin, the protein to store iron in a wide variety of live organisms, where the mean size of the Fh NPs is controllable, ranging from 6 to 3 nm, located in a cavity of 8 nm. In the search for finding smaller NPs a synthetic preparation method, based on the reduction of iron acetilacetonate, Fe(acac)3, with metallic sodium, later fixed and protected with PVP (Polyvinylpirrolidone) led to 1.4 nm NPs. To characterize those NPs we employed various physical methods necessary to have the best description with complimentary informations : Mössbauer spectroscopy, SQUID Magnetic susceptibility measurements, HRTEM, WAXS. WAXS and HRTEM allowed to determine that the sample is principally Fh and that the size is 1.4 nm. The maximum in the ZFC of the SQUID magnetic susceptibility is in agreement with this result. The Mössbauer results obtained between 1.5 K and 17K allowed to see the linear decreasing behaviour which is expected in temperature for the hyperfine field(HF), due to the collective excitations: ¡Hhf(T,V)¿= Hhf(0) (1 - kBT/2KV) From the slope we can calculate the anisotropy constant K by taking a volume V assuming spherical particles of diameter 1.4 nm obtained from the WAXS result: K = 4.4 x 105 J/m3. This value is in excellent agreement with other determinations.

[06/11/06 - 10:20h]
In-Field Mössbauer Study of Core-Shell Magnetic Structure in Ferrite Nanoparticles, E. C. Sousa, , M. H. Sousa, F. A. Tourinho, J. Depeyrot, *Complex Fluids Group, University of Brasilia, 70919-970 Brasília (DF)*, H. R. Rechenberg, *Institute of Physics, University of*

São Paulo, 05315-970 São Paulo (SP) ■From the design of new magneto-pharmaceuticals to ultra high-density information storage, magnetic nanoparticles bear a host of promising applications. On a fundamental level, reducing the size of magnetic solids down to the nanometric scale drastically increases the weight of surface effects with respect to bulk magnetic behavior. It may induce spin-canted structures, freezing of disordered spins in a disordered state [1] as well as enhanced surface anisotropies. Nickel ferrite nanoparticles, well known to present important surface effects, were chemically synthesized by hydrothermal precipitation. Four powder samples of mean nanoparticle sizes ranging from to 4 to 9 nm were probed by Mössbauer spectroscopy at low temperatures. At zero applied field the temperature variation of hyperfine fields has shown that the anisotropy energy possesses a strong surface contribution [2]. Mössbauer data were collected at 5 K in the presence of applied fields ranging up to 12 T. Our spectra are well fitted with three hyperfine fields, two associated to Fe ions at A and B sites of the spinel structure, and the third one corresponding to superficial Fe ions. Under external field, the disordered surface contribution decreases while the contribution of core spins, well aligned along the field direction, increases. By fitting the experimental data we show that the estimated average thickness of the spin-disordered surface layer, which is of the order of 1 nm in zero field, decreases by a factor of 0.3 to 0.4 as the field increases up to 12 T.

[1] R. H. Kodama et al., Phys. Rev. Lett. 77 (1996) 394 [2] E. C. Sousa et al., J. Magn. Magn. Mater. 272 (2004) e1215

[06/11/06 - 10:35h]
Structural and Hyperfine Characterization of Zinc Substituted Magnetites, ANTONIO CARLOS SARAIVA DA COSTA, IVAN GRANEMANN DE SOUZA JUNIOR, MARCELO AUGUSTO BATISTA, *Departamento de Agronomia - Universidade Estadual de Maringá*, ANDREA PAESANO JUNIOR, KLEBSON LUCENILDO DA SILVA, JUSMAR VALENTIN BELLINI, *Departamento de Física - Universidade Estadual de Maringá* ■Ferrimagnetic materials are intensely investigated because of their important applications to the industry and to the environment. Recently, special attention has been focused on the synthesis methods based on co-precipitation from aqueous solutions, with different cations substituting the iron in the spinel structure and how this affects its magnetic properties. Structurally and magnetically zinc substituted magnetites, were prepared from $FeCl_2$ e $ZnCl_2$ aqueous solution in the mole fraction 0.025 - 0.35. The resulting powder material was analyzed by total chemical analysis, X-ray diffraction, Mössbauer spectroscopy and other techniques. Total chemical analysis showed that the co-precipitation method was successful and isomorphous substitutions were 0.22, 3.53, 6.54, 11.80, 17.72, 25.75 and 34.95 cmol mol^{-1} of zinc. X-ray diffraction showed planes associated with the presence of the magnetite and, possibly, with maghemite. The diffraction lines shifted to low angles, revealing an increasing lattice parameter as the isomorphous substitution increases. Mössbauer spectra showed a magnetic combined pattern, confirming the occurrence of the magnetite and maghe-

mite phases. The later, present as a minor phase, is due to oxidation of the very fine as-prepared particles. As the zinc content increases, only the magnetite phase is observed, revealing that substitution favors the chemical stabilization of the solid solution. In addition, the hyperfine magnetic fields of both sites of the spinel structure decreased (B^A_{hf} slower than B^B_{hf}) indicating the progressive weakening of the magnetic interaction intra and inter sublattices. For x >> 0.33, B^B_{hf} is virtually collapsed whereas B^A_{hf} reduced only 10 percent of its initial value. The isomer shifts for sites A and B showed a linear decline with increasing x (IS_A slower than IS_B), with IS_B changing from a value typical of mixed valence to a value corresponding to trivalent iron. The subspectral areas presented good agreement with the theoretical occupation formula $(Zn^{2+}_X Fe_{1-X})[Fe^{2+}_{1-X} Fe^{3+}_{1+X}]O_4$.

[06/11/06 - 11:20h]
Characterization of Marine Sediments of Casqueiro River, São Paulo, Brazil, by Mössbauer Spectroscopy, PIXE and Magnetic Susceptibility: a Study of Environmental Magnetism, F.O. Jorge, , M.H. Tabacniks, W.M. Pontuschka, C.S.M. Partiti, *Instituto de Física da USP, Caixa Postal 66318, CEP 05315-970 - São Paulo - SP, Brazil,* M.M. Mahiques, C.C. Martins, *Instituto Oceanográfico da USP, São Paulo, Brazil,* R.C.L. Figueira, *Universidade Cruzeiro do Sul, São Paulo, Brazil* ■Cubatão city ocean bay was chosen to supply the set of sediment samples, since this is a heavily polluted region. Thus, a specific interest to study samples collected in this region is justified. With the proposal above, a set of marine sediments were collected from the Casqueiro River at Cubatão, São Paulo, at different depths ranging from 0 to 222cm, dated from 1612 to 2002 years. The samples were characterized by Mössbauer Spectroscopy (MS), Magnetic Susceptibility and by PIXE (Particle Induced X-ray Emission). Magnetic susceptibility measurements indicated low values that remained quite constant for the totality of samples, except the one collected at the depth of 3cm that showed a peak. The Mössbauer measurements at 4.2K presented Fe^{2+} and Fe^{3+} sites at the proportions of 17% and 83%, respectively, for the samples of depth higher than 6cm. The sample of 3cm depth exhibited a greater proportion of Fe^{3+} (95%) than that of Fe^{2+} (5%). The samples less profound (0 to 2cm depth) contained two Fe^{3+} sites and the Fe^{2+} was not detected, but an additional sextet was observed, probably due to the presence of goethite. Thus, we observed an increase of oxidation inversely proportional to the sample depth, i.e., the more recent are the most oxidized. The presence of trace metals was detected and quantified using the PIXE technique. The combined results of MS and PIXE allowed us to perform the fitting of a magnetic susceptibility curve and the experimental data. We conclude that our results of MS, PIXE and Magnetic Susceptibility are in good agreement and may be used in models with the objective to study the environmental impact effects.

[06/11/06 - 11:45h]

^{57}Fe Mössbauer spectroscopy for ordinary chondrites of the Atacama Desert (Chile): Constraining the weathering processes on desert meteorites., MILLARCA VALENZUELA, DIEGO MORATA, *Dep. Geología, Universidad de Chile, Santiago, Chile.*, ROSA B. SCORZELLI, YASSIR ABDU, MATHIEU DUTTINE, *Centro Brasileiro de Pesquisas Físicas (CBPF/MCT), Río de Janeiro, RJ, Brasil.*, JOSÉ B. DE CAMPOS, ROBERTO R. DE AVILLEZ, RONALDO P. DA SILVA, *Dep. Ciencias dos Materiais e Metalurgia PUC/Rio, RJ, Brasil.* ■ We report the results of a RT ^{57}Fe Mössbauer spectroscopy study, involving 21 meteorites from the Atacama Desert (Chile), complemented with X ray diffraction for the determination of mineral phases present in the samples. The meteorites are weathered ordinary chondrites (OC) and include the three chemical groups (H, L, and LL). The goal of this study is the identification and quantification of the weathering products of these meteorites, in order to understand the weathering processes acting in the Atacama Desert.

As recently fallen equilibrated OC contain iron only as Fe^0 (kamacite and taenite) and Fe^{2+} (olivines, pyroxenes and troilite), the abundance of ferric iron is directly related to the level of terrestrial weathering and can be measured by Mössbauer spectroscopy [1].

We obtained the percentage of the Fe-bearing phases for the primary minerals: olivine, pyroxene, troilite and Fe-Ni metal, and for the ferric alteration products (paramagnetic and magnetically ordered Fe^{3+} components). This last percentage gives the oxidation of the samples, which was found to range from $\tilde{5}\%$ to $\tilde{6}0\%$. The amount of silicate and opaque phases decreases in a constant rate with increasing oxidation level, and an oxidation frequency histogram shows a pattern similar to samples of the Sahara Desert [2]. Low temperature measurements are in progress in order to define the oxides that are in a superparamagnetic state.

References

[1] P. A. Bland, F. J. Berry, A. J. T. Jull, t. B. Smith, A.W. R. Bevan, J. M. Cadogan, A. S. Sexton, L. A. Franchi and C. T. Pillinger. 2002. "^{57}Fe Mössbauer Spectroscopy Studies of Meteorites...". Hyperfine Interactions 142: 481-494.

[2] E. M. Valenzuela, Y. Abdu, R.B. Scorzelli, J.B. de Campos, M. Duttine and D. Morata. 2006. "Weathering of ordinary chondrites from the Atacama Desert..." 69^{TH} Annual Meeting of the Meteoritical Society, Zürich, Switzerland.

[06/11/06 - 12:00h]

FABRICATION AND MÖSSBAUER STUDIES OF Al-Cu-Fe QUASICRYSTAL, SUZANA NÓBREGA DE MEDEIROS, , SCHEYLA CADORE, IVAIR APARECIDO DOS SANTOS, ANDREA PAESANO JÚNIOR, *UEM - PR - Brazil*, FERNANDO LUIS DE ARAUJO MACHADO, *UFPE - PE - Brazil* ■Quasicrystalline materials have long-range rotational order but lack of long-range translational order and they are not truly periodic. Quasicrystalline alloys are usually prepared by rapid or conventional solidification from the melt. However, in the last few years it has been reported that quasicrystalline alloys can also be prepared by mechanical alloying. In the present work, the formation of $Al_{70}Cu_{20}Fe_{10}$ icosahedral phase by mechanical alloying of the elemental metallic powders was investigated by X-ray diffractometry and Mössbauer spectroscopy. The $Al_{70}Cu_{20}Fe_{10}$ samples were prepared varying the milling time and using two different mills.

In a planetary mill, milling of 20 h, 40 h or 60 h produces the $\beta - Al(Cu, Fe)$ cubic phase and a small amount of the Al_2Cu intermetallic phase. The samples milled for 80 h and 100 h present the icosahedral phase besides the earlier observed phases. The X-ray diffraction pattern of the sample milled for 40 h and heat-treated at 623 C shows, essentially, only the icosahedral phase. The Mössbauer spectrum for this sample was fitted with two doublets, one of them assigned to the icosahedral phase.

In the case of a shaker mill, the occurrence and evolution of the icosahedral phase was faster than in the planetary mill. Just 6 h of milling was enough to form the icosahedral phase along with the cubic $\beta - Al(Cu, Fe)$ phase and a small amount of Al_2Cu phase. For 12 h of milling, the XRD pattern and the Mössbauer spectrum shows mainly the icosahedral phase. Therefore, no heat treatments were necessary to produce the quasicrystalline phase in samples obtained in this mill. The results are discussed on the basis of a model according to the evolution of the icosahedral phase in mechanical milling takes place by a reaction between the $\beta - Al(Cu, Fe)$ and Al_2Cu phases.

[06/11/06 - 12:15h]

Hyperfine and magnetic characterization of recent soils around 38° South in the Province of Buenos Aires, Argentina, A. A. Bartel, , *Facultad de Ciencias Exactas y Naturales, Universidad Nacional de La Pampa, Av. Uruguay 151, 6300 Santa Rosa, Argentina,* J. C. Bidegain, *Laboratorio de Entrenamiento Multidisciplinario para la Investigación Tecnológica. Calle 52 e/ 121 y 122, 1900 La Plata, Argentina,* A. M. Sinito, *Facultad de Ciencias Exactas, Campus Universitario Paraje Arroyo Seco, Universidad Nacional del Centro de la Provincia de Buenos Aires 7000 Tandil, Argentina,* F. R. Sives, R. C. Mercader, *Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, IFLP, C.C. 67, 1900 La Plata, Argentina.* ■In order to establish a correlation between the different types of soils using hyperfine and magnetic parameters as climatic and environmental proxies, we have studied the differentiation of soil types developed around 38° South Latitude in the central pampas of Argentina, by means of Mössbauer spectroscopy and environmental magnetism. The soils transect (climosequence) investigated stretches from the drier west in La Pampa Province to the more humid east in the Buenos Aires Province, covering a distance of 600 km. The soils studied were developed during recent Holocene geologic times in a landscape characterized by small relict plateaus, slopes and depressions, dunes and prairies. The parent material consists of Aeolian sandy silts overlying calcrete layers. The humidity in the western soils is lower than in the eastern ones. The low mean annual precipitation in the western parts of the region gives rise to soils without B horizons, which limits the agricultural use of land. The preliminary results show a variation of the hematite-to-magnetite ratio in the soils investigated. Magnetite is probably the main responsible for the enhancement of susceptibility values. The magnetic parameters which depend on concentration show a relative enhancement of values in the soils at the top. In some cases this behavior can be attributed to fires. However, this can also be caused by more recent amounts of large quantities of magnetic particles carried by strong winds. In this contribution we show that the hyperfine and the magnetic parameters are appropriate tools for differentiating soil horizons in both arid and humid areas of Argentina.

[06/11/06 - 14:25h]
The outstanding contribution of Mössbauer spectroscopy to the elucidation of properties of matter at very high-pressures, MOSHE P PASTERNAK, GREGORY KH. ROZENBERG, WEIMING XU, *School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, ISRAEL*, R. DEAN TAYLOR, *MPA, Los Alamos National Laboratory, Los Alamos, NM 87545* ■Following a short introduction of the modern diamond anvil cells techniques and a brief history of early Mössbauer DAC-based high-pressure studies (with some nostalgia), the presentation will concentrate on: • The modern foundations of conventional 57Fe Mössbauer spectroscopy methodology at static pressures using Diamond Anvil Cells. Special considerations in pressure cells design, the miniature very high specific activity Rh(Co57) source, absorbers and gaskets, cryostats, pressure measurements. • The discovery of new and verification of classical phenomena at extremely high-pressures: (i) The role of Hunds rules at mechanical energy density (= P) exceeding that of the crystal-field density, leading to low spin regimes at very high pressures. (i) (i) (ii) Correlation breakdown of the highly correlated Mott-Hubbard magnetic insulators resulting in non-magnetic states and insulator-metal transition. Examples will be given of representative iron halides and oxides. (iii) The final resolution of the Verwey transition dilema attained by Mössbauer HP spectroscopy and the discovery of inverse-normal spinel. • The experimental observation Mott-Hubbard phase diagram in highly correlated oxides: A first time observation of a Mott-Hubbard phase diagram obtained by HP Mössbauer spectroscopy in RFeO3. • High-pressure induced REDOX. The mechanism behind the pressure-induced oxidation of Fe2+(OH)2 and the reduction of Fe3+CuO2 • Contribution of Mössbauer spectroscopy to Earth sciences and mineral physics and chemistry. The effect of spin crossover in perovskites containing iron and magnesion wustite.

[06/11/06 - 15:00h]
Magnetic Properties of Molecular Magnets and Spin Chains Studied by Mössbauer Spectroscopy, H.-H. KLAUSS, , F. GOUIDER, J. KREITLOW, S. SÜLLOW, F.J. LITTERST, *TU Braunschweig, Inst. for Physics of Condensed Matter, 38106 Braunschweig, Germany*, R. FEYERHERM, A. LOOSE, *Hahn-Meitner-Institut, 14109 Berlin, Germany*, T. ISHIDA, T. NOGAMI, *Dept.of Appl. Phys. and Chem.,*

University Chofu, Tokyo 182-8585, Japan, K. Doll, *TU Braunschweig, Inst. for Mathematical Physics, 38106 Braunschweig, Germany*, D.J. Price, *Dept. of Chemistry, University of Glasgow, UK* ■We present spectroscopic studies on two $Fe(II)$ S=2 based molecular magnets, $FePM_2Cl_2$ and $FePMCl_2$ ($PM = N_2C_4H_4 = pyrimidine$), and the spin chain compounds $K_2Fe(C_2O_4)_2$ and $Na_2Fe_2(C_2O_4)_3(H_2O)_2$. These materials are of interest due to their macroscopically observed magnetic properties indicating quantum magnetic effects. From Mössbauer spectroscopy we can get a closer insight into the local magnetic coupling and thus can contribute to a better understanding of the magnetic ground states and their spin dynamics. $FePM_2Cl_2$ crystallizes in a chiral lattice. 3-D magnetic order is established via magnetic exchange interaction mediated by the PM molecule. Combined magnetization, Mössbauer and neutron diffraction studies reveal canted antiferromagnetism below $T_N = 6.4K$ with an ordered moment of $\sim 4\mu_B$. The low temperature B_{hf} is only -32 T. The canting angle resolved from Mössbauer spectroscopy is unusually large (14° from their general antiferromagnetic alignment). The measured electric field gradient is in very good agreement with density functional theory calculations. In $FePMCl_2$ anisotropic magnetic interactions are provided via PM molecules and Cl^- ions. This leads to long range antiferromagnetic magnetic order below $T_N = 11K$ with an ordered moment of $3.2\mu_B$. The Mössbauer experiments reveal a strongly reduced B_{hf} of only 4 T. $K_2Fe(C_2O_4)_2$ is an antiferromagnetic spin chain compound with a maximum in magnetic susceptibility at 20 K. The intra-chain interaction is J $\sim$ 5 K. Our Mössbauer data indicate long range magnetic order below 6.8 K which we attribute to an inter-chain interaction with $J_{perp}/\text{J} \sim 0.1$. Also $Na_2Fe_2(C_2O_4)_3(H_2O)_2$ reveals a maximum in susceptibility around 25 K. In this case its origin is the formation of antiferromagnetically coupled $Fe(II)$ dimers. The Mössbauer data clearly prove that no long range order occurs down to low temperatures. The quadrupole data are compatible with an orbital and spin singlet ground state of $Fe(II)$.

[06/11/06 - 15:15h]
Structural, Mössbauer and Magnetic Studies on Mn-substituted Barium Hexaferrite Prepared by High Energy Ball Milling, Puneet Sharma*, , Raquel A. Rocha, Suzana N de Medeiros, Andrea Paesano Jr., Bachir Hallouche, *UEM-PR-Brazil* ■Barium hexaferrite, isostructural with magnetoplumbite ($MFe_{12}O_{19}$, M = Ba, Sr, Pb) is extensively used for permanent magnets and high density magnetic recording media. The barium hexaferrite unit cell is built up of two formula units, in which iron ion occupy the five different crystallographic sites: i.e. tetrahedral ($4f_1$), octahedral (12k, 2a, $4f_2$) and hexahedral (2b). In the magnetically ordered state of $BaFe_{12}O_{19}$, the 12k, 2a, and 2b sites have their spins parallel to crystallographic c axis, whereas, those of $4f_1$ and $4f_2$ points in anitparallel, constitute a net magnetic moment of 40 bohr magneton. In order to tailor its magnetic properties, iron ions can

be partially substituted by various di, tri and tetravalent metal ions, considering the possibility to occupy spin down sites.

In the present study, Mn-substituted barium hexaferrite powders with composition $BaFe_{12-x}Mn_xO_{19}$ (x = 0.0 - 2.0) were prepared by high energy ball milling and subsequent thermal annealing. The phase characterization was carried out by X-ray diffraction and Mössbauer spectroscopy. All the X-Ray diffraction patterns were refined using Rietveld method. The analysis showed that the hexagonal M-type phase is the main phase in all the samples. The magnetic properties were measured by vibration sample magnetometer. Increasing the substitution amount, the saturation magnetization decreases with corresponding increase in coercivity. The decrease in magnetization is mainly attributed to non collinear magnetic structure. The increase in coercivity is due to decrease in crystallite size with the substitution. The site preferences of Mn ions have been studied by Mössbauer spectroscopy. It is observed that Mn ion occupies the spin up (12k, 2a) and spin down ($4f_2$, $4f_1$) sites. The analysis was made by calculating the site occupation fraction for Mn ions.

[06/11/06 - 16:00h]

Pair-breaking field and structural effects in the magnetically diluted antiferromagnetic superconductor $DyNi_2B_2C$, D. R. SÁNCHEZ, E. M. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Físicas. Xavier Sigaud 150, Urca, 22290-180, RJ, Brazil*, H. MICKLITZ, *II. Physikalisches Institut, Universitaet zu Köln, Zülpicherstrasse 77, 50937 Köln, Germany*, SUNG-IK LEE, *Department of Physics, Pohang University of Science and Technology, Pohang 790-784, South Korea* ■Coexistence of superconductivity and commensurate antiferromagnetic order is observed in the rare earth (R) nickel borocarbides RNi_2B_2C ($R = Dy$ and Ho). The superconducting transition temperature T_c of $DyNi_2B_2C$ rapidly decreases if Dy is substituted by non-magnetic Lu ($T_c < 2K$ for a Lu concentration $x = 0.15$) as has been found by Cho et al. [1]. The work of Morozov [2], in principle can explain this reduction: according to this work the effect of non-magnetic impurities in antiferromagnetic superconductors in the region of coexistence of superconductivity and antiferromagnetism is analogous to the pair-breaking effect of paramagentic impurities in ordinary superconductors. Therefore, one should expect that such a pair-breaking field also should be observable in magnetically diluted AF superconductors. Mössbauer spectroscopy on ^{57}Fe doped $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R' = non magnetic rare earth or Y) offer the possibility to detect this magnetic pair breaking field through the appearance of a magnetic hyperfine field B_{hf} at the $^{57}Fe(Ni)$. Our ^{57}Fe Mössbauer study show that such a magnetic hf field exists for the magnetically diluted $Dy_{0.8}R'_{0.2}Ni_2B_2C$ ($R' = Y, La, Lu$) below their antiferromagnetic ordering temperature ($T_N \sim 10K$). No magnetic hyperfine field was observed in pure AF $DyNi_2B_2C$, as expected. This hyperfine field can explain the reduction in the superconducting transition temperature for $Dy_{0.8}Y_{0.2}Ni_2B_2C$, however, it is too small to explain the complete breakdown of superconductivity in the case of La and Lu doping, respectively. [1] B. K.Cho, et al. Phys. Rev. Lett. **77**, 163 (1996). [2] A. I. Morozov, Sov. Phys. Solid State **22**, 1974 (1980).

[06/11/06 - 16:15h]
Composition of Rust Layers Formed on Low Carbon Steels Exposed to Total Immersion Tests for Different NaCl Concentrations, FREDDY RAFAEL PÉREZ, , *Grupo de Óptica y Espectroscopía, Universidad Pontificia Bolivariana, Circular 1 70-01, Medellín,* FREDDY RAFAEL PÉREZ, CÉSAR AUGUSTO BARRERO, ÓSCAR ARNACHE, LUIS CARLOS SÁNCHEZ, *Grupo de Estado Sólido, Universidad de Antioquia, A. A. 1226, Medellín,* KAREN GARCIA, *Instituto de Química, Universidad de Antioquia, A. A. 1226 Medellín* ■Coupons of low carbon steels with dimensions of 30x100x3 mm3 were submitted to total immersion tests in NaCl solutions, during seven days. Before immersion, the coupons were sandblasted until white metal degree, then cleaned and degreased with water, detergent and ethyl alcohol. Afterwards, four coupons were immersed vertically in three different vessels containing 3000 ml of 0.05, 0.2 and 0.6M solutions, respectively. After seven days, the coupons were extracted. That rust formed in the coupons and that was collected by scrapping the steel surface was called the adherent rust (AR). The rust that is loosely bound to the metal surface was collected for each vessel. This is called the non-adherent rust (NAR). The composition of AR and NAR were investigated by Mossbauer spectroscopy (MS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). In addition, a relation between the grain sizes measured by scanning electronic microscopy (SEM) and the corrosion rate, measured by the weight-loss method, has been established. The hyperfine parameters and the DRIFT vibrational bands showed that the AR samples are composed of magnetite, goethite and lepidocrocite, whereas the NAR contains lepidocrocite, akaganeite and goethite. In all samples lepidocrocite is the most abundant phase. The effects of the immersion time and the grain sizes on the corrosion rates were also investigated. A possible relation between the corrosion rates and the grain sizes for AR samples is also discussed. The amount of corroded iron that completely converts into AR was calculated for all NaCl concentrations. These results can be used to provide important information for corrosion protection.

Poster Session

T1-Catalysis

[06/11/06 - P001]
$LaFe_xMn_yMo_zO_3$ Catalysts for the Oxidation of Aromatic Organic Contaminants, JULIANA C. TRISTÃO, FLÁVIA C. C. MOURA, ROCHEL M. LAGO, *UFMG - MG - Brazil,* JOSÉ D. ARDISSON, *CDTN - MG - Brazil* ■Catalytic oxidation of volatile organic compounds (VOCs) have been studied with several ABO_3 -type perovskite oxides. In this work, mixed perovskites $LaMO_3$ (M = Mn, Fe, Mo) were prepared, characterized and investigated as catalyst for the total oxidation of toluene, used as a probe molecule. The perovskites $LaFe_xMn_yMo_zO_3$

were prepared from a citric acid and ethyleneglycol precursor and characterized by XRD, TPR (Temperature Programmed Reduction), BET (Surface Area) and Mössbauer spectroscopy. XRD data showed the formation of single phase perovskite and the incorporation of all metals. Mössbauer measurement showed for $LaFe_{0,27}Mn_{0,73}O_3$ and $LaFe_{0,54}Mn_{0,46}O_3$ only a duplet which are related to the octahedric Fe^{3+} dispersed, with σ $0,33mms^{-1}$, Δ $52mms^{-1}$ and σ $0,33mms^{-1}$, Δ $62mms^{-1}$, respectively. The spectrum splits into two sextets for higher concentration of Fe assigned to the well and poorly crystallized $LaFeO_3$ structure. The proximity of the Mo to the octahedric Fe^{3+} centers induces an important change in the perovskite structure. For the $LaFe_{0,90}Mo_{0,02}Mn_{0,08}O_3$ perovskite, the relative intensity of the more crystalline phase decrease to 36% (σ $0,36mms^{-1}$, Δ $-0,05mms^{-1}$ and B_{hf} 50,9 T) with a slight increase to 64% of the poorly crystallized phase (σ $0,37mms^{-1}$, Δ $0,09mms^{-1}$ and B_{hf} 48,4 T). The catalytic reactions were carried out with toluene in the gas phase. It was observed that small amounts of Fe ($Fe_{0,27}$) produced a more active catalyst decreasing the oxidation temperature of the toluene. On the other hand, higher concentrations of Fe or the presence of Mo produced a decrease on the catalytic activity.

[06/11/06 - P002]
Mössbauer Investigation of $LaFe_xMn_yMo_zO_3$ Supported on Al_2O_3 as Precursor of Nanodispersed Fe^0 Catalyst, Juliana C. Tristão, Márcio C. Pereira, Flávia C. C. Moura, José D. Fabris, Rochel M. Lago, *UFMG - MG - Brazil* ■In this work, controlled reduction of perovskites supported on Al_2O_3 was used to prepare thermally stable nanodispersed iron catalysts based on $Fe^0/La_2O_3/Al_2O_3$. The perovskites composites $LaFe_{0,90}Mn_{0,08}Mo_{0,02}O_3/Al_2O_3$ were prepared from a citric acid-ethylene glycol precursor with 25, 33 and 50 wt

[06/11/06 - P003]
(Co, Mn)-Doped Magnetites as catalysts, Pegoretti, V. C. B., Coelho, F. S., Pereira, M.C., Tavares, C. M, *Departamento de Química, ICExUFMG, Belo Horizonte 31270-901, MG, Brazil,* Lelis, M.F.F, *Departamento de Química, CCE - UFES, Vitória, ES, Brazil,* Fabris, J.D., *Departamento de Química, ICExUFMG, Belo Horizonte 31270-901, MG, Brazil* ■Spinel-ferrites present interesting characteristics for their use as catalysts. The spinel structure allows accommodate many single or mixed metallic ions, in different oxidation states. This feature makes it possible to modify their catalytic properties according to the chemical reaction of interest and also to vary their chemical behavior, according to the expected effect of different doping metals, without changing the oxide structure. This work was focused on the study of the catalytic effect of magnetites doped with Co and Mn. The pure and (Co, Mn)-doped magnetites were synthesized by the method of the co-precipitation. These materials were characterized with conventional chemical analyses, powder X-ray diffractometry (XRD) and Mössbauer spectroscopy. The H_2O_2 (3.5 mol L^{-1}) decomposition kinetic was studied by quantifying the

formed gaseous O_2 in a volumetric glass system. The oxidation reaction of methylene blue at a concentration of 0.05 g L^{-1} with H_2O_2 was monitored with UV-Vis at $\lambda = 663$ nm. XRD data of samples evidenced characteristic reflections of magnetite; the values of the lattice parameter, obtained from the Rietveld refinement, indicated that the doping ions are replacing iron in the crystalline structure of the magnetite. The Mössbauer spectra of samples showed that the substitution of ions Co^{2+} and Mn^{2+} occurs preferentially in the octahedral coordination sites. Further tests of H_2O_2 decomposition indicated that the substituted catalysts are about 5 times more efficient than the pure magnetite. The tests of discoloration of the methylene blue indicated that the pure magnetite is practically inactive, whereas the doped ferrites are very active, totally discoloring the dye within the first 10 minutes from the beginning of the reaction.

T2-Applications in mineralogy, geology and soils

[06/11/06 - P004]

Study of colombian auriferous ores by means of X-rays diffraction, Mössbauer spectrometry, SIMS and LAM-ICP-MS,

HUMBERTO BUSTOS RODRIGUEZ, DAGOBERTO OYOLA LOZANO, YEBRAYL A. ROJAS MARTÍNEZ, *Departamento de Física, Universidad del Tolima, A. A. 546, Ibagué, Colombia*, GERMÁN ANTONIO PÉREZ ALCÁZAR, *Departamento de Física, Universidad del Valle, A. A. 25360, Cali, Colombia*, ADAM G. BALOGH, STEFAN FLEGE, *Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany*, LOUIS J. CABRI, *Cabri Consulting Inc., Ottawa, Ontario Canada*, LOUIS J. CABRI, MICHAEL TUBRETT, *Memorial University of Newfoundland, St. Johns, Newfoundland, Canada* ■X-ray diffraction (XRD), Mössbauer spectrometry (MS), secondary ions mass spectroscopy (SIMS) and Laser-Ablation Microprobe - Inductively Coupled Plasma - Mass Spectrometry (LAM-ICP-MS) were used to study minerals samples of Colombian auriferous ores. The ores were collected from El Diamante mine, located in the municipality of Guachavez-Nariño (Colombia), and the samples were prepared by means of polished thin sections and polished sections. By XRD analysis, phases like the quartz, sphalerite and pyrite were detected and their respective cell parameters calculated using the adjustment program MAUD. By MS, the phases pyrite, arsenopyrite and chlacopyrite were detected and by using MOSFIT adjustment program it was obtained their respective hiperfine parameters and their respective texture. Multiple regions of approximately 200 μm x 200 μm of area in each mineral sample were analyzed by SIMS registering the presence of "invisible gold"associated mainly with the pyrite and secondarily with the arsenopyrite. This technique proves also that the pyirite is of the arsenian type. Spots of 30 μm to 40 μm of diameter were analyzed by LAM-ICP-MS in pyrite, arsenopyrite and sphalerite, and it was observed that the Au is "homogeneously"distributed inside the structure of the arsenian pyrite and the arsenopyrite (it is not presented as inclusions); the chemical likeness of the "invisible gold"is with the arsenian pyrite and with the arsenopyrite and it is dissolved (solid solution) inside the respective structures. 119 ppm and 62 ppm of invisible gold was quantified in 21 spots analyzed on pyrite and in 14 spots analyzed in arsenopyrite, respectively.

Key words: Mössbauer, invisible gold, SIMS, XRD, LAM-ICP-MS, pyrite, arsenopyrite.

[06/11/06 - P005]

Iron oxide ratio and the soil color attribute,

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■Color is an important attribute in soil grouping that is related to the parent material and to pedogenetic processes. It has been widely used in the Brazilian Soil Classification System to distinguish between yellowish red and yellow soils by the hue 5YR, assuming that the main coloring minerals, namely hematite (Hm) and goethite (Gt) , are present at a ratio $R = \mathrm{Hm}/(\mathrm{Hm}+\mathrm{Gt})$ smaller than 0.2 for the yellow hues. Evaluating reliable R-values is a quite complex task and depends upon the accurate quantification of these minerals, which often occurs as low proportions of cryptocrystalline phases. This imposes serious problems to the quantification with conventional powder X-ray (XRD) analysis. The difficulties were evidenced in a previous work dealing with five soil samples from a toposequence, in a transect located in a soil color transition zone, in a sampling site near the Sete Lagoas, MG, Brazil, for which XRD patterns showed only small and broad reflections due to iron oxides. The corresponding 80 K-Mössbauer analyses were somewhat limited in giving further quantitative information, as some spectral (super)paramagnetic doublet still remained unresolved. In this work, the same samples were again prepared and their chemical compositions determined. Mössbauer measurements (MS) were now performed at 278 K, 110 K, 77 K and 23 K, in an attempt to completely identify and block any superparamagnetic relaxation due small sized iron oxides. From the present results, R-values in the range of 0.14 to 0.66 behave well linearly with hues. This is a clear confirmation of the usefulness of the Mössbauer analysis on the detailed mineralogical quantification of iron oxides of such complex soil samples.

[06/11/06 - P006]

Multivariant analysis in provenance studies: Cerrillos obsidians case, Peru.,

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■In the present work, a total of 21 samples of obsidians coming from the Archaeological Project site have been analyzed by Mössbauer Spectroscopy. The obsidian was the preferred material to make knives of stone, lance and arrows with end, and other tools through prehistoric world due to its characteristics of fracturing and their level of pointed work. Since a volcanic flow is very homogenous, the profile of its elements plans can solely be characteristic of a given source. On the other hand, obsidian is stable to the chemical alteration, so an analysis of an obsidian device can reliably reflect the composition of the original source of the flow. Cerrillos is located in the high Valley of the Province of Ica, in the Ica Region, Peru. The site corresponds to the Paracas culture (600 to the 800 a.C.), Formative Period. In Peru several obsidian sources have been located, in the Central and South zone of the Andes, from Ayacucho Region (for Ayacucho, Coracora and Quispisisa) and from the Arequipa Region (Cotallaulli, Valley of the Colca, Alca and Ccampa). Multivariant analysis was done using Mössbauer hyperfine parameters obtained at room temperature. The Mössbauer spectra in high and low velocity are formed by asymmetric doublets due to the superposition of at least three quadrupole doublets corresponding to Fe2+ in sites A and B and one small proportion of Fe3+, and magnetic phases (due to the presence of small particles of iron oxides like magnetite). The corresponding dendograms obtained reflect the presence of two groups of objects. Group 1 is formed by three sub-groups, whereas the second group presents two sub-groups, evidencing the different origins. Chemical and EPR analysis is under way.

[06/11/06 - P007]

Provenance Studies of geologic prehistoric obsidian sources in Peru, for provenance studies: an approach by Mössbauer spectroscopy and magnetic properties, A. Bustamante, *Facultad de Ciencias Físicas, Universidad Nacional Mayor de San Marcos, Apartado Postal 14-0149, Lima 14, Perú.*, M. Delgado, *Qallta, Jr. Luis Romero 1065 - Urb. Roma - Lima 01, Perú*, G. Cernicchiaro, *3Centro Brasileiro de Pesquisas Fisicas, Rua Xavier Sigaud 150, 22290-180, Rio de Janeiro, Brasil* ■The volcanic glass denominated obsidian was the preferred material to make knives of stone, lance and arrows with end, and other tools through prehistoric world due to its characteristics of fracturing and their level of pointed work. In resistance to the flint, obsidian is only produced by volcanic action. Since a volcanic flow is very homogenous, the profile of its elements plans can solely be characteristic of a given source. On the other hand, obsidian is stable to the chemical alteration, so an analysis of an obsidian device can reliably reflect the composition of the original source of the flow. In Peru several obsidian sources have been located, in the Central and South zone of the Andes, from Ayacucho Region (for Ayacucho, Coracora and Quispisisa) and from the Arequipa Region (Cotallaulli, Valley of the Colca, Alca and Ccampa). Here we present the study of 11 obsidian samples using Mössbauer spectroscopy and magnetization. A plot of the Mr/Ms versus Hc/Hm shows that there is accumulation of points in certain areas depending on the obsidian origin. The magnetization of the saturation (Ms) depends on the origin and it reaches a maximum value of 0,14 emu/g after the obsidian of Quispisisa, indicating the presence of a magnetic phase. The Mössbauer spectra exhibit broad asymmetric doublets, corresponding to two Fe2+ and one of Fe3+ sites. In addition, some samples present a magnetic component attributed to magnetite and/or hematite, in small proportion. A detailed multivariant analysis using the hyperfine Mössbauer parameters and the magnetic properties is under way.

[06/11/06 - P008]
Study of Tropical Forest Soil in the Huanuco Region, Peru, MIRIAN E. MEJIA, JORGE A. BRAVO, JULIO FABIAN, *UNMSM - Perú*, JOSÉ D. FABRIS, *UFMG - Brasil* ■The purpose of this work is the mineralogical characterization of the clay fraction of soils from an area within the Reserved Forest of the Universidad Agraria de la Selva, located in the Region of Huanuco, Peru, with emphasis on the iron oxides and clay minerals, with the help of methods such as selective dissolution of oxides with low crystalline order using sodium dithionite,and analytical techniques such as X ray diffractometry (XRD) and transmission Mössbauer spectroscopy (TMS). For the untreated samples their XRD analyses report the presence of quartz, aluminum silicates (illite and muscovite), and goethite. In the case of samples subjected to the selective dissolution treatment, the X ray diffractograms show aditionally the presence as partheite and mixed layered clay minerals, along with hematite and goethite.It should be noted that quartz remains present even after the fore mentioned chemical treatments. The results from the TMS analysis at room temperature (RT) for the untreated clay fractions indicate the presence of magnetic sites attributed to hematite and Fe^{3+} sites possibly assignment to aluminium silicates (illite and halloysite). In the case of samples subjected to the selective dissolution treatment, only some of them show a slight decrease in the presence of the magnetic sites.

Key words: clay fraction, transmission Mössbauer spectroscopy, X ray diffratometry, selective dissolution.

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[06/11/06 - P009]
Electron Spin Resonance and Mössbauer spectroscopy of Kaolin from Borborema-Seridó Region, F.A.N.G. SILVA, *CETEM-COPPE/UFRJ - Rio de Janeiro*, L.C. BERTOLINO, *FFP/UERJ - São Gonçalo - RJ*, R.B. SCORZELLI, M. DUTTINE, *CBPF - Rio de Janeiro*, A.B. LUZ, J.A. SAMPAIO, *CETEM - Rio de Janeiro*, F.T. SILVA, *COPPE/UFRJ - Rio de Janeiro* ■Kaolin is a finely granulated rock, usually white and chemically inert. Due to its properties, it is widely used in many industrial

fields. A key element in the paper industry, kaolin is also used as raw material in paints, ceramic articles, rubber, plastics, medicine, fiberglass, catalysts, fertilizers and other products. The most important and commonly used mineral of kaolin is kaolinite $[Al_2Si_2O_5(OH)_4]$. The theoretical chemical composition of kaolinite is 39.50% Al_2O_3, 46.54% SiO_2 and 13.96% H_2O. The main contaminants in commercial kaolin are iron (goethite, hematite, magnetite, pyrite and ilmenite) and titanium (rutile, anastase and ilmenite) bearing minerals. The Fe^{3+} can also be found in the structure of kaolinite, substituting the Al^{3+} in octahedral sites and the amount of structural iron can vary depending on the geology of kaolin. The studied sample comes from the Borborema-Seridó area, located in Rio Grande do Norte and Paraiba states (Northeast of Brazil), where there are large deposits of kaolin associated with pegmatite rocks. The beneficiation process was based on magnetic separation (high-intensity magnetic field - $14,000$ G) and bleaching with sodium dithionite ($Na_2S_2O_4$), aiming to eliminate impurities from the kaolin and produce a material compatible with the paper industry specifications, $80-90\%$ ISO brightness.

The mineralogical characteristics were determined by using X-ray diffraction, scanning electron microscopy and chemical analysis.

The X-band Electron Spin Resonance (ESR) spectra of the kaolin samples exhibit, in the $g = 4.2$ region, two superposed signals attributed to Fe^{3+} (substituting for Al^{3+}) in two types of sites with different degrees of distortion. Broad resonance lines mainly due to iron oxides (present in kaolinite external phases) and a $g = 2.0$ line associated with radiation-induced defects (RID) were also detected. The Mössbauer spectra obtained for these samples shown the $Fe^{2+} - Fe^{3+}$ paramagnetic species and the magnetic oxides Fe_2O_3 and Fe_3O_4.

[06/11/06 - P010]

A Comparison of Deferration Methods for Soils,

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■The classical method of Mehra and Jackson uses an 8:1 citrate-bicarbonate buffer solution (C-B buffer) and dithionite (2 g dithionite/1 g clay) in order to concentrate silicate. The method of Stucki is an adaptation of that of Roth et al. who modified the Jackson procedure to study redox processes in clay minerals. In this method dithionite (100 mg dithionite/30 mg clay) is added to a suspension of the clay mineral in C-B buffer. The objective of the study was to identify the differences of these methods with respect to the removal of iron oxides, changes in iron oxidation state, and introduction of defects into the clay structure. The Na-saturated clay fraction from two Brazilian soils a Vertisol and a Cambisol were submitted to the two methods under an inert (nitrogen) or ambient (air) atmosphere, freeze dried, and analyzed by Mössbauer spectroscopy. Maghemite is the principal mineral in the unaltered Vertisol and goethite and hematite in the Cambisol. All treatments removed iron oxides. Spectral differences were observed only in the doublet of structural iron in the clay mineral. Relative Mössbauer Fe(II)/Fe(III) peak areas of the air-reduced samples were only 0.02, revealing that deferration in air reduces little of the structural iron in the clay. The quadrupole distribution for Fe(III) and Fe(II) was the same in air-reduced samples regardless of the deferration method used. Differences were observed between the two methods, however, when performed under an nitrogen atmosphere. The Stucki method yielded a greater Fe(II):Fe(III) ratio, probably due to the greater dithionite:clay ratio used, and more Fe(III) sites were present, due to the introduction of structural defects by the longer exposure time (4 h versus 15 min for the Jackson method). These findings indicate that deferration conditions influence the extent of structural iron reduction and introduce structural defects.

[06/11/06 - P011]

OBSERVATION OF THE VERWEY TRANSITION IN MAGNETITES BY MÖSSBAUER SPECTROSCOPY AND HIGH RESOLUTION X-RAY POWDER DIFFRACTION (SYNCHROTRON LIGHT) AT LOW TEMPERATURE,

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■Transition of Verwey is a crystallographic transition of the magnetite at low temperature, where the cubic crystalline structure is changed to the monoclinic structure. The phase transition at low temperature would be associated with the ceasing of the electron transfer after the ordering of the Fe^{2+} and Fe^{3+} ions. This transition happens in temperatures below 120K, being very sensitive to the size of particles, to the oxidation of the mineral and to the cation substitution. The main purpose of the present work was to study the Verwey transition of magnetites from steatite rocks, sampled in the "Quadrilátero Ferrífero" area, in Minas Gerais state, Brazil. The magnetic fractions from the rock were magnetically separated with a hand magnet and submitted to chemical treatment with citrate-bicarbonate-dithionite (CBD). The resulting materials were characterized by powder X-ray diffraction (XRD) at the XPD line of the Brazilian Synchrotron Light Laboratory, under varied temperatures, by Mössbauer spectroscopy (298K and 110K) and by chemical analysis. The chemical analysis revealed the occurrence of minerals with small isomorphic substitution. The analysis of the diffractograms of the sample at 298 K led to the identification of only one mineralogical phase, the magnetite. Even in the diffractograms at the temperatures below the transition (100 and 60K), it was not possible to observe the occurrence of this phenomenon. Only the characteristic reflections of the cubic phase of the magnetite were observed. The Mössbauer results at 298K showed a magnetite with high crystallinity. In the measurement at 110 K, the split of the octahedral site in two subspectra is observed. This is, possibly, because the measure was performed close to the transition temperature. Probably, smaller temperatures (4K) and external magnetic field application would allow a better separation of the relative sextets of the tetrahedral and octahedral sites.

[06/11/06 - P012]

DISTRIBUTION OF Fe-FORMS IN AN ULTISOL AS DETERMINED WITH SELECTIVE CHEMICAL DISSOLUTION AND MÖSSBAUER SPECTROSCOPY,

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■Electric charges on the surface of iron oxide (FeO_x) particles greatly influence the ion dynamics in the solid-solution relationship. The mineralogical composition and the way these minerals are inter-related or chemically and spatially distributed determine the soil chemical properties. The identity and distribution of Fe-forms in the silt ($\phi = 0.002$-0.053 mm) and clay fractions from soil samples collected at a depth of 15 - 30 cm from an Ultisol profile (sampling site, 36°58' S 72°09' W) in southern Chile, were determined in this study. The mineralogical analysis was carried out mainly with Mössbauer spectroscopy at 298 K, 80 K and 6 K, for samples before and after treatment with ammonium oxalate (OX). The 298 K-Mössbauer spectra reveal relatively complex mineral assemblages for all samples, with heterogeneous chemical compositions, rendering patterns mainly formed by an intense central doublet, due to (super)paramagnetic Fe^{3+}. A less intense high-spin ferrous doublet is assignable to ilmenite and an incipient broad-line sextet to coexisting magnetically ordered forms of FeO_x. The sextet signals are more intense for the silt sample. Goethite, hematite and maghemite were identified from the Mössbauer spectral analysis of patterns obtained at 6 K, numerically fitted with hyperfine field distributions. The relative area for maghemite in non-treated samples was found to be 46 % (silt) and 13 % (clay). These results are consistent with the measured values of specific saturation magnetization. Some low hyperfine fields are identified for both silt ($B^{max}{}_{hf} = 43.7$ T; RA = 16 %) and clay (44.2 T and 47.3 T; 31 %) samples. These species are likely due to poorly crystalline iron oxyhydroxides, which are more easily removed with OX. In this volcanic soil, maghemite tends to remain in the coarse fraction, whereas poorly crystalline forms do occur mainly in the clay fraction.

[06/11/06 - P013]
INDUCED GEOCHEMICAL BARRIER TO MITIGATE THE MINE ACID DRAINING, ASSIS, , I.R., ABRAHÃO, W.A.P, *Departamento de Solos, Universidade Federal de Viçosa, 36571-000 Viçosa, Minas Gerais, Brazil,* PEREIRA, M.C., FABRIS, J.D., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Brazil,* DIAS, L.E., SOARES, T.M., *Departamento de Solos, Universidade Federal de Viçosa, 36571-000 Viçosa, Minas Gerais, Brazil* ■Sulfide-containing rejects from mining areas present enormous risks to the environment if exposed to air. Their oxidation leads to acidic waters, in a phenomenon better known as acid mine drainage, that tend to incorporate and redistribute heavy metals (as Pb, Cd, Ni) and metalloids (As, B) that reach the food chain. The objective of this work was to induce, in the laboratory, the formation of jarosite and/or natrojarosite, in a sulfide-containing substrate, in order to form a geochemical barrier to further oxidation of sulfides. Sulfide-rich samples from a reject material of a mining area for gold in the state Minas Gerais, Brazil, were conditioned in lisimeters, with different covering layers, sealing and capillarity. Salt was also added to the column. During one year, these lisimeters were eluted with de-ionized water in amounts and mean frequency equivalent to the rainfall of the mining area. The pH, Fe and S contents of the eluted solution were monitored. Finally, portions with characteristic oxidation colors were collected from the solid column and analyzed with powder X-ray diffractometry (XRD) and Mössbauer (MS) spectroscopy. It was observed that contents of Fe and S in the liquid was significantly reduced due to the inductive salt treatments, confirming the effect of the chemical barrier, when compared with the blank treatment, suggesting a ferric micro-encapsulation of sulfides by oxides or sulfates. XRD data alone were not enough to clearly elucidate the mineralogy of the neo-formed ferric materials, due to abundance of silicates in the samples. MS revealed to be an adequate tool for the detection and quantification of the iron-bearing neo-formed minerals. It was observed the occurrence of pyrite ($\delta = 0.361$ mm s^{-1}, $\Delta = 0.555$ mm s^{-1}), jarosite ($\delta = 0.383$ mm s^{-1}, $\Delta = 1.078$mm s^{-1}) and ilmenite ($\delta = 1.069$ mm s^{-1}, $\Delta = 0.707$ mm s^{-1}).

[06/11/06 - P014]
Placic Horizons Developed in Soils of Coastal Tablelands in the in the Northeastern Region of Brazil, J.C. DE ARAÚJO FILHO, , *1Embrapa Solos/UEP Recife, Recife - PE, Brasil,* A. CARVALHO, *Instituto de Geociências, USP, São Paulo - SP, Brasil,* F.O.

JORGE, C.S.M. PARTITI, *Instituto de Física, USP, Caixa Postal 66318, CEP 05315-970 - São Paulo - SP, Brasil* ■The lack of information moved the study of three placic horizons developped in soils of coastal tablelands in Northeastern region of Brazil. The samples of placic horizon were obtained from two profiles of Ultisols order and from one profile of Spodosols order. The main goal was the characterization of the iron oxides mineralogy that plays the role as cementing agents. We were also concerned to clarify if the placic horizons show spodic materials properties. The results confirmed that, independently from the type of soils, the placic horizons show spodic materials properties suggesting that the podzolization process could be an active factor involved in the genesis of these horizons. On the other hand, the low content of iron extracted from the organic matter suggested that the accumulation of this element in placic horizons might be more influenced by the oxide-reduction processes. Oxalate-extractable aluminum and silicon also suggested a possible presence of non-crystalline or poor crystalline hydrous aluminosilicates probably acting as accessory cements. According to several authors the identification of ferryhidrite when it is mixed with others minerals requires special techniques like Differential X-ray Diffraction. However, about ten percent of Fe extracted by acid ammonium oxalate probably correspond to ferryhidrite minimum detection. An alternative technique is Mössbauer spectroscopy that has been used extensively in the study of Fe compounds in soils. The advantage of Mössbauer spectroscopy is that it is non-destructive and it is sensitive to valence states, chemical structure and magnetic properties of iron. Our Mössbauer spectroscopy results allowed identify that the main iron forms in placic horizons are ferryhidrite and aluminum-substituted goethite. In according with our results, the decrease of hyperfine field is associated with the increase of aluminum content in samples.

[06/11/06 - P015]

EFFECTS OF SODIUM HYDROXIDE- SELECTIVE CHEMICAL TREATMENT ON SAMPLES OF SEDIMENTS,

M. L. CERÓN LOAYZA, M. MEJÍA SANTILLAN, A. TRUJILLO QUINDE, *Facultad de Ciencias Físicas. Universidad Nacional Mayor de San Marcos, Apartado 14-0149, Lima 14.Perú* ■The main purpose on this work is to essay the NaOH method in the silt and clay fractions of samples of Peruvian sediments in order to selectively concentrate iron oxides in variable degrees dissolves and removes phyilosilicates and determine the mineralogical composition of the samples. The chemical selective treatment of the sodium Hydroxide (NaOH) was applied to the grain sized fractions of silt and the clay of the sediment sample. These samples are sediments derived from the "Salinas de Chilca"that are located in the District of Chilca, province of Cañete, Department of Lima, Perú. This treatment is an important step for the mineralogical determination of the samples in soils and sediments. A previous treatment to the sample with the Hydrogen Peroxide method was made and thus to be able to reduce the percentage of organic matter existing and to obtain better results.

For the magnetic characterization we utilized the Mossbauer spectroscopy (ME) using the isotope natural of 57Fe; that we let detected and measure in form selective the presence of sesquioxides and other minerals that contain iron (Fe), and for the structural characterization we used X ray diffraction (XRD). The treatments of NaOH was applied in form sequential and submit sequentialy to the techniques of Mössbauer Spectroscopy by Transmisión (EMT) and X Ray diffraction (X-RD). The result by Mössbauer spectroscopy show paramagnetic doublets and the presence of the magnetite partially oxidized The results by DRX of the sample without treating show the Quartz presence, phyilosilicates like: Vermiculite y Halloysite, nevertheless when it is continued with the selective chemical treatment is possible to be observed that phyilosilicates can been eliminated almost in their totality and we can observed the main reflection (311) of iron oxide spinel.

Keywords: Sediments, Mossbauer Spectroscopy, X ray diffraction.

[06/11/06 - P016]

Advances in the mineralogical characterization of agricultural soils at Fundo Majin, Miracosta, Cajamarca,

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■The present work tries to determine the mineralogical composition of the agricultural soils putting special emphasis in iron oxides and argillaceous minerals that contains the clay fraction. The samples in study come from the vicinity of Fundo Majín, District of Miracosta, Province of Chota, Department of Cajamarca, Perú.

Have been made the chemical physical analyses to each one of the 42 samples that represent the zone in study. Additionally, for aims of this study, of this universe of samples one has selected some for the analyses by X ray diffraction (by the powder method) and of Mössbauer espectroscopy of transmission (TMS), as much of the samples in gross like of his fraction clay. In the cases that are necessary, chemical techniquel of selective extraction of iron of the mineralogical components in crystalline and/or amorphous form are being applied, to obtain one better resolution in the measures by the mentioned techniques.

This work is being carried out jointly with the Faculty of Agronomy of the National University Pedro Ruiz Gallo of Lambayeque, where the chemical physical analyses have been made. In the faculty of physical sciences of te National University of San Marcos the analyses by X ray diffraction and Espectroscopy Mössbauer are being made.

With works of this nature it is tried to create bonds of interdisciplinary cooperation with the Peruvian technicians of the agricultural sector, who have showed the necessity to count with information more detailed about the mineralogical composition of the soils, specially of the clay fraction.

[06/11/06 - P017]
CHARACTERIZATION OF CLAYS IN AGRICULTURAL SOILS:NORTH AND SOUTH OF ICA, M. L. Cerón Loayza, C. J. Rodríguez Palomino, *Facultad de Ciencias Físicas. Universidad Nacional Mayor de San Marcos, Apartado 14-0149, Lima 14.Perú.* ■The study of agricultural soils have a relevant importance due to their magnetic properties and to the content of the clay fraction (¡2mm) that is the that is related directly to the fertility of the soil. In the present work we reported a preliminar study over the mineralogical characterization of agricultural soils by Mossbauer spectrosocpy (ME), using the natural isotope of 57Fe; which we let detected and measure in form selective the presence of sesquioxides and other minerals that contain iron (Fe) and as complementary tecnique we used X ray diffraction (XRD) and the physical-chemical treatement. The samples analized come of the south and north of the district of Salas, Guadalupe localized en the deparment of Ica, south of Peru, both was extracted in two different depth: 10 cm and 50 cm. The results by ME for the sample south show the presence of a magnetic component with a hiperfine field mean of 36.0 T which is asociated to the presence of Goethite, furthermore are identified the presence of Illite/Smectite and the phase spinel, while the samples of the part north show a magnetic component associated to the presence of Hematite and states of valence Fe2+ y Fe 3+. The results of X ray diffraction of the samples of the south part for the two depth studied show the presence of phases asociated to the minerals : Quartz, Albite, Illite, Montmorillonite and chlorite; while in the samples of the part north we found phases associated to the minerals : Quartz, Albite, Illite, Montmorillonite and Muscovite. The mineralogical components that we find with less than of 5
Key words: Clays, Mossbauer Spectroscopy, X ray Diffraction.

[06/11/06 - P018]
Mössbauer, FTIR spectroscopy of lazulite-scorzalite samples from Diamantina District (Minas Geraes, Brazil)., Giovanna Maria L. Gardini, Adolf Heinrich Horn, *Federal University of Minas Gerais-Geological Institute- Av. Antônio Carlos, 6627 31.000-000 Belo Horizonte-MG*, Yvs Fuchs, *Université Marne la Vallée, Laboratoire des Géomatériaux et de Géologie de lIngénieur*, Jorge Linares, *Université Versailles-Saint Quentin, Laboratoire Magnétisme et Optique, UMR* ■Near Diamantina, p-sedimentary rocks of the paleo-proterozoic Rio Paraúna Supergroup have locally contact parallel lazulite and dumortierite rich parts. That mineralization is the result of the formation of the Espinhaço Supergroup by rifting, metamorphism and intemperism. A lot of transformations are observed probably indicating the formation of important mineral deposits. Lazulite is formed of infinite chains of face sharing octahedral oriented along [110] and [110], connected along [001] by corner sharing PO4-tetrahedra and (OH)-hydroxyl groups (Giusepetti& Tadini, 1983). The central octahedron is occupied by a R2+-cation and the two other octahedral by a R3+-cation. Substitution of Mg2+ by Fe2+

characterizes the solid-solution lazulite-scorzalite. Mössbauer studies (Selke et al. 2003) on synthetic lazulite-scorzalite showed that Fe2+ is located in the central octahedron and that Fe3+ could occupy 2 octahedral sites (Selke et al 2003). In the Espinhaço Range lazulite occurs in: –some particular levels as amygdaloidal lenses –crosscutting quartz veins. The Fe content in the vein lazulite is higher as in the stratiform one. Calculation of number of atoms per structural unit shows the samples having dominant lazulite composition (95.2 for type 1, 93.1 for type 2). Mössbauer spectra show two doublets. Spectra performed at 150K preclude that Fe3+ could be located in a tetrahedral position. IS and QS parameter for Fe2+ and Fe3+ are similar with those of Selke et al. (2003) but the Fe3+/Fetotal ratio increases with Fe content, differently from the results obtained by R. Selke et al. (2003) on synthetic lazulite-scorzalite. FTIR spectra show a strong peak at 3405 cm-1, attributed to the OH stretching of OH surrounded by Mg (in central octahedron) and 2 Al. The shoulder at 3381 cm-1 is attributed to Fe substituting for Mg. The existence of shoulders at 3460/3550 cm-1 can be related to some disordering of the octahedral chains.

[06/11/06 - P019]
Thermally Induced Phase Transformations in Zinc Magnetites, Antonio Carlos Saraiva da Costa, Ivan Granemann de Souza Junior, Marcelo Augusto Batista, *Universidade Estadual de Maringá. Departamento de Agronomia. Av. Colombo 5790. Maringá-PR. 87020-190.*, Andrea Paesano Junior, Kleberson Lucenildo da Silva, Denise Adorno Lopes, Jusmar Valentin Bellini, *Universidade Estadual de Maringá. Departamento de Física.* ■Ferrimagnetic iron oxides of natural origin such as magnetite and maghemite are an important group of minerals to soil, geology, and environmental studies The isomorphous substitution of iron for different cations (Zn, Cu, Ni, Cd, Pb, etc.) in these minerals, affects most of their magnetic properties. Studies on the phase transformations thermally induced of chemically synthesized substituted magnetites and maghemites can help to understand the evolution of these minerals generated by the weathering processes. In the present work $Fe_{3-X}Zn_XO_4$ magnetites were prepared by co-precipitation in the range 0.025 to 0.35 cmol mol^{-1} and, further, annealed at 800^oC, under free atmosphere for 4 h. The as-annealed powders were characterized by total chemical analysis, X-ray diffraction and Mössbauer spectroscopy. The XRD and MS results showed that the annealed samples were oxidized and converted in hematite and franklinite ($ZnFe_2O_4$), in relative amounts that vary with X. The oxidation reaction may be represented by the stoichiometric equation: $Fe_{3-X}Zn_XO_4 + (1-X)/4.O_2 =$ 3(1-X)/2.Fe_2O_3 + X.$ZnFe_2O_4$. The diffraction lines did not present any regular displacement in the angular position for both formed phases, as the zinc concentration varies. Similarly, the isomer and quadrupole shifts for both phases, and the hyperfine magnetic field for hematite, did not show any significant variation with increasing zinc content. This indicates that

the compositions and structures of the resulting oxides do not depend on the starting magnetite. The nature and relative amounts of the final oxides are explained based on a Gibbs free energy diagram, having iron-zinc oxides as end compounds in concentration axes, given the pressure, temperature and atmosphere in which the annealing process was conducted.

[06/11/06 - P020]
Rock magnetism and Rock magnetism and paleomagnetic studies on Paleozoic rhythmites (Paraná Basin, Brazil)paleomagnetic studies on Paleozoic rhythmites (Paraná Basin, Brazil), Franco, D.R., Ernesto, M., *Universidade de São Paulo, Instituto de Astronomia, Geofísica e Ciências Atmosféricas (IAG-USP), Departamento de Geofísica, São Paulo, SP, Brasil.*, Berquó, T.S., *Department of Geology and Geophysics, Institute for Rock Magnetism, University of Minnesota - Minneapolis, MN 55455 USA*, Fabris, J.D., *Departamento de Química-ICEx, Universidade Federal de Minas Gerais, Campus Pampulha, 31270-901, Belo Horizonte, MG, Brazil.*, Rosière, C.A., *Instituto de Geociências, Universidade Federal de Minas Gerais, Campus Pampulha, 31270-901, Belo Horizonte, MG, Brazil.* ■The discussions about future global heating has pointing at the importance of increasing the knowledge concerning to paleoclimatic changes in different regions of Earth, for a better understanding of dynamics and amplitude of the present climatic system. During the last two decades, ciclostratigraphy studies have suffered a great development, and nowadays it is possible to investigate climatic signals by geological record. One of the most important tools in such kind of studies is the Paleomagnetism, which is the record of ancient magnetism preserved in rocks through geological time. Its basic phenomenon is the acquisition of a permanent magnetization by rocks, from and parallel to the then existing magnetic field direction, indirectly its strength, at or near the time of formation of the rock. Such magnetization is called primary magnetization, but it could be possible to verify secondary magnetizations which are acquired along geological time. Therefore, it is of fundamental importance to investigate the nature of remanence, through magnetic mineralogy studies for identification the magnetic carriers. In the present work, we investigated the presumable annual sedimentation character of Paleozoic rhythmites (laminated glacial rocks, which show alterning of sandstone-siltstone and siltstone-argilite beds) from Paraná Basin, Brazil. Outcrops in the cities of Itu and Rio do Sul (Paraná and Santa Catarina states, respectively) correspond to one of most interesting problems concerning to Paleozoic Gondwana glaciation. Spectral analysis on previous paleomagnetic and thickness data revealed a periodicity of 11 and 22 years in sedimentation compatible with annual sedimentation, considering that the layers do correspond to one-year sedimentation. Rock magnetism studies (Thermal demagnetization, thermomagnetic and IRM acquisition curves, Mössbauer spectroscopy, hysteresis loops and ZFC-FC curves) provided explanations for the very stable magnetic remanence found in such rocks, which is probably related to magnetic mine-

rals of high coercivity.

[06/11/06 - P021]
Structural and hyperfine characterization of zinc substituted magnetites, Antonio Carlos Saraiva da Costa, , Ivan Granemann de Souza Junior, Marcelo Augusto Batista, *Departamento de Agronomia - Universidade Estadual de Maringá,* Andrea Paesano Junior, Klebson Lucenildo da Silva, Jusmar Valentin Bellini, *Departamento de Física - Universidade Estadual de Maringá* ■Ferrimagnetic materials are intensely investigated because of their important applications to the industry and to the environment. Recently, special attention has been focused on the synthesis methods based on co-precipitation from aqueous solutions, with different cations substituting the iron in the spinel structure and how this affects its magnetic properties. Structurally and magnetically zinc substituted magnetites, were prepared from $FeCl_2$ e $ZnCl_2$ aqueous solution in the mole fraction 0.025 - 0.35. The resulting powder material was analyzed by total chemical analysis, X-ray diffraction, Mössbauer spectroscopy and other techniques. Total chemical analysis showed that the co-precipitation method was successful and isomorphous substitutions were 0.22, 3.53, 6.54, 11.80, 17.72, 25.75 and 34.95 cmol mol^{-1} of zinc. X-ray diffraction showed planes associated with the presence of the magnetite and, possibly, with maghemite. The diffraction lines shifted to low angles, revealing an increasing lattice parameter as the isomorphous substitution increases. Mössbauer spectra showed a magnetic combined pattern, confirming the occurrence of the magnetite and maghemite phases. The later, present as a minor phase, is due to oxidation of the very fine as-prepared particles. As the zinc content increases, only the magnetite phase is observed, revealing that substitution favors the chemical stabilization of the solid solution. In addition, the hyperfine magnetic fields of both sites of the spinel structure decreased (B^A_{hf} slower than B^B_{hf}) indicating the progressive weakening of the magnetic interaction intra and inter sublattices. For x >> 0.33, B^B_{hf} is virtually collapsed whereas B^A_{hf} reduced only 10 percent of its initial value. The isomer shifts for sites A and B showed a linear decline with increasing x (IS_A slower than IS_B), with IS_B changing from a value typical of mixed valence to a value corresponding to trivalent iron. The subspectral areas presented good agreement with the theoretical occupation formula $(Zn^{2+}_X Fe_{1-X})[Fe^{2+}_{1-X} Fe^{3+}_{1+X}]O_4$.

T3-Amorphous, nanocrystals and small particles

[06/11/06 - P022]
A Mössbauer Investigation of Nanocrystalline Iron with A Mössbauer Investigation of Nanocrystalline Iron with Zirconium Additions, Michael Martin, , Yusef Fahmy, Airat Khasanov, Amar Nath and *John Stevens, *UNCA Mossbauer Research Group, University of North Carolina at Asheville, Asheville, NC 28804 United States* ■Iron nanocrystals have been studied extensively during the past decade with particular interest in their potential

applications in several fields including computing, medicine, and metallurgy. In order for wide scale implementation in these specified industries, iron nanocrystalline alloys must be stabilized such that their unique properties are retained post processing and/or in service. Thus, it is of both scientific and technological interest that the thermal stability and grain growth of such nanocrystalline systems be studied and understood. This research project undertakes a study of the structure, stability and characteristics of nanocrystalline iron and iron with minor zirconium and hafnium impurity additions prepared by high energy ball milling. Mechanically milled nanocrystalline iron, and zirconium-doped and hafnium-doped iron powders have undergone a series of heat treatments and x-ray diffraction measurements to characterize structure and estimate grain size using Bragg reflection linewidths and the Scherrer formula. Using crystalline growth measurements, and assuming grain growth under ideal conditions such that a grain growth constant of n=0.5 applies where D(1/n)-Do(1/n) = kt, the rate constant, k, is determined for the different iron systems. Rate constants are used to determine the activation energy for isothermal grain growth revealing enhanced stability of the doped iron. Crystalline size in milled iron increased 646

[06/11/06 - P023]
Determination of the Growth Mechanism of Catalytically Grown Carbon Nanotubes, C. M. CAMERON, , A. NATH, A. M. KHASANOV, J. G. STEVENS, J. M. SCHMELTZER, *UNCA Mossbauer Research Group, University of North Carolina at Asheville, Asheville, NC 28804 United States*, G. KESKAR, K. YANG, J. GAILLARD, AND A. P. RAO, *Department of Physics and Astronomy, Clemson University, Clemson, SC 29631 United States* ■Carbon nanotubes are cylindrical carbon networks composed of single sheets of graphite rolled and capped at the ends. They exhibit extraordinary tensile strength, novel electrical properties, and efficient thermal conduction. When grown with a metal catalyst, a mixture of metallic and semiconducting nanotubes is obtained. Semiconducting carbon nanotubes have found application in subminiature transistors and the metallic ones as electrical conductors. Understanding the growth mechanism of carbon nanotubes has great importance; by attaining this knowledge, nanotubes can be tailored for specific applications where their physical and chemical properties play a significant role. Our investigations into nanotube growth are attempting to address the question of the role of nanoparticulates of gamma-iron mixed with carbon clusters on the surface of the 200-nm iron carbide (originally alpha-iron), which is the focal region of the growth of nanotubes. Very interestingly, we find that the nanoparticles of gamma-iron, which induce catalysis, are migrating rapidly on the surface of the 200 nm iron carbide particles, and consequently the hyperfine interactions are washed away. Currently, further studies are taking place in order to provide additional spatial information about the iron as well as to verify and reinforce our results. We are preparing a synthesis of ferrocene, the catalytic precursor, with the spectroscopically active 57Fe.

Carbon nanotubes grown from this sample will improve results overall by producing reliable and unambiguous spectra. In addition, a thorough examination by TEM is in progress, which would help to confirm the size distribution and location of alpha- and gamma-iron nanoparticles. We believe that gamma-iron nanoparticulates are stabilized by carbon nanoclusters, while the gamma-iron particles are clinging to the nanotube walls.

[06/11/06 - P024]
Formation of Al-doped Iron Silicides by Ball Milling, S. M. COTES, , M. TAYLOR, J. MARTÍNEZ, J. DESIMONI, *Dto. Física, Fac. Cs. Exactas, UNLP, IFLP/CONICET, 1900 La Plata, Argentina,* J. RUNCO, *Dto. de Física, Fac. Cs. Exactas, UNLP, 1900 La Plata, Argentina.*
■Phases obtained in the Fe-Si system are extremely depending on the experimental conditions of synthesis. Non-equilibrium processing techniques like mechanical alloying allow the formation of stable and metastable phases at room temperature. Among the nine known types of iron silicides, the semiconducting β-$FeSi_2$ disilicide has attracting the attention of the researchers in the last recent years due to its technological potential applications in the field of optoelectronic and as a material for thermoelectric conversion. The doping with Al atoms makes the semiconducting β-$FeSi_2$ disilicide to become n-type semiconductor and consequently some interesting fundamental issues arise. This facts are related to the occurrence of metastable phases and to the impurity location at the two non-equivalent Fe site of the β-$FeSi_2$ lattice structure. In this frame, a study of the sequence of phase formation of stoichiometric $Fe_{1-x}Al_xSi_2$ ($0.03 \leq x \leq 0.50$) mixtures prepared by mechanical alloying from elemental Fe, Al and Si powders is presented. The milling process was performed at room temperature in Ar atmosphere in a horizontal mill device during 15 h. Mössbauer Spectroscopy and X-ray diffraction were used to identify the phases produced during sample preparation and to follow the relative fraction of the obtained phases as Al concentration is increased.
The diffractograms and the Mössbauer patterns are characterized by broad lines indicating the formation of different disordered iron silicides. The observed phases could be associated with stable and metastable room temperature phases like β-$FeSi_2$, α-$FeSi_2$ and ϵ-FeSi. No traces of the pure elements were detected. The present results are compared with those obtained on Pt and Mn doped β-$FeSi_2$ prepared by the same method, where chemical driving forces predominate over the diffusion process.

[06/11/06 - P025]
Milling time effects on the magnetic and structural properties of the $Fe_{0.7}Si_{0.3}$ system, RUBY ROCIO RODRIGUEZ, HECTOR SANCHEZ STHEPA, GERMAN PEREZ, *Universidad del Valle, Calli, Colombia,* JEAN-MARC GRENECHE, *Universite du Maine, Le Mans, France*
■The magnetic and structural properties of the $Fe_{0.7}Si_{0.3}$ alloy are analyzed by using X-Ray diffraction and Mössbauer spectrometry at 300 K and 77 K in transmission geometry. The samples were prepared by mechanical alloying in a planetary ball mill pulverisette 5 during 1, 5, 9, 15, 75 and 100 hours milling, with a

ball mass to powder mass relation of 10:1, under argon atmosphere. The evolution of the properties of the $Fe_{0.7}Si_{0.3}$ alloy obtained by mechanical alloying at different milling times is presented. The X-ray diffraction patterns showed a coexistence of BCC, DO3 and FeSi structural phases, however, for 1 h to 5 h process, we observed additional peaks which correspond to iron and silicon elements. These results indicate us that the alloy is still a non-fully consolidated sample. The present milling conditions allow to extend until 30 at. Si the BCC structure, contrasting with melted Fe-Si alloys in which this phase is obtained until 10 at Si. The grain size of the BCC phase is about 18 nm for 1 h, then decreases down to 9 nm for 5 h and finally is nearly constant at about 6 nm for 75 h and 100 h milling. In addition, the crystalline grains tend to have a cubic-shaped morphology. The lattice parameter for each phase remains nearly constant (2,838 A for the bcc structure). The shape of hyperfine field distributions used to describe the Mössbauer spectra is discussed. A theoretical binomial model to interpret the experimental hyperfine field distribution is presented and discussed.

[06/11/06 - P026]

MAGNETIC PROPERTIES OF NANOPARTICLES OBTAINED THROUGH DIFFERENT CHEMICAL ROUTES,

Souza, , D. M., Andrade, A. L., Pereira, M. C, Fabris, J.D., Domingues, R. Z., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Brazil.*

■Improving synthesis condition to prepare nanosized magnetite with controlled chemical, morphologic and magnetic characteristics has increasingly been of technological interest. Nanosized magnetic structures are currently key materials for advancements in electronics, optoelectronics, medicine and a variety of applications in magnetic storage devices. So, various approaches have been developed to synthesize and utilize iron oxides This work reported three chemical synthesis of magnetite: (i) by direct reduction-precipitation method, (Mt025); (ii) reduction of the hematite precursor with H_2 at 250 °C (MtH2) and (iii) with coal, at 600 °C (MtC). X-ray diffractometry data suggest the formation of single-phased samples of magnetite, MtH2 (a = 8.3948(3) Å) and Mt025 (a = 8.383(7) Å) and a multi-phased sample MtC, containing maghemite (a = 8.3605(5) Å), hematite (a = 5.184(2) Å) and c = (13.561(8) Å) and magnetite (8.3957(8) Å). The estimated average particle sizes are 10, 26 and 33 nm for samples Mt025, MtC and MtH2, respectively. The 298 K Mössbauer parameters for the sample MtH2 are characteristic of magnetite, whereas magnetite, maghemite and hematite are identified from the corresponding spectrum for sample MtC. The broader-line pattern for sample Mt025, with the smallest mean particle size of this set, reveals rather a relatively lower hyperfine. Differently from the other samples, the 110 K spectrum indicates that the magnetite of sample MtH2 undergoes the Verwey transition. Values of saturation magnetization measurements for samples MtH2, MtC and Mt025 are found to be 87, 78 and 60 J T^{-1} kg^{-1}, respectively. The authors are grateful to CAPES, CNPq and FAPEMIG for financial support.

[06/11/06 - P027]

EFFECT OF THE CONCENTRATION OF THE HCl ON THE SYNTHESIS OF MAGNETITE BY A CHEMICAL REDUCTION-PRECIPITATION METHOD, ANDRADE, , A. L., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Brazil,* SOUZA, D. M., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Brazi,* FABRIS, J.D., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Bra,* DOMINGUES, R. Z., PEREIRA, M. C., *Departamento de Química, ICEx, UFMG, 31270-901 Belo Horizonte, Minas Gerais, Brazil* ■In this work, it was studied the influence of the HCl concentration on the chemical nature and properties of synthetic magnetic nanocomposites. Five magnetite samples were synthesized using ferric chloride as precursor. Samples Mt3, Mt2, Mt1, Mt05 and Mt025, corresponding to 3, 2, 1, 0.5 and 0.25 mol L^{-1} HCl, respectively, were characterized by XRD, ^{57}Fe Mössbauer spectroscopy at 298 K and 110 K and saturation magnetization measurements. The cubic lattice parameter for magnetite of samples Mt025, Mt05 and Mt1 were determined to be a = 8.383(7), 8.354(2) and 8.3707 Å, respectively. The sample Mt2 contained magnetite (a = 8.386(3) Å); maghemite (a = 8.34(3) Å) and goethite (a = 4.615(5), b = 9.96(1) and c = 3.034(3) Å); for Mt3, it was observed only characteristic reflections of maghemite (a = 8.342(1) Å), and goethite (a = 4.585(3), b = 9.911(5) and c = 3.0207(9) Å). XRD patterns present line broadenings presumably due to small particle sizes. Estimations of the particle size for all these magnetite is about 9 nm. In effect, Mössbauer spectra at 298 K showed hyperfine fields lower than the expected fields for pure magnetite. For all samples, some superparamagnetic relaxation effects, very likely due to goethite, may explain the central doublets in Mt2 and Mt3 spectra. For all but sample Mt3, the spectra at 110 K the doublet nearly disappear. The Verwey transition in magnetite was not observed at least down to 110 K, for all samples. Saturation magnetization (σ) values are 60, 58 and 60 J T^{-1} kg^{-1} for samples Mt025, Mt05 and Mt1, respectively. For samples Mt2 and Mt3, σ is 31 and 10 J T^{-1} kg^{-1}, respectively. These results suggest that the concentrations of 2 M and 3 M HCl lead to the formation of side-products to magnetite, namely goethite and maghemite.

[06/11/06 - P028]

Synthesis and Structure of Biocompatible Ferrofluids, BEATRIZ PORTUGAL GONÇALVES DA MOTTA, , ADRIANA SILVA DE ALBUQUERQUE, JOSÉ DOMINGOS ARDISSON, WALDEMAR AUGUSTO DE ALMEIDA MACEDO, *Centro de Desenvolvimentoda Tecnologia Nuclear CDTN/CNEN-MG- Brazil,* ANAYIVE PEREZ REBOLLEDO, *Departamento de Química / UFMG, MG, Brazil* ■Nanostructured magnetic oxides for biological applications has been largely investigated nowadays. In this direction, we have investigated the synthesis and characterization of ferrofluids based in iron oxide nanoparticles dispersed in a surfactant. The nanoparticles of stoichiometric Ni-Zn ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$, NZF) were prepared by chemical coprecipitation in a dextran solution and the ferrofluid was obtainded after heating the mixture for 30 minutes at 50 ^{o}C. Dried samples, as obtained and after heat treatment, were characterized by X-ray diffraction (XRD), infrared, and 57Fe Mössbauer spectroscopy. XRD results show that the as-obtained samples present low crystallinity. Annealing at 600 ^{o}C results in the formation of NZF of high crystallinity and complete carbonization of the dextran. As obtained and heat treated samples present average particle size of 9 nm and 21 nm, respectively. The Mössbauer spectra at room temperature indicate superparamagnetic behavior for both NZF samples. At 100 K, the Mössbauer spectra indicate the formation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, confirming XRD results. The infrared spectra show C-O-C bands at 1158 and 1100 cm^{-1}, suggesting that the dextran is covering the ferrite particles. For the annealed samples, the bands at 575 cml can be associated with Fe-O bonds present in NZF. Neverthelesss, no conclusive information about the bonding between the NZF core and the dextran shell can be drawn from our infrared spectroscopy results. Ferrofluid samples with added organic materials maintained in suspension after centrifugation at 12.000 rpm. The analysis of these materials indicated satisfactory values of zeta potential (-20 mV), pH (7-7.5) and hydrodynamic volume (100-250 nm). In conclusion, the applied methodology made possible obtaining surfactaded stable ferrofluids based on stoichiometric NiZn ferrite, superparamagnetic at room temperature.

[06/11/06 - P029]
X-ray diffraction and Mossbauer spectrometry study of $Fe_{50}Al_{50}$, $Fe_{60}Al_{40}$, $Fe_{40}Al_{60}$, $Fe_{50}Al_{25}Co_{25}$, $Fe_{25}Al_{25}Co_{50}$ mechanical alloys., JUÁN DAVID ARBOLEDA JIMÉNEZ, , JOHANS RESTREPO CÁRDENAS, *Grupo de Estado Sólido - GES, Universidad de Antioquia, Medellín, Antioquia, Colombia,* CÉSAR AUGUSTO LA ROTTA RODRÍGUEZ, WILLIAM ALFONSO PACHECO SERRANO, *Grupo de Magnetismo e Interacciones Hiperfinas - MIH - Escuela de Física, Universidad Pedagógica y Tecnológica de Colombia - UPTC, Tunja, Boyacá, Colombia* ■Nanostructured alloys have great potential as soft magnetic materials. In particular, nanocrystalline Fe-Co based alloys are believed to be good candidates for imparting improved magnetic behavior in terms of higher permeability, lower coercivity, reduced hysteresis losses and higher Curie temperatures. The other hand, Fe-Al based alloys have a great potential for structural applications at high temperatures as they possess an outstanding high - temperature corrosion resistance and they have a lower density compared to other iron - base materials such as cast iron and stainless steels. In view of their melting temperatures, which have range between 1200 °C and 1400 °C,Fe-Al based alloys may be used for structural applications up to service temperatures of 1000 °C. As strength and creep resistence are still insufficient at these high temperatures further alloy development is needed to improve these properties [1]. It represents an actual basic research goal, where nanostructural processes can give special findings. Mechanical alloy powders of FeAl and FeAlCo by planetary milling

ball technique were sinthesized. The ratio of the weight of the balls to the weight of the powder was about 10 to 1. Several different grinding times were considered ranging from 30 min to 6 hours. Samples were structurally characterized by means of high resolution X-ray diffraction and Rietveld analysis. Hence, information regarding the mean grain size, lattice parameters, phase distribution and microstrain, were obtained. On the other hand, the nuclear properties were obtained by means of ^{57}Fe transmission Mossbauer spectrscopy at room temperature. Both, the structural and the different hyperfine parameters were correlated in order to elucidate the influence of the micro and nanostructural properties upon the hyperfine properties.

[1] M. Palm, Intermetallics, V. 13, Issue 12, 12 (2005), pages 1286 - 1295, Published by Elsevier Ltd

[06/11/06 - P030]
Magnetic Properties of Ferrihydrite Nanoparticles with Diameter d=1.4 nm, César Augusto La Rotta Rodríguez, William Alfonso Pacheco Serrano, *Grupo de Magnetismo e Interacciones Hiperfinas - MIH - Escuela de Física, Universidad Pedagógica y Tecnológica de Colombia - UPTC, Tunja, Boyacá, Colombia* ■

[06/11/06 - P031]
Synthesis and characterization of CoFe$_2$O$_4$ nanoparticles using a combustion method, André Ben-Hur da Silva Figueiredo, , Ronaldo Sergio de Biasi, *IME - RJ - Brazil,* Antonio Alberto Ribeiro Fernandes, Carlos Larica, *UFES - ES - Brazil* ■Ferrite nanoparticles have been recently investigated by many researchers because they have interesting magnetic properties, such as superparamagnetic relaxation and magnetoelectric transport, as well as a good potential for application in areas such as high-density data storage, magnetocaloric refrigeration, magnetic resonance imaging and magnetic drug delivery. Among them, cobalt ferrite has attracted considerable attention due to its large magnetocrystalline anisotropy, high coercivity, large magnetostrictive coefficient, chemical stability and mechanical hardness. In recent years, several methods to prepare nanoparticles of cobalt ferrite have been proposed, such as sonochemical reactions, sol-gel techniques, microwave plasmas, microemulsions and coprecipitation. Most of these methods, however, are not suitable for large scale applications, since they require expensive and time-consuming processing steps. The combustion method seems to be a good alternative, because it is fast and relatively inexpensive. Is this work, CoFe2O4 nanoparticles were prepared using the homogeneous combustion method and characterized by Mossbauer spectrometry and X-ray diffraction. CoFe2O4 nanoparticles were prepared by igniting a mixture of iron nitrate, cobalt nitrate and glycine. The Mossbauer spectra were obtained at different temperatures between 13 K and 180 K. At low temperatures, the material is completely ordered, but shows a relatively broad distribution of hyperfine fields that suggests the existence of nonequivalent Fe sites and thus random occupancy of cationic sites by Fe and Co ions. When the temperature increases, the particles become superparamagnetic, with a broad transition between 100 and

150 K. X-ray diffraction patterns, obtained at room temperature, confirm the fact that the particles are in the nanosize range and provide an independent estimate of the average particle size.

T4-Chemical applications: electronic structures, bounds, etc

[06/11/06 - P032]
Mössbauer Studies of the Dynamics of Hexaferrocenylbenzene vis-à-vis Ferrocene, J. Fitzpatrick, , A. Khasanov, J. Stevens, A. Nath, *UNCA Mossbauer Research Group, University of North Carolina at Asheville, Asheville, NC 28804*, P. W. Leonard and P. Volhardt, *Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720* ■In hexaferrocenylbenzene, six ferrocene molecules are attached to the benzene ring in an interesting configuration. We are making a comparative Mössbauer study of the two compounds, namely hexaferrocenylbenzene and ferrocene . The basic goals of our studies are threefold. First, we want to learn about the electronic communication between the cyclpentadienyl and the benzene rings. Secondly, we would like to detect any distortion of the cyclopentadienyl rings due to steric hindrances,. Thirdly and most importantly, we would like to find out whether the rings are floppy or rigid. We find that the isomer shift of hexaferrocenylbenzene is larger than that of ferrocene. It suggests that the electron density in the d-shell is higher than that for ferrocene presumably due to the ?-electrons from the benzene ring being delocalized over cyclopentadienyl rings. This observation may help to decide between the merits of the different electronic structural models proposed for ferrocene, in the literature. If the rings in the hexaferrocenylbenzene molecule are rigid,then one would expect a larger fraction of recoil-free events as compared to that for ferrocene. Very interestingly, our observations show clearly, that the hexaferrocenylbenzene molecule is very much more floppy than that of the ferrocene, which would result in a lower Mössbauer Debye temperature. The stereochemistry of the molecule allows considerable oscillation of the cyclopentadienyl rings. It is reasonable to assume that the intermolecular interactions in the molecular crystals cannot contribute to a very large difference in the Mössbauer effect, namely a factor of about three. Detailed Mössbauer studies at different temperatures will give an insight into the nature of the floppiness of the molecule.

[06/11/06 - P033]
MÖSSBAUER SPECTRA MODELING, A. Amulevicius, K. Mazeika, V. Remeikis, and A. Undzenas, *Institute of Physics, Savanoriu 231, LT-02300, Vilnius* ■The electron transfer in iron phthalocyanine and related molecular crystals has been studied in the temperature range 100 – 350K. The Mössbauer spectra can be best described by three doublets whose population and line halfwidth depend on the measurement temperature. The parameters of two doublets correspond to those of Fe^{2+} and Fe^{3+} ions, however the values of the third doublet are intermediate ones. They were assigned to the virtual $Fe^{2.5+}$ ionic state that is caused by the electron

transfer between the central iron ion and the surrounding ligand ring. At some ratio of the measurement duration and the transfer time, the separate spectra of Fe^{2+} and Fe^{3+} ions become a resultant one whose Mössbauer parameters (isomeric shift and quadrupole splitting) are averaged. The real values of parameters depend on the population of ionic states. We made use of the model describing the spectra of magnetic moment relaxation [1] and modified it. Sharp changes of spectral lines are caused by the electron transfer and the alteration of the iron ionic state from Fe^{2+} to Fe^{3+} and back in time. The doublet with large quadruopole splitting of Fe^{2+} transforms to doublet with small quadruopole splitting of Fe^{3+}. We obtained the model spectra reflecting the dependence of changes in the spectrum shape and line half-width on the transfer time and population of ionic states. The superposition of Fe^{2+} and Fe^{3+} spectra, as well as the transition into the virtual $Fe^{2.5+}$ ionic state occur when the electron transfer time τ varies from 10^{-7} s to 10^{-9} s.

[1] D.H. Jones and K.K.P. Srivastava: "Many-state relaxation model for the Mössbauer spectra of superparamagnets", Phys. Rev. B, Vol. 34 (1986), pp.7542-7548.

[06/11/06 - P034]

Synthesis, Characterization and Mössbauer Studies of Mixed Ligand Complexes of Iron (III) with 2-9-Dimethyl-1,10 Phenantroline (DMP) and Inorganic Ligands,

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■Methyl substituents in the 2,9 positions of 1,10-phenanthroline create a steric hindrance, which limits the extent of coordination to Fe(III) (tris complexes form) and restricts the number of possible geometries. The two solid forms, green (moist) and maroon (dry), which are obtained with the ligand 2,9-dimethyl-1,10-phenanthroline have been studied briefly. It is suggested that five- and four-coordinate geometries, respectively, differing by a coordinated H_2O, are relevant. Electron-transfer reactions involving the Fe(II)-Fe(II) couple are unusual in that, for simple complexes at least, the two oxidation states differ either in coordination number and/or stereochemistry. Because of the extensive reorganization requirements attendant on electron-transfer, inner sphere mechanisms are generally preferred. Mössbauer spectroscopy is a versatile technique that can be used to provide information in many areas of science such as Physics, Chemistry, Biology and Metallurgy. It can give very precise information about the chemical, structural, magnetic and time-dependent properties of a material. Six complexes of iron (III) were prepared and characterized by elemental analysis, IR and Mössbauer spectroscopy: [1] $(H_3O)_2(dmp)_2Cl_6O$, [2] $Fe(dmp)Cl_3 2H_2O$, [3] $Fe(dmp)_2(NO_3)_3 3H_2O$, [4] $Fe(dmp)(HC_2O_4)Cl_2$, [5] $Fe(dmp)_2(HC_2O_4)_3.2H_2$, and [6] $Fe(dmp)_2(NCS)_3$. Infrared spectral data indicates the existence of Fe-O-Fe bridge in samples [1] and [2], and coordination of Cl^- to iron as monodentate or bidentate bridge in [1], and [2], and coordination NO_3^- and $HC_2O_4^-$ in [4] and [5], respectively. Magnetic moment $\mu_{eff}/Fe(III)$ data indicate the existence of antiferromagnetic coupling in compounds [1]-[4] and [6]. Magnetic moment data and Mössbauer spectral results, both at room temperature and liquid nitrogen temperature, are indicative of the existence of binuclear complexes involving $Fe - O - Fe$, $Fe - Cl - Fe$ and $Fe - HC_2O_4 - Fe$ and $Fe - NCS - Fe$ bridges.

[06/11/06 - P035]
Artificial muscles of the Polyacrylonitrile studied by Mössbauer spectroscopy, Adilson Ribeiro Prado, Eloi Alves da Silva Filho, Gisele Martins Fidelis, *Departamento de Química - UFES*, Luiz Carlos Pimentel de Almeida, *Departamento de Química - UENF*, Evaristo Nunes Filho, Jair Carlos Checon de Freitas, Alfredo Gonçalves Cunha, *Departamento de Física - UFES*, Hans-Jorg Andreas Schneebeli, *Centro Tecnologico - UFES* ■The artificial muscles of the Polyacrylonitrile (PAN) fibers doped with $FeCl_3$ were studied by the application of Mössbauer, FTIR spectroscopy, X-ray, DSC, TGA, viscosity and electric conductivity. The Polymerization of acrylonitrile (AC) to Polyacrylonitrile was synthesized with 3 mL of acrylonitrile and 0.5 wt of benzoyl peroxide as polymerization initiator that were intensively mixed using water as solvent.

The product was then heated in a closed flask at 60 °C for 24 h to polymerize the AN. The viscosity-average molecular weight of the PAN was found to be 44000 g/mol in agreement with the literature. The PAN fibers were doped by soaking them in range of 5 wt aqueous solution of $FeCl_3$ for 3 h and doping level was evaluated by Mössbauer spectroscopy confirmed that doped of PAN with $FeCl_3$ shows a quadrupole splitting. X-ray shows differences can be observed between the PAN samples without doped and doped with $FeCl_3$. First of all, an intense peak at 0.5 nm

The thermal gravimetric analysis (TGA) of PAN samples pure and doped with 5 wt of ferric chloride shows that occur a mass loss at around 276 °C and 357 °C respectively. The FTIR spectrum of PAN revealed absorption frequencies at 2920 cm^{-1}(C-H streching) and 2244 cm^{-1} (N-H bending and C=N streching) that is characteristic of the polyacrylonitrile fibers. The results of the present experiments reveal that PAN samples pure and doped with 5 wt. of $FeCl_3$ during its synthesis is partially crystalline. This study of PAN fibers indicate that doping with ferric chloride were very important to characterization of this polymer that exhibits a greater potential for application as linear actuators and artificial muscles.

T5-Corrosion and environments

[06/11/06 - P036]
ON THE FORMATION OF AKAGANEITE IN THE PRESENCE OF Al, Cr, Cu, Ti IONS AND UREA., Karen Edilma García, , *Instituto de Química, Universidad de Antioquia, Medellín, Colombia*, Cesar Augusto Barrero, Alvaro Luis Morales, *Instituto de Física, Universidad de Antioquia,*

Medellín, Colombia., JEAN MARC GRENECHE, *Université du Maine, Le Mans, France.* ■This work deals with the influence of Al, Cr, Cu and Ti ions on the formation of akaganeite when is obtained from hydrolysis of FeCl3 solutions. In the case of Al ions, we have also added urea to modify the pH values and to increase the Al concentration in the solution. XRD, FTIR and Mössbauer spectrometry show that akaganeite is the only phase being formed, i.e. they do not promote the formation of another phase. Very small differences in some of the crystallographic parameters for samples obtained in the presence of Cr and Cu ions were observed. In addition, the Mössbauer parameters and infrared absorption bands are not appreciably affected. Because the physical properties of the akaganeites prepared by hydrolysis are not significantly affected by the presence of those cations, one concluded that only a very small amount of these cations entered into the structure. At low concentrations (less than 10 mol %), Al does not affect the physical properties of akaganeite in an appreciable way. However at 30 mol %, its presence is able to reduce the average grain size of the final products. Among the cations studied, Ti is the one that most drastically affects the physical properties of the akagenites: its presence originates a decrease of the particle size, a reduction of the unit cell parameters and favors the presence of defects into the crystallographic structure. The presence of urea does not help to incorporate in an appreciable amount the Al into the akaganeite structure, at least in the present concentration range, but gives rise to ultrafine crystalline grain. The present results imply that in the design of a steel meant to alter the properties or even to inhibit the akaganeite formation, Al, Cr, and Cu are not the appropriate metallic cations.

[06/11/06 - P037]

ON THE RUST PRODUCTS FORMED ON WEATHERING AND CARBON STEELS EXPOSED TO CHLORIDE IN DRY-WET CYCLICAL PROCESSES,

KAREN EDILMA GARCÍA, , CESAR AUGUSTO BARRERO, ALVARO LUIS MORALES, *Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, Colombia*, JEAN MARC GRENECHE, *Université du Maine, Le Mans, France.* ■In this work, the adherent (AR) and non-adherent (NAR) rusts formed on weathering (WS) and carbon (CS) steels exposed to drying-wetting cycles in solutions containing various chloride concentrations were studied using different characterization techniques. Special emphasis is given to the methodology of analysis of the experimental data using variable temperature Mössbauer spectrometry and X-ray diffraction. The NAR for both steels and all chloride concentrations are composed of lepidocrocite (L), goethite (G), hematite (H), and traces of akaganeite (A), independent of the investigated exposure times and chloride concentrations. H is probably formed via the transformation of L, G or A in the solution. The scraped and hit AR were composed of L, S, G and A. Several differences in the crystallographic structure, microstructure, relative amounts, physical and chemical properties of the iron oxides present in the different rust on both steels were evidenced. The spinel phase was only observed in the AR, whereas H was only observed in the NAR. A was present in the AR but only traces were found in the NAR. We have also calculated the amount of iron coming from both steels that converts into AR, NAR and that is loss for the different chloride concentrations. Our results suggest that the perfect conversion of corroded iron into AR is never equal to one in chloride rich environments. In fact, there is an appreciably amount of iron that is lost and other part that it is converted into NAR. The results described here give keys about the possible corrosion mechanism driving the corrosion process at high concentrations of chlorides. Indications are also given about the necessity of including rust composition in mathematical models describing corrosion processes. These results are important to understand and assess the behaviour of WS and CS at high levels of chlorides.

[06/11/06 - P038]

Highly reactive Fe^0/Fe_3O_4 composites: potential application for the reduction of Cr(VI) toxic environmental contaminants,

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■Chromium is a groundwater contaminant, being widely used for electroplating, leather tanning and corrosion protection. In water, oxidizing Cr(VI)-containing species are highly mobile, exerting hazardous effects on biological systems. In this work, the effectiveness of Fe^0/Fe_3O_4 composites on Cr(VI) removal was studied. The composites were characterized with powder XRD, SEM, transmission and conversion electron Mössbauer spectroscopy (CEMS) at room temperature. The chemical reduction assays were performed by using initial solutions of 100 ppm of Cr and a solid/solution ratio of $24gL^{-1}$. The composite Fe^0/Fe_3O_4 1/3 was found to be the most efficient (70% of Cr(VI) removed in 3 h). The pure Fe_3O_4 was less active (25%) and Fe^0 alone presented the lowest performance (16%). The alloying process promoted a strong interaction between the powders of Fe^0 and Fe_3O_4, as it could be confirmed by comparing the Cr(VI) removal efficiency of the composite and the individually milled and mixed powders. The former was much more efficient on the Cr(VI) removal (65% of removal in 3 h) than the latter (5%). The transmission Mössbauer spectrum of the composite confirmed the co-existence of magnetite and elemental iron. On the other hand, when the same composite was analyzed by CEMS, no signal of Fe^0 was observed in the spectrum. Preliminary results indicate that the pH is a determining factor on the total Cr(VI) removal, instead of the passivation of the composite surface. The high activity of the composite on the Cr(VI) removal can be understood in terms of the presence of donors of electrons as Fe^{2+} and Fe^0 in the original solids and of electron transference from Fe^0 in the more internal part of the composite to the Fe^{3+} in the surface, leading to the formation of reactive Fe^{2+} on the surface of composite.

[06/11/06 - P039]
Plasma nitriding of ASTM F138 biomaterial - Corrosion study, SYLVIO DIONYSIO DE SOUZA*, , MARISTELA OLZON-DIONYSIO, *DF-UFSCar-SP-Brazil,* RODRIGO BASSO, *UNICAMP-SP-Brazil,* SOLANGE DE SOUZA, *IQ-USP-SC-SP-Brazil* ■ The practice of using metals and alloys to repair or replace human body parts is now well established. Two of the most important parameters in determining the suitability of a material for biomedical applications are its biocompatibility and corrosion resistance. Materials such as stainless steels, like as ASTM F138, are used despite their poorer corrosion resistance, occasionally with undesirable consequences. Nitriding is nowadays a good solution for improving tribological properties, such as surface hardness and corrosion resistance of austenitic stainless steels, because a metastable phase with a large nitrogen concentration is formed. This phase, known as supersaturate or expanded austenite gamma N has proved to have higher hardness and higher pitting corrosion resistance, in comparison with the untreated material . In this work we show some interesting results obtained for ASTM F138 stainless steel nitreded at several conditions. Direct current (DC) plasma at 400 oC in a mixture of 80 percent H2 - 20 percent N2 was used to nitride samples F138 stainless steels with treatment times varying between 1h and 7h. Conversion Electron Mössbauer Spectroscopy (CEMS), Corrosion tests, X-Ray Diffraction (XRD) and Scan Electron Microscopy (SEM), were used as analytical techniques. A modified layer of about 8 micrometer was observed for all the nitrided samples, independently of the nitriding time. The results indicate that the gamma N is correlated with Fe4N phase. If the gamma N fraction decreases, the Fe4N fraction increases. The gamma N magnetic nature was analyzed. When the nitriding time increases, the results indicate that there is a significant reduction in the relative fraction of the magnetic phase. On the contrary, the paramagnetic phase increases.

[06/11/06 - P040]
Rust formed on cannons of XVIII century under two environment conditions, A. CAYTUERO, E. M. BAGGIO SAITOVITCH, *CBPF,* M. P. CINDRA FONSECA, *UFF - Universidade Federal Fluminense, PGMEC,* I. N. BASTOS, *IPRJ - Instituto Politécnico do Rio de Janeiro / UERJ, Nova Friburgo-RJ, Brazil* ■Metals exposed to atmosphere may represent a high risk for costs to our society when they no longer present the design properties of aesthetic, security and functionality due to corrosion. Thus, only the understanding the formation mechanism of these rusts allows the development and use of effective methods to minimize this metallic degradation. For reaching this aim the physical characterization of naturally formed rusts of ancient ferrous artefact is an essential step. The scientific study of ferrous objects allows to determinate the phases that reduce corrosion, give the corrosion rate for long-term exposure of steels, and show procedures to stabilize ancient artefact surface from a conservational perspective. The corrosion products (goethite α-FeOOH, akaganeite β-FeOOH, lepidocrocite γ-FeOOH, magnetite Fe_3O_4 and also amorphous and

non-stoichiometric phases) of two ancient cannons exposed to atmospheric corrosion were analysed by X-ray powder diffraction, transmission Mössbauer spectroscopy and scanning electron microscopy-SEM. After almost three centuries exposed in marine environment one of them was moved to a rural region and was maintained in this environment for approximately 30 years. The inland region has an altitude of 1000 m above sea level and consequently low aggressiveness. The studied rusts were obtained from external and internal surfaces of the cannon barrels. This investigation, using three different techniques, was done to check if the relatively short time (ca. 30 years) in rural area was sufficient to change the characteristics of the thick rust formed during long time exposure (ca. 300 years) in marine atmosphere. The time-environment effects change the physical nature of rust, mainly observed by Mössbauer spectroscopy results.

T6-Experimental techniques and data analysis

[06/11/06 - P041]
Multipurpose Spectrometer for Depth Selective Investigation of Surface, <u>SOBIR IRKAEV</u>, VALENTIN SEMENOV, VITALIY PANCHUCK, *IAI Russia - SPSU Russia* ■An automated multipurpose spectrometer intended for depth selective investigation of phase, elemental and physical and chemical properties of the surface and bulk of condensed matter is presented. The optical scheme of the multifunctional spectrometer TERLAB realizes the capabilities of Mossbauer and X-ray florescence spectroscopy at normal and grazing incidence angles [1,2,3]. The spectrometer also allows measurement in X-ray reflectivity and X-ray and Mossbauer standing waves modes. The spectrometer, allows one to define depth selective physical and chemical properties of the surface and bulk, such as, for example a phase state, parameters of hyperfine electric and magnetic interactions, electron density, a nuclear susceptibility and their depth distribution (Mossbauer and Grazing Incidence Mossbauer Spectroscopy mode); the roughness of the surface or interfaces, thickness of layers in thin films and artificial multilayer structures, electron susceptibility profiles on the surface and inside a layer (X-ray Reflectometry mode); element composition and its change with depth (X-ray fluorescence spectroscopy mode); crystal structure of a substance, the sizes of an elementary cell, phase properties, defects of crystal structure, the sizes of particles (X-ray diffraction mode). Experimental data obtained on the spectrometer TERLAB allow adding data obtained by other analytical methods (mass spectrometry, ESCA, Auger spectroscopy) to the data on microphase, structural and magnetic properties, and also surface roughness, density and thickness.

1. Stoev K.N., Sakurai K., Spectrochimica Acta, Part B, 54, 41 (1999). 2. Irkaev S.M., Andreeva M.A., Semenov V.G. et al., Nucl. Instr. Meth., B74, 545(1993), ibid., B103, 351(2005). 3. Klockenkamper R., Total -reflection X-ray fluorescence analysis., Wiley, 1997, pp 245.

[06/11/06 - P042]
Methodological Problems of Mossbauer Spectroscopy Applied to Quantitative Analysis, VALENTIN SEMENOV, SOBIR IRKAEV, *Institute for Analytical Instrumentations RAS, Saint Petersburg, Russia,* VITALIY PANCHUCK, VLADIMIR VOLODIN, *St.Petersburg State University, Saint Petersburg, Russia* ■The Mossbauer spectroscopy technique belongs to few methods of defining the phase state of a substance. The Mossbauer spectra bear information on various hyperfine interactions, many of which are indirectly related to the chemical nature of the Mossbauer atom and its nearest environment. Determination of parameters of hyperfine interaction that can be extracted from Mossbauer spectra and used for qualitative analysis is a routine task. The nice description the most important parameters are given in excellent review [1] and [2]. However the most difficult are analytical tasks when it is required to define absolute quantities of phases in a multiphase system. Quantitative analysis is based on the assumption that the area under a lines in the partial subspectra proportional to the number of atoms containing Mossbauer nuclei in the same microenvironment. We studied the influence of various factors on experimental errors encountered in defining the phase composition of the substance under study. Such as measurements geometry, Lamb - Mossbauer coefficients, absorber thickness, efficiency and dead time of the detection system and spectral line shape. Experimental data are presented for phase analysis of siliceous ferrous metalore. Carbonylic iron 1-100 nm and 30 mkm particle diameter), sodium nitroprusside $Na_2[Fe(CO)_5NO]_2H_2O$ and yellow potassium prusside $K_4Fe(CO)_6$ are used as calibration samples. The obtained results are compared with the chemical analysis data. Fe(II) and combined iron were determined by redox titration with preliminary decomposition of the sample.

1. E.Kuzmann, S.Nagy, A.Vertes. Pure Appl.Chem., (2003), V.75, No. 6, pp. 801-858 2. E.Kuzmann, S.Nagy, A.Vertes. In Chemical Analysis by Nuclear Methods, (1994), Wiley, New York.

[06/11/06 - P043]
Design and Construction of a Velocity Transducer and a Sample Change System for Mössbauer Spectroscopy, A.A. VELÁSQUEZ, J. RESTREPO VÉLEZ, J.A. OTÁLORA AND J.TOBÓN, *Universidad de Antioquia, Instituto de Física - Universidad de Antioquia, Instituto de Física - Universidad de Antioquia, Instituto de Física-Universidad de Antioquia, Instituto de Física* ■A low cost velocity transducer as well as a system for automatic change of the samples in a Mössbauer spectrometer has been designed and built. Both systems include very simple components, which can be implemented in any Mössbauer laboratory. The velocity transducer is an electromechanical oscillator, built mainly with two permanent magnets, two coils and two acetate membranes which operate as springs. The system for sample change is based on a step motor, which rotates a disk in whose border are placed four samples uniformly spaced. Once a Mössbauer spectra acquisition finishes, the step motor rotates the next sample to the position between the radioactive source and the

detection system, to perform a new spectra acquisition. The sample change system is useful specially when the operator of the spectrometer is absent from the laboratory. In this manner the radioactive source can be used, for example, during nocturnal hours and vacation periods, and the spectrometer can be used more efficiently. On the other hand, the exposition of the users of the spectrometer to the radioactive sources can be reduced to one fourth part. The frequency of the velocity transducer motion as well as the sequence of the sample positioning can be programmed by software. The system includes a graphic interface made in LabVIEW software, which allows to the user make supervision and control of the Mössbauer spectrometer from remote places. The system has been tested with several samples, giving satisfactory results. Mössbauer spectra obtained with samples of a-Fe and analytic grade a-Fe2O3 are here presented.

[06/11/06 - P044]
Mössbauer Magnetic Scans technique development, GUSTAVO A. PASQUEVICH, , PEDRO MENDOZA ZÉLIS, MARCELA FERNANDEZ VAN RAAP, ALEJANDRO VEIGA, NOLBERTO MARTINEZ, <u>FRANCISCO SÁNCHEZ</u>, *Departamento de Física, Fac. Cs. Exactas, Universidad Nacional de La Plata* ■In this work the experimental set-up and data analysis procedures for Mössbauer Magnetic Scans (MMS) technique are discussed. The MMS are obtained by measuring the Mossbauer transmission at a fixed Doppler energy while the sample is subjected to an a.c. external magnetic field, recording the Mössbauer transmission versus applied magnetic field. From these scans, information on magnetic hysteresis mechanisms could be retrieved.

The first work [Phys B, 384 (2006) 348] dealing with MMS technique was devoted to the study of 20 μm NANOPERM ribbons. In that work the feasibility of the technique was demonstrated for field frequencies between 0.001 and 200 Hz. The experimental results suggested that for data analysis the effect of saturation and polarization absorption phenomena should be taken into account. To elucidate how the underlying physics can be uncovered, simpler systems were chosen: a sputtered film with a thickness lower than 1 μm and a 12 μm sheet, both of α-Fe. The dependence of the spectral lines relative absorption with an a.c. magnetic field (Hmax= 6.3 kA/m) parallel to the sample and perpendicular to the gamma ray was determined.

For the film, the line intensities magnetic field dependence was in agreement with the thin absorber approximation predictions. In this case, the magnetic moments orientation dependence on the magnetic field could be modeled.

For the analysis of the sheet results, it was necessary to use the exact expression for the Mössbauer absorption.

We conclude that the MMS technique allows the study of magnetic hysteresis mechanisms. With available analysis procedures, quantitative information can be retrieved in the case of thin absorbers, while for thick ones, data analysis using the Mossbauer absorption exact expression is under progress. We expect this technique be useful to study the different dynamic responses of iron moments at particular structural sites in more complex samples.

T7-Magnetism and magnetic materials

[06/11/06 - P045]
The investigation of non-collinear magnetic structures by angle dependent Mossbauer spectroscopy, Valentin Semenov, Sobir Irkaev, *Institute for Analytical Instrumentations RAS, Saint-Petersburg, Russia*, Valerii Uzdin, Vitalii Panchuk, *Saint-Petersburg State University, Saint-Petersburg, Russia* ■Non-collinear magnetism is quite general phenomenon, which was detected in a number of low-dimensional systems. It is usually connected with the competition of several interactions and with the existence of different metastable states close in energy. If iron is used as magnetic material in non-collinear magnetic structures, magnetic texture can be derived from an analysis of Mossbauer spectra measured for different orientation of radiation beam relative to the crystallographic axes of the sample [1]. For this purpose we developed setup, which allows performing the measurements for different beam incidence angle in the temperature range from the liquid nitrogen till the room temperatures. External magnetic field can be introduced into the system via proximity of 2 permanent magnets placed on the varied distance from the sample. Increase of resonant absorption of radiation by subsurface atoms at low temperature ensures high sensitivity of the method. Examples of Mossbauer spectra and their evolution with temperature and magnetic field will be presented. For the interpretation of Mossbauer data we suggested the theoretical approach, which includes modelling of the epitaxial growth with subsequent self-consistent calculations of magnetic moments localized at each atomic site within the framework of vector Anderson model [2]. Self-consistent calculations are performed for the system in external local magnetic field [3]. It makes possible to separate particular non-collinear state from the set of self-consistent solutions and to trace the evolution of non-collinear ordering with external magnetic field. Calculated distributions of magnetic moments are compared with hyperfine field distributions extracted from the Mossbauer spectra. This work was partially supported by RFBR (Grants 06-02-16722) 1. V.V. Panchuck, V.G. Semenov, V.M. Uzdin Hyperfine Interactions 156/157 (2004) 643 2. V.M. Uzdin, N.S. Yartseva, Comp. Mat. Sci., 10 (1998) 211 3. V.M. Uzdin, C. Demangeat, J. Phys.: Condens. Matter 18 (2006) 2717

[06/11/06 - P046]
On the effect of nanocrystallization and disorder on the magnetic properties of Cu-rich, FeMnCu alloys, S. J. Stewart, , *Departamento de Física, Facultad de Ciencias Exactas, UNLP, IFLP-CONICET C.C.N? 67, 1900 La Plata, Argentina*, J. F. Marco, J.R. Gancedo, *Instituto de Química-Física “Rocasolano*, P. Crespo, J. J. Romero, A. Martínez, A. Hernando, *Instituto de Magnetismo Aplicado - UCM, P.O. Box 155, 28230 Las Rozas (Madrid), Spain*, F.J. Palomares, *Instituto de Ciencia de Materiales de Ma-*

drid, CSIC, C/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain, J. M. GONZÁLEZ, *Unidad Asociada ICMM-IMA, C/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain, and P.O. Box 155, 28230 Las Rozas (Madrid), Spain* ■We report on the temperature dependencies of the Mössbauer spectra and the AC magnetic susceptibility measured in Cu-rich, FeMnCu samples. The samples were prepared by mechanical alloying using, on the one side, Cu and prealloyed FeMn powders and, on the other, Cu, Mn and Fe pure elemental powders. From the correlation of the Mössbauer spectra and the AC susceptibility data we propose a rough description of the spatial phase distribution present in the synthesized materials. Those distributions are a consequence of both the nanostructure induced upon milling and of the different signs of the Mn/Cu and Fe/Cu enthalpies of mixing (negative and positive, respectively. Those distributions are significantly different in the samples prepared from different precursors. So, the material prepared by alloying Cu and pre-alloyed FeMn powders are composed of grains having a core/shell structure in which the inner region corresponds to a Fe rich, FeMnCu alloy and the outer one to a FeMnCu one which is probably richer in Cu. In both regions local MnCu and (smaller in size and number) FeCu clusters could be present. The Mn diffusion out from the precursor FeMn grain should originate a significant amount of MnCu alloy regions (located in the precursor Cu grains) whereas the minority diffusion of the Fe atoms should result on isolated Fe atoms embedded into the Cu grains. In the materials prepared from Fe, Mn and Cu pure elemental powders the Fe atoms should be present essentially outside the Cu and Mn grains, either at the Cu and Mn grain boundaries (where, consequently, FeMnCu and/or FeCu clusters can be present) or at Fe-rich regions. The occurrence of some out-from-the-equilibrium diffusion could make possible the presence of a minority percentage of isolated Fe atoms at the outermost region of the Cu grains.

[06/11/06 - P047]
Magnetically modified bentonite as a possible contrast agent in MRI: Mössbauer study, MIROSLAV MASHLAN*, , HELENA BARTONKOVA, IVO MEDRIK, DALIBOR JANCIK, RADEK ZBORIL, *Research Centre of Nanomaterials, Palacky University,,Svobody 26, 77146 Olomouc, Czech Republic* ■The role of magnetic resonance imaging (MRI) as important medical diagnostic method increases at last years. On the one hand, MRI shows a very good sensitivity to tissue differences. On the other hand MRI is an expensive, but risk-free procedure. Partially, the application of MRI in gastrointestinal tract is limited by various problems, including the necessity to use the oral contrast agents for the improvement of the image contrast. A composite of superparamagnetic iron oxide nanoparticles and mineral matrix, which can be used as an oral contrast agent for MRI of GI tract, has been synthesized. Magnetic modification of natural bentonite is two step process. First step is based on replacing original interlayer cations by iron (II) cations and adsorption of another amount of these cations on the mineral surface. Second

step is their conversion to magnetic iron oxide, maghemite or magnetite. Nanoparticles of superparamagnetic magnetite or maghemite guarantee contrast effect and bentonite could act as inert matrix reducing absorption of iron and as an agent improving dispersion of iron oxide particles in whole volume. Both components are non-toxic and low-cost. A composite of iron oxide nanoparticles and mineral matrix has been studied by XRF analysis, X-ray diffraction, Mössbauer spectroscopy, transmission electron microscopy, nuclear magnetic resonance and magnetic resonance imaging. The optimal concentration of nanocomposite "iron oxide nanoparticles-bentonite", when the MRI signal is fully reduced, has been determined for using this composite as the negative oral contrast agent. Magnetite, superparamagnetic magnetite and interlayer Fe(II)have been identified by Mössbauer spectroscopy in the nanocomposite.

[06/11/06 - P048]
Mössbauer and Impedance Spectroscopy Studies of Zr_xTi_{1-x}-Doped Lithium Ferrites, IGOR F. VASCONCELOS, *Department of Metallurgy and Materials Science, Universidade Federal do Ceará, Brazil,* MARCELO ANTONIO SANTOS DA SILVA, JOSÉ AIRTON CAVALCANTE DE PAIVA, ANTÔNIO SÉRGIO BEZERRA SOMBRA, *Department of Physics, Universidade Federal do Ceará, Brazil* ■Among the various families of ferrites, the lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ has appealing electric and magnetic properties for microwave and memory core applications. It has also been shown that many physical properties of lithium ferrites are considerably stable in a wide range of temperatures. Nevertheless, their applications in microwave devices are considerably limited due to a few undesirable physical properties such as high dielectric and magnetic losses. Because of a number of factors that can affect the performance of microwave devices, lithium ferrites are heavily doped to optimize the properties of interest. Improvement of these properties can be attained by substituting lithium and iron ions by other elements like Ti, Co, Mn, Zn, and Bi. These substitutions are made without structural modifications with the ferrites keeping their original spinel structure. In this contribution, we present studies of the dielectric loss and thermal stability on Li ferrites doped with Zr and Ti. The ferrites were produced from commercial oxides in stoichiometric proportions using a regular furnace. The samples were then homogenized in a mechanical mill and annealed for 10 hours at 900°C. Structural and electrical properties were investigated using ^{57}Fe Mössbauer Spectroscopy, conventional X-Ray diffraction and a number of dielectric measurements. The results obtained indicate formation of lithium ferrites with substitution in the original spinel structure. It was also found that the aforementioned substitution of Li and Fe for other elements improved the dielectric properties suggesting a wider range of applications for these materials.

[06/11/06 - P049]
Fe Nanoparticles in Cd Films, P. MUNAYCO, J. LARREA J., Y. T. XING, E.M. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Físicas,* F.J.LITTERST, *Technical*

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■Films of Cd, with 0.5 and 1.5 at.% Fe, were prepared by vapor quenching technique deposition at low temperatures (20 K and 80K). The two metals were thermal evaporated from two Ta crucibles with independent deposition controlling. Since Fe is immiscible with Cd in the whole composition range of the equilibrium phase diagram, precipitation occurs by warming up leading to Fe nanoparticles dispersed in Cd non magnetic metallic host. The nanoparticles size depends on the host and thermal treatment. The films are initially characterized by *in-situ* ^{57}Fe Mössbauer spectroscopy showing isolated Fe atoms in Cd hosts as well as some other components assigned to Fe clusters. At 300 K, all isolated Fe atoms in the Cd host diffuse and form clusters. The magnetic properties were studied using SQUID magnetization combined with Mössbauer spectroscopy in a variable temperature and in applied external magnetic field ^{4}He cryostat with a built-in superconducting magnet ($B \leq 7$ T). Spectra above the blocking temperatures (T_B ~10 K) allow estimating the moment and diameter of the Fe nanoparticles. The results show Fe nanoparticles with an average size ~ 0.6 nm. *In-situ*electrical resistance measurements on these films show resistance minima at T_K (T_K = 5 K for c = 0.5 at %) which disappear in an external magnetic field B_{ex} = 5 T and, therefore, are interpreted as Kondo minima.The samples with higher concentration of Fe (1.5 ~ 2 %) do not show this effect.The Mössbauer spectroscopy study also shows that there is some magnetic transition around 8 K.

[06/11/06 - P050]

Spin glass like behaviour in nanogranular FeMnCu samples,

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■Nanogranular magnetic materials have been received much attention in the last decade due to their rich phenomenology and intensively researched from the fundamental and technological point of view. Frustration of the exchange interactions, disorder and surface effects have been claimed to interpret their structural and magnetic properties. In order to get deeper insight into the nanoestructurated metallic systems, allowed powders of $(Fe_{79}Mn_{21})_{1-x}Cu_x$(x = 0.2, 0.25 and 0.3) were prepared by milling the elemental species in a horizontal vibrating device with steel ball and vial, under Ar atmosphere during 15 h at 33 Hz. A detailed analysis of structural aspects and magnetic properties has been obtained via Mössbauer spectroscopy (MS), X-ray diffraction (XRD) and magnetic measurements (AC-susceptibility, ZFC-FC: zero field cooling and field cooling and M vs H). The X- ray diffraction patterns indicate mainly the presence of the FCC phase. The Mössbauer spectra are characterized by broad lines that were fitted with three interactions: two single lines and a sextet. One of the paramagnetic interaction and the magnetic one have similar isomer shifts. This fact could be indicating grain size distributions in the sample, driving to different ordering temperatures as determined by the low temperature Mössbauer measurements. On the other hand, the AC-susceptibility curves show the existence of a characteristic temperature Tc ($\approx 150K$) which shifts to lower temperatures with increasing Cu content. These results, associated with magnetization measurements as function of temperature and applied field, provides strong evidence for a highly disordered magnetic system with spin-glass-like behavior.

[06/11/06 - P051]
Magnetic properties of Fe-doped TiO_2 and SnO_2 by wet chemical synthesis, A.F CABRERA, *Departamento de Física, Facultad de Ciencias Exactas UNLP, IFLP-CONICET, Argentina*, S. JACOBO, C. HERME, *Facultad de Ingeniería, Universidad Nacional de Buenos Aires, Argentina*, C.E. RODRÍGUEZ TORRES, F.H. SÁNCHEZ, *Departamento de Física, Facultad de Ciencias Exactas UNLP, IFLP-CONICET, Argentina* ■Oxide-based diluted magnetic semiconductors (O-DMS) have currently attracted much attention due to the reports of the room temperature ferromagnetism observed in TiO_2, ZnO, SnO_2 and Cu_2O doped with transition metals (V, Mn, Fe, Co, Ni, Cu). Much work has been focused on the study of these doped oxides thin films, however, the magnetic origin of the room-temperature magnetism is not clearly understood at the moment. Nowadays, there are controversial interpretations about the origin of magnetism. Some authors attribute the magnetic behavior to the presence of defects in the sample, like anion vacancies and/or surfaces and interfaces. In order to check the effect of interfaces we prepared bulk TiO_2 and SnO_2 (rutile phase) samples doped with iron by wet chemical synthesis. The samples with different Fe composition (between 6 and 25 at. %) were characterized using X-ray diffraction, Mössbauer spectroscopy and magnetic measurements. X-ray diffraction patterns show a good dilution of iron in the rutile phase for both systems. From the magnetic measurements, preliminary results indicate a paramagnetic behavior for low Fe concentration in the case of TiO_2 samples, while evidence of hematite phase was detected by Mössbauer spectroscopy for the higher (11 at. %) Fe concentration investigated. On other hand, all SnO_2 samples are mainly paramagnetic, but for the lower Fe concentration they also present a ferromagnetic-like component. In order to discuss the interfaces influence, these results will be compared with those reported in the literature for samples of nominally the same materials prepared in the form of thin films.

[06/11/06 - P052]
Magnetic and structural properties of nanostructured $Tb_{0.257-x}Nd_xFe_{0.743}$ alloys, with x=0 and 0.257, YEBRAYL ROJAS MARTÍNEZ, HUMBERTO BUSTOS RODRÍGUEZ, DAGOBERTO OYOLA LOZANO, *UNIVERSIDAD DEL TOLIMA*, GERMÁN ANTONIO PÉREZ ALCÁZAR, JUAN CARLOS PAZ, *UNIVERSIDAD DEL VALLE* ■The alloys between a metal of transition and a rare earth present magnetic and magneto optical properties of exceptional interest for the production of magnetic devices for the information storage [1]. In this work we report the magnetic and structural properties obtained by Mössbauer spectrometry and X-ray diffraction

of nanostructured $Tb_{0.257-x}$ Nd_x $Fe_{0.743}$ alloys with x =0 and 0.257 obtained by mechanical alloying. These alloys were obtained for the manufacture of targets in order to growth thin films with magneto-optical properties. The samples were milling during 12, 24 and 48 hours, to study the influence of the milling time in their magnetic and structural properties. The samples were investigated by means of transmission 57 Fe Mössbauer spectrometry. For all the times, the spectra were fitted by means of a sextet and a doublet associated to Fe and an amorphous iron-based phase, respectively. Structural and microstructural parameters were derived from high statistics X-ray patterns and discussed as a function of milling time. The X-rays results for all the samples indicate that they are amorphous with a tendency to be crystallized for milling times greater than 48 hours. Due to the preparation conditions method, the samples shown some mixing between the iron-terbium and iron-neodymium for x=0 and x=0.257 respectively, which appears as an amorphous phase by x-ray and a paramagnetic doublet obtained by Mössbauer spectrometry. With milling time the NdFe samples presents a bigger tendency to paramagnetic state.

Key words: Mössbauer spectrometry, mechanical alloying, X-rays, magnetooptical.

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[06/11/06 - P053]

Comparative study of magnetic and structural properties of the $Nd_2(Fe_{100-x}Nb_x)_{14}B$ system prepared by mechanical alloying and arc melting,

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[06/11/06 - P054]
Synthesis and Characterization of Magnetites in Presence of Cu2+, A.L. Morales, A.A.Velásquez, J.P. Urquijo, and E. Baggio-Saitovitch, *Universidad de Antioquia, Instituto de Física - Universidad de Antioquia, Instituto de Física - Universidad de Antioquia, Instituto de Física - CBPF* ■Samples of magnetite doped with Cu2+ divalent cations, Fe3-xCuxO4, where x = 0, 0.05 and 0.2, were synthetized hydrothermally. Temperature and oxidant concentration were controlled in the experiments. Samples were characterized by magnetic, structural as well as chemical analysis techniques, such as: Mössbauer spectroscopy (TMS), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Infrarred Transform (FTIR), SQUID magnetometry and Atomic Absorption Spectroscopy (AAS). Final products had concentrations of copper near to the nominal values used in the precursor solutions. A simultaneous reduction in: hyperfine magnetic interactions at the octahedral sites, Mössbauer factor, magnetisation parameters, particle size as well as a morphologic degradation of the magnetite particles were also observed as the Cu2+ concentration increases. Based on the diamagnetic nature of Cu2+ as well as its smaller ionic radius compared with that of Fe2+ ions, a possible incorporation of Cu2+ ions at the octahedral sites of magnetite, where that ions substitute a percentage of Fe2+ ions is suggested.

Key words: doped magnetites, divalent copper, Mössbauer Spectroscopy, magnetic and structural characterization.

1. Introduction

Magnetite is an iron oxide with many technological, industrial and biological applications such as: fabrication of magnetic tapes and sensors, pintures, contrast mean for clinical analysis, among others. In the field of corrosion magnetite may appear in the rust formed on steels exposed to enviroments with high chloride concentration and high relative humidity [1]. Several routes for chemical synthesis of magnetite, both pure as doped with magnetic and nonmagnetic cations have been proposed in order to study the behavior of the magnetic and structural properties of this iron oxide in different chemical enviroments.

[06/11/06 - P055]
57Fe Mossbauer spectroscopic and bulk magnetic study of the spinel system: CuAlxCrxFe 2-2xO4, Uday N. Trivedi*, , M. C. Chhantbar, H. J. Shah, K. B. Modi, H.H. Joshi and H.C.Verma2, *Department of Physics, Saurashtra University, Rajkot, 360 005, India.2Indian Institute of Technology, Kanpur, India* ■The spinel oxide system CuAlxCrxFe2-2xO4 with compositions x =0.0, 0.2,0.4, 0.6 and 0.8 was synthesized by double sintering ceramic techni-

que in two sets of specimen with different thermal history i.e. quenched and slow-cooled. The chemical stoichiometry of each specimen was checked through EDAX mapping. The X-ray diffraction patterns showed that all the samples were found to be single phase spinels having tetragonal structural deformation. It was found through the XRD intensity analysis that the CuFe2O4 has 90
Slow cooled (SC): (Cu2+0.1 Al3+0.6xFe3+0.9-0.6x)A [Cu0.92+Al3+0.4xCrx3+Fe3+1.1-1.4x]B O42-
Quenched (Q): (Cu2+0.1Al3+xFe3+0.9-x)A [Cu2+0.9 Cr 3+x Fe3+1.1-x]B O42-
The cation distribution for SC-samples shows partial occupancy of Al3+ for both A& B sites, which results in simultaneous site dilution. The variation of saturation magnetization is explained by Random Canting of Spins model. The Curie temperature (Tc) determined through thermal variation of AC susceptibility for all the samples showed that the Q-samples have much lower Tc than that of their slow-cooled counter parts indicating severe reduction in A-B superexchange magnetic linkages in Q-samples due to greater occupancy of non-magnetic Al3+ ions. The hyperfine interaction parameters were deduced through computer simulation of Mössbauer spectra. The Mössbauer spectra for the compositions x=0.2 and 0.6 Q- and SC- samples were analyzed and the hyperfine interaction parameters were refined using NORMOS computer software using nonlinear least squares minimization method. The 57Fe Mössbauer spectra recorded at room temperature shows the effect of dilution of A-B interaction (frustration) more in case of Q-samples compared to SC-samples. The Mössbauer studies of the samples reveal that the distribution of cations and therefore their bulk and microscopic properties are sensitive to the thermal history of the specimen which, in turn becomes a decisive factor for synthesizing the ferrites with desired properties.

[06/11/06 - P056]

Pyrochlores containing iron: Structural and Magnetic Characterization,

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■Pyrochlores are oxides with ideal formula $A_2B_2O_7$, where A is a rare earth and B is a transition metal ion. These compounds show magnetic frustration and, by this reason, have been objects of intensive studies in the last years. The literature does not report pyrochlores with only iron atoms occupying the B site. However, it is possible to prepare single phase systems containing iron combined to other metal or semi metal ion. In the present work, pyrochlores containing iron, such as A_2FeBO_7 (where A=Y, Ce, Gd, Eu, Sm and Dy; B= Sb, Ta and Nb) were synthesized by solid state reaction, from oxides precursors. The compounds were structurally and magnetically characterized by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements. The

X-ray diffraction analyses revealed that the crystallographic structures depend, fundamentally, on the type of B atom used in the synthesis. For antimony, the lattice remains cubic, with Fd3m symmetry, although for niobium and tantalum there are evidences of deviation from that symmetry. The Mössbauer spectroscopy studies reinforce the relative differences caused by the atom partner of the iron. The room temperature spectra show only one doublet, independent of the A atom, for antimony. Diversely, in the case of niobium and tantalum, the spectra reveal two doublets and one sextet, indicating that the iron occupies more than one different crystallographic site. Low temperature Mössbauer measurements revealed the superposition of magnetic patterns, regardless the B atom. The magnetic characterizations carried out at room temperature showed the presence of hysteresis loop for all pyrochlores samples. This hysteresis was not expected for pyrochlores where the iron ion does not have magnetic moment.

[06/11/06 - P057]
Synthesis, characterization and magnetic properties of NiFe2O4.SrFe12O19 nanocomposites prepared using aerosol route, Sonal Singhal and Kailash Chandra*, , *Department of Chemistry, Panjab University and Institute Instrumentation Centre, Indian Institute of Technology-Roorkee, Roorkee* ■Strontium ferrite with hexagonal structure is known for high performance permanent magnetic material, owing to its fairly large magnetocrystalline anisotropy, high Curie temperature and relatively large magnetization as well as excellent chemical stability. On the other hand nickel ferrite with inverse spinel crystal structure has been extensively used in many electronic devices because of their high permeability at high frequency, remarkably high electrical resistivity, chemical stability and reasonable cost. In this paper we report the synthesis of nano composites of these ferrites by aerosol route and their characterization by TEM, XRD, magnetic susceptibility and Mössbauer spectral studies. In order to prepare nano size composite of SrFe12O19 and NiFe2O4 ferrite, in different molar ratio, two solutions of 0.05 M concentration, one of strontium and iron nitrates and other of nickel and iron nitrates were prepared. These were further diluted in the desired molar ratio and passed through two separate nebulizers having same solution uptake. The aerosols of the two were passed through a common furnace maintained at 600 oC and these were collected on a Teflon coated metal pan. The elemental analysis of Ni, Sr and Fe using EPMA matches within ± 2Coercivity has been found to increase with concentration of strontium ferrite phase and annealing temperature due to the increase in crystallite size. Mössbauer spectrum of the as obtained sample at RT exhibited a doublet suggesting super paramagnetic nature. However, after annealing at 1000 oC this doublet is converted into magnetic sextets suggesting increase in particle size with annealing. These observations are in conformity with TEM and XRD results.

[06/11/06 - P058]

Mössbauer investigation of maghemite-based glicolic acid nanocomposite, JUDES G. SANTOS, LUCIENE B. SILVEIRA, *Fundação Universidade Federal de Rondônia, Departamento de Ciências Exatas e da Natureza, 78961-970, Ji-Paraná-RO, Brazil,* ANSELMO F. R. RODRIGUEZ, ADERBAL C. OLIVEIRA, BRUNO M. LACAVA AND PAULO C. MORAIS, *Universidade de Brasília, Instituto de Física, Núcleo de Física Aplicada, 70910-900, Brasília-DF, Brazil,* ANTONIO C. TEDESCO, *FFCLRP- USP, Universidade de São Paulo, 14040-903, Ribeirão Preto-SP, Brazil* ■In recent years the design and synthesis of biocompatible magnetic nanocomposite (BMNC) has attracted intense interest, with special emphasis on their applications in cell sorting, contrast agents for magnetic resonance imaging, diagnosis and cancer therapy, among others [1]. In the present study, glicolic acid-based micro-spheres were used as a template to host maghemite nanoparticles (average diameter of 6.6nm)obtanied from electron microscopy thus producing BMNC, in nanoparticle concentration.The X-ray data showed that the structure is maghemite. The BMNC sample were labelled, containing 1.4 10^{16} $particle/cm^3$ with molar concentration of 0.5 were synthetized. The BMNC were investigated using Mössbauer Spectroscopy (MS), following the standard experimental setup [2]. Measurements were realized in room temperature and liquid nitrogen. Typical Mössbauer spectra of the composite sample in room temperature and 77 K showed that the isomers shifts (0.37; 0.33) and (0.60; 0.45; 0.42) respectively. The transitions us levels isomerics shifted in Mössbauer spectra were curve-fitted with sextet and singlet the room temperature. The Mössbauer spectra at liquid nitrogen were curv-fitted using two sextet and one doublet. The resulted showed also that magnetic field is 396.14 Oe in room temperature and 505.84 Oe in liquid nitrogen, showing that the ions of the Fe^{2+} are distributed in octhaedral site probably.As expected from bulk maghemite crystal at 77 K and no expected at 300 K, is related to the oxi-hydroxy molecular layer builted up at the maghemite surface incapsulled during the nanoparticle synthesis. This work also show the temperature dependence of the total absorption area and discuss the effects of lattice vibrations.

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[06/11/06 - P059]

Mössbauer study of oriented FeO(100) ultra-thin films, GUILHERME JEAN PEREIRA DE ABREU, HANS-DIETER PFANNES, ROBERTO MAGALHÃES PANIAGO, *Universidade Federal de Minas Gerais* ■Iron oxide thin films, such as FeO, Fe_3O_4 and Fe_2O_3, are important in a several of scientific, technological and industrial applications and present a variety of physical and chemical properties. Some of their properties are already well known, however the study of these oxides as thin films can still reveal important physical properties. With the development of nanotechnology, the presence of nanoparticles in several technological systems and the miniaturization of electronic devices, it happens that the surface atoms play more and more important functions, because chemical reactions and the electric and magnetic interactions occur basically at the surfaces. Therefore it is important to study these materials by surface techniques, such as CEMS (*Conversion Electron Mössbauer Spectroscopy*), XPS (*X-ray Photoelectron Spectroscopy*) and LEED (*Low Energy Electron Diffraction*).

In the present investigation FeO ultra-thin films were prepared on a Ag(100) substrate, with the intention to obtain this phase oriented in the (100) direction. The motivation of the work is the lack of studies of the FeO phase as ultra-thin films. Besides, it is very well-known that it is very difficult to prepare FeO without the coexistence of Fe_3O_4. FeO crystallizes if in the NaCl cubic structure and it has a Néel temperature of 198K. The preparation was done in ultra-high-vacuum by evaporating ^{57}Fe pure in a low oxygen pressure. The films were analyzed *in-situ* by XPS in order to check the absence of contamination, as well as to verify the stequiometry of the sample. LEED was used to determine the orientation of the films and Mössbauer spectroscopy (CEMS) to check and to quantify the obtained phases (FeO, Fe_3O_4 and metallic iron). We established the best parameters to prepare films with a high concentration of FeO. Low temperature (100K) measurements were also performed to characterize the FeO antiferromagnetic phase.

[06/11/06 - P060]

Mössbauer Investigation of Magnetite Nanoparticles Incorporated in a Mesoporous Polymeric Template,

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■Iron oxide-based nanoparticles can be conveniently synthesized and maintained as stable single units using a variety of polymeric templates, though it is quite clear that the oxidation procedure, nature of polymer matrix, and polymer morphology strongly affect the chemical composition of the obtained nanoparticles. Mössbauer spectroscopy was used to investigate chemically cycled magnetite-based nanocomposites using mesoporous sulfonated styrene-divinylbenzene (Sty-DVB) copolymer as template. Six composite samples were prepared using the Sty-DVB template immersed in ferrous sulfate aqueous solution at 30 mmol/L. The preparation cycle follows a four step procedure. The mixture was first stirred for 1 h at room temperature. Second, the polymer particles were separated by filtration and washed thoroughly with water until no iron was detected in the eluent. Third, the oxidation of the ferrous ion was performed in alkaline medium following a standard recipe used in the synthesis of magnetite microcrystals from ferrous ion in aqueous solution. Fourth, obtained black composite was filtered, washed with water until the pH of the eluent was neutral, and dried at 60 Celsius. The described procedure was performed six times in order to obtain composite samples with increasing amount of magnetic material. Plots of hyperfine field and line-wide as a function of number of template chemical cycles were used to get information about the particle size. Besides supporting the amount of magnetic material incorporated in the polymeric template the Mössbauer parameters also indicate changes on the average nanoparticle diameter and diameter dispersion. These findings will be discussed and correlated with transmission and scanning electron microscopy data taken from the nanocomposite samples. The narrowing of the nanoparticle size distribution and the linear dependence of the magnetite mass incorporation versus number of chemical cycles are key issues for the interpretation of Mössbauer data.

[06/11/06 - P061]
The study of the aging effect of a ferrofluid sample, <u>SUHAILA MALUF SHIBLI</u>, FÁBIO DE OLIVERIA JORGE, CARMEN SILVIA DE MOYA PARTITI, *Instituto de Física, Universidade de São Paulo, São Paulo, Brazil - Caixa Postal 66318 CEP: 05315-970* ■We present, here, a study of the aging process in a magnetic colloid by Mossbauer spectroscopy. The sample is an aqueous ferrofluid sample (EMG 607), produced by the Ferrotec Co., composed by magnetite nanoparticles covered by an unknown surfactant. The aging effect in such fluids is not thoroughly understood. Nowadays, a good number of researchers are interested to acquire a better knowledge of this problem, and, indeed, publications about it have been increasing. Magnetite compositions range from that of stoichiometric Fe3O4 with eight Fe3+ ions in tetrahedral sites and eight Fe2+ plus eight Fe3+ ions in octahedral sites, to that of maghemite with eight Fe3+ ions in tetrahedral and thirteen and one-third Fe3+ ions in octahedral sites of the unit cell. The relative areas of the Mossbauer spectral components are close to ratio of 2:1 expected for stoichiometric magnetite(1,2). On oxidation the intensity of the component with the smaller field decreases relative to the intensity of the component with the larger field. Two Mossbauer spectra were obtained for the same sample with an interval of time of eleven months. The ratio described above is 1.098 for the first spectra and 1.080 for the last one. This result indicates that an oxidation of the sample occurred, evidencing the presence of the aging effect.

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[06/11/06 - P062]
Magnetic and valence instability in $CeSn_3$ and $CeSn_{3.1}$ seen by Mössbauer spectroscopy, <u>J. LARREA J</u>, D. R. SANCHEZ, E. M. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Físicas,Rua Xavier Sigaud, Rio de Janeiro,Brazil*, R. K. SINGHAL, *Department of Physics, Rajasthan University, Jaipur, India* ■Ce intermetallic compounds has been

attracted a lot of attention because of their ground state may show different unconventional phenomena. This is mainly due to the strength of the electronic correlation which may be very much higher than in common metals leading to the formation of new class of materials such as the heavy fermions.

Between the variety of Ce intermetallic compounds, the ground state of $CeSn_3$ has been extensively investigated, and the intermediate valence and non-magnetic state on Ce sites are well established. More interesting are the physical properties measured at low temperatures. The magnetic susceptibility ($\chi(T)$) measurements show a small broad maximum around $T_V \sim 150$ K while for temperatures below $T_S \sim 30$K $\chi(T)$ increases drastically. While the former may be explained inside a simple model of hybridization between the electronic bands of the f electrons on Ce sites and the surrounding conduction electrons, the later susceptibility anomaly is an unusual and requires a different framework. Some of the physical scenarios proposed to account that unusual behavior are the influence of the atomic disorder and the quenching of the spin fluctuations.

In this work, we will report our recent ^{119}Sn Mössbauer measurements on $CeSn_3$ and $CeSn_{3.1}$ single crystals as function of temperature, from 300 K down to 20 K. Following the temperature dependence of the hyperfine parameters we may characterize two different temperature transitions, at $T_V \sim 150$ K and $T_S \sim 50$K. Bellow 50K, the spectra become broadening and the first attempt to fit our spectra suggests the presence of fast spin fluctuations. It is very relevant and unique to compare the presence of these spin fluctuations in both $CeSn_3$ and $CeSn_{3.1}$ systems .

[06/11/06 - P063]

SYNTHESIS AND CHARACTERIZATION OF $FeNb_{11}O_{29}$,

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■The $FeNb_{11}O_{29}$ compound was synthesized by high temperature solid state reaction. In the phase diagram $Fe_2O_3 - Nb_2O_5$, the conditions for obtaining the pure phase depend from synthesis temperature. The polycrystalline ferric niobate obtained was a light green crystalline powder. In this work it is presented the results obtained by characterization with Mössbauer spectroscopy, X ray diffraction and magnetic susceptibility measurements. Also it has been obtained three different phases from iron niobium oxide: $FeNb_{11}O_{29}$ orthorhombic type and few traces of FeNbO4 monoclinic phase. The phase percentage depends of the duration (number of hours) of annealing of materials.

The study of the phase diagram $Fe - Nb - O$ has recently been of interest due to the metallurgical implications of special steels containing of niobium; when studying the phase diagram the materials $FeNb_{11}O_{29}$ ways appears mixed with other phases of iron niobium oxide. The first report of synthesis this compounds of orthorhombic type by Trunov, conformation of

Kitayama, Brunner and Gruehn reported of $FeNb_{11}O_{29}$ monoclinic type mixed with $FeNbO_4$ monoclinic type. The $FeNb_{11}O_{29}$ described in the literature that hace poliformic structure monoclinic and orthorhombic, as being monoclinic where prepared at 1150 C and orthorhombic for temperature of 1300 C, this structure has been discussed in Trunov et al, the orthorhombic and monoclinic modification of $FeNb_{11}O_{29}$ that found in isostructural with the corresponding modifications of $Ti_2Nb_{10}O_{29}$.

Keywords: Phase equilibrium, double oxides of niobium, high temperature, orthorombic structure, mixed oxides iron and niobium, x-ray phase analysis, refinement.

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[06/11/06 - P064]

REINVESTIGATION OF VERWEY TRANSITION IN NIOBIUM MAGNETITE BY MÖSSBAUER SPECTROSCOPY,

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■The ordering of bivalent and trivalent ions from iron in magnetite (Fe_3O_4) below the Verwey temperature ($T \approx 120K$) has been the subject of research for many years; since the phenomenon interconnects problems of the charge transfer, magnetism and lattice symmetry in oxides. As a result of many investigations, it has been established that this type of ordering is accompanied by monoclinic distortions of the original cubic crystal, by corrected atomic displacements. The presence of impurities atoms or vacancy in magnetite causes a considerable lowering of the ordering temperature T_v.

A careful investigation with Mössbauer of the influence of Nb^{5+} substitution on the Verwey transition of the spinel system $Nb_xFe_{3-2x}O_4$, with $0 < x < 0.2000$, has been carried out; it has shown a decreasing transition temperature with increasing composition for x. By mean of Mössbauer Spectroscopy with temperature T(K) between 94 and 98, all spectra were decomposed in their components tetrahedral (A site) and octahedral (B site). The obtained results are consistent with the fact that at low temperatures above T_v the spin lie along a domains [100] axis.

Keywords: Verwey transition, pentavalent doped magnetite, magnetic susceptibility measurements.

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[06/11/06 - P065]

Low dimensional $A_{n+2}Co_{n+1}O_{3n+3}$ $(A = Ca, Sr, Ba; n = 1-5)$ system studied by ^{57}Fe Mössbauer spectroscopy, D.R. SANCHEZ, M. ALZAMORA, E. M. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Fisicas. Rua Xavier Sigaud 150. Urca. CEP 22290-180. RJ, Brazil*, M. CINDRA, *Universidade Federal Fluminense, CT/DEM. Rua Passo da Patria, 156/302 Bloco D. São Domingos 24210240. Niteroi, RJ. Brasil*

■Low-dimensional materials have attracted interest among physicists owing to their highly anisotropic and rather unique physical properties leading naturally to the question of the interrelationship between magnetism and dimensionality [1-2]. The Co oxides $A_{n+2}Co_{n+1}O_{3n+3}$ includes columnar structures, between which the alkaline-earth metal A is located, offering the possibility to study this kind of interrelationship. Furthermore, regarding technological applications, these compounds have been attracted considerable attention as thermoelectric materials that are stable in air and at high temperature. It was found that for $Ca_3Co_2O_6$ $(n = 1)$ the intrachain interaction is ferromagnetic and an antiferromagnetic interaction between ferromagnetic chains take place at low temperatures [2].

The static and dynamic properties of the magnetically ordered $A_{n+2}(Co_{0.99}{}^{57}Fe_{0.01})_{n+1}O_{3n+3}$ have been studied by Mössbauer spectroscopy. The room temperature Mössbauer spectra for all the samples show a broadened asymmetrical doublet, typical for electronic spins relaxation systems. The 4.2 K spectrum for $n = 1$ is resolved into two static magnetic components. The $IS = 0.39$ mm/s and the quadrupole splitting $\Delta E_Q = 1.23$ mm/s are almost identical for both components in agreement with a previous work [2]. Indicating a high-spin Fe^{3+} located in a trigonal prism (with lower local symmetry). The 4.2 K spectrum for $n = 2$ shows, additionally to a broadened sextet, a high temperature remaining relaxation single line. For $n = 3-5$ the 4.2 K spectra are even more complicated, indicating a complex dynamic magnetic state. Such a behavior may be related to the increase of the distance between neighboring $Fe(Co)$ located at the prisms as n increases. Magnetization and Mössbauer under external magnetic field as a function of temperature experiments are in progress.

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[06/11/06 - P066]

High-Spin → Low-Spin Transition in $Cs_{0.7}Co_4[Fe(CN)_6]_{2.9}[\square]_{1.1} \cdot 16H_2O$, D. R. SANCHEZ, E. BAGGIO-SAITOVITCH, *Centro Bra-*

sileiro de Pesquisas Fisicas. Rua Xavier Sigaud 150. Urca. CEP 22290-180. RJ, Brazil, IGNACE JARRIGE, J.J. LEE, *National Synchrotron Radiation Research Center. 101 Hsin-Ann Road. Hsinchu Science-Park. Hsinchu 30076, Taiwan* ■In the field of molecular magnets, Prussian blue $M_xCo[Fe(CN)_6]_y \cdot zH_2O$ analogues, where $M = Na, K, Rb$, and Cs have provided a wealth of attractive results: high-T_C magnet, photoinduced ferrimagnetism, photocontrolled pole inversion, photo- and thermochromism, etc. [1]. Their (photo)-magnetic properties depend on several factors linked to the chemical environment, namely, the presence of $Co^{III}(LS) - Fe^{II}(LS)$ diamagnetic pairs, leading to $Co^{II}(HS) - Fe^{III}(LS)$ magnetic pairs by optical electron transfer (LS = low spin, HS = high spin), the presence of $[Fe(CN)_6]$ vacancies in sufficient amount, and the nature of the counterion C; the first two factors are related to the Co/Fe ratio which has to be in the range $1.2 - 1.4$ for efficient photoeffect. The room temperature Mössbauer spectrum of $Cs_{0.7}Co_4[Fe(CN)_6]_{2.9}[\square]_{1.1} \cdot 16H_2O$ shows a slightly asymmetrical doublet, attributed to the electronic $Fe^{III}(LS)$ state with a small admixture ($\sim$ 5%) of the $Fe^{II}(LS)$ state. The low temperature spectra (after slow cooling to avoid frozen-in effects) evidences a clear superimposition of two absorption doublets associated with the coexistence of $Fe^{II}(LS)$ and $Fe^{III}(LS)$ species. At $30K$ there are a contribution of $\sim 75\%$ corresponding to $Fe^{II}(LS)$ and $\sim 25\%$ to $Fe^{III}(LS)$. The obtained values are consistent with previous literature data on $Na_{0.32}Co[Fe(CN)_6]_{0.74} \cdot 3.4H_2O$ [2] and confirm the mechanism of the transition, based on the electron transfer

$$Fe^{III}(LS) + Co^{II}(HS) \rightarrow$$
$$Fe^{II}(LS) + Co^{III}(LS)$$

Mössbauer data obtained at 4.2 K after immersion of the sample in liquid Helium, shows basically Fe^{II} contribution. As the sample is heated up above $\sim 330K$ a dehydrating process seems to take place. For the dehydrated sample an inhibition of the low temperature charge transfer was observed. Magnetization measurements as a function of temperature are in progress to complement these results.

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[06/11/06 - P067]

Magnetic ordering in 57Fe doped EuNiO3 and NdNiO3 studied by Mössbauer spectroscopy,

ALEXANDER CAYTUERO VILLEGAS, ELISA BAGGIO SAITOVITCH, HANS MICKLITZ, J. LITTERS, *Centro Brasileiro de Ciencias Físicas*, J. A. ALONSO, *CSIC, Cantoblanco, E-28049 Madrid, Spain*, M. M. ABD-ELMEGUID, *Physikalisches Institut, Universität Köln, D-50937 Köln, Germany* ■The rare earth nickel perovskites RNiO3 have attracted considerable interest due to their unusual electronic/magnetic properties including phenomena as charge and orbital ordering. While charge ordering has been found for the RNiO3 with small R = Y, Lu by means of ^{57}Fe Mössbauer spectroscopy, this was not found using this for the nickelates containing the larger R-atoms Nd and Sm. Orbital ordering was proposed for R = Pr, Nd, Sm and Eu. Studies about magnetic order in $NdNiO_3$ and $EuNiO_3$ (1 at % Ni substituted by ^{57}Fe) are reported. About 50 % of the Fe atoms show a magnetic hyperfine interaction which follows the macroscopic magnetization: a second order magnetic phase transition is observed for $EuNiO_3$ at T_N = 190 K, while an abrupt onset of Bhf indicates a first order magnetic transition for $NdNiO_3$ at T_N = 150 K. The other 50 % of the Fe atoms reveal a slowing down of fluctuating hyperfine fields on lowering temperature indicating that these sites are magnetically frustrated. Mössbauer spectroscopy results on $NdNiO_3$ and $EuNiO_3$ are compatible with a charge ordered state below the Metal Insulator Transition (MIT). In contrast to the earlier proposed orbital ordered state where two different possible orbital surroundings are expected, one with weaker and one with stronger frustration, the charge disproportionation derived from resonant x-ray scattering lets expect one Fe site which reflects very well the undisturbed magnetic surrounding and another one which is frustrated. This can be well explained by a charge disproportionation occurring at the Ni sites.

[06/11/06 - P068]

MAGNETIC AND MÖSSBAUER INVESTIGATIONS IN MECHANICALLY PROCESSED MULTIFERROIC MAGNETOELECTRIC COMPOUNDS, V. F. FREITAS, , S. N. DE MEDEIROS, A. PAESANO JR., AND I. A. SANTOS, *Universidade Estadual de Maringá, Departamento de Física, Av. Colombo, 5790, Maringá-PR, 87020-900, Brazil,* L. F. CÓTICA, *Universidade Estadual do Centro Oeste, CEDETEG, Simeão Camargo Varela de Sá, 3, Guarapuava-PR, 85040-080, Brazil,* A. A. COELHO, *Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, Barão Geraldo, Campinas-SP, 13083-970, Brazil* ■Multiferroic magnetoelectrics present potential applications in those areas where electrically and magnetically ordered materials are extensively employed. In fact, the electric and magnetic order parameter coupling opens the possibility of integration between the multiferroic physical properties through the magnetoelectric effects, and can promote interesting technological advances in many advanced technologies, as spintronics and magnetoelectronics. In this context, the magnetoelectric properties of the perovskite compounds had received considerable attention in the last years, mainly due to the coexistence of ferromagnetism and ferroelectricity in some of these materials. Nevertheless, practical applications of polycrystalline perovskite magnetoelectrics are only possible in monophasic samples, whereas spurious or secondary phases can strongly contribute to the degradation of the electrical, magnetic and dielectric properties of processed ceramics. In this context, several works, concerning alternative processing routes for synthesize monophasic magnetoelectric compounds; have been also employed to prepare magnetoelectric ceramic compounds. Among them, the high-energy ball milling can be used mainly due to its potentiality to produce monophasic and high reactive powders in nanoparticle scale. In this work, magnetic and Mössabuer spectral properties of high-energy ball milled $BiFe_{1-x}Mn_xO_3$, $Bi_{1-x}Eu_xFeO_3$ and $Bi_{1-x}Gd_xFeO_3$ powders were carefully investigated through Mössbauer spectroscopy and magnetization measurements. The whole set of the results point to considerable alterations in the powders properties as a function of the composition. The influence of the processing route on the ceramics properties has also been carefully investigated. As it will be shown, the synthesis route employed provides high-quality nanosized ceramic powders that possess potential application for magnetoelectric sensors and lead-free piezoelectric actuators.

[06/11/06 - P069]

Magnetocaloric Effect in NiMnSn Heusler Alloys,

FABIO XAVIER, MAURÍCIO GOMES DAS VIRGENS, CARLOS LARICA, EDSON PASSAMANI CAETANO, *Departamento de Física, Universidade Federal do Espírito Santo*, ANGELO GOMES, *Instituto de Física, Universidade Federal do Rio de Janeiro*

■Magnetocaloric effect (EMC) has been used for reducing temperature by isothermally applying magnetic field and removing it adiabatically. This effect has been used in the past to obtain temperatures below than 1 K. In nowadays, the research of new materials with large EMC has opened up the possibility of using it for room-temperature refrigeration as an environment-friendly alternative to conventional vapour-cycle refrigeration. In the present decade, reseachers are looking for materials cheaper, safer and easier to be prepared by conventional experimental thecniques. In this work, structural and magnetic properties in the Heusler-based system $Ni_2(Mn_{1-x}Fe_x)_{1.44}Sn_{0.56}$, to x=0, 0.25, 0.50, 0.75, were studied by X-ray diffraction, Mössbauer spectroscopy and magnetization. While X-ray diffraction data show that structures, obtained by replacing Mn with Fe, are L21-like, ^{57}Fe Mössbauer results suggest two components for the spectra; one being paramagnetic even at 12 K, whereas the other one is magnetically ordered at 12 K with magnetic hyperfine field of about 22 T. The relative fractions of the components are aproximatly 1:9. In addition, Fe increasing content shifts to lowers values the compound magnetic ordering temperatures and also the magnetization, following a linear-like behavior. The L21-like structures do not display martensitic transformation for temperature down to 100 K. Martensitic transition will be investigated in alloys with appropriated Sn contents. Hyperfine interactions in Fe and Sn sites of martensitic phase will be studied in a near future. Finally, since one can set the compound ordering temperature by Fe replacement, this system can be suitable to future applications in magnetic refrigeration near room temperature.

[06/11/06 - P070]

Surface morphology and magnetic properties of CoFe2O4 films prepared by the proteic sol-gel process and deposited by dip-coating technique,

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MG.Brazil, JOSEÉ G. DOS SANTOS DUQUE, MARCELO MACEDO, *UFS-S-Brazil* ■Thin films of cobalt ferrite (CoFe2O4) have been prepared by a sol-gel process on glass substrates. A CoFe2O4 sol was prepared from dissolution of Fe(NO2)3.9H2O and Co(NO2)3.6H2O in processed coconut water. The films were grown using the dip-coating technique, followed by a heat treatment at 773K during 2 hours. After the treatment, two films (A1 and A2-samples) were inmediately taken off the furnace and exposed to room temperature and a third sample (A3) was cooled down inside the switched off furnace. The first sample (A1-sample) consists of a film with a layer thickness of 300nm annealed at 673 K during 2 hours. Sample A2 has thickness of approximately threefold the thickness of A1. The heat treatment of A2 was the same as for A1. The microstructure of the films was investigated by means of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The X-ray patterns of the all samples can be ascribed to spinel CoFe2O4. The magnetic properties were investigated by transmission Mössbauer spectroscopy. The AFM images showed morphological changes in the surface, which depended of preparation conditions. AFM examination of the CoFe2O4 films surfaces revealed molecular-scale details of some granular structure as mostly observed on nanocrystalline materials. When we increase the films thickness the surface roughness increases due to increases of the grain size. From the XPS Fe 2p3/2, Co 2p3/2 and O 1s peak intensities the surface composition of the samples was determined. Samples submitted to different cooling conditions presented small differences in the surface stoichiometry. The Mössbauer spectra of all samples showed a well-resolved sextet at 300 and 4.2 K. Magnetic properties measured at room temperature showed that the films did not have any magnetically preferred orientation. The motivation of the study is investigate the structure and surface properties of these CoFe2O4 films in according with of preparation conditions.

[06/11/06 - P071]

^{119}Sn Mössbauer Study of $Gd_5Ge_2(Si_{1-x}Sn_x)_2$ (x=0.23 and 0.40) compounds,

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[1] J.C.P.Campoy et al. Magnetocaloric effect and transport properties of $Gd_5Ge_2(Si_{1-x}Sn_x)_2$, (x = 0.23 and 0.40) compounds, submittted to Journal of Magnetism and Magnetic Materials.

(Work supported by CNPq, Fapemig and Fapesp).

T8-Physical metallurgy and materials science

[06/11/06 - P072]

Study of Fe-doped TiO_2 and SnO_2 by Mossbauer spectroscopy and FP-LAPW calculations, A. F. Cabrera, L. A. Errico, A. Mudarra Navarro, C. Rodríguez Torres, M. Rentería, F. H. Sánchez, *Departamento de Física, Facultad de Ciencias Exactas UNLP, IFLP-CONICET, Argentina,* M. Weissmann, *Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina* ■During the last years the study of transition metal doped TiO_2 and SnO_2 semiconductors has become a topic of interest, not only because of the many current industrial applications of these materials, as for example in catalysis, but also because of their potential use in spintronic devices. There is a great deal of new experimental and theoretical work on these TM-doped systems (TM= Mn, Co, Fe, Ni, Cu), focused on their magnetic properties. In the case of Fe doping, Mössbauer studies were performed in order to elucidate the local atomic structures associated to the observed interactions [1]. Despite the several reports published on quadrupole splitting data, a unique consensus on the hyperfine parameters associated to Fe substitutional in the rutile structure has not been achieved yet. Several questions remain open concerning the Fe dopants location in the host structure, and/or the short range orders around impurities, as well as to their assignment to the observed hyperfine interactions. In 2002 we demonstrated the capability of the ab initio full potential linearized augmented plane waves (FP-LAPW) method to predict the hyperfine parameters at impurity sites. Following this approach, in this work we present a comparative Mössbauer and FP-LAPW study of the hyperfine parameters at Fe impurity in the rutile phase of TiO_2 and SnO_2. Samples of TiO_2 and

SnO_2 doped with 7 and 10 at. % of Fe were prepared by mechanical alloying. The samples were characterized by X-Ray diffraction, ^{57}Fe Mössbauer, and magnetometry measurements. The calculations were performed assuming substitutional and interstitial Fe locations and for different impurity concentrations. The effect of oxygen vacancies is also discussed.

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[06/11/06 - P073]

Mössbauer and Calorimetry Study of Fe-Mn-Si Shape Memory Alloys, JAVIER MARTÍNEZ, , SONIA MARCELA COTES, JUDITH DESIMONI, *Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, IFLP-CONICET, C. C. No. 67, 1900 La Plata, Argentina* ■The Fe-Mn-Si system hold a large attention of researchers in the last 25 years because of the presence of the so-called shape memory effect along with good thermomechanical properties, and a relative cheap preparation cost on industrial scale. These characteristics make this kind of alloys attractive for practical uses. Anyhow, it was experimentally observed that some properties (i.e. resistance to corrosion) can be improved by a small addition of one or more components, like Cr and Ni. The shape memory effect in Fe-Mn-Si alloys is governed by the martensitic transformation between γ (FCC) and ϵ (HCP) phases, which are metaestable phases of the system. A quenching from about 1000°C is needed in order to retain these phases around room temperature. To produce a thermodynamic description of the phases in multicomponent systems capable of predicting alloys with better properties, complete information about physical properties of γ and ϵ are needed even for the basic system Fe-Mn-Si.

We are interested in the acquisition of new experimental data on γ and ϵ phases in the Fe-Mn-Si system which can be useful to assess the most recent thermodynamic description of both phases, γ and ϵ. We use a combination of Mössbauer spectroscopy and differential scanning calorimetry (DSC) to investigate the martensitic transformation. Mössbauer spectroscopy was used in retrodispersion geometry with the electron conversion technique (CEMS). Hyperfine parameters and phase fractions were obtained as a function of the Mn and Si. A discussion about the effect of the components on the magnetic states of both phases, γ and ϵ , is also performed. The enthalpy of transformation as a function of alloying elements was obtained from the DSC study of alloys and phase fractions obtained from Mössbauer spectra.

[06/11/06 - P074]

Mechanochemical Activation of Titanium-Magnetite Mixtures, A. A. CRISTÓBAL, , J. M. PORTO LÓPEZ, *Instituto de Investigaciones en Ciencia y Tecnología de Materiales, INTEMA, División Cerámicos, Av. J. B. Justo4302, B7608FDQ Mar del Plata, Argentina,* E. F. AGLIETTI, *Centro de Tecnología de Recursos Minerales y Cerámica, CETMIC, Camino P. Centenario y 506, 1897 M. B. Gonnet, Argentina,* F. R. SIVES, R. C. MERCADER, *Departamento de Física, IFLP, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. C. 67, 1900 La Plata, Argentina* ■Mechanochemical processes involving reactions between metals and crystalline oxides are of interest because –in addition to their potential technological applications in structural, magnetic or electric materials through the development of metastable and non-crystalline materials with controlled properties– they add to the understanding of the natural occurring processes that lead to the formation of minerals and soils. On the other hand, natural series of minerals in the solid solution series between magnetite (Fe_3O_4) and Ulvöspinel (Fe_2TiO_4) and their intermediate members, titano-magnetites, also display differences in the degree of oxidation and their cation distribution among the spinel structural sites. The controlled studies of how the distribution of cations takes place can help toward building a model for the nature of their magnetism, and, since they are the primary carriers of rock and soil magnetism, are therefore intensively investigated in many experimental and theoretical studies. Toward a better understanding of the thermal, physical-chemical, magnetic and hyperfine behavior, we have set about to study a series of titanium and magnetite mixtures with diverse activation conditions. We have studied the development of new phases other than the initial Ti and Fe_3O_4 ones by x-ray diffraction (XRD), scanning electron microscopy, differential thermal analysis, AC susceptometry and Mössbauer spectrometry. As a result of the mechanochemical activation produced by high-energy ball-milling of the mixtures in Ar atmosphere at room temperature, the Ti reduces the Fe ions in the Fe_3O_4 spinel, partly to $Fe^{2}+$ and partly to metallic Fe. By Mössbauer spectrometry, magnetic measurements and XRD, we have been able to follow the evolution of the changes in the contents of the main phases, α-Fe, γ-Fe, Ilmenite and Ulvöspinel. The values obtained by the diverse techniques are discussed according to the different materials properties on which the techniques are based.

[06/11/06 - P075]

Characterization of Austenitic Steel SAE 304 Samples Treated with Plasma Nitration at Different Temperatures

JOSÉ FLÁVIO MARCELINO BORGES, FRANCISCO CARLOS SERBENA, CARLOS EUGÊNIO FOERSTER, SILVIO LUIZ RUTZ DA SILVA, *Departamento de Física, Universidade Estadual de Ponta Grossa, Ponta Grossa, Paraná.*, ANDREA PAESANO JUNIOR, *Departamento de Física, Universidade Estadual de Maringá, Maringá, Paraná*, IRINEU MAZZARO, *Departamento de Física, Universidade Federal do Paraná, Curitiba, Paraná* ■The austenitic steels are considered resistant to highly corrosive environments. These grades of steel are also resistant to heat, keeping good tensile strength at low temperatures and are ductile at high temperatures. They can be produced with good surface aspect, are not magnetic and can be hardened by cold deformation, reaching high limits for traction and ductility. The introduction of hydrogen in their structure causes micro-structural changes and delayed fracturing, in the form of an intensive superficial cracking, that occurs during degassing at room temperature even when no mechanical tension is applied. Within the utilized processes for surface modification, while keeping the original volume properties, is the steel nitration. The aim of this technique consists in the formation of nitrates of the source material that exhibit higher mechanical, tribologic and corrosive resistance. In the present work samples of austenitic steel SAE 304 mechanically and electrically polished were treated in a plasma nitration chamber. The plasma nitration was performed at three different temperatures: 400°C, 500°C and 600°C, for 4 hours in and atmosphere of 60% N_2 + 40%H_2. The structural and hyper-thin characterization of the samples were done through: X rays from Cu radiation, optical microscopy, and Mössbauer spectrography of conversion electrons using a radiation of ^{57}Co diluted in a matrix of Rh, at room temperature. The nitrated samples were tested for micro-strength and the results were compared with the non-treated samples. The aim is to study the alterations of the structural and physical properties on the surface of nitrated steel. It is noticeable an increase in the penetration of the N and the superficial wrinkling of the steel surface as a function of the temperature increase.

[06/11/06 - P076]
SYNTHESIS AND CHARACTERIZATION OF Fe6W6C BY MECHANICAL ALLOYING, William Barona Mercado, , JulioCesar Cuevas, Modesto Fajardo Ruiz, German Antonio Perez Alcazar, Hector Sanchez Stepha, *Univesidad Santiago de Cali, *Universidad del Valle** ■The properties of the double iron and tungsten carbide prepared by mechanical alloying technique (MA) from elemental powders are reported. Iron, tungsten and carbon Powders were used to prepare the initial mixture. The powders were mixed in a flask and transferred into anvils of hardened heat treated Cr-steel with steel balls of the same composition; the balls mass to powder mass ratio was 20:1. Ten balls of 20mm in diameter and ten of 11 mm in diameter were used. MA was carried out in an inert atmosphere (Ar) in a planetary ball mill Fritsch pulverisette 7.

The samples were milled for 1, 3, 5, 10, 15, 20, 25 and 30 hours. The alloy progress for each milling time was evaluated by X- ray diffraction (XRD) and 57Fe Mössbauer spectroscopy. The XRD patterns were performed with a D8 Bruker AXS diffractomer, using the Cu-Ka radiation (l = 1.54056 Å). Mössbauer procedure was carried out by the transmission geometry with a 20 mCi (57 Co/Rh) source using a ranger MS 1200 Spectrometer in the constant acceleration mode at room temperature. The spectra were fitted by using MOSFIT program. After ten hours of milling the double carbide Fe6W6C begins to appear. Once the alloy was consolidated two sorts of paramagnetic sites were detected according to the Mössbauer fit. The bigger doublet could correspond to Fe6W6C carbide, the other could be Fe3W3C. The Vickers microhardness measurements of 20, 25 and 30 hours milled samples were conducted at room temperature with a load of 0.49N for 20s. and mean values of 1650 Hv were founded.

Keywords: Double carbide; Mechanical alloying; Mössbauer spectros-

copy.

[06/11/06 - P077]
^{119}Sn-Mössbauer on the unconventional superconductor Sr_2RuO_4, I. Souza Azevedo, , E. Baggio-Saitovitch, *Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud, 150, Urca, Rio de Janeiro - Brazil,* Ada López, *Universidade do Estado do Rio de Janeiro, IF - Rua São Francisco Xavier 524, Maracanã, Rio de Janeiro, Brazil* ■Superconductivity - one of the best understood many-body problems in physics - has again become a challenge following the discovery of unconventional superconducting materials. The strontium ruthenate (Sr_2RuO_4) has a lattice structure very similar to the layered structure of the cuprates $La_{2-x}Ba_xCuO_4$, but shows an exotic mechanism for superconductivity, since it is widely believed to be a spin-triplet pairing superconductor[1-3]. That compound and the correspondent Ca-doped ($Ca_{2-x}Sr_xRuO_4$) have been subject of extensive studies, making part of a new group of materials in this area. μSR experiments indicated the emergence of random magnetic fields upon entering the superconducting state[4]. Nakatsuji and Maeno[5] show that Ca-doping promotes a metal-nonmetal transition, structural changes, and the existence of a region of instability.

^{119}Sn-atom, as Mössbauer-probe, is very suitable to investigate the existence of magnetism at microscope level. Using the solid state reaction method, we have prepared polycrystalline samples of $Sr_2(Ru_{1-x}Sn_x)O_4$ doped with Sn (x = 0, 0.01, 0.02 and 0.10). Tetragonal space group I4/mmm was assumed for all samples, and the data were fitted with the Rietveld method for structural refinements. The ^{119}Sn-Mössbauer spectra for the $Sr_2(Ru_{1-x}Sn_x)O_4$ system were done at room temperature and 4.2 K.

We report our preliminary studies about the structural effects of the substitution of a nonmagnetic Sn^{4+} in the superconductor (Sr_2RuO_4). The x-ray diffraction and the ^{119}Sn-Mössbauer spectra analysis suggest that Sn substitutes the magnetic Ru at the RuO_2 layers.

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T9-Other correlated subjects

[06/11/06 - P078]
Inka Metallurgic Furnaces at the Curamba site (PERU): A Study by Mössbauer Spectroscopy and X Ray Diffractometry, Yezeña Huaypar, Jorge Bravo, *UNMSM - Peru,* Luisa Vetter, *PUCP - Peru* ■In the Province of Apurimac, in the Southern highlands of Peru, the Inka site of Curamba is located where, according to some historians, several thousands furnaces used for gold, silver and cooper smelting were found [1]. For this work, three samples of burned soil were gathered

from these furnaces, classified as Curamba1, Curamba2 and Curamba4 and studied using X ray diffractometry (XRD) and transmission Mössbauer spectroscopy (TMS) techniques.

By XRD the mineralogical composition of the samples was determined. By TMS the structural sites in the minerals occupied by iron cations were identified. Moreover, an attempt was made to determine the maximum temperature reached in these furnaces using the refiring technique of the samples in an oxidizing environment and monitoring the structural modification of the iron sites by changes in the Mössbauer hyperfine parameters [2,3]. The MS results of Curamba2 show that the maximum temperature reached in these furnaces were 900°C it is in according with the mineralogy found in XRD. For Curamba1 and Curamba4 the temperature reached were 400°C.

Key words: furnaces, smelting, refiring, oxidizing environment, Mössbauer spectroscopy, X ray diffractometry.

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[06/11/06 - P079]

Study of the Structural Modifications in Activated Clays by Mössbauer Spectroscopy and X Ray Diffractometry,

YEZEÑA HUAYPAR, JORGE BRAVO, *UNMSM - Perú*

■In this work we study the changes induced on the structure of smectite clays by chemical acid activation with HCl [1] using X ray diffractometry (XRD) and transmission Mössbauer spectroscopy (TMS) techniques. By XRD we were able to determine the mineralogical composition of the clay samples and measure the changes in the interplanar distance associated to the structural modifications in the clays [2]. We appreciate a reduction in the interplanar distance and intensity as the acid concentration in the activation process increased.

TMS allowed us identify and characterize the structural sites occupied by ferric and ferrous iron cations [3]. In addition, we were able to follow the effects caused by the chemical acid activation on the valence state of the iron cations that occupy these structural sites in the clay. For the treatment at low acid concentration, keeping time and temperature of activation constant, we can notice in our results a strong effect on the ferrous and ferric iron sites, reducing and increasing their adsorption relatives areas respectively. Similar behavior is observed when the acid concentration and temperature have kept constant but time of treatment varied.

Key words: Smectite, chemical acid activation, X-ray diffractometry, interplanar distance, transmission Mössbauer spectroscopy.

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[06/11/06 - P080]

New hierarchic theory of Mössbauer effect and its computerized illustration on examples of ice and water.,

ALEX KAIVARAINEN, *Dept. of Physics, University of Turku*

■This new approach to theory of Mössbauer effect (http://arxiv.org/abs/physics/0003070) and number of others, including theories of total internal energy, heat capacity, surface tension, vapor pressure, thermal conductivity, viscosity and self-diffusion, state equation, refraction index, Brillouin light scattering, etc., are based on Hierarchic theory of condensed matter (Kaivarainen http//arxiv.org/physics/0102086). Special computer program was used for this theory quantitative verification on examples of water and ice. Condensed matter was considered as a hierarchic system of 3D standing waves (collective excitations) of different nature: a) the de Broglie waves (waves B) of molecules; b)IR photons and c) thermal phonons. This model, makes it possible to evaluate, more than 300 physical parameters of matter, using CAMP computer program and 4 input parameters: sound velocity; density; refraction index and positions of translational and librational bands in oscillatory spectra. The demo version of program [pCAMP] can be downloade from the front page of site: web.petrsu.ru/∼alexk. The main parameter, characterizing Mössbauer effect, is the probability of recoilless effect just after emission of&;-quanta by radioactive atom, like Fe(57), incorporated in matter. The resulting probability of elastic effects is determined by the sum of contributions of primary and secondary effectons (see eq. 10.13) from article: http//arxiv.org/physics/0102086. This approach makes it possible to get temperature dependences of total probability (f) of elastic effect and different contributions to this effect without recoil and phonon excitation in the ice, in the water and in the range of phase transition (Fig.33 in the same paper). Our theory makes it possible to calculate also Doppler broadening in spectra of nuclear gamma-resonance (NGR), when the energy of recoil exceeds the energy of phonons and photons excitation (see section 10.3 in http://arxiv.org/pdf/physics/0102086). The correlation between theoretical and experimental data is good. For details see also http://arxiv.org/abs/physics/0003070 and my homepage: web.petrsu.ru/∼alexk

[06/11/06 - P081]
Hydrogen Storage and Production from Ethanol using Iron Based Redox Systems,

MARCELO G. ROSMANINHO, GUILHERME M. GOMES, RAFAEL F. ZICA, MÁRCIO C. PEREIRA, FLÁVIA C.C. MOURA, JOSÉ D. FABRIS, MARIA H. ARAÚJO, ROCHEL M. LAGO, *Departamento de Química - ICEx. Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil, 31270-901*

■Hydrogen, the "fuel of the future", will replace fossil energy sources with higher efficiency and several environmental advantages. However, the use of H_2 faces two main challenges: its production and storage. In this work, an alternative solution for these problems is presented: the use of redox systems based on Fe^o/Fe_2O_3. This system operates in a 2 steps process: (i) a fuel, e.g. methane or ethanol, is used to reduce the iron oxide to Fe^o; (ii) when H_2 is needed, Feo can be reacted with H_2O to produce CO_2-free hydrogen. The Fe_2O_3 produced can be reduced again to Fe^o making this system reversible. To produce a more reactive system, a highly dispersed Fe_2O_3 was prepared using Al_2O_3 as support with Fe contents of 10, 20, 30 and 50wt% (Fe10 to Fe50). These samples were submitted to Temperature Programmed Reaction (TPRe), using a mixture of $EtOH/N_2$ from 30 up to 900°C at 5°C/min. The samples, before and after TPRe, were characterized by XRD, SEM, BET, TG and Mössbauer Spectroscopy. BET analyses showed that the surface areas of the /alpha-Fe_2O_3/Al_2O_3 between 43 and 62m^2/g. Mössbauer analyses showed that the samples before TPRe presented mainly the /alpha-Fe_2O_3 phase, but also some amounts of Fe_3O_4 and superparamagnetic Fe^{3+} (possibly nanometric hematite particles or surface Fe^{3+} species). After reaction with EtOH in the TPRe experiments, the sample presentedalpha-Fe_2O_3 and Fe_3O_4 (30% for Fe10 and 12% for Fe50), Fe^o (30 and 56% for Fe10 and Fe50, respectively). Also, Fe_3C phases and some carbon deposition are formed. These results are confirmed by XRD, TG and SEM analyses. As next steps, we are investigating the use of these reduced samples to produce H_2 by the reaction with H_2O.

Session 2

[07/11/06 - 09:30h]

MÖSSBAUER SPECTROSCOPY AS A KEY TECHNIQUE TO CHARACTERIZE IRON OXIDES AND TRACE THEIR TRANSFORMATIONS IN NATURAL SYSTEMS,

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■Iron-bearing minerals are of very wide occurrence in the Earth crust. Their oxidized forms are dominant in most geosystems under tropical environment. The chemical pathways through which they are formed and transformed in such systems are not always clear. For instance, magnetite (ideal formula, Fe_3O_4; cubic system, space group Fd3m), a ferrimagnetic iron oxide with inverted spinel structure, may be oxidized to hematite (αFe_2O_3, hexagonal system, space group R3c), which is thermodynamically more stable, either directly or via the intermediate formation of maghemite (γFe_2O_3, also with the spinel structure). The crystallographic mechanisms related to this transformation are still controvertial. The literature reports this conversion as being dependent upon the nature (chemical composition, size of the crystals) of the precursor (magnetite). In this discussion, two examples are used to illustrate the powerfulness of the Mössbauer analysis on: (i) the characterization of a magnesioferrite from a magnetic soil derived from a pyroclastic material and (ii) the attempt to obtain evidences about structural and chemical mechanisms involved on the oxidation of magnetite of a weathering sequence developing on stetatite, both geosystems in Minas Gerais, Brazil. The analyses were mainly based on structural Rietveld refinement of powder X-ray diffraction data from the synchrotron radiation source and Mössbauer measurements at various temperatures. Mössbauer data for the rock-magnetite were also collected with externally applied magnetic field.

ACKNOWLEDGEMENTS This work has was supported by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D10B - XPD 4157, by the Federal University of Minas Gerais, the University of Patos de Minas (MG), CNPq and FAPEMIG (Brazil).

[07/11/06 - 10:05h]

MÖSSBAUER STUDY AND STRUCTURAL CHARACTERIZATION OF COMPOUNDS $UO_2-TR_2O_3$ (TR=Gd and Eu),

FLÁVIO F. IVASHITA*, , KLEBSON L. SILVA, REGINALDO BARCO, SUZANA N. MEDEIROS, ANDREA PAESANO JR., *Departamento de Física - Universidade Estadual de Maringá - Brasil,* RICARDO G. GOMIDE, SELMA L. SILVA, ANA E. L. CLÁUDIO E LUCIANO PAGANO JR., *Laboratório de Materiais Nu-*

cleares - Centro Tecnológico da Marinha em São Paulo - Brasil ■The $UO_2 - TR_2O_3$ (TR = Gd and Eu) systems are used to nuclear application as burnable poison fuel. The Rare-Earth oxides are added to improve the core's physics and to extend the irradiation in water reactors. However, the occurrence of grains in these oxides, even nano sized, is undesirable in ceramics, because spoils the properties of thermal transport of ceramics. The objective of the present work is to verify the homogeneity of the solid solution $(U,TR)O_2$ formed by solid state reaction, and to compare results when it is used Eu_2O_3 or Gd_2O_3. The samples were prepared mixing the precursors UO_2 and TR_2O_3, in the ratio of 7 percent in weight of Rare-Earth oxides. Cylindrical pellets were obtained by mechanical pressures with a load of 3.5 ton/cm2 performed in a die punch. The sintering of the pellets was done under a reducing atmosphere. The pellets were sintered at conditions which consists of up and dwell of temperatures varying between 900 C and 1750 C, for periods up to 4 h. The sintered samples were sprayed and the material was analyzed by X-Ray Diffraction and Mössbauer spectroscopy in 155Gd and 151Eu. The results show that the diffusion of Rare-Earth oxides in the uranium oxide is favored by the increase of the temperature. For samples annealed up to 900 C, the spectra show which Rare-Earth oxide remains not-reacted, as disclosed for the Mössbauer spectra of these samples. For the sample longest heat treated, the Mössbauer spectrum reveal only one site. This evidences a progressive and complete diffusion of Rare-Earth atoms into the uranium oxide matrix, occupying a site of cubical symmetry, as would be in the case of a substitution. For intermediate temperatures, the occurrence of a mixed oxide phase, badly crystallized, is indicated by both characterization techniques.

[07/11/06 - 10:20h]
PROVENANCE STUDY OF OBSIDIANS FROM THE ARCHAEOLOGICAL SITE OF LA CADENA - QUEVEDO (ECUADOR)., M. Duttine, R.B. Scorzelli, *CBPF - Rio de Janeiro - Brazil*, G. Poupeau, *CRP2A - Pessac - França*, A.V. Bellido, R.M. Lattini, *Instituto de Química, Dep. de Físico-Química, UFF - Rio de Janeiro - Brazil* ■The potentialities of ^{57}Fe Mössbauer spectroscopy, SQUID Magnetometry and Electron Spin Resonance for provenance research of prehistoric obsidians have already been demonstrated in the Western Mediterranean basin. The aim of the present study is to apply these methods to provenance research of Andean obsidians. The geological samples were collected in four primary sources and a secondary one, all located around Quito (Ecuador). According to the Fission Track dating results[1], these sources may have been used by prehispanic populations. The archaeological samples were collected in tolas (from Preceramic period to Spanish conquest) located between the Ecuadorian cities of Quevedo and La Cadena.

Magnetization of the samples was measured at room temperature with a commercial SQUID magnetometer. Arising from the M vs. H cycles, the saturation magnetization, the magnetic remanence and the coercive force appear to be discriminant parameters.

ESR spectra of the samples were recorded at 9.5 GHz and at room temperature. They mainly present a broad and intense signal due to iron oxides or iron and titanium oxides, a narrower one at $g_{eff} \approx 4.3$ with a shoulder at about $g_{eff} \approx 9.8$ associated to isolated Fe^{3+} ions and another line at $g \approx 2$ due to Fe^{3+} clusters. Peak-to-peak intensity and linewidth of these signals were used to differentiate the samples.

^{57}Fe Mössbauer spectra were also recorded at room temperature for all the geological samples. They are mainly composed of broad asymmetric doublets, associated to Fe^{3+} and Fe^{2+} in two different sites. Some samples exhibit a magnetic component attributed to iron oxides (hematite and/or magnetite). Measurements on the archaeological samples are still in progress.

Multivariate statistical analyses (cluster analysis methods) of all these results allow to differentiate the Ecuadorian obsidian sources and to determine the origin of some archaeological samples.

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[07/11/06 - 10:35h]

Mössbauer Analysis of Gas-Metallized Iron Ore Pellets, CATIA CASAGRANDE, PAULO FREITAS NOGUEIRA, MARIA BEATRIZ VIEIRA, *DITF, Companhia Vale do Rio Doce - Vitória*, JOSÉ DOMINGOS FABRIS, MÁRCIO CÉSAR PEREIRA, *Departamento de Química, ICEx, UFMG*, FLÁVIO BENEDUCE NETO, *Instituto de Pesquisas Tecnológicas do Estado de São Paulo - IPT* ■The metallization process of iron ore pellets is an issue that has been gathering significant attention over the last fifty years. The metallization rate has a significant impact on the productivity and performance of the blast furnace, thereby influencing the overall economics of the ironmaking operations. The present paper is part of a project aimed at measuring intrinsic chemical reaction rates of the reduction of iron oxides through the analysis of the gas off-stream. The homogeneity and intensity of the pellet metallization is influenced by several variables. To examine these effects, the furnace chamber was loaded with two layers of iron ore pellets. These pellets were sandwiched between layers of alumina grains six times thicker than that of the iron ore, to ensure a homogeneous radial distribution of gases. After heating the chamber environment up to the reaction temperature, under a nitrogen stream to purge the air out, a reducing mixture of hydrogen and carbon monoxide was injected trough the pellet column. After reduction, the pellets are cooled under a nitrogen stream before unloading. In this work, six samples were collected from three points along the radius of each layer of pellets. The samples were first ground in a pan mill. Room temperature 57Fe Mössbauer spectra were obtained with a gamma backscattering portable equipment and with a conventional transmission setup. In both cases, only metallic iron and wüstite were identified. These results show that (i) the degree of metallization is higher in the bottom pellet layer; (ii) the relative amount of metallic iron is found to be higher on the outer shell of grains obtained from grinding pellets after the reduction process, as expected, and (iii) the metallization is reasonably homogenous along a same pellet layer.

[07/11/06 - 11:20h]
XMCD applied to magnetic thin films investigations, Ana Paula Dornelles De Alvarenga, *Inmetro* ■The investigation of spin-dependent phenomena such as the behavior of magnetic materials has being increasingly enhanced by the use of circularly polarized synchrotron radiation. The technique of X-ray magnetic circular dichroism (XMCD) is actually well established for the study of magnetic thin films and multilayers. It uses the absorption of circularly polarized synchrotron radiation to probe the unoccupied states near the Fermi Level. The values of the orbital and spin magnetic moments can be obtained by direct integration of the experimental data combined to developed sum rules. Here we present the technique of XMCD on experiments performed at the SGM beam line of the Brazilian National Synchrotron Light Laboratory (LNLS) with samples prepared and characterized at the Thin Film Laboratory of CBPF/MCT-RJ.

[07/11/06 - 11:45h]
Interfacial magnetic properties of NiFe/FeMn/NiFe exchange-biased trilayers, Valberto Pedruzzi Nascimento, *Universidade Federal Rural do Rio de Janeiro*, Edson Caetano Passamani, *Universidade Federal do Espírito Santo*, Ana Paula Dornelles Alvarenga, *INMETRO*, Armando Biondo, *Universidade Federal do Espírito Santo*, Fernando Pelegrini, *Universidade Federal de Goiás*, Elisa Baggio Saitovitch, *Centro Brasileiro de Pesquisas Físicas* ■The exchange bias effect (EB) is characterized by a shifting of the hysteresis loop along the magnetic field axis (called here as: exchange field (H_{ex})), when a sample with two magnetic phases is cooled under an applied magnetic field throughout the antiferromagnetic Néel temperature (T_N). In general, this phenomenon emerges from the interfacial magnetic coupling between a ferromagnetic and an antiferromagnetic material. Here we report on the influence of the roughness on the exchange bias effect in trilayers of NiFe/FeMn/NiFe deposited on water-cooled Si substrates by dc magnetron sputtering at the Thin Films Laboratory of CBPF/MCT-RJ. These samples were prepared under different Ar gas pressures (2, 5 and 10 mTorr) in order to produce distinct interface roughness. During the deposition an applied magnetic field of 460 Oe was applied in order to induce the unidirectional anisotropy on the films. Magnetization results have shown very asymmetrical hysteresis loops due to different layer thickness for up and down NiFe layers. The exchange bias field (H_{ex}) is inversely proportional to the NiFe/FeMn interfacial roughness, while the coercive field (H_C) runs in the opposite way. From Mössbauer spectroscopy measurements, it can be proposed an interface composed by three phases of NiFeMn alloys: a) antiferromagnetic, b) paramagnetic and c) ferromagnetic. Extra planar spins were observed at the interfaces of samples prepared at higher pressures. Ferromagnetic resonance and Mössbauer spectroscopy results show that the "magnetic roughness"is bigger than the root mean square roughness obtained by reflectivity which includes structural and chemical disorders. The "magnetic roughness"is more pronounced in the up NiFe/FeMn

interface.

[07/11/06 - 12:00h]
Bcc-Mn Magnetism and Magnetic Couplings in Fe/Mn/Fe Trilayers Grown by Molecular Beam Epitaxy on MgO(001) Substrate., B. SEGATTO, E. C. PASSAMANI, V.P. NASCIMENTO, J.R. PROVETI, *Depto. Física, Universidade Federal do Espírito Santo Federal, 29075-910, Vitória, Brazil*, F. ALMEIDA, A. VANTOMME, *Instituut voor Kern-en Stralingsfysica, Katholieke Universiteit Leuven, B-3101 Leuven, Belgium*, F. PELEGRINI, *Depto. Física, Universidade Federal de Goiás, Goiânia, Brazil* ■Fe/Mn superstructures have had considerable attention from the scientific community due to the complex magnetic structures found in their magnetic phase diagram. The present work searches for better understanding of the mechanism responsible for the magnetic couplings between Fe layers (collinear and non-collinear) spaced by magnetic bcc-Mn layers, all grown by MBE. Fe(5 or 20nm)/Mn(0.5-15nm/Fe(5nm) films were deposited directly on the MgO(001) substrate after it has been annealed at 900°C or on a thick Ag buffer layer deposited on the MgO substrate. Several experimental techniques (RHEED, XRD, CEMS, XMCD, FMR and magnetization) have been used to characterize the film structure and the magnetic couplings often found in this system. In-plane and out-of-plane epitaxy of the Fe and Mn layers have been confirmed by RHEED and X-ray \ φ-scan experiments. The Fe fractions affected by interfaces were determined by performing CEMS in a thin 57Fe layer (1nm) deposited at the interfaces and also by FMR measurements. The CEMS results indicate that both interfaces are not similar one each other, being the upper interface rougher than the lower one. Moreover, CEMS and FMR results suggest formation of Fe/Mn alloys at the interfaces when non-collinear Fe layer coupling is presented. XMCD method (L2,3 edge) has been used to have basic information of the bcc-Mn magnetism. The Fe coupling angles were evaluated from fitting the M(H) curves using Heisenberg (passive spacer = non-magnetic) and Slonczewski (active spacer = magnetic) models. The M(H) fitting and XMCD results indicate antiferromagnetic state in the bcc-Mn layers. Finally, different Fe coupling angles (almost larger than 90°) were found in the investigated samples, which were associated with the interface roughness caused by step edge, defects, inter-diffusion (not a continuous alloys formation) as will be discussed during the poster presentation.

[07/11/06 - 12:15h]
Magnetoelastic Effect in Al/Amorphous Ribbons/Al Trilayers Observed by Mössbauer Spectroscopy, P. S. MOSCON, , E. C. PASSAMANI, C. LARICA, *Departamento de Física-CCE, Universidade Federal do Espírito Santo, (29060-900), ES, Vitória, Brazil.*, F. H. SANCHEZ, *Departamento de Física-FCE, Universidad Nacional de La Plata, Casilla de Correos 67 (1900), La Plata, Argentina*, E. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, 22290-180, RJ, Brazil*, V. A. P. RODRIGUEZ, *Facultad de Ciencias Física, Universidad Nacional Mayor de SanMarcos,P.O. Box 14-149, Lima 14, Perú* ■In

this work, thermally induced spins reorientation effect observed in soft magnetic ribbons (FINIMET, MetGlass 2605 and Vitrovac) covered by Al layers has been investigated. Stress induced has been simply produced by coupling materials with different expansion coefficients in form of trilayer-like samples. The trilayer magnetoelastic effect has been studied by *Mössbauer* spectroscopy in a temperature interval from 12 K up to 423 K. The spectrum relative absorption line intensity (D23), associated with a magnetic phase, mainly depend of the incident gamma rays angle relative to sample magnetization direction. In our *Mössbauer* set-up, the incident gamma rays direction has been used to be perpendicular to the ribbons planes, consequently, one may get information about the average magnetization distribution in the ribbons at different temperatures. In general, the trilayer-like samples display: (*i*) magnetic sensibility with temperature as well as with Al layer thickness, (*ii*) positive magnetostriction, (*iii*) opposite variation concerning the thermal behavior of the magnetic hyperfine field ($\langle B_{HF}(T)\rangle$) and of the isomer shift ($\delta(T)$) with increasing *Al* layer thickness and (*iv*) finally, the full sample magnetization direction does not saturate out of ribbons planes even for the stress of 0.2GPa, obtained for the largest Al thickness $(20/mum)$. It has also been investigated: i) changes in the $\vec{M}$ (T) directions of the ribbons simply by covering them with an organic material (polymer sellotape) and ii) modifications of the $\vec{M}$ directions with the temperature in pure FINIMET and MetGlass 2605 ribbons. In summary, the spins thermomagnetic dynamics and spatial spin configurations suffer significant modifications dependent on the cover layer thickness, magnetic ribbons compositions and parameters associated with the ribbons formation process. Particularly, the covered layers thickness is an external parameter that can be easily controlled and it is very important for the magnetoelastic effect observed in the studied trilayers.

[07/11/06 - 14:25h]

Nano science in Catalysis-Bridge of conventional to surface experiences, MARTIN SCHMAL, *COPPE/UFRJ/NUCAT*, CARLOS ANDRE PEREZ, *Nucat/COPPE/UFRJ*, NIELSON FERNANDO DA PAIXÃO RIBEIRO, *PEQ/COPPE/UFRJ*, FABIANA M. T. MENDES, *IMETRO*, HANS JOACHIM FREUND, S.K. SHAIKHUTDINOV, *Fritz Haber Institut- Berlin*

■This paper presents the research work on nano science on supported catalysts and on metallic crystal films aiming to make corralation between catalysis and surface science experiments. We present supported metals prepared by impregnation and applied for methane decompositon and CO hydrogenation with CVD preparations on UHV. These systems were tested and characterized using different techniques at normal pressure and under UHV. Results show interesting correlation between surface properties and particle sizes, as well as interaction between particles and supports, showing well defined nano particles on different systems. In order to understand the reactivity of oxide and metal/oxide surfaces and structure-reactivity relationship, we follow the "surface science" approach where highly dispersed catalysts are modelled by metal nanoparticles deposited on well-ordered oxide films. Within this approach, the preparation and structure determination of well-ordered niobium oxide films is essential for modelling niobia based catalysts. Niobia films were grown on an oxygen implanted Cu3Au(100) substrate, which has recently been suggested as a good substrate for epitaxial growth of various transition metal oxides films[3]. The films were prepared by vapor deposition of Nb on the oxygen pre-sputtered Cu3Au(100) surface in an ultra-high vacuum and subsequent oxidation in O2 at elevated temperatures. The structure of the films was studied by low energy electron diffraction (LEED), scanning tunnelling microscopy (STM), vibrational spectroscopy (IRAS and HREELS) and photoelectron spectroscopy (PES) using the synchrotron facilities at BESSY (Berlin). The experimental results were complemented with density functional theory (DFT) calculations. This work presents studies from the Humbolt Research Award of the author.

[07/11/06 - 15:00h]
Mossbauer Effect of Eu-151 Carboxylic Acid Salts, CLIVE I. WYNTER, D.H. RYAN, OLGA TRICHTCHENKO, D.E. BROWN, S.G. SOBEL, LEOPOLD MAY, ***Nassau Community College, USA, McGill University, Canada, North Illinois University, USA, Hofstra University, USA, The Catholic University of America, USA*** ■A number of rare earth ion complexes with dianion carboxylic acids have been reported over several decades; they continue to be of interest because these metal coordination polymers provide a link between synthetic chemistry and materials science. The study is fascinating and intriguing because the actual complex formed depends on such factors as lanthanide ion, the pH, the dicarboxylic ion, and other modes of preparation like the temperature of the solution. Further their practical utility in fluorescence, electrical and magnetic technology makes them very desirable material.

To date their study and characterization have been primarily by single crystal x-ray diffraction, infrared and Raman vibrational studies and thermal gravimetric studies.

We have prepared the much studied europium malonate hexahydrate complex by a different method; additionally we have prepared three new complexes, namely, europium succinate pentahydrate, europium malide hydrate and europium maleide haxahydrate.

These white salts were characterized by infra-red spectra to substantiate bridging and chelating dicarboxylic dianions in these polymers while magnetic and Mossbauer measurements were used to get better insight into the heterocyclic "cages" containing the trivalent europium ions and the three dianions.

No conclusions were drawn based on the magnetic susceptibility measurements.

The Mossbauer spectra validated not only trivalent europium ions but also the lattice dynamic calculations of the Debye temperatures reflected the order of stability of the heterocyclic rings in these polymeric complexes.

[07/11/06 - 15:15h]

Mössbauer Studies of Non-Cubic Garnets,

SHALIMAR CALEGARI ZANATTA, ANDREA PAESANO JÚNIOR, SUZANA NÓBREGA DE MEDEIROS, PAULO WILLIAN C. SARVEZUK, *Universidade Estadual de Maringá - UEM Brazil*, JOÃO BATISTA MARIMON DA CUNHA, *Universidade Federal do Rio Grande do Sul - UFRS Brazil*, BACHIR HALLOUCHE, *Universidade de Santa Cruz - RS UNISC Brazil*, FLAVIO FRANCISCO IVASHITA, PUNNET SHARMA, *Universidade Estadual de Maringa - UEM Brazil* ■Garnets are considered cubic systems with the space group symmetry Ia3d. In this structure, iron occupies octahedral and tetrahedral sites labeled 16a and 24d, respectively. Usually, the Mössbauer spectra of these compounds are fitted with two or three sextets. However, some recent publications have reported evidences of a deviation from cubic to romboedral symmetry, showed by some garnets such as YIG, DyIG and EuIG. The few results reported in literature indicate that Mössbauer spectroscopy may discern the romboedral structure whereas X-ray or neutron diffraction studies are not conclusive in this respect. In the present work, we prepared the YIG, SmIG and EuIG garnets by solid state reaction and characterized them by X-ray diffraction and Mössbauer spectroscopy. An original and physically consistent fit routine was developed taking in account a rombohedral symmetry for these compounds. To proceed the fit, 6 crystallographic Mössbauer sites were considered: 4 octahedral and 2 tetrahedral. The atomic positions of the cations and oxygen ions were obtained by the Rietveld analysis. From that, each particular iron site in the unitary cell had its symmetry axis determined, resulting in two subgroups for the octahedral sites and three for the tetrahedral sites. Each subgroup was assembled by sites that reveal a similar angle (q) between the symmetry axis and the direction of easy magnetization. The isomer shifts (IS), the quadrupolar splittings (QS) and hyperfine magnetic fields (Bhf) were constrained to be equal for sites of same coordination. In addition, the relative areas were constrained according to the site populations of each subgroup. Thus, 5 sextets were employed for each spectrum, with IS, QS , Bhf and q varying according to the above constraints. The fits for the pointed out REIGs revealed to be consistent with the applied model.

[07/11/06 - 16:00h]

Nanocrystalline and amorphous Nanoperm phases prepared by mechanosynthesis.,

R. D. PEREIRA, E. C. PASSAMANI, C. LARICA AND J. C. C. DE FREITAS, *Depto. Física, Universidade Federal do Espírito Santo Federal, 29075-910, Vitória, Brazil.* ■Nanoperm alloys are amorphous materials with composition ($Fe_{84-x-y}Zr_{9-y}Cu_1B_y$) and that present soft magnetic properties. In this work, mechanical alloying process was applied to produce Nanoperm alloys in amorphous as well as in nanocrystalline states. Powder mixtures, with the $Fe_{84}Zr_9Cu_1B_6$ composition, were milled under an Argon atmosphere in high-energy mills. In order to demonstrate the alloy structural state (amorphous or nanocrystalline), they were prepared in two different ways; either by milling the mixture of the constituents powders (series I) or by performing milling of partial powder mixtures (Series II = $Fe + Zr \rightarrow FeZr + Cu \rightarrow FeZrCu + B \rightarrow FeZrCuB$). Structural and kinetic crystallization characterizations of the milled powders were done with X-ray diffractometer (Cu-$K\alpha$) and differential scanning calorimetry (Shimadzu DSC-50 equipment), respectively. XRD results suggest a formation of the Nanoperm amorphous phase, as the dominant phase in Series II, while in Series I the XRD results indicate presence of nanocrystalline phases. DSC curves, recorded at different rates for the Series II, show two crystallization stages, with the activation energy values of 208 kJ/mol and 453 kJ/mol, respectively. Fe environments were studied by transmission Mössbauer spectroscopy using source ^{57}Co/Rh radioactive. The central shifts of the subspectra are given relative to the α - Fe at RT. Mössbauer measurements clearly show that amorphous phase in Nanoperm alloys is highly dependent of the preparation procedure, being gotten in a larger fraction (92%) in the second procedure (Series II). Therefore, our results suggest that Nanoperm alloys can be prepared by mechanosynthesis from sequences of blended powder exercising influence in the final product.

[07/11/06 - 16:15h]
The Next Generation of Mössbauer Researchers, J. G. STEVENS, A. K. KHASANOV, N. F. HALL, AND I KHASANOVA, *Mössbauer Effect Data Center, University of North Carolina at Asheville* ■The scientific leadership in the Mössbauer community is undergoing drastic changes as retirements over the past five to ten years have had a major impact. However, we are seeing a new generation of Mössbauer researchers emerging to contribute challenging research. Examples of this change can be seen in various regions of the Mössbauer community; Japan is a good example. In Japan, we have seen the retirement of Teruya Shinjo (228 Mössbauer publications), Hirotoshi Sano (219 Mössbauer publications), Saburo Nasu (226), Yusuke Ujihira (130), Yoshimasa Takashima (126), Atsuko Ito (115), Takeshi Tominaga (114), and Fumitoshi Ambe (105), and have learned of the retirement of Masuo Takeda next year (124 Mössbauer publications) Together, these individuals have contributed over 1,000 Mössbauer publications. To balance this trend, there are new Japanese Mössbauer scientists, who constitute the next generation of Mössbauer researchers. These include such individuals asTakateru Kawakami, Yoshiki Ohgo, Junhu Wang, Yoshitaka Yoda, Kaori Kuzushita, Hisao Yamauchi, Shotaro Morimoto, Yukio Hinatsu, and Shuji Kawasaki. Similar changes are being experienced throughout the international Mössbauer community.

Of particular note is that much of the development of the new generation of Mössbauer researchers is occurring regionally. For all of us to become better informed about what is happening in the various parts of the international Mössbauer community, the Mössbauer Effect Data Center is establishing a group of Regional Editors. The initial group includes Peter Schaaf for Germany, Denis Rancourt for Canada, George Fern for the UK, Stewart Campbell for Australia, and Clive Wynter for the US. These Regional Editors are working with MEDC and IBAME to establish regional Mössbauer Web pages.

New research areas are developing as a result of this next generation of Mössbauer researchers. One of the obvious areas is the new research efforts with Synchrotron Mössbauer. Other new frontiers will be examined.

Session 3

[08/11/06 - 09:30h]
Systematic Approach to Mössbauer Spectroscopy in Archaeology, Ursel Wagner[1], Izumi Shimada[2], Fritz E. Wagner[1], [1]*Physik Department E15, Technische Universität München, 85747 Garching, Germany;* [2]*Southern Illinois University, Institute of Anthropology, Carbondale 62901* ■Mössbauer spectroscopy has proved to be a powerful tool in the characterization of archaeological ceramics and in the assessment of ancient production techniques, since iron in pottery clays undergoes typical transformations during firing. Here we report on an in-depth investigation of pottery production in Northern Peru at the Formative Poma Canal kiln site (1000 - 700 BC) and in the Huaca Sialupe workshop during the Middle Sicán period (AD 950 - 1050). The final aim of this investigation is a comprehensive characterization of pre-Hispanic pottery production in Northern Peru.

In such a study the physical and chemical transformations taking place during firing of appropriate model clays under various conditions should be established in laboratory firing experiments. Field firings of replica pottery in authentic or replica kilns provide additional information in the assessment of ancient firing procedures. The clays used in such experiments should resemble those used in antiquity. For the Huaca Sialupe site clays already treated by ancient potters and unfired pottery found during the excavations are available. Mössbauer spectra are usually taken at RT and at 4.2K. Measurements in external magnetic fields help in identifying different iron phases.

In laboratory firing experiments, firing in air under reducing conditions and in changing atmospheres were emulated. These data were used in the interpretation of the data gained from numerous sherds, moulds and samples from kilns and furnaces at the archaeological sites. Also future finds can be studied. The results of Mössbauer spectroscopy supplement the archaeological findings and allow us to obtain a holistic picture of the cultural and technological development of the region. According to this picture, careful purification of the raw material and the control of the firing temperature by the use of charcoal as a fuel appear to have been major steps towards the perfection of a purpose-driven pottery production.

[08/11/06 - 11:20h]
Spin Density Waves in the layered compound CuFeTe$_2$: direct evidence of the coexistence of the normal and condensate states, A. Rivas[1], F. Gonzalez-Jimenez[2], J.M. Broto[3], Jesus Gonzalez[4], [1] *Departamento de Física, FACYT, UC, Valencia 2001, Venezuela;* [2] *Departamento de Física, Fac. de Ciencias, UCV, Apdo. 47586, Caracas 1041A, Venezuela* ■In this work we achieved a rigorous study of the magnetic and electric behavior of the layered compound CuFeTe$_2$. The magnetic measurements results, performed in a Faraday balance and in a SQUID magnetometer, indicate the appearance of an antiferromagnetic order below about 300 K, with a Pauli paramagnetic behavior above this temperature. This behavior is attributed to the formation of a Spin Density Wave (SDW) state in this compound. Another element in favor of

the existence of the SDW is given by the Mössbauer effect measurements: In the temperature range 2-310 K a variety of spectra are observed, going from an incommensurate magnetic structure, to whom is superposed a non magnetic contribution as temperature raises, until the complete disappearance of the first one. To confirm the itinerant character of the observed magnetism, a spectrum recorded under a magnetic field of 6.5 T shows that iron doesn't hold a magnetic moment.

These results allowed us to give a new interpretation of the Mössbauer spectra observed in SDW, because one can see how the proportions of the condensed state (spectra of the incommensurate SDW) and of the normal state (paramagnetic doublet) evolve according to the temperature.

The electric properties indicate the appearance of a metal-semiconductor transition around room temperature as the consequence of the opening of a gap at the Fermi level in the metallic layers, by the formation of a SDW state. The resistance increase, as temperature decreases, is due to the condensation of the conduction electrons down to 100 K; the results suggest a static regime, which means that the SDW is pinning. The unpinning of the SDW is observed in the non linear behavior in the I-V curves.

[08/11/06 - 11:45h]

Evidence for Kondo effect in Zn:Fe films: A ^{57}Fe Mössbauer effect study, P. MUNAYCO, J. LARREA J., Y. T. XING, E.M. BAGGIO-SAITOVITCH, *Centro Brasileiro de Pesquisas Físicas*, H. MICKLITZ, *II.Physikalisches Institut, Universitaet zu Koeln* ■Due to advances in sample preparation methods nowadays it is possible to investigate the behavior of impurities in metals. It has been shown that it is possible to prepare samples of Zn or Cd hosts, which contain ^{57}Fe impurities at a concentration of the order of 1 at %, by using the vapor-quenching method. The main interest of these former studies was to get information on the isomer shift (IS) of ^{57}Fe atoms sitting on substitutional lattice sites in the hcp Zn lattice. We now have extended these experiments to (i) in-situ resistance measurements and (ii) ^{57}Fe ME studies in an external magnetic field. While experiments (i) may give us information about the possible existence of a Kondo state via the finding of a resistance minimum, studies (ii) will give information on the local magnetic moment μ of Fe in Zn and the possible change of μ with B_{ex}. Zn films doped with ^{57}Fe (atomic concentration c between 0.2 and 2.0 at %) have been prepared by the co-evaporation of the two metals onto a cooled substrate ($T_s = 80$ K). *In-situ*electrical resistance measurements on these films show resistance minima at T_K ($T_K = 10$ K for c = 1.0 at %) which disappear in an external magnetic field $B_{ex} = 5$ T and, therefore, are interpreted as Kondo minima. ^{57}Fe Mössbauer effect studies on the films with c = 0.6 at % taken at T = 4.3 K and for various B_{ex} values, reveal that the effective paramagnetic Fe moments, μ, are $\mu < 0.1\ \mu_B$ for $B_{ex} = 3$ T. For larger magnetic fields the magnitude of μ is increasing with increasing B_{ex} [$\mu \sim 0.30(3)\ \mu_B$ for $B_{ex} = 7$ T], as expected for a spin-compensated Kondo state.

[08/11/06 - 12:00h]
Effect of Mn and Cu in Fe-Mn-Al-C-Cu alloys study by ICEMS and XRD, Juan David Betancur-Ríos, , Jesus Anselmo Tabares, German Antonio Pérez-Alcázar, Victor Fernando Rodríguez, *Departamento de Física, Universidad del Valle, A.A. 25360, Cali-Colombia* ■Experimental analysis of magnetic and structural properties of melted Fe-Mn-Al-C-Cu alloys with compositions $Fe_xMn_{0.915-x}Al_{0.075}C_{0.01}$ (series A) and $Fe_xMn_{0.912-x}Al_{0.075}C_{0.01}Cu_{0.003}$ (series B), $0.500 \leq x \leq 0.800$, in steps of 0.050, is presented and discussed. The analysis was performed by Integral Conversion Electrons Mössbauer Spectroscopy and X-ray Diffraction at room temperature. In order to obtain the alloys, high purity powders of Fe, Mn, Al, C and Cu were melted in an arc furnace, in argon atmosphere. These samples were melted again in an induction furnace and ingots were formed. The ingots were put under the following thermo-mechanical treatment: forged at 1473 K, laminated at 1073 K until 2.3 mm, homogenized at 1323K during 15 minutes, and finally a fast tempering was done in oil at room temperature. Then, discs of 25mm diameter and between 2.0 and 2.5 mm thickness were cut. Finally, the discs were grinded by means of different abrasive papers (grain size from 400 to 1200), polished to mirror brightness with an alumina solution, cleaned ultrasonically in an acetone bath and dried in air. The results suggest, for both series of alloys, that for the highest Mn content, samples exhibit an antiferromagnetic behavior, typical of the FCC or austenite FeMn phase rich in Mn; for low Mn contents, the coexistence of paramagnetic austenite, typical of the FeMn alloy poor in Mn, and ferromagnetic BCC or ferrite phases can be observed, while for the lowest Mn content, only FM phase tends to prevails. The ferromagnetic phase is associated to the BCC FeMnAl as is corroborated by X-ray diffraction. In samples with highest Mn content, the influence of Cu content is to reduce the mean hyperfine field and to stabilize the antiferromagnetic behavior

[08/11/06 - 12:15h]
Structural and hyperfine properties in nanocrystalline ball-milled iron, J. Restrepo, J. Mazo-Zuluaga, *Grupo de Estado Solido. Instituto de Fisica. Universidad de Antioquia. A.A. 1226, Medellin, Colombia* ■Nanocrystalline iron powder was obtained via high-energy ball milling. A wide range of milling times between 15 minutes and 48 hours was considered. The as-milled samples were characterized by 57Fe Mössbauer spectrometry at room temperature and Rietveld analysis of high-resolution X-ray diffractograms. Hence, correlations between the different hyperfine parameters and the structural ones are obtained. Concretely, for those samples having an average grain size in the range of some few nanometers, results reveal the presence of two distinguishable phases ascribed to the core of the nanograins and the inter-grains region in between. No evidence of iron oxide was detected. In particular, the intergranular region gives rise to a broad distribution of hyperfine magnetic fields typical of an amorphous-like structure. Moreover, such distribu-

tions reveal the occurrence with a non-zero probability of hyperfine fields slightly greater than 33 T at room temperature, which are attributed to those iron atoms located along the edge of the grain boundary. This fact suggests a slightly increase in the average coordination number and consequently in the atomic density. In contrast, those iron atoms in the intergranular region with lower hyperfine fields suggest a decrease in the average coordination number due to the presence of defects. In order to endorse this scenario, a modeling of the hyperfine field distributions based on the idea of Schottky vacancies and its corresponding equilibrium density is implemented. The employed model is based on the binomial method and allows inferring the most probable local configurations involving vacancies within the first coordination shell.

Session 4

[09/11/06 - 09:30h]

Two Years of Mössbauer Exploration on the Surface of Mars: Results from MIMOS II at Gusev Crater and Meridiani Planum,

GÖSTAR KLINGELHÖFER, *Institut Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, Germany* ■The Mars Exploration Rovers Spirit and Opportunity have explored the Martian surface at Gusev Crater and Meridiani Planum for more than two and a half Earth years, traveling more than 9km (Opportunity) and 8km (Spirit), each carrying our Mössbauer Spectrometer MIMOS II. More than 15 different minerals have been identified so far by the Mössbauer instruments on board the two rovers [1,2,3]. Mössbauer spectroscopy identified the secondary Fe3+-bearing minerals jarosite, hematite, and nanophase iron oxides in the sulfate-rich outcrop rocks at Meridiani Planum [2]. Pyroxene may be a remnant primary Fe2+-bearing mineral. No precursor material to the sulfate-rich outcrop has been identifieded to date, but it has been inferred to be basaltic in composition [4,5]. At Gusev Crater rocks are much more diverse, ranging from little altered basaltic material in the plains to pervasively altered basalt in the Columbia Hills [3,6]. Primary minerals include the Fe2+-bearing minerals olivine, pyroxene, and ilmenite, as well as the mixed-valence iron oxide magnetite. Secondary minerals include the Fe3+-bearing minerals hematite, goethite, nanophase iron oxides, and an unspecified iron sulfate phase. The relation between primary and secondary minerals varies over short spatial scales. In particular the minerals jarosite and goethite found at Meridiani Planum and Gusev Crater, respectively, are clear mineralogical evidence for aqueous weathering processes active at both landing sites in the past. New results will be reported. Recent results from Gusev Crater indicate the presence of hematite in greater abundance than in many targets at Meridiani.

References [1] Morris, R.V. et al. (2004) Science 305, 833-836. [2] Klingelhöfer, G. et al. (2004) Science 306, 1740-1745. [3] Morris, R.V. et al. (2006) JGR 111, E02S13. [4] McLennan, S.M. et al. (2005), EPSL 240, 95-121. [5] Tosca, N.J. et al. (2005), EPSL 240, 122-148. [6] Ming, D.W. et al. (2006) Journal of Geophysical Research, Vol. 111, E02S12, doi: 10.1029/2005JE002560

[09/11/06 - 11:20h]

Growth of Single-Wall Carbon Nanotubes using Maghemite Nanocatalyst,

RAMA BALASUBRAMANIAN, JAKE BENNETT, RICHARD GRANT, *Roanoke College, Salem, VA 24153, USA*, YANFEI YANG, PAOLA BARBARA, *Department of Physics, Georgetown University, Washington D.C. 20057, USA* ■Carbon nanotubes are cylindrical nanostructures with hexagonal networks of carbon atoms with interesting electronic and mechanical properties. The growth of carbon nanotubes in specific configurations and geometry is crucial to developing useful applications in nanoelectronics, nanosensors and smart coatings. We have shown that single wall carbon nanotubes (SWNTs) of diameters less than 2 nanometers can be grown directly from catalyst particles comprising of maghemite on a Silicon substrate using the conventional chemical vapor deposition (CVD)process. The sizes of SWNT were measured using Atomic Force Microscopy. The average tube diameter was measured to be 1.5±0.2 nm. Scanning Electron Microscopy measurements revealed that the catalyst oxide particles formed in micron sized clusters. Transmission Mössbauer measurements at room temperature showed the presence of a magnetic sextet corresponding to maghemite with a particle size approximately 100 nm and a superparamagnetic phase. The presence of superparamagnetic phase indicates the presence of maghemite particles with diameters less than 20 nm. Our results also indicate that the superparamagnetic phase of maghemite with average particle size of about 5 nm plays a critical role in the formation of SWNT with specific tube dimensions. Using the nanophase maghemite as catalyst particles in CVD growth, we have also been able to successfully synthesize several Y-junction nanotubes. Experiments are currently underway to characterize the relaxation rates of the superparamagnetic phase of maghemite. The fundamental role of arrays of metal nano-catalysts and superparamagnetic nanoclusters of maghemite in the selective growth of single wall carbon nanotubes and Y-junction nanotubes will be presented.

[09/11/06 - 11:45h]
Improving Detector Signal Processing with Pulse Height Analysis in Mössbauer Spectrometers, JIRI PECHOUSEK, MIROSLAV MASHLAN, JIRI FRYDRYCH, DALIBOR JANCIK, ROMAN PROCHAZKA, *Department of Experimental Physics, Palacky University, Svobody 26, 771 46 Olomouc, Czech Republic* ■A plenty of different programming techniques and instrument solutions are used in the development of Mössbauer spectrometers. Each of them should provide a faster spectra accumulation process, increased productivity of measurements, decreased nonlinearity of the velocity scale, etc. The well known virtual instrumentation programming method has been used to design a computer-based Mössbauer spectrometer. Hardware solution was based on two commercially-available PCI modules produced by National Instruments Co. Data acquisition was realized via NI 5124 digital oscilloscope which was used as a multichannel analyzer. The NI 5401 function generator was used to the drive transducer system. Virtual Mössbauer spectrometer is implemented by the graphical programming language LabVIEW 7 Express. This design environment allows to emulate the multichannel analyzer on the digital oscilloscope platform. This is a novel method based on Waveform Peak Detection function which allows detailed analysis of the acquired signal. This solution of the Mössbauer spectrometer, equipped with an appropriate detector, allows to build a wide variety of measurement arrangements (e.g. TMS, CEMS, and CXMS). The optimal treatment of the detector signal from various detector types is achieved by mathematical processing only. As a result, the possibility of an increase of signal/noise ratio is presented. It was shown that the number of the velocity channels in the Mössbauer spectrum is given by the

sampling frequency of the acquired signal and frequency the of velocity signal. In this work, the optimal sampling frequency-determination procedure for various detector types by calibration spectra comparison is presented.

1. J. Pechousek, M. Mashlan: Mössbauer spectrometer in the PXI/CompactPCI modular system. Czech. J. Phys. 55, No. 7 (2005) 853-863.

[09/11/06 - 12:00h]
MÖSSBAUER SPECTROMETER. The Past. The State of the Art. Quo Vadis?, Sobir Irkaev, Valentin Semenov, *Institute for Analytical Instrumentations RAS, Saint-Petersburg, Russia* ■The paper describes the state of the Mossbauer spectroscopy instrumentation. It is stressed that the current trend in Mossbauer spectrometer design is continuous improving of technical parameters of various instrument parts and experiment automation systems [1]. In fact, this does not involve extension of the information potential of the nuclear gamma resonance technique. The most important lines of Mossbauer spectroscopy instrumentation development are discussed. The analysis shows that additional information may be obtained by the use of resonance converters of spectral lines (resonance detectors, filters, shutters and polarizes). In this connections, special attentions is paid to a set of multidimensional parametric Mossbauer spectrometry (MPMS) instruments [2,3] which considerably extends the functionality of conventional spectroscopy, increases the resolution and speed of the method almost for any resonance isotope and greatly expands the information potential. We are present the set of the MPMS spectrometers which are consist of three types of multipurpose (SM 2201 and SM 3201), problem-oriented (SM 2201DR and SM 1101TER) and technological (SM 2101TURBO and SM 1101). The detailed description of features of each types of spectrometers is present. The capabilities of spectrometers and their experimental opportunities are illustrated on examples of investigation of different samples. Some examples are given to illustrate experimental capabilities of certain spectrometers.
S.M. Irkaev <<Trends in Mossbauer Spectrometer Designs>>, Mossbauer effect Reference and Data Journal, 28, No 10 (2005) 314-323. S.M. Irkaev <<Research and Development in the Field of Mossbauer Spectroscopy Instruments and Methods>>, Scientific Instrumentation, 9, No 3 (1999) 21-32 (In Russian). Semenov V.G., Andreeva M.A., Irkaev S.M. <<Nuclear Gamma Resonance Optics of Surfaces>>, Scientific Instrumentation, 9, No 1 (1999) 19-32 (In Russian).

[09/11/06 - 12:15h]
Mössbauer Scans, G. A. Pasquevich, , P. Mendoza Zélis, M. B. Fernandez van Raap, F. H. Sánchez, *Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata* ■A Mössbauer scan can be defined as the recording of the Mössbauer transmission at a fixed Doppler energy while a physical quantity, such as temperature, is continuously varied. The first Mössbauer thermal scan was performed by Rudolf L. Mössbauer in 1957, when he measured the temperature dependence of the nuclear resonant ab-

sorption effect on ^{191}Ir at zero Doppler velocity. Shortly after that, well known Mössbauer specialists as U. Gonser, S. Hanna, and others, explored this experimental approach. In 1962 R.S. Preston, S.S. Hanna and J. Heberle, applied this technique to metallic Iron and published a precise determination of its Curie temperature. In the late seventies C.L. Chien published a few inspiring papers showing how this method, in combination with Mössbauer spectroscopy and other techniques can help to detect and identify sequential thermally induced reversible and irreversible changes on amorphous metastable materials.

Despite these important antecedents, the potential of Mössbauer scans can be substantially enhanced. Here we discuss how this can be done and the steps we have taken so far to accomplish it. Firstly, the method can be upgraded from a semiquantitative to a fully quantitative one, by developing the appropriate theoretical expressions for analysing the experiments. Secondly, the effect of varying different physical parameters, such as temperature, degree of solid state reaction advance, external fields, etc., can be explored. Thirdly, the optimal experimental set up, procedures, and working conditions for a given scan can be studied and improved.

We present experimental results of thermal, isothermal, and magnetic Mössbauer scans recently obtained by our group. Examples of studies of the hyperfine field temperature dependence on $FeSn_2$, thermal evolution of a Finemet amorphous precursor, and the magnetic response of $\alpha - Fe$ and a Nanoperm alloy to an ac external field will be presented.

[09/11/06 - 14:25h]
Using Mössbauer spectroscopy as a key technique in the investigation of nanosized magnetic particles, PAULO C. MORAIS, *Universidade de Brasília - Instituto de Física, 70910-900 Brasília DF, Brazil* ■Mössbauer spectroscopy has already proved itself as a key technique in the investigation of nanosized magnetic nanoparticles. For decades the signature of the superparamagnetic behavior has been fully accomplished via the temperature dependence of Mössbauer spectra. In addition, the literature provides huge number of examples of the size effect, via the onset of the superparamagnetic behavior. Finally, the temperature dependence of the internal field has long been used to disclose the very fine aspects of the magnetic phase transition in nanosized systems. Despite all the knowledge accumulated in about half of a century, regarding the use of the Mössbauer spectroscopy in investigating iron-based magnetic nanoparticles, the technique is far from being exhausted on its capability to provide useful and complementary information about such material systems. This work provides new insights while using Mössbauer spectroscopy as a key technique for complementary information regarding the magnetic behavior of nanosized magnetic particles.

[09/11/06 - 15:00h]
Methodology and Applications of Elastic and Inelastic Nuclear Resonant Scattering, ERCAN ALP, WOLFGANG STURHAHN, JIYONG ZHAO, T. TOELLNER, *Argonne National Laboratory, Argonne, Illinois 60439, USA* ■ Nuclear resonant scattering of synchrotron radiation as a tool

for investigating chemical, magnetic and vibrational properties of materials under extreme conditions have received favorable response from various scientific disciplines including condensed matter physics, materials science, biophysics, geophysics and mineral physics. This is rather remarkable given the fact that the technique itself is undergoing substantial development in terms of instrumentation and data evaluation. The isotopoes that can be studied have been extended to more than a dozen, including Tm, Fe, Sn, Eu, Dy, Kr, Sb, and Sm. Today, it is possible to learn about phonon density of states under pressures exceeding 1 Mbar, and temperatures as high as 3000 K, or as low as 4 K. This information, which can be converted into Debye velocity of sound, as well as an accurate test of force constants turned out to be very relevant to geophysics, and to those who perform density functional calculations. Similarly, vibrational and magnetic properties of a isotopically decorated monolayers, carefully placed at a particular depth can be studied. Interesting studies of iron proteins, model compounds like single crystal porphyrins, with different ligand substitutions provides important clues to the mechanisms of enzymes. This talk will review the recent trends from development point of view and will try to put some perspective for various opportunities at the Advanced Photon Source with respect to optics, different isotopes and sample environments.

(*) Work performed in collaboration with W. Sturhahn, T. Toellner, and J. Zhao, all of Argonne National Laboratory, and their collaborators. This work is supported by US DOE-BES Materials Science under contract number W-31-109-ENG-38.

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