

REFERENCE

IC/82/62



**INTERNATIONAL CENTRE FOR  
THEORETICAL PHYSICS**

AMORPHOUS Cu-Ag FILMS WITH HIGH STABILITY

I.M. Reda

J. Hafner

P. Pongratz

A. Wagendristel

H. Bangert

and

P.K. Bhat

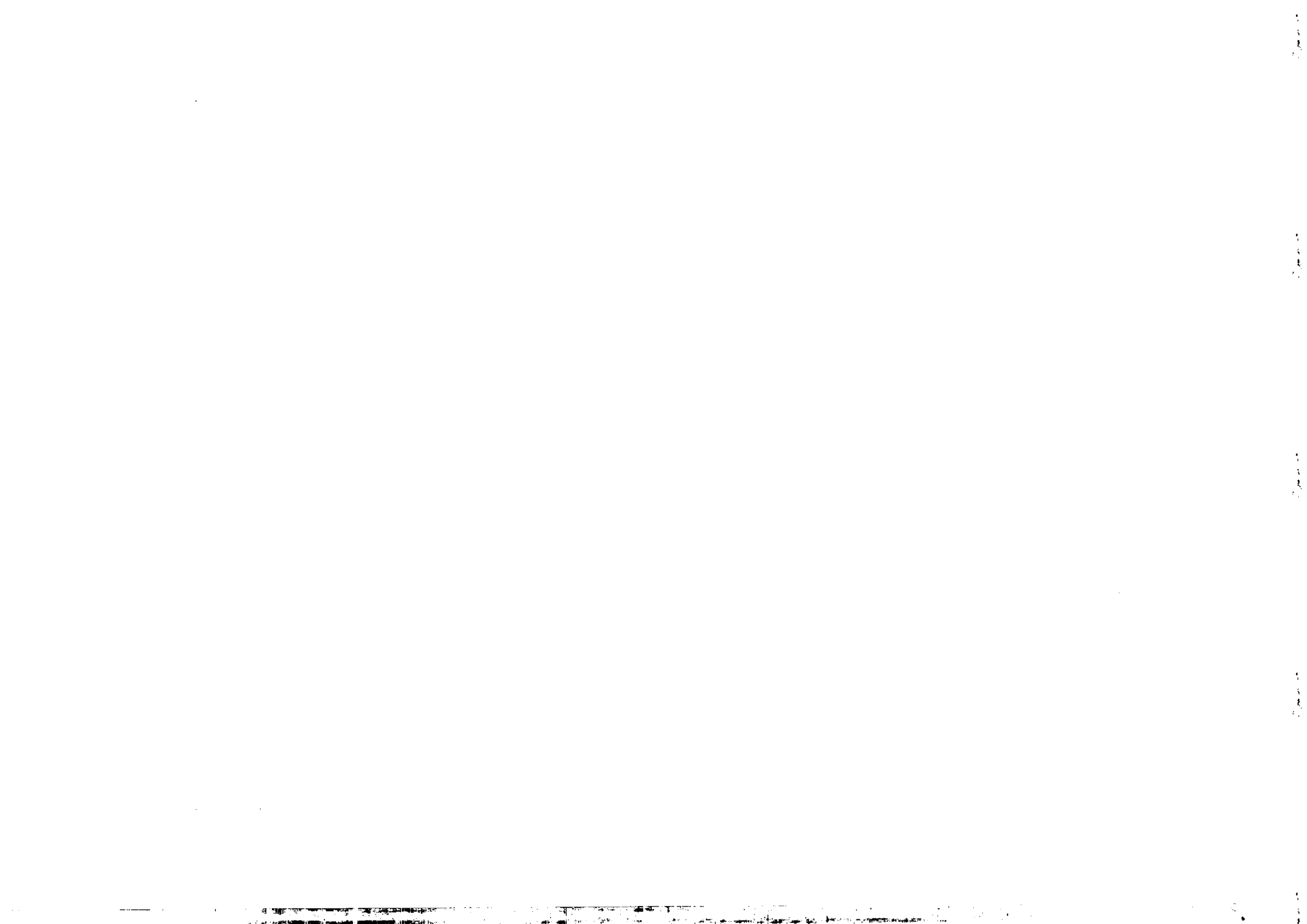


**INTERNATIONAL  
ATOMIC ENERGY  
AGENCY**



**UNITED NATIONS  
EDUCATIONAL,  
SCIENTIFIC  
AND CULTURAL  
ORGANIZATION**

1982 MIRAMARE-TRIESTE



International Atomic Energy Agency  
and  
United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

AMORPHOUS Cu-Ag FILMS WITH HIGH STABILITY \*

I.M. Reda \*\* J. Hafner \*\*

International Centre for Theoretical Physics, Trieste, Italy,

P. Pongratz, A. Wagendristel, H. Bangert and P.K. Bhat  
Institute of Applied and Technical Physics, Institute of Theoretical Physics,  
Technical University, Vienna, Austria.

MIRAMARE - TRIESTE

June 1982

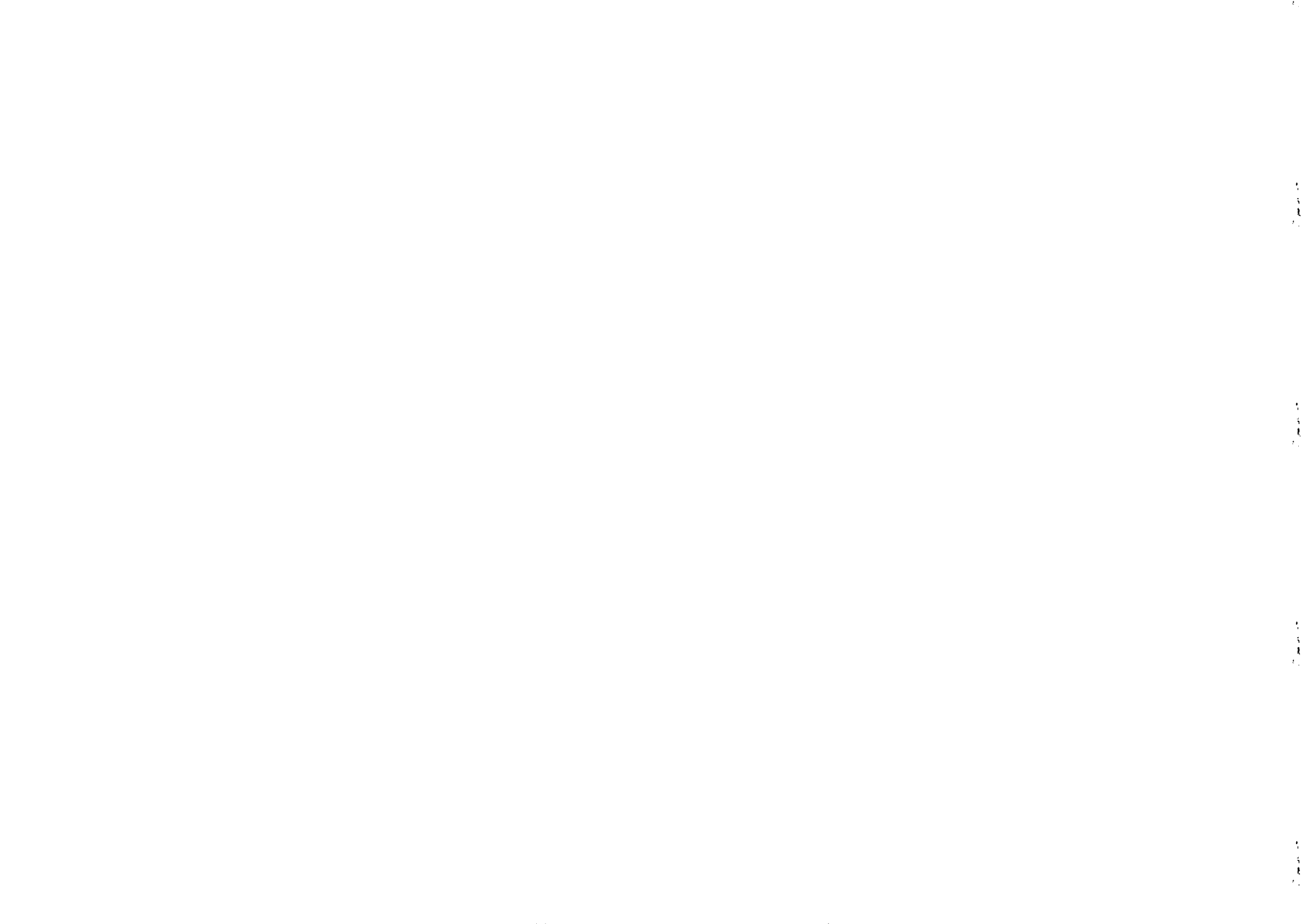
\* Submitted for publication.

\*\* On leave of absence from Institute of Applied and Technical Physics,  
Institute of Theoretical Physics, Technical University, Vienna, Austria.



ADDENDUM TO ACKNOWLEDGMENTS:

I.M. Reda and J. Hafner would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.



IC/82/62

International Atomic Energy Agency  
and  
United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

AMORPHOUS Cu-Ag FILMS WITH HIGH STABILITY \*

I.M. Reda \*\* J. Hafner \*\*

International Centre for Theoretical Physics, Trieste, Italy,

P. Pongratz, A. Wagendristel, H. Bangert and P.K. Bhat  
Institute of Applied and Technical Physics, Institute of Theoretical Physics,  
Technical University, Vienna, Austria.

MIRAMARE - TRIESTE

June 1982

\* Submitted for publication.

\*\* On leave of absence from Institute of Applied and Technical Physics,  
Institute of Theoretical Physics, Technical University, Vienna, Austria.

Films produced by quenching Cu-Ag vapour onto cooled substrates at liquid nitrogen temperature have been investigated using electron microscopy, electron diffraction and electrical resistivity measurements. In the composition range from 30 to 70 at% Cu the as quenched films are amorphous, and within the range of 35 to 63 at% Cu the amorphous phase is stable above room temperature with a maximum crystallization temperature  $T_c = 381$  K at 47.5 at% Cu. Crystallization results in the formation of a supersaturated fcc solid solution which decomposes in a second crystallization step. The effect of deposition rate, film thickness, temperature and surface of the substrate, and most importantly of the composition on the transition temperatures has been investigated. A comparative study of the formation of amorphous phases in a wide variety of Cu-based alloys is presented.

### 1. Introduction

The formation of the amorphous phase of metals and alloys is normally achieved by:

- (a) liquid quenching (splat cooling or melt spinning)
- (b) co-deposition of two or more elements using vacuum techniques or electrochemical processes, and
- (c) deposition onto substrates which are sufficiently cold to inhibit atomic mobility.

Pure amorphous metals may only be prepared by the third technique /1,2/, Cu-based alloys are known to be very tendent to form amorphous phases. Amorphous alloys with alkaline-earth metals (e.g. Cu-Mg/3/, Cu-Ca/4/), polyvalent simple metals (Cu-Al/5/, Cu-Sn/1,6/), metalloids (Cu-P/7/, Cu-Ge/8/ with small additions of Ag), transition-metals (Cu-Zr/9/, Cu-Ti/10/), rare-earth metals (Cu-La/11/, Cu-Gd/12/), actinides (Cu-Th/13/) and nobel metals (Cu-Ag/14-18/) have been prepared. Amorphous Cu-Ag alloys belong to the rare examples where two elements from the same row of the periodic table form an amorphous alloy and there is still some uncertainty concerning the structure and the stability of the as-quenched alloy. The early X-ray diffraction analysis of Wagner /15/ and Lukens /16/ on  $\text{Cu}_{45}\text{Ag}_{55}$  alloys coevaporated on beryllium substrates at a vacuum of  $10^{-3}$  Pa showed clear evidence for the liquid-like

and hence amorphous structure of the condensate. On the other hand, Lukens reported that  $\text{Cu}_{48}\text{Ag}_{52}$  films vapour-quenched in a better vacuum but on vitreous silica are definitely microcrystalline. There is also a discrepancy concerning the stability of the amorphous phase: Mader /14/ reported a crystallization of the amorphous state to the metastable fcc solid solution at about 375 K, whereas according to Chopra /18/, the noncrystalline state is stable only up to 120 K.

In this paper we present a re-investigation of vapour-quenched Cu-Ag alloys over the whole concentration range using electron microscopy, electron diffraction and electrical resistivity measurements. The influence of composition, deposition rate, film thickness, substrate temperature and surface on the stability of the amorphous phase was studied. In the second part we present a comparative study of the formation of amorphous Cu-based alloys and of their stability.

## 2. Preparation

At pressures between  $1 \times 10^{-6}$  to  $6.5 \times 10^{-5}$  Pa, Cu and Ag were simultaneously evaporated from the individually controlled tungsten boats, the boat for Cu was covered with a thin layer of aluminium oxide. Polished glass slides 0,2 mm thick predeposited with a set of Cr(10 nm) /Au(100 nm) contacts for resistance measurements served as substrates. They were ultrasonically cleaned in freon and then dried in the vapour zone of this solvent. Before being exposed to the metal vapour, the substrates were annealed at 200°C for 60 minutes and then rapidly cooled to liquid nitrogen temperature. The substrate temperature was measured by a Ni-NiCr thermocouple 0,2 mm in diameter, attached to the substrate with

silver paste. In each run additional samples for electron microscopic investigations, for X-ray optical determination of the thickness /19/ and accurate determination of the film composition by atomic absorption spectrometry were prepared. For electron microscopy glass substrates were coated with a thin intermediate Movital® film (10 nm thick) which dissolves easily in chloroform to detach the alloy film from the substrates. The deposition rates were monitored by a quartz crystal balance facing both sources during the co-evaporation or either one of them before as well as after deposition.

## 3. Structural characterization

Immediately after deposition, the films were isothermally annealed in steps of 10°C. During this treatment the resistance of the films was measured. After stabilisation at each particular temperature the next step was carried out. At several temperatures the anneal was interrupted and the samples were cooled down again in order to detect irreversible changes in the resistance as well as to measure the temperature coefficient of resistance. As a typical example of such measurements we first show the resistivity versus temperature plot of a  $\text{Cu}_{48}\text{Ag}_{52}$  alloy film (fig.1). The main features are two pronounced irreversible drops in the resistivity at distinct temperatures. In order to assign the type of the structure to the three plateau regions, electron micrographs and diffraction patterns of the sample were taken at different temperatures starting at room temperature. Fig. 2 shows diffraction patterns taken during heating in the electron microscope. In the temperature range where the first plateau of the resistance is observed, the electron diffraction pattern



consists of two diffuse halos only. Hence we may regard this state as amorphous. In some cases, however, dark field images taken in the (111)-reflection revealed some few small crystals (about 10 nm in diameter) in the amorphous matrix. The film transforms to a crystalline one at the temperature of the first drastic irreversible change in the resistivity. This change manifests itself in the electron diffraction pattern by the splitting of the second halo into the well separated (220), (113) rings characterising the substitutional solid solution Cu Ag fcc alloy. Continuing the heat treatment makes the initially very fine crystals growing to dimensions giving rise to a sharp ring system corresponding to a lattice parameter of 0,3783 nm, which fairly satisfies Vegards law. This indicates that the alloy is a highly supersaturated substitutional mixed crystal. After raising the temperature up to the third plateau of resistance we observe the decompositions of the single phase alloy to the heterogeneous equilibrium mixture of almost pure Cu and Ag crystals.

#### (a) Composition dependence

The structural transitions show a strong composition dependence (fig.3). Two transitions were observed only in a composition range between 30 and 70 at% Cu. Beyond this range only a single drop of resistivity, the one characterising the decomposition, was observed. As the composition approaches that of the pure components this drop decreases and moves towards lower temperatures. Alloys with a concentration lower than 10 and higher than 90 at% Cu do not show any drop but only a continuous annealing of the resistance is observed. A thermodynamical model for the composition dependence of the transition temperatures will be discussed in sec. 4.c.

#### (b) Thin film thickness and deposition rate

Altering the film thickness in the range from 8.3 nm up to 62.5 nm showed no marked influence on the transition temperatures. According to Herold et.al./23/ the transition temperature of the thin film is usually slightly lower than that of a bulk amorphous alloy ( $\Delta T_c \approx 5-15$  K). This is thought to be associated with the larger surface energy in films which consequently enhances the driving thermodynamic potential for crystallization. A small influence of the deposition rate on the stability of the films was observed (fig.4). Due to the higher degree of disorder films deposited more rapidly show a fairly increased crystallisation temperature.

#### (c) Substrate temperature and surface

The substrate temperature, however, proved to be a very critical parameter. In fig.(5) the transition temperatures of films of concentration Cu 48 at% and thickness  $20 \pm 1$  nm deposited at temperatures ranging from 80 up to 160 K are plotted. As can be seen, it is not possible at all to obtain the amorphous phase for films deposited at temperatures  $\geq 160$  K. The decrease of the transition temperature with increasing substrate temperature is not surprising, since the amount of crystalline nuclei in the amorphous matrix is larger if the substrate temperature and hence the ad-atom mobility is higher.

To study the effect of atomic structure of the substrate surface a mica substrate of thickness 0.1 mm freshly cleaved and a glass substrate both supplied with electric contacts for resistivity measurements were used. Both substrates were exposed simultaneously to  $\text{Cu}_{55}\text{Ag}_{45}$  vapour to a thickness of 2 nm, and subsequently annealed in the same vacuum cycle. The result is plotted in fig.(6). The film on mica shows a continuous resistivity decrease with temperature until  $\approx 338$  K

where the film crystallizes giving rise to the first drop in resistivity. The reference film on the glass substrate crystallizes at  $\approx 350$  K with a rather deep resistivity drop. This suggests that the film on a mica substrate is amorphous as well but exhibits some crystalline nuclei which are not able to stimulate crystallization all over the film, however, they continuously cause a limited induced crystallization during annealing. The amount of crystalline material was estimated between 5 and 10 % of the amorphous matrix.

#### 4. Comparative study of the formation of amorphous Cu-based alloys

It is now generally believed that all metallic materials other than pure close-packed metals would undergo a transition to an amorphous state provided they are cooled rapidly enough from the liquid or vapour state. It is still interesting, however, to predict which system may produce amorphous phases of useful stability and at practicable quenching rates. The stability of the amorphous state depends on thermodynamic conditions that favour the amorphous rather than the crystalline phase and furthermore on kinetic conditions that inhibit nucleation to the crystalline state. Cu forms amorphous alloys with a vast variety of other metals. This allows for a comparative study for these conditions.

##### (a) Rapid assessment of the glass-forming ability

Numerous attempts have been made to find empirical parameters which can be employed to estimate the ability of a system to form an amorphous phase. Donald and Davies /20/ have shown that the departure of the alloy's liquidus temperature  $T_1$  from the rule of mixtures liquidus temperature

$\bar{T}_m = C_A T_m^A + C_B T_m^B$ ,  $\Delta T^* = (\bar{T}_m - T_1) / \bar{T}_m$  is a very useful parameter. According to Donald and Davies a value of  $\Delta T^* \approx 0.2$  separates the systems to be made amorphous by liquid-quenching (cooling rates  $< 10^7$  K.s<sup>-1</sup>) from those requiring higher cooling rates. In table I we have compiled  $\Delta T^*$  for several Cu-based systems.

##### (b) TTT-diagrams and critical cooling rates

We have seen that it is possible to estimate in a rather simple way the ability of a system to form an amorphous phase. In order to make even a guess of the cooling rate necessary to avoid crystallization, we must have a deeper insight into the transformation kinetics. The classical work of Uhlmann /21/ and of Davies and co-workers /22/ seems to describe the transformation kinetics of the liquid-quenching process rather well, whereas the transformation kinetics of the vapour quenching process is only poorly understood. However, Herold et.al. /23/ have shown that Fe-B liquid-quenched metallic glasses and their vapour deposited thin films equivalents show the same crystallization modes. Quantitative differences in the transformation kinetics are shown to depend on the thickness of the films and result from surface energy terms. Keeping this difference in mind, we shall use the Davies-Uhlmann (DU) theory to estimate critical cooling rates of some copper-based alloys. The DU theory is based on theories of nucleation, crystal growth, and atomic transport. It allows to express the time  $t$  necessary to crystallize a fraction  $X$  of a volume as

$$t \approx \frac{93n_c(T)}{kT} \left\{ \frac{\bar{f}^3 X \cdot \exp\left(\frac{\Delta G^*}{RT}\right)}{\left[ 1 - \exp\left(\frac{\Delta H_m^f \cdot (T - T_1)}{kT T_1}\right) \right]} \right\} \quad (1)$$

Here  $\Delta H_m^f$  is the molar heat of fusion.  $\bar{v}$  is the average atomic diameter,  $N_v$  is the volume concentration of atoms /24/,  $f$  is the fraction of sites available at the growth interface ( $f = 1$  for a smooth interface),  $\eta(T)$  is the viscosity and  $\Delta G^*$  is the molar free energy barrier to homogeneous nucleation of a crystalline phase.  $\Delta G^*$  is related to the interfacial tension and to the thermodynamic driving force ( $\sim (T-T_1) \cdot \Delta H_m^f$ ) and may be written as /22/

$$\frac{\Delta G^*}{RT} = 1024 \cdot \Delta T_l^{-2} T_r^{-3} \quad (2)$$

with the reduced temperature  $T_r = T/T_1$  and  $\Delta T_r = 1 - T_r$ . Assuming  $\Delta G^*/RT \approx 50$  at a reduced undercooling of  $\Delta T_r = 0.2$ . (For a discussion of the influence of  $\Delta G^*$  see Tanner and Ray /25/. There is evidence that  $\Delta G^*/RT$  varies only weakly for different systems). The viscosity  $\eta(T)$  is interpolated from the experimental value at the liquidus temperature (since experimental information is missing for most binary systems, we take the experimental value  $\eta_{Cu}(T_l) = 41 \text{ cP}$  for pure Cu /26/ valid for all systems) to an assumed viscosity of  $\eta = 10^{13} \text{ P}$  at the glass-transition temperature. For simplicity, we assumed an Arrhenius behaviour for the viscosity, though other empirical relations might be used as well. For our simple analysis, the influence of a slightly different form of  $\eta = \eta(T)$  is not so effective. Time-Temperature-Transformation diagrams  $t(T)$  for  $x=10^{-6}$  are shown in Fig. 7 for some Cu-based alloys. The shape of the curves reflects the competition between the driving force for nucleation and the atomic mobility, as expressed by  $\eta$ .

They clearly show the trend from easy-glass forming systems (Cu-Zr, Cu-La, Cu-Ca) to difficult glass-formers, which

can be liquid quenched in very thin splats (Cu-Al) and finally to systems which can be made amorphous only by vapour quenching methods (Cu-Ag, Cu-Sn). The reduced glass-temperature turns out to be the most important parameter (note that we have in fact done the calculations with a fixed viscosity  $\eta(T_1)$  which is justified because at  $T_1$  most liquid metal viscosities fall within a rather narrow range of a few cP). This is even more evident if we use the TTT-diagrams to derive critical cooling rates: the cooling curve must bypass the "nose" of the TTT-diagram, hence the critical cooling rate is given by

$$R_c = \frac{T_1 - T_n}{t_n} \quad (3)$$

where  $T_n$  and  $t_n$  are the coordinates of the "nose" (strictly speaking, the TTT-curves should be corrected first for the effect of continuous cooling and converted into CCT (continuous cooling transformation curves)). In Fig. 8  $R_c$  is plotted against  $T_{g,r} = T_g/T_1$ , the reduced glass temperature, which is shown to be the controlling parameter.

### (c) Reduced glass-transition (or crystallization) temperatures

Evidently what we need for an easy formation of an amorphous alloy is a high value of  $T_{g,r}$ . This can be achieved in two different ways: (i) by making  $T_g$  very high or (ii) by making  $T_1$  rather low. The nature of the glass transition is still open to discussion: it is yet

unknown whether in the limit of infinitely slow cooling or heating, the glass-transition would become a true thermodynamical phase transition. It was first pointed out by Kauzmann /27/ that the extrapolation of the configurational entropy of the liquid would possibly yield meaningless negative to the crystalline state below a certain temperature  $T_g$ .

The existence of a vanishing-excess-entropy temperature  $T_g$  points to the possible occurrence of a real phase transition, the "ideal glass transition" at a temperature  $T_{ig}$ ,  $T_g \leq T_{ig} \leq T_0$ . The entropy-theory of Gibbs et.al. /28/ predicts a second order phase transition, while the free volume theory of Cohen and Grest /29/ predicts a first order transition. On this basis, a first-principle estimation of the glass-temperature is now possible, provided we have a rather accurate information on the thermodynamic potentials of the system as a function of temperature /30,31/. Unfortunately this information is not available for Cu-based alloys. Nevertheless, a few useful correlations may be pointed out. Chen and Jackson /34/ and Donald and Davies /20/ pointed out that the thermal stability and hence  $T_g$  should depend on the interatomic potentials and hence on the cohesive energy. This relationship is demonstrated for the Cu-base alloys in Fig. 9, with the cohesive energy approximated by the mean sublimation energy  $H_g$ . Where a glass-transition was not thermally manifest, the lowest crystallization temperature was taken as an estimate. All the points are very close to the empirical relation of Donald and Davies. There is some scatter in the data, which may be discussed in relation to the phase diagram /33/. However, this very simple estimate does not yield any information about the composition dependence of the transformation temperature. Allen and co-workers /30/ have pointed out that based on Kauzmann's paradox, a first principle estimate of  $T_g$  (the lower limit of the glass transition temperature) is possible, pro-

vided that accurate experimental or theoretical thermodynamic potentials for the solid and liquid (including the supercooled liquid) phase over a wide temperature range are available. In this case the temperature dependence of  $T_g$  defined by the relation  $S_l(T_g) = S_s(T_g)$  may be studied /30/. Based on the accurate thermodynamic data of Castanet et.al. /34/ for the Au-Si system Allen et.al. were able to show that a finite  $T_g$  is defined only for concentrated alloys and that  $T_g$  has a maximum close to, but not exactly at the eutectic concentration. This concentration dependence of  $T_g$  (and hence  $T_g$ ) is shown to be due to a strongly temperature dependent excess entropy of the liquid alloy: for  $T \gtrsim 800$  K the excess entropy is positive, whereas for  $T \lesssim 800$  K it becomes increasingly negative. This effect works against the formation of a very deep eutectic, but is overwhelmed by the negative enthalpy of formation of this system. On the other hand a negative excess entropy of the liquid contributes to an increase of  $T_g$ . As has been emphasized by Turnbull and co-workers /35/, a negative entropy of formation reflects strong A-B interaction and a certain degree of chemical short range order.

A theoretical calculation of  $T_g(c)$  has been presented by Hafner /31/ for the Ca-Mg system. Unlike the Au-Si system, the excess entropy varies only weakly with temperature and concentration. Consequently  $T_g$  is found to be nearly independent of the concentration, in agreement with the experimentally observed trend in the transition temperatures /36/. Hence the composition dependence of the transition temperature is closely related to the thermodynamical properties of the system. Unfortunately we are not in possession of sufficiently detailed knowledge of the thermodynamical properties of the Cu-Ag system to allow for a similar estimate of  $T_g$ . However, we expect the system to behave very much like the Au-Si system: both systems form simple eutectic phase diagrams and the decreasing excess entropy and the tendency to chemical ordering is also found in the Cu-Ag system. We find that the excess entropies of liquid Cu-Ag alloys at  $T = 1423$  K are already smaller than those of

solid alloys at  $T = 800 \text{ K}$  /26/. A measurement of the temperature dependent specific heat  $C_p(T)$  would be very valuable. The most important parameter for the glass forming ability is the reduced glass temperature  $T_{r,g}$ . In most systems, the composition variation of  $T_{r,g}$  comes mainly from the variation of the liquidus temperatures. Different models have been brought forward for the explanation of eutectic phase diagrams, the liquid phase is thought to be stabilized with respect to the crystalline phase either by packing effects /37/ or chemical bonding /38/ effects or electronic /39/ effects. Microscopic calculations /38/ have shown that indeed all three effects do contribute, but their relative importance varies from one system to another: for alloys of Cu with polyvalent metals or metalloids, the electronic effect is most important, quite as for the crystalline Hume-Rothery phases. The Nagel-Tauch rule /39/  $Q_p \approx 2k_f$  is a Hume-Rothery rule for the amorphous phase /33/ and amorphous alloys such as Cu-Al, Cu-Sn, Cu-Ge, Cu-Ag-Ge, Cu-Ag-P may indeed be considered as amorphous Hume-Rothery phases /8/. In these cases, the generalized Faber-Ziman-Baym theory also provides a satisfactory explanation of their electronic transport properties /5/. In alloys of Cu with early transition metals or lanthanides and actinides (Cu-Ti, Cu-Zr, Cu-La, Cu-Th), the large negative enthalpies of formation are explained by a shift of the Cu-d band which does not depend on the long-range order /40/. Hence the heat of crystallization turns out to be small. In Cu-Mg, Cu-Ca, Cu-Sr packing effects are as important as electronic effects.

On the other hand, Cu-Ag behaves very much like an ideal solid solution. The stabilization of the disordered (liquid or amorphous) phase relative to the ordered (crystalline) one has a strong influence on  $T_i$  which is determined by the competing free enthalpies of formation and some influence on the concentration dependence of  $T_g$  (for Cu-Al and related alloys, Leitz and co-workers /5/ have demonstrated that  $T_g$  (or  $T_c$ ) is largest at the concentration where the  $Q_p = 2K_F$  is satisfied). The main influence on the composition dependence of  $T_g$  comes from the excess entropy. Hence the

quotient  $T_g/T$  rules the easiness of glass formation, the thermal stability on the other hand is related to  $T_g$  alone.

## 5. Conclusions

We have shown that it is possible to produce amorphous Cu-Ag films with high stability using co-evaporation. The most important parameter is the composition of the film: Only in the concentration range between 30 and 70 at% Cu are the as quenched films amorphous, and only within the range between 35 and 63 at% Cu does the crystallization temperature lie above room temperature.

The relative easiness of formation of Cu-based amorphous alloys may be understood within the Davies-Uhlmann transformation theory. The composition dependence of the stability is shown to be related to the chemical short range order.

## Acknowledgements:

This work was sponsored by the Austrian "Fonds zur Förderung der Wissenschaftlichen Forschung" and the "Jubiläumsstiftung der Stadt Wien" and was performed in cooperation with Siemens Forschungslabor Munich. One of the authors (I.M.R.) would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

## REFERENCES

- 1) W. BUCKEL, Z.Phys.138, 136(1954); W. BUCKEL and R. HILSCH, Z.Phys.138, 109(1954).
- 2) J.G. WRIGHT, IEEE Transactions on Magnetics, MAG12, 95(1976); Proc. 3<sup>rd</sup> Int.Conf. in Liquid Metals, ed. by R. EVANS and D.A. GREENWOOD, Inst. of Physics - Conference Series, vol.30, 251(1977).
- 3) F. SOMMER, G. BUCHER and B. PREDEL, J. Physique 41, C8-563 (1981).
- 4) R.St. AMAND and B.C. GIESSEN, Scr.Met. 12, 1021(1978).
- 5) A. LAMBRECHT, H. LEITZ and J. HASSE, Z.Phys. B38, 35(1980); N.M. MAYER, Thesis, Univ. Rgënsburg (1980).
- 6) D. KORN, W. MÜRER and G. ZIBOLD, J.Physique 35, C4-257(1974); Z.Phys. 270, 195(1973).
- 7) K. SHIRAKAWA, J. KOBAYASHI and T. MASUMOTO, Science Reports of the Research Institutes, Tohoku University. A28, 255(1980).
- 8) U. MIZU TANI and J. YAZEWA, Scr.Met. 14, 637(1980).
- 9) N. COWLAM, M. SAKATA and H.A. DAVIES, J.Phys.F9, L203 (1979).
- 10) T. MIZOGUCHI, T. KUDO, T. IRISAWA, N. WATANABE, N. NIIMURA, M. MISAWA and K. SUZUKI, Proc. 3<sup>rd</sup> Int.Conf. on Rapidly Quenched Metals, ed.by B. CANTOR (The Metals Society-London), vol.2, 384(1978); H.S. CHEN and J.T. KRAUSE, Scr. Met. 11, 761(1977).
- 11) K.H.N. BUSCHOW, J.Appl.Phys. 41, C4(1980).
- 12) K.H.N. BUSCHOW and N.M. BEEKMANS, Proc. 3<sup>rd</sup> Int. Conf. on Rapidly Quenched Metals, ed.by B. CANTOR (The Metals Society - London), vol.2, 133, 471(1978).
- 13) K.H.N. BUSCHOW and N.M. BEEKMANS, Sol.State Comm.
- 14) S. MADER, J.Vac.Sci.Techn. 2, 23(1965); S. MADER, A.S. NOWICK and H. WIDMER, Acta Met. 15, 203(1967); S. MADER and A.S. NOWICK, Acta Met. 15, 215(1967).
- 15) C.N.J. WAGNER, J.Vac.Sci,Techn. 6, 650(1969); W.D. LUKENS, Yale Univ., 1971, cited by Ref. 16.
- 16) G.S. CARGILL, Solid State Physics 30, 227(ed. by H. EHRENREICH, F. SEITZ and D. TURNBULL, Academic Press, N.Y., 1975).
- 17) C.N.J. WAGNER, T.B. LIGHT, N.C. HALDER and W.E. LUKENS, J.Appl.Phys. 39, 3690(1968).
- 18) K.L. CHOPRA, A.T. THAK, S.K. BARTHWAL and P. NATH, Phys.Stat.Sol. (a)40, 247(1977).
- 19) H. KIESSIG, Ann.Phys.10, 729(1931).
- 20) I.W. DONALD and H.A. DAVIES, J.Non-Cryst.Sol.30,77(1978).
- 21) D.R. UHLMANN, J.Non-Crystl.Sol. 7, 337(1972); 25, 43(1977).
- 22) H.A. DAVIES, Phys.Chem.Glasses 17, 159(1976); B.G. LEWIS and H.A. DAVIES, Proc. 3<sup>rd</sup> Int.Conf. on Liquid Metals, ed. by R.EVANS and D.A. GREENWOOD, Institute of Physics - Conference Series, vol.30,274(1977).
- 23) U. HEROLD, U. KÖSTER and A.G. DIRKS, J.Magn.Mat. 19, 152 (1980).
- 24) Experimental values of  $\Delta H_m^f$ ,  $N_v$  and  $T_L$  are taken from CRC Handbook of Chemistry and Physics, (ed. by R.C. WEAST), CRC 1975 and Selected Thermodynamic Properties of the Elements, ed. by R. HULTGREN et.al. (American Society for Metals, 1973).
- 25) L.E. TANNER and R. RAY, Acta Met. 27, 1727(1979).
- 26) T.E. FABER, An Introduction to the Theory of Liquid Metals, Cambridge, Univ. Press (1972), p. 168.
- 27) W. KAUZMANN, Chem.Rev. 43, 219(248).
- 28) J.H. GIBBS and E.A. DI MARZIO, J.Chem.Phys. 28, 373(1958); G. ADAM and J.H. GIBBS, J.Chem.Phys. 43, 139(1965).
- 29) M.H. COHEN and G.S. GREEST, Phys.Rev. B20, 1077(1979); D. TURNBULL and M.H. COHEN, J.Chem.Phys. 34, 120(1961).
- 30) J.W. ALLEN, A.C. WRIGHT and G.A.N. CONNELL, in "Frontiers in Glass Science", J.Non-Cryst.Sol. (in print).
- 31) J. HAFNER, Phys. B21, 406(1980) and to be published.
- 32) H.S. CHEN and K.A. JACKSON, in "Metallic Glasses", ed. by J.J. GILMAN and H.J. LEAMY (American Society for Metals, Metals Park 1978)p. 74.

- 33) J. HAFNER, in "Nuclear Methods Applied to the Investigation of Metallic Glasses", ed. by U. GONSER, Atomic Energy Review (in print).
- 34) R. CASTANET, R. CHASTEL and C. BERGMANN, Mat.Sci.Eng. 32, 93(1978).
- 35) D. TURNBULL, J. Physique 35, C4-1(1974); P. CHAUDCHARI and D. TURNBULL, Science 199, 11(1977).
- 36) B.C. GIESSEN and J. HONG, private communication.
- 37) C.H. BENETT, D.E. POLK and D. TURNBULL, Acta Met. 19, 1259(1971).
- 38) H.S. CHEN and B.L. PARK, Acta Met. 21, 395 (1973).
- 39) S.R. NAGEL and J. TAUC, Phys. Rev. Lett. 35, 380(1975).
- 40) P. OELHAFEN, J. Phys. F11, L41(1981).

Alloy	x	T	Classification	note
Cu Ce	30	0.37		★
Cu Ti	30	0.35	AMORPHOUS	★
Cu La	30	0.32	BY	★
Cu Ca	50	0.32	QUENCHING	★
Cu Si	30	0.32	FROM	
Cu Zr	60	0.30	THE	★
Cu Sr	30	0.28	MELT	★
Cu Ge	65	0.28		
Cu Th	50	0.26		
Cu Sb	50	0.26		
Cu Be	30	0.24		
Cu Mg	30	0.21		★
Cu Al	30	0.19	AMORPHOUS BY	★
Cu Ag	50	0.16	QUENCHING	★
Cu Mn	50	0.16	FROM	
Cu Sn	70	0.11	THE VAPOUR	★
Cu Au	50	0.12		
Cu In	50	0.07		
Cu Pd	50	0.06		
Cu Cd	50	0.04	CRYSTALLINE	
Cu Ni	50	- 0.03		
Cu Fe	50	- 0.07		
Cu Zn	50	- 0.12		

Table 1

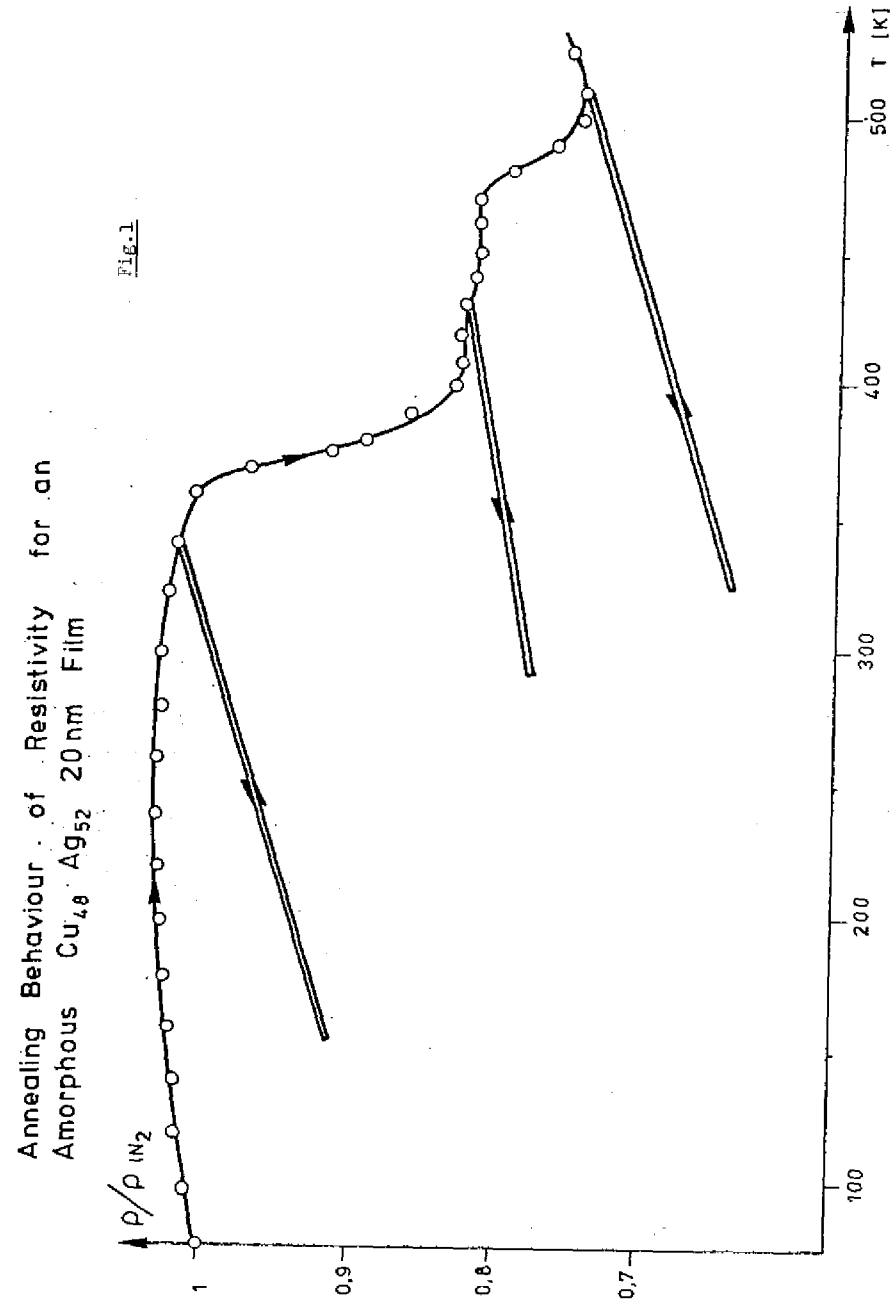
x = Cu concentration (at%)

★ indicates that the corresponding result was confirmed experimentally.

- fig.1) Annealing behaviour of resistivity for an amorphous  $\text{Cu}_{48}\text{Ag}_{52}$  - 20 nm film.
- fig.2) Electron diffraction patterns for a  $\text{Cu}_{48}\text{Ag}_{52}$  film at different temperatures.
- fig.3) Transformation temperatures as a function of the Cu-concentration.
- fig.4) Change of the crystallisation temperature with the deposition rate.
- fig.5) Dependence of crystallisation and decomposition temperatures on the deposition temperature.
- fig.6) Annealing behaviour of two  $\text{Cu}_{55}\text{Ag}_{45}$  films on glass and mica substrates.
- fig.7) TTT diagrams for some Cu-based alloys.
- fig.8) Critical cooling rate  $R_c$  vs reduced glass temperatures for amorphous Cu-based alloys.
- fig.9) Glass transition temperature vs mean heat of sublimation.

Table 1)

Classification of Cu-based alloys with respect to their glass forming ability according to the liquidus temperature depression.





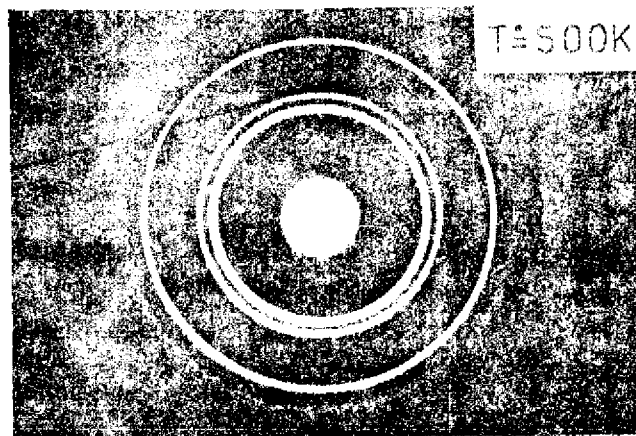
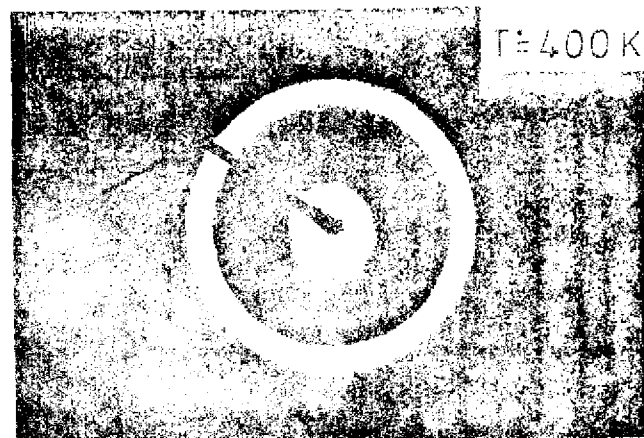
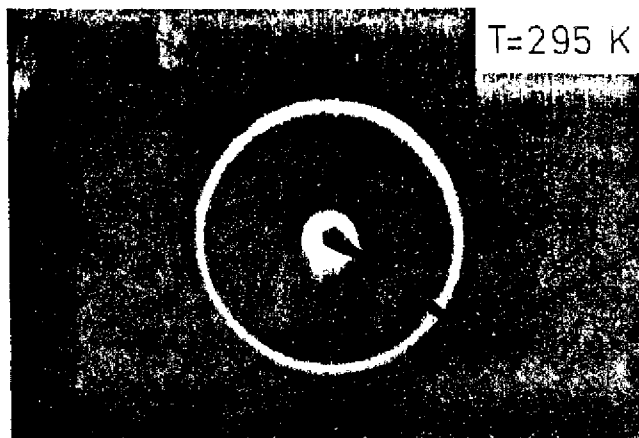
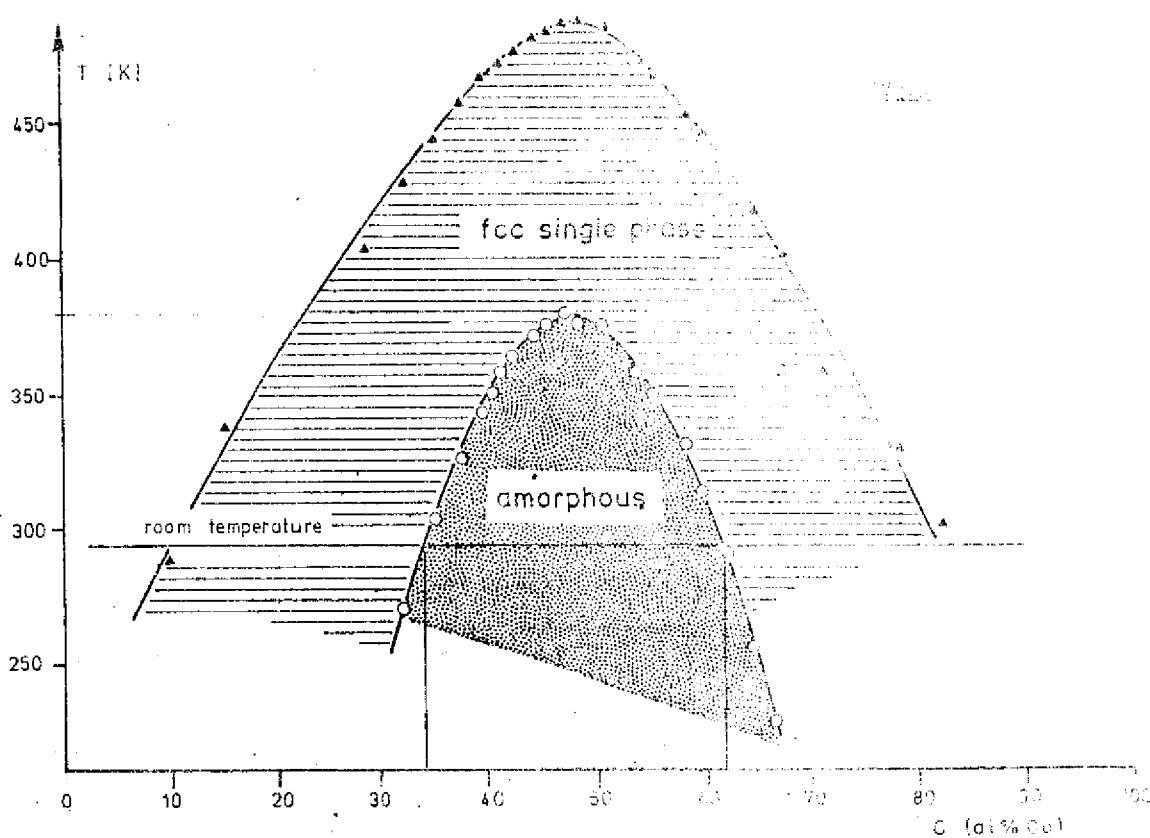


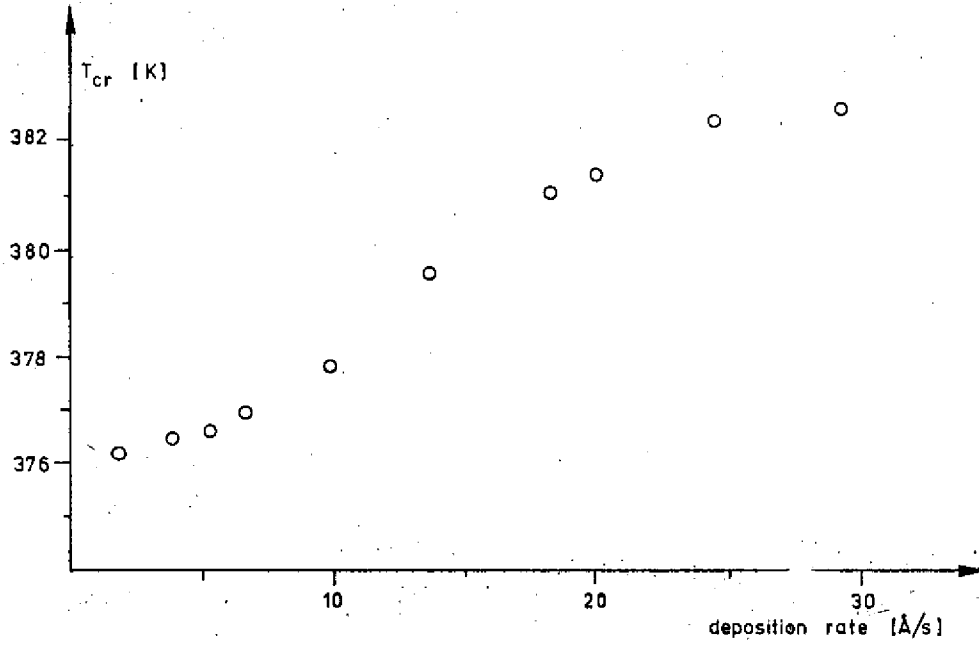
Fig. 1

Transformation Temperatures as Function of the Cu Concentration in the Nobel Metal



Change of Crystallisation Temperature  
with the Deposition Rate

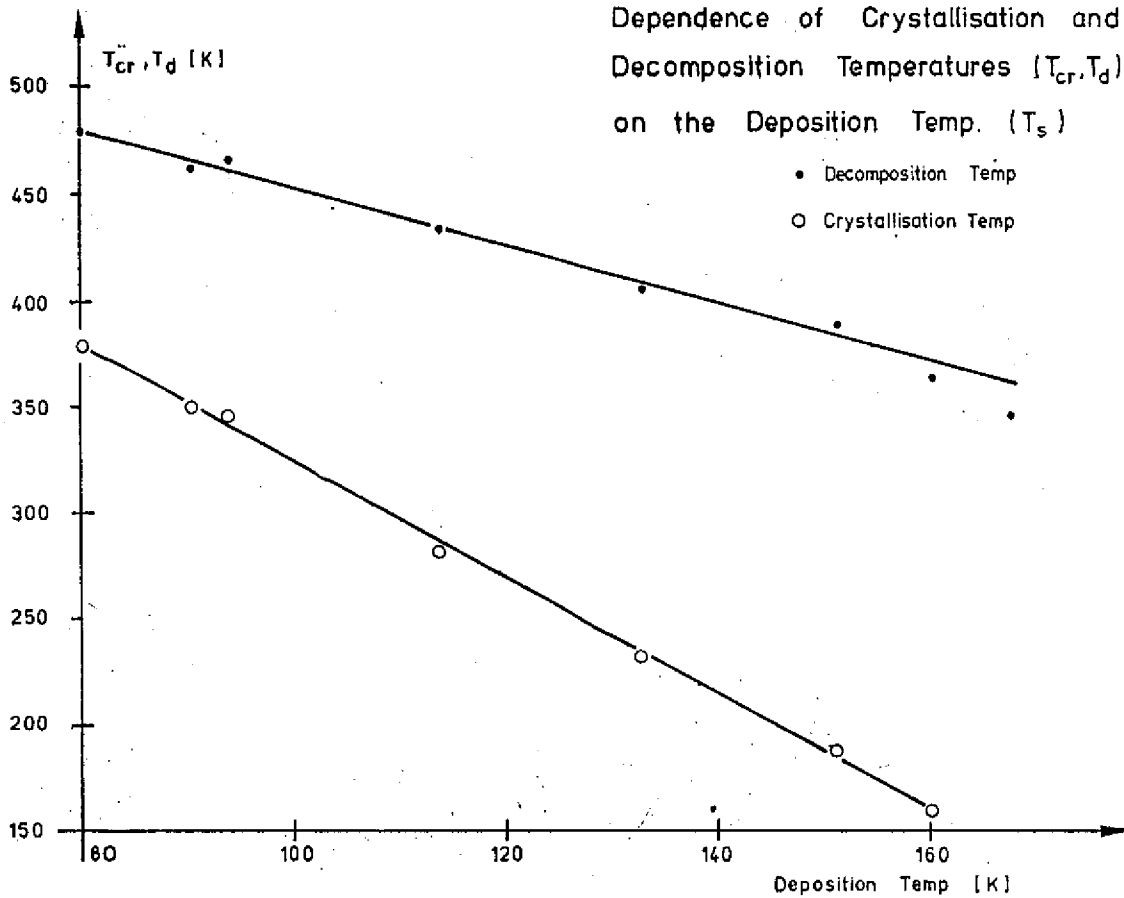
Fig.4



Dependence of Crystallisation and  
Decomposition Temperatures ( $T_{cr}, T_d$ )  
on the Deposition Temp. ( $T_s$ )

- Decomposition Temp
- Crystallisation Temp

Fig.5



Annealing Behavior of Two Cu<sub>55</sub>Ag<sub>45</sub> Films on Glass and Mica Substrates

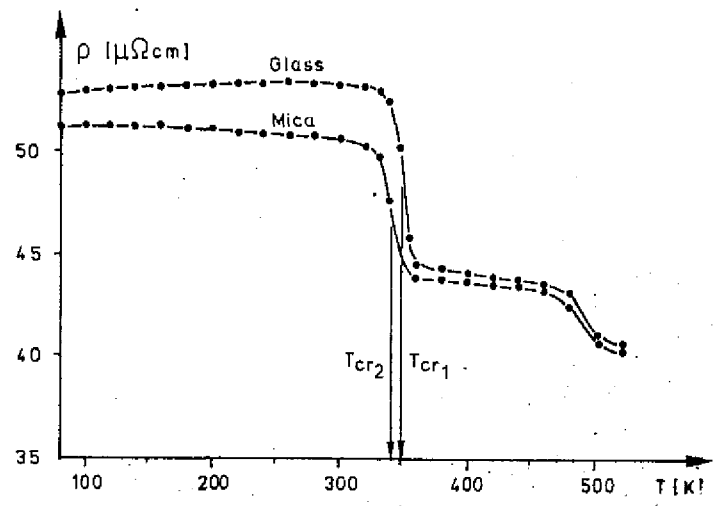


Fig. 6

TTT - Plot for Cu-Based Alloys

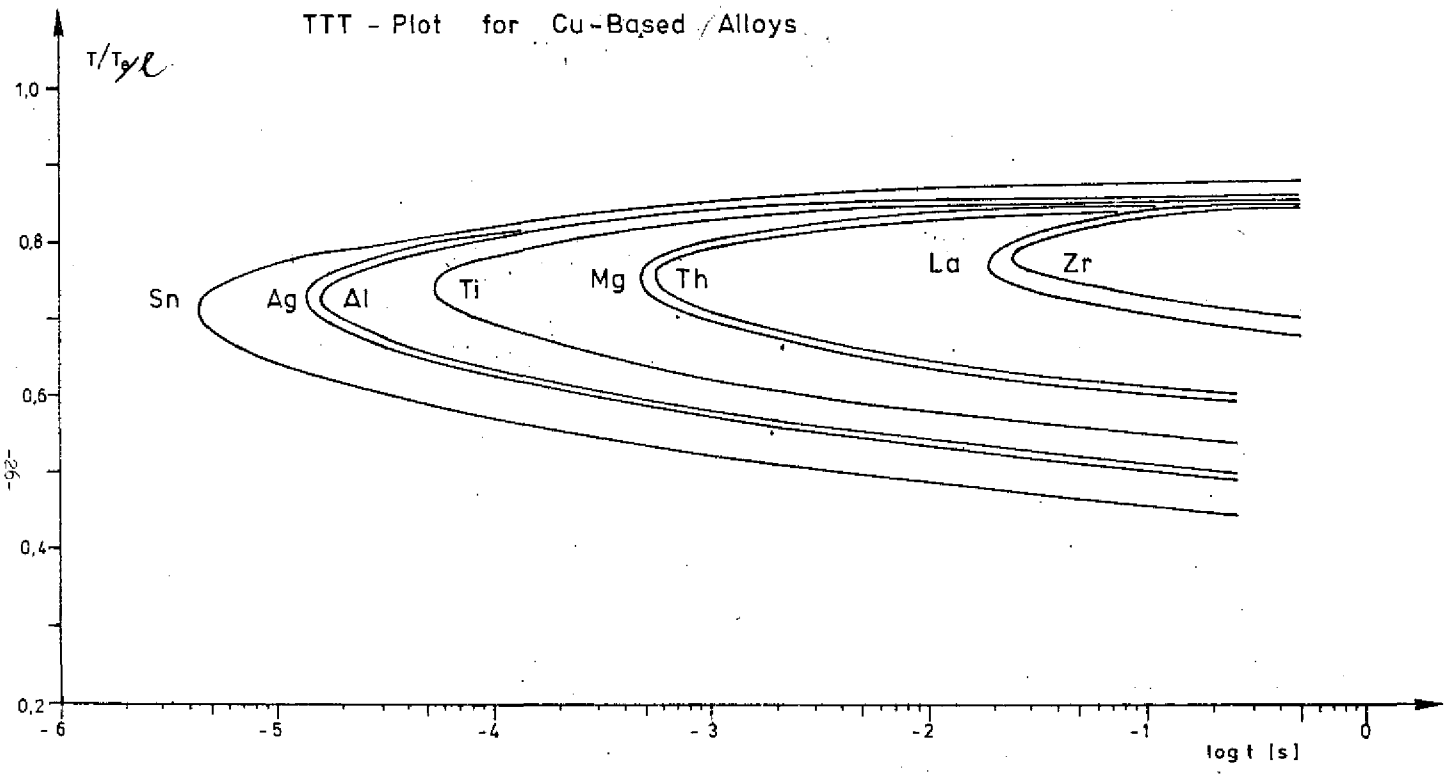
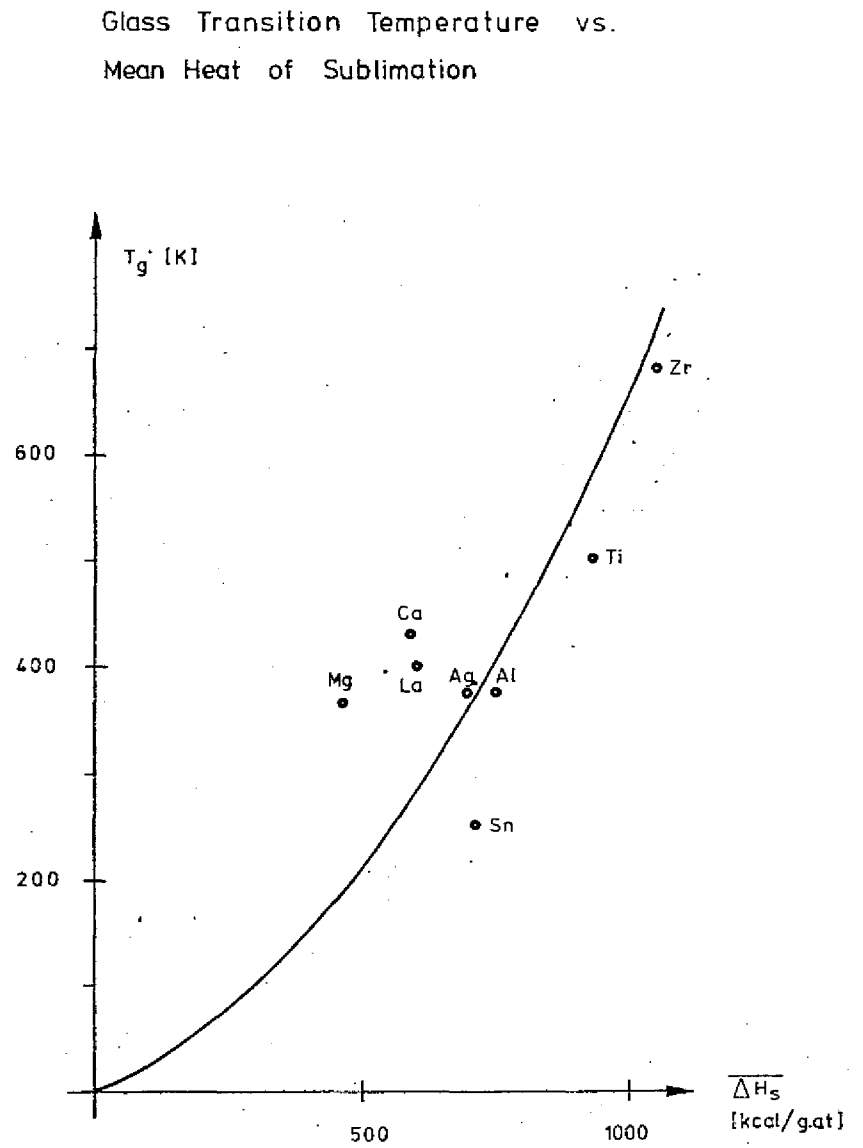
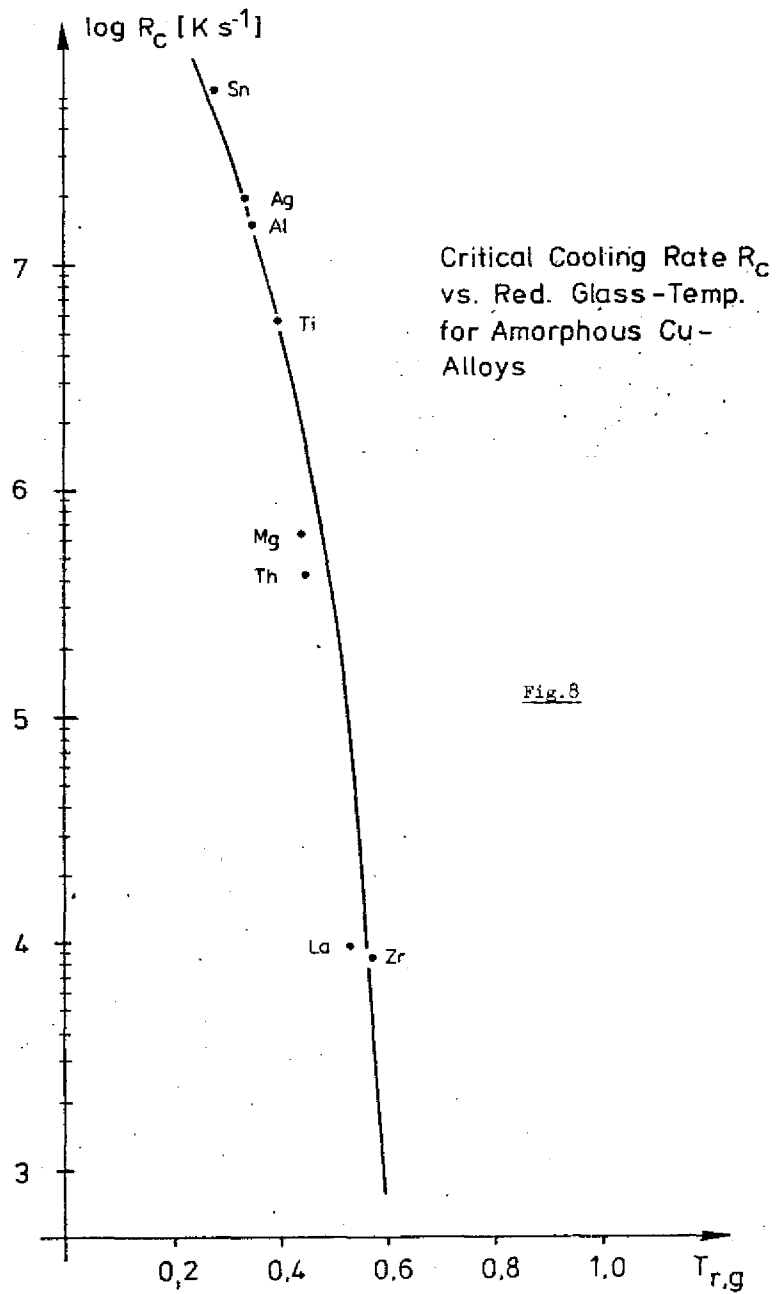


Fig. 7

-25-

-26-



IC/82/1 TH.M. EL-SHERBINI - Excitation mechanisms in singly ionized krypton laser.  
INT.REP.\*

IC/82/2 CHR.V. CHRISTOV, I.I. DELCHEV and I.Z. PETKOV - On direct mechanism of light-particle emission in incomplete-fusion reactions  
INT.REP.\*

IC/82/3 F. CLARO and V. KUMAR - Phase diagrams for a square lattice with two- and three-body interactions.

IC/82/4 E. ROMAN, G. SENATORE and M.P. TOSI - A simple model for the surface energy of ionic crystals.

IC/82/5 G.A. CHRISTOS - "Loop the loop".  
INT.REP.\*

IC/82/6 H.R. KARADAYI - L-R asymmetry in GUT's.

IC/82/7 YASUSHI FUJIMOTO and JAE HYUNG YEE - The electron magnetic moment at high temperature.  
INT.REP.\*

IC/82/8 T.S. SANTHANAM - Charge structure of quarks and the number of valence quarks in the nucleon.  
INT.REP.\*

IC/82/9 TH.M. EL-SHERBINI and A.A. RAHMAN - Auto-ionizing states in MgI.  
INT.REP.\*

IC/82/10 K.P. JAIN and G.S. JAYANTHI - Quasibound exciton-LO phonon intermediate state in multi-phonon Raman scattering of semiconductors.  
INT.REP.\*

IC/82/11 T. SRIVASTAVA - A two-component wave equation for particles of spin  $\frac{1}{2}$  and non-zero rest mass (Part II).

IC/82/12 T.S. SANTHANAM and S. MADIVANANE - The structure of the Hamiltonian in a finite-dimensional formalism based on Weyl's quantum mechanics.  
INT.REP.\*

IC/82/13 J.A. MAGPANTAY, C. MUKKU and W.A. SAYED - Hot gauge theories in external electromagnetic fields.

IC/82/14 H.R. KARADAYI - The derivation of the conventional basis for the simple Lie algebra generators.

IC/82/15 H.R. KARADAYI - SO(14) unification of 3+1 families.

IC/82/16 W. NAHM - The construction of all self-dual multimonoles by the ADHM method.

IC/82/17 B. GRUBER and T.S. SANTHANAM - Indecomposable representations for parabolic algebra.

IC/82/18 R. PERCACCI and S. RANDJBAR-DAEMI - Kaluza-Klein theories on bundles with homogeneous fibres - I.

IC/82/19 W. ANDREONI, M. ROVERE and M.P. TOSI - Co-ordination of heterovalent cation impurities in molten salts.

IC/82/20 L. SMRČKA - A "quadratized" augmented plane wave method.  
INT.REP.\*

IC/82/21 V. de ALFARO, S. FUBINI and G. FURLAN - Some remarks about quantum gravity.

IC/82/22 G. CHABRIER, G. SENATORE and M.P. TOSI - Ionic structure of solutions of alkali metals and molten salts.

THESE PREPRINTS ARE AVAILABLE FROM THE PUBLICATIONS OFFICE, ICTP, PO BOX 586, I-34100 TRIESTE, ITALY.

IC/82/23 SUN KUN OH - Mass splitting between  $B^+$  and  $B^0$  mesons.  
INT.REP.\*

IC/82/24 A. BREZINI - Self-consistent study of localization near band edges.  
INT.REP.\*

IC/82/25 C. PANAGIOTAKOPOULOS - Dirac monopoles and non-Abelian gauge theories.  
INT.REP.\*

IC/82/26 CAO CHANG-qi and DING XING-fu - Intermediate symmetry  $SU(4)_{EC} \times SU(2)_L \times U(1)_Y$  and the  $SU(N)$  unification series.

IC/82/27 H.B. GHASSIB and S. CHATTERJEE -  $^4\text{He}$ -impurity effects on normal liquid  $^3\text{He}$  at low temperatures - I: Preliminary ideas and calculations.

IC/82/28 C. PANAGIOTAKOPOULOS, ABDUS SALAM and J. STRATHDEE - Supersymmetric local field theory of monopoles.

IC/82/29 G.A. CHRISTOS - Concerning the proofs of spontaneous chiral symmetry breaking in QCD from the effective Lagrangian point of view.  
INT.REP.\*

IC/82/30 M.I. YOUSEF - Diffraction model analyses of polarized  $^6\text{Li}$  elastic scattering.  
INT.REP.\*

IC/82/31 L. MIZRACHI - Electric-magnetic duality in non-Abelian gauge theories.

IC/82/32 W. MECKLENBURG - Hierarchical spontaneous compactification.  
INT.REP.\*

IC/82/33 C. PANAGIOTAKOPOULOS - Infinity subtraction in a quantum field theory of charges and monopoles.

IC/82/34 M.W. KALINOWSKI, M. SEWERYNSKI and L. SZYMANOWSKI - On the F equation.  
INT.REP.\*

IC/82/35 H.C. LEE, LI BING-AN, SHEN QI-XING, ZHANG MEI-MAN and YU HONG - Electroweak interference effects in the high energy  $e^+ + e^- \rightarrow e^+ + e^- + \text{hadrons}$  process.  
INT.REP.\*

IC/82/36 G.A. CHRISTOS - Some aspects of the U(1) problem and the pseudoscalar mass spectrum.

IC/82/37 C. MUKKU - Gauge theories in hot environments: Fermion contributions to one-loop.

IC/82/38 W. KOTARSKI and A. KOWALEWSKI - Optimal control of distributed parameter system with incomplete information about the initial condition.  
INT.REP.\*

IC/82/39 M.I. YOUSEF - Diffraction model analysis of polarized triton and  $^3\text{He}$  elastic scattering.  
INT.REP.\*

IC/82/40 S. SELZER and N. MAJLIS - Effects of surface exchange anisotropy in Heisenberg ferromagnetic insulators.  
INT.REP.\*

IC/82/41 H.R. HAROON - Subcritical assemblies, use and their feasibility assessment.  
INT.REP.\*

IC/82/42 W. ANDREONI and M.P. TOSI - Why is AgBr not a superionic conductor?

IC/82/43 N.S. CRAIGIE and J. STERN - What can we learn from sum rules for vertex functions in QCD.

IC/82/44 ERNEST C. NJAU - Distortions in power spectra of digitised signals - I: General formulations.  
INT.REP.\*

