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MÖSSBAUER STUDY ON PHASE SEPARATION IN FeNi MULTILAYERS UNDER ION BOMBARDMENT

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ABSTRACT

We investigated the effect of noble gas irradiation (He, Ne, Ar and Xe) on Fe-Ni multilayers with a very thin modulation and nominal composition in the invar region $Fe_{0.63}Ni_{0.37}$. The evaluation of the formation/stability of the Fe-Ni phases formed under irradiation with different ions and doses was followed by conversion electron Mössbauer spectroscopy (CEMS).

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Keywords: ion implantation; Mössbauer spectroscopy; Fe-Ni multilayers.

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1. INTRODUCTION

The Invar alloys, which are based on the composition Fe-36 wt% Ni, have a near zero thermal expansion coefficient over a substantial temperature range. Many other high temperature properties and parameters including lattice parameter, electrical resistivity, magnetization and elastic moduli show anomalies which have been found experimentally [1,2]. These observations indicate that there is a phase instability in the Fe-Ni phase system at approximately the Invar composition. Several authors have suggested the presence of a low temperature miscibility gap to explain the anomalies and have proposed a variety of phase diagram for the Fe-Ni system [3, 4, 5, 6,].

Phase decomposition in thermally annealed Fe-Ni materials is experimentally difficult to observe because of the slow diffusion rate of nickel in iron at low temperatures. However, iron-nickel meteorites, due to their extremely slow cooling rates (1° C/10^6 years), are a unique source of material that allow the study of phase separation in the Fe-Ni system [6].

Extensive studies [7,8] have shown that Fe-Ni Invars undergo phase separation after enough irradiation (neutrons or electrons) to enhance diffusion. It has also been found that the alloys with composition in the range in which the so called Invar anomalies occurs are those with the greatest response to irradiation.

Other alternative ways of achieving a state closer to the true thermodynamical equilibrium (which for this system means atomic ordering and phase separation), is to use special techniques for increasing diffusion, like ultrafine particles [9,10,11] or ion bombardment [12].

In this work we investigated the effect of noble gas irradiation (He, Ne, Ar and Xe) on iron-nickel multilayers with nominal composition $Fe_{0.63}Ni_{0.37}$, through Conversion Electron Mössbauer Spectroscopy (CEMS).

2. EXPERIMENTAL

The FeNi multilayers were prepared using e-gun source in a ultra-high vacuum system at the Kyoto University. Several pieces were cut into 15x15 mm^2. Before deposition the SiO_2/Si substrates were heated up to 100° C for 2 hours to clean the surface. Then, the substrates were cooled down to room temperature and Fe and Ni layers were alternately deposited. The vacuum during the deposition was better than $5x10^{-8}$ Torr. In these conditions it was produced multilayers with total thickness of 102 nm and a very thin modulation

(Λ=0.33nm/Fe+0.18nm/Ni), that means 200x[ϕ_{Fe}=0.33nm/ϕ_{Ni}=0.18nm] or a nominal composition $Fe_{0.63}Ni_{0.37}$.

The ion irradiations were done at the HVEE 400-kV ion implantor of the Institute of Physics, Porto Alegre. The implantation current density was always lower than 1 $\mu A/cm^2$ in order to avoid undesirable heating of samples. The implantation energies (He-14 KeV, Ne-70 KeV, Ar-130KeV and Xe-400 KeV) were set up using the TRIM code [13] in order to match the projected range and range straggling with middle of sample thickness. The annealing treatments were performed in a vacuum better than $2x10^{-7}$ Torr.

The as deposited as well as the irradiated samples were characterized by Rutherford Backscattering (RBS) in order to investigate sputtering effects during irradiation and reaction with the substrate.

Conversion Electron Mössbauer Spectroscopy (CEMS) was performed at room temperature using a conventional spectrometer with a flowing gas (90% He - 10% CH_4) proportional counter and a $^{57}Co(Rh)$ source. The 14.4 keV γ-ray direction was perpendicular to the film plane, but no texture effects were expected to occur. The CEMS spectra were analysed using the NORMOS code [14].

3. RESULTS AND DISCUSSION

The characterization by RBS (not shown) clearly indicates that there is no diffusion of Fe and Ni towards the substract and no sputtering effects.

We investigated by CEMS the effect of noble gas irradiation on iron-nickel multilayers with total thickness of 1020Å and a very thin modulation Λ = 3.3 Å Fe +1.8 Å Ni. This modulation corresponds practically to the distances that one atom can move in lattice positions. Then, if mixing or formation of phases occur only in the next near neighbours it would be more evident than in samples with thicker layers of ~ 100 Å [15].

CEMS data are particularly usefull to evaluate phase changes induced by irradiation, giving information on microstructural aspects of the mixed layer such as chemical environment, local atomic arrangement, magnetic ordering, etc. [16]. It is known that the hyperfine field in iron-nickel alloys contains information on composition and structure and can be used to study the mixed region.

Typical CEMS spectra of films irradiated using Ne+ ions (70 keV) and doses in the range $1x10^{15}$-$1x10^{17}$ ions/cm^2 are shown in figure 1. The corresponding hyperfine parameters

are listed in Table 1. The spectrum of the as deposited sample as well as the $5x10^{15}$ Ne/cm^2 irradiated sample, display only the typical sextet of bcc α-Fe. From $1x10^{16}$ Ne/cm^2 on it is clearly seen the formation of two other γ-FeNi phases with different Ni compositions: one corresponding to a magnetic phase atomically ordered - Fe50Ni50 - (B_{hf}=29T and ΔE_Q= 0.15-0.20 mm/s) and another one corresponding to a non-magnetic phase Ni≤30%. With increasing doses the ordered phase increases up to 18% while the non-magnetic component presents a remarkable enhancement up to 10^{17} ions/cm^2, accounting for 40% of the spectrum at this doses. An increase of about 50% in the irradiation doses did not lead to any alteration in the spectra, suggesting that there is a saturation effect. This two phase region has also been observed in particle irradiated Invar alloys [17] and meteorites [18,19] and has been considered as the equilibrium state. It has been recently proposed [20] that the non-magnetic phase seen by Mössbauer spectroscopy is a low-spin γ-phase (γ_{LS}), related to the close packed low-spin phases seen in the pressure-temperature phase diagrams of both metalic Fe and synthetic Fe-Ni alloys, and many other Fe-alloy system. This γ_{LS} in meteorites as well as in particle irradiated alloys coexists with the ordered FeNi phase (named tetrataenite in meteorites). The two phases have practically the same lattice parameters and form a very fine-grained intergrowth. This intergrowth is indicative of the low-temperature equilibrium state at the Invar compositions. Since the γ_{LS} phase is never seen alone, but always in coexistence with the ordered phase (having various degrees of atomic order) it has been proposed [20] that this γ_{LS}-phase always occurs in close microstructural association with the ordered phase

The effect of irradiation with other ions (He, Ar and Xe) can be seen in fig. 2. Irradiation with He showed to be less effective than with Ne for similar doses. In the He irradiated sample a high proportion of the α-Fe (79%) still remains even at $1x10^{17}$ He/cm^2 and only a low proportion (7%) of the non-magnetic phase is formed together with 14% of the ordered 50/50 phase. In the case of the irradiation with Ar, a large distribution of hyperfine fields appear showing a spectral component centered around 29T, indicating formation of the Ni-rich phase (18%), and other low field contributions. In the spectrum, the γ_{LS}-phase is also present but in a very low proportion (~3%).

In the Xe irradiated sample besides other low field contributions, the large hyperfine field distribution displays the presence of the component centered at 29T and another one centered around 23T, attributed to the Invar phase, already observed in Kr irradiated samples [Toselli]. Nevertheless the γ_{LS} was not detected in the Xe irradiated sample. This can be due to

an instability of this Fe-rich phase in relation to Xe irradiation that seems to favour the formation of phases in the Invar compositions.

The results obtained bombarding Fe-Ni multilayers with very thin modulation with Ar and Xe are very similar to that obtained with Kr^{2+} irradiation by Toselli et al. [15] using not so thin layers, suggesting that the mixing process occurs for more than the distance of a few lattice parameters.

In order to investigate the well known Radiation Enhanced Diffusion (RED) phenomena [21] in our system we performed two more experiments that can be seen in fig.3: a thermal annealing at 350° C and a simultaneous irradiation at the same temperature.

If we compare figure 3c with fig. 1e we can see that irradiation at RT or at 350° C does not show any difference. On the other side a sample treated at 350° C for ~50 hours (fig.3b) exhibits the same spectrum as the as deposited one (fig. 3a), indicating that only temperature doesn't promote any phase transformation.

Finally, another question that still remains open is related to the phase stability under irradiation. To get more information about this question we submit our samples to a sequential bombardment (fig. 4) and remarkable effect was observed. For samples previously implanted with Ne the γ_{LS}-phase (associated with Ne implantation) is completely destroyed by Xe ions.While changing the order of implantation, i.e., the sample is first implanted with Xe and then bombarded with Ne, no modifications appear in the CEMS spectrum.

4. CONCLUSIONS

From our results obtained irradiating Fe-Ni multilayers, with nominal composition in the Invar region, with a series of noble gas, He, Ne, Ar, Xe it is possible to evaluate the formation/stability of the Fe-Ni phases formed by ion irradiation. In the case of Ne there is an increasing formation of the two phase region: ordered and γ_{LS}, with a saturation effect at doses as high as 10^{17} ions/cm^2. The same effect but much less effective was observed He irradiation. The γ_{LS} phase formed by Ne irradiation showed an instability, vanishing completely when further irradiated with Xe. If we change the order of irradiation (fig. 4), first Xe and then Ne trying to form the two phase region, phase segregation does not occur, at least the γ_{LS} is not obtained and the CEMS spectrum displays the same distribution produced by Xe irradiation, showing that the phases produced by Xe predominates over the others. For bombardment with

heavier ions like Ar and Xe the mixing effect was similar to reported data obtained on Kr irradiated samples[15], showing a large distribution of hyperfine fields.

These results can be interpreted as evidencing that for lighter ions (He, Ne) phase separation is obtained and equilibrium-like state for this system is achieved, whereas for heavier ions (Ar, Xe and Kr) the mixing effect is predominant.

FIGURE CAPTION

Fig.1 - CEM spectra of Fe-Ni multilayers:
a) as deposited, and Ne irradiated to the doses: b) $5x10^{15}$ Ne/cm^2; c) 10^{16} Ne/cm^2;
d) $5x10^{16}$ Ne/cm^2; e) 10^{17} Ne/cm^2.

Fig.2 - CEM spectra of Fe-Ni multilayers irradiated:
a) 10^{17} He/cm^2; b) 10^{17} Ne/cm^2; c) 10^{17} Ar/cm^2; d) 10^{17} Xe/cm^2.

Fig.3 - CEM spectra of Fe-Ni multilayers:
a) as deposited; b) annealed 52h at 350° C; c) irradiated with 10^{17} Ne/cm^2 at 350° C.

Fig.4 - CEM spectra of irradiated Fe-Ni multilayers:
a) $5x10^{16}$ Xe/cm^2; b) $5x10^{16}$ Xe/cm^2 + $5x10^{16}$ Ne/cm^2; c) $5x10^{16}$ Ne/cm^2 + $5x10^{16}$ Xe/cm^2.

TABLE CAPTION

Table 1 - Hyperfine parameters and relative phase area for the Ne irradiated Fe-Ni multilayers.

Table 2 - Ion doses, hyperfine parameters and relative phase area for the Fe-Ni irradiated multilayers.

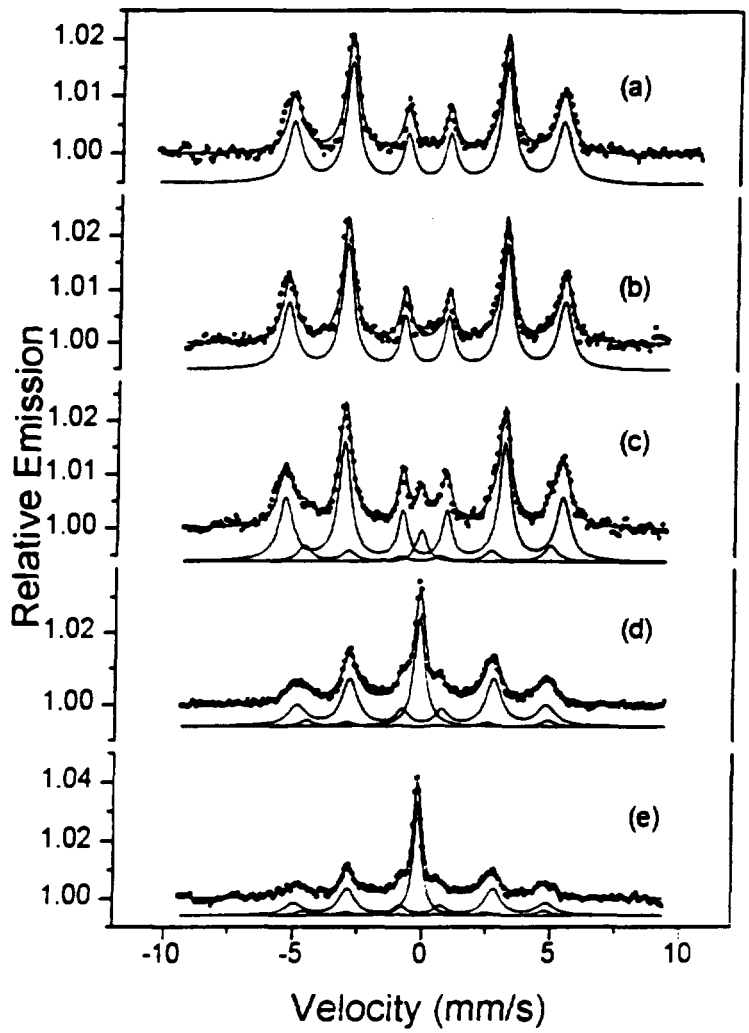
Relative Emission
1.02
1.01
1.00
(a)
(b)
(c)
(d)
(e)
1.04
-10
-5
0
5
10
Velocity (mm/s)

FIG. 1

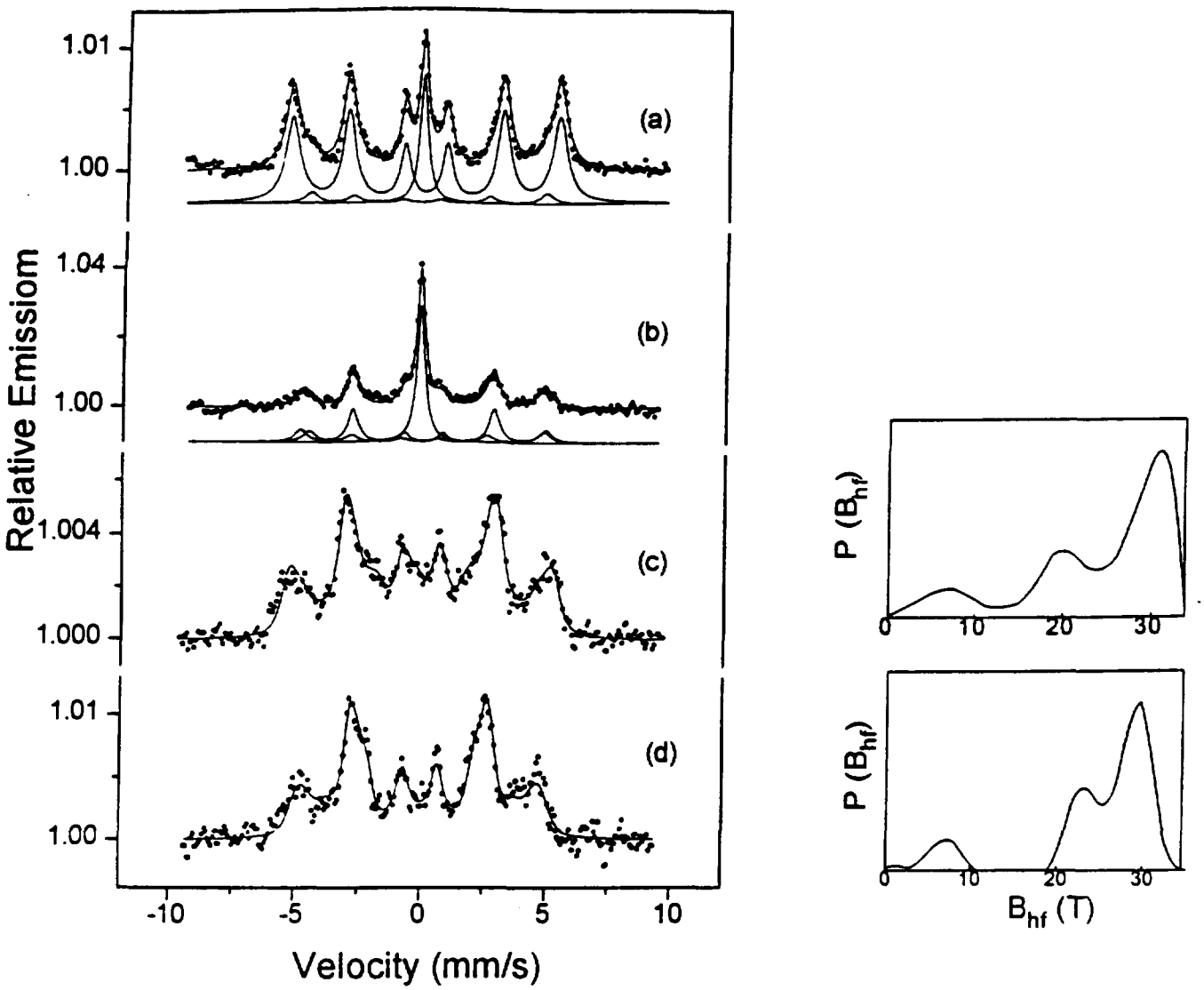
Relative Emission
1.01
1.00
(a)
1.04
1.00
(b)
1.004
1.000
(c)
1.01
1.00
(d)
-10
-5
0
5
10
Velocity (mm/s)
P (B_hf)
0
10
20
30
P (B_hf)
0
10
20
30
B_hf (T)

FIG. 2

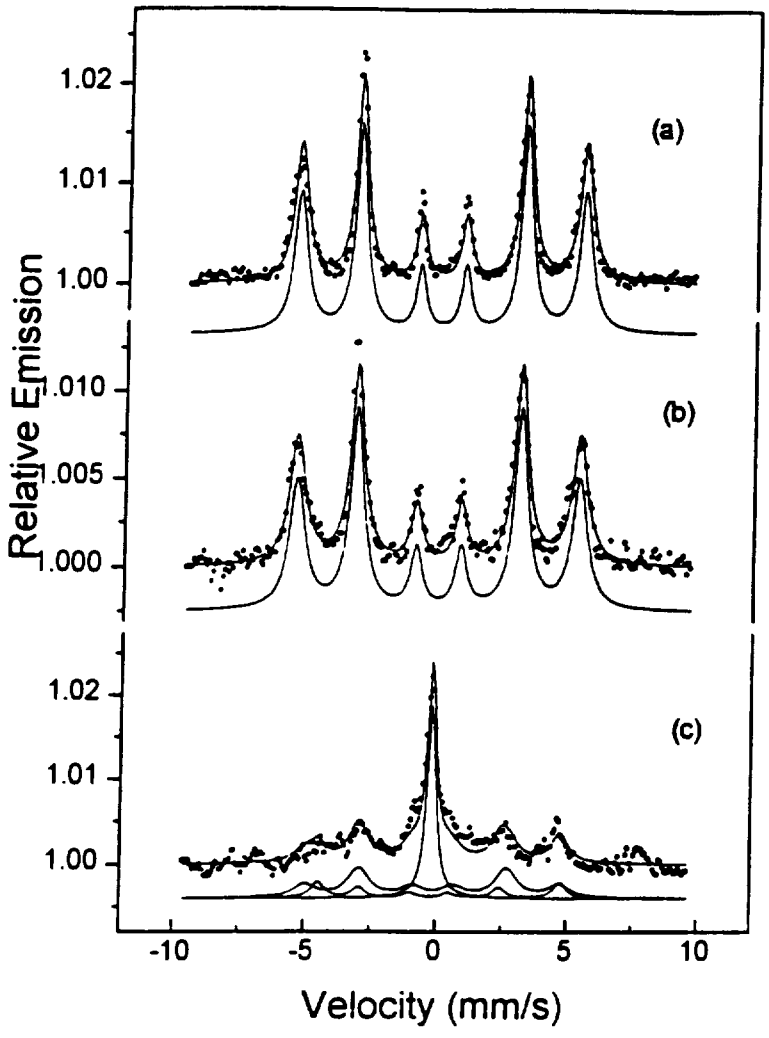
Relative Emission
1.02
1.01
1.00
(a)
1.010
1.005
1.000
(b)
1.02
1.01
1.00
(c)
-10
-5
0
5
10
Velocity (mm/s)

FIG. 3

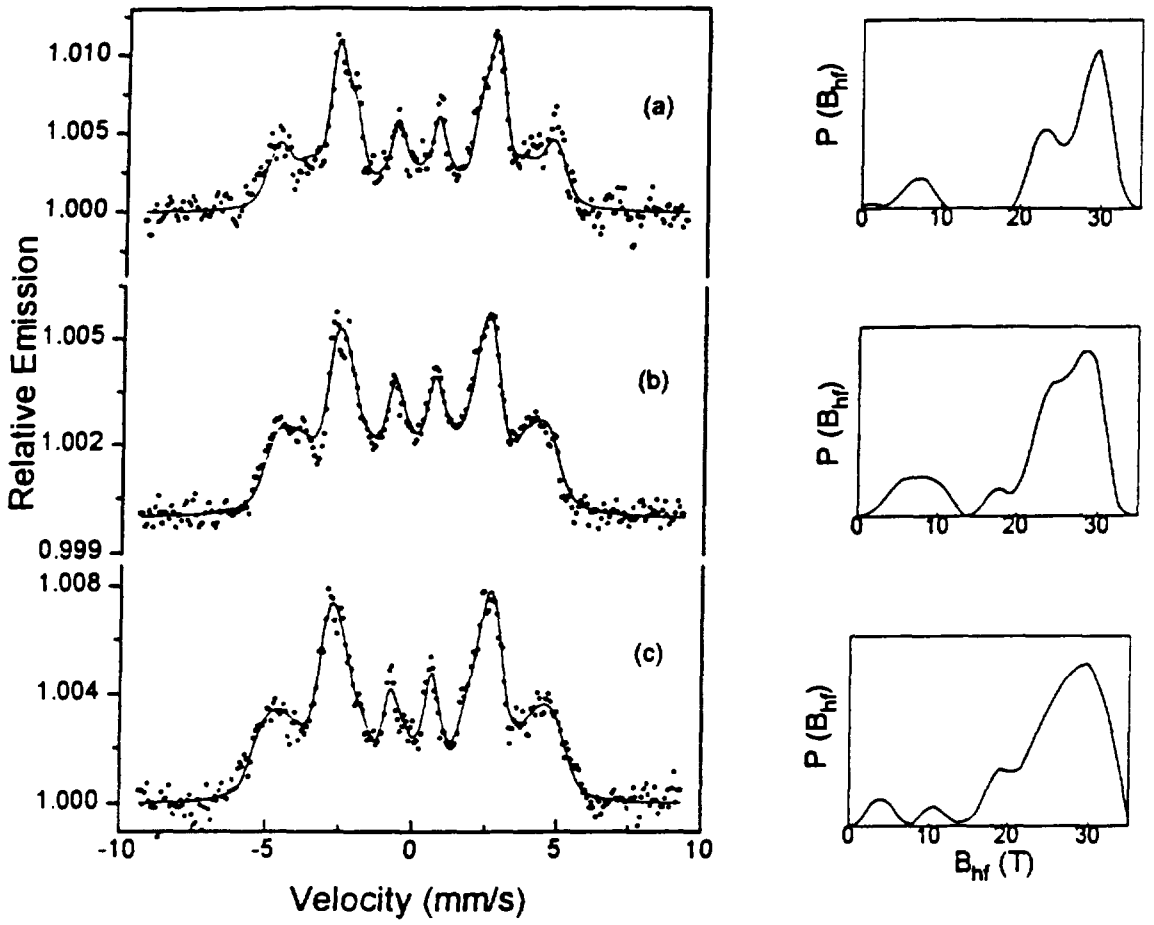
Relative Emission
1.010
1.005
1.000
(a)
1.005
1.002
0.999
(b)
1.008
1.004
1.000
(c)
-10
-5
0
5
10
Velocity (mm/s)
P (B_hf)
0
10
20
30
B_hf (T)

FIG. 4

TABLE 1

Sample	H (T)	IS (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	A (%)
As dep	33	-0.07	-	0.48	100
10^{17} He/cm^2	33	-0.06	-	0.50	79
	29	-0.07	0.15	0.60	7
	-	-0.18	-	0.40	14
10^{17} Ne/cm^2	30	-0.04	-	0.40	41
	29	-0.05	0.20	0.60	18
	-	-0.18	-	0.40	41
10^{17} Ar/cm^2	Large magnetic distribution Non-magnetic phase < 5%				
10^{17} Xe/cm^2	Large magnetic distribution Only magnetic contribution				

TABLE 2

Sample	H (T)	IS (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	A (%)
As dep	33	-0.07	-	0.48	100
5.10^{15} Ne/cm^2	33	-0.06	-	0.45	100
1.10^{16} Ne/cm^2	33	-0.06	-	0.46	82
	29	0.05	0.15	0.60	13
	-	-0.17	-	0.41	5
5.10^{16} Ne/cm^2	30	-0.04	-	0.40	57
	29	-0.05	0.20	0.60	11
	-	-0.18	-	0.40	32
1.10^{17} Ne/cm^2	30	-0.05	-	0.60	41
	29	-0.05	0.20	0.60	18
	-	-0.18	-	0.40	41

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