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PLASMON ELECTRON LOSS SPECTROSCOPY AND ELECTRICAL CONDUCTIVITY AT 300 K OF CRYSTALS AND QUASICRYSTALS IN AlMn AND AlMnSi

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Abstract The plasmon excitation in quasi-crystals and crystals of AlMn and AlMnSi is studied by electron energy loss spectroscopy in a scanning transmission electron microscope (STEM). One deduce an estimate of the “microscopic” electrical resistivity at 300 K. The weak or negligible effect of the aperiodicity, as compared with periodicity or randomness of the Mn atoms distribution seems to be consistent with a description in uncoupled virtual bound states.

Résumé L'excitation des plasmons dans les phases quasi-cristallines et cristallines de AlMn et AlMnSi est étudiée par spectroscopie des pertes d'énergie électronique réalisée dans un microscope à balayage et à transmission (STEM). On en déduit une estimation de la résistivité électrique “microscopique” à 300 K. Le faible ou négligeable effet de l'apériodicité comparée à la périodicité ou au désordre aléatoire dans la position des atomes Mn semble être cohérent avec une description en états liés virtuels découplés.

I - INTRODUCTION

The role played by aperiodicity and 5 fold symmetry long range orientational order in the physical properties of the quasicrystals is evidently an exciting problem. However the experimental determination of these properties, particularly those related to propagating waves, suffers from the absence of macroscopic and homogeneous single quasi crystalline specimens : the melt-spun ribbons are aggregates of quasicrystalline grains exceeding rarely a few microns in size, eventually embedded in a crystalline matrix when the melt chemical composition is off the quasicrystalline stoichiometry.

For example, the analysis of electrical resistivity measurements made by the classical four point method on a ribbon Al_6Mn containing quasicrystals such as those shown in Fig. 1 is evidently tricky : such a specimen is composite ; it contains a volume fraction of $\sim 40\%$ of aluminum matrix supersaturated in Mn with a large area of irregular interface with the icosahedral (i) phase, and whose contribution to the resistivity is probably far from being negligible ; furthermore the i-phase contains defects and probably microcracks, the i-phase being brittle ; finally the geometry of the ribbons is badly defined and presents macroscopic irregularities inherent to the melt-spinning process.

In this extent, transmission electron microscopy (TEM) appear well suited to the investigation of quasicrystals as well as the associated analytical techniques. For example, X-ray-EDS analysis has allowed to determine the composition of the icosahedral phase in $AlMn$, $\sim Al_4Mn$, and the Mn content of the matrix [1/ [2/.

In this work we present an investigation of electron energy loss spectroscopy (EELS), performed in a 100 kV scanning transmission electron microscope (STEM). We study

Fig. 1 - Transmission electron micrograph of icosahedral phase particles (in black). The Al matrix has been removed during the electrolytic thinning process.

the plasmon loss domain, in both quasicrystals (i- and decagonal or T-phase) and crystals in AlMn and AlMnSi. From these results we make an estimate of their electrical resistivity, as it has been done before for small Al particles /3/ and glassy metals /4/. Due to the very small diameter of the electron probe, we get an insight into a "microscopic" resistivity, free of the defect contributions previously mentioned.

II - EXPERIMENTAL

In three melt-spun alloys ($\text{Al}_{86}\text{Mn}_{14}$, $\text{Al}_{80}\text{Mn}_{20}$, $\text{Al}_{74}\text{Mn}_{20}\text{Si}_6$) the i-phase, the decagonal or T phase, the f.c.c. α solid solution of Mn in Al have been analyzed, as well as the crystallization products after heating, i.e. the orthorhombic Al_6Mn and hexagonal Al_4Mn .

The EELS was performed in thin regions of the foils in order to avoid multiple scattering. Mn and Si local concentrations were measured by X-EDS in the analyzed regions.

The VG HB 501 STEM was operated in conditions minimizing the plasmon peak broadening i.e. with minimum specimen illumination angle α_i and collection angle θ_c of the inelastic electrons through the energy analyzer. In these conditions the electron beam focussed on the specimen has a diameter of 4 nm, and the maximum scattering vector is $q_{\text{max}} = .311 \text{ \AA}^{-1}$.

The loss function has to be corrected for its shift and broadening due to the integration over $q < q_{\text{max}}$ and the finite energy width of the incident electrons ($\sim .5 \text{ eV}$, for the field emission gun). A first-order deconvolution procedure of the loss function for the position of the plasmon loss $E_p = \hbar\omega_p$ and its half-height width $\Delta E_{1/2}$ is given in reference /5/, which first necessitates the determination of the plasmon dispersion relation E_p or $\Delta E_{1/2}$ vs. q^2 .

III - RESULTS : PLASMON LOSSES, RESISTIVITY

Examples of the loss function obtained in $\text{Al}_{86}\text{Mn}_{14}$ for the i-phase and the α -f.c.c. matrix are shown in Fig. 2. The bulk plasmons are clearly separated, with an energy shift sufficiently large to be able to make filtered images of each phase.

Fig. 3 shows the variations of E_p and $\Delta E_{1/2}$, after energy and angular corrections, as a function of the Mn content-determined by X-EDS- for each phase investigated. The increase of E_p has also been found by XPS /6/ on coevaporated Al-Mn alloys, without,

Fig. 2 - Loss function vs. energy loss in $\text{Al}_{86}\text{Mn}_{14}$, the probe being focussed on the i-phase and on the f.c.c. matrix.

however, specifying the amorphous or crystalline state of the specimens. Similarly, a linear increase of $\Delta E_{1/2}$ with Mn content, as determined by optical measurements also on coevaporated alloys /7/ fits reasonably well our data for Mn concentrations lower than 0.05.

In a free electron model, the bulk plasmon loss is

$$E_p = \hbar \omega_p = \hbar \left(\frac{ne^2}{m \epsilon_0} \right)^{1/2} \quad (1)$$

where ω_p is the plasmon frequency, n the electron density and ϵ_0 the permittivity of free space. The half-height width of the lorentzian loss function can be written /8/

$$\Delta E_{1/2} = \hbar \tau_p^{-1} \quad (2)$$

τ_p being the plasmon life time, provided that $\omega_p \tau_p \gg 1$; such a condition is here pretty well fulfilled ($\omega_p \approx 2.5 \times 10^{16} \text{ s}^{-1}$, τ_p varying between .3 and .95 $\times 10^{-15} \text{ s}$).

If we make the assumption that the plasmon life time is necessarily limited by the relaxation time τ , we get for the electrical conductivity, combining (1) and (2) with $\tau = \tau_p$:

$$\sigma = \frac{ne^2 \tau}{m} = \frac{\epsilon_0}{\hbar} \cdot \frac{E_p^2}{\Delta E_{1/2}} \quad (3)$$

Fig. 3 - Bulk plasmon value E_p (a) and half-height width $\Delta E_{1/2}$ (b) for the various phases investigated.

The resistivity $\rho = \sigma^{-1}$, calculated from the measured values of E_p and $\Delta E_{1/2}$, is given in Table 1 and plotted in Fig. 4, as a function of the Mn concentration. The uncertainty is particularly high for the reference Al which has a small half-height width close to the limit of energy resolution. These measurements have been made at 300 K, which is probably the specimen temperature, if one considers that a local heating by the electron beam should be small for such a metallic specimen.

Fig. 4 - 300 K electrical resistivity for crystals and quasicrystals, calculated from the plasmon loss data, vs. the Mn content.

Alloy	Phase	C_{Mn} (at.%)	ρ ($\mu\Omega$ cm)
$Al_{86}Mn_{14}$	α -Al	3.1	24 ± 20
	orthorhombic	14 ± 4	51 ± 21
	i	20	66 ± 29
$Al_{80}Mn_{20}$	T	20	58 ± 26
	hexagonal	20	66 ± 30
$Al_{74}Mn_{20}Si_6$	i	19.5	68 ± 25
	α -Al	$1.8 \pm .4$	23 ± 20
pure Al	Al	0	24 ± 20

Table I - Quasicrystals and crystals resistivity. $T \approx 300$ K. The extremal bounds are determined by the first-order deconvolution procedure.

IV - DISCUSSION AND CONCLUSION

The Matthiessen rule, $\rho = \rho_{Al} + \rho_{Mn} C_{Mn} (1 - C_{Mn})$, would lead for fully disordered Mn solid solutions, on the basis of ρ_{Al} (300 K) = $2.77 \mu\Omega$ cm and a specific residual resistivity $\rho_{Mn} = 612 \mu\Omega$ cm /9/, to the following 300 K resistivities : $21.1 \mu\Omega$ cm for α -Al ($C_{Mn} = 3.1$ at.%), $76.4 \mu\Omega$ cm for $Al_{86}Mn_{14}$, $100.7 \mu\Omega$ cm for $Al_{80}Mn_{20}$. On the other

hand, Dunlop et al. /10/ report for the 300 K resistivity of the orthorhombic compound Al_{16}Mn 80 $\mu\Omega\text{cm}$.

Discarding the pure Al resistivity, which is too small to be measured by E.E.L.S. for energy resolution mainly, the comparison with our data shows :

i/ the E.E.L.S. resistivity of α -Al is in good agreement with the Matthiessen estimate.

ii/ for orthorhombic Al_{16}Mn the E.E.L.S. resistivity is 37 % lower than the value measured by Dunlop et al. /10/, itself close to the Matthiessen estimate. Such effects already noted by Reda et al. for amorphous Cu-Ag films /4/, are understandable in terms of the "microscopic" nature of the EELS resistivity.

iii/ the most interesting point is certainly the weak, if any, EELS resistivity change between crystal and quasicrystal with the same Mn content (1).

Two facts may help in understanding this result :

- the crystallization of glassy metals gives a drop of resistivity generally of a few to 20 % ; the i-phase which is long range orientationally ordered, should give still a smaller decrease.

- a special reference has to be made to the dilute Al-T3 (T3 = transition metal of the third row) compounds investigated by Dunlop et al. /10/. The main result of their investigation, analyzed in terms of Mn virtual bound states array, was the almost equivalence between solid solution and crystalline compound of same composition, suggesting the importance of the T3 local environment by Al atoms. A periodical stacking of local units in the compound, or at random in the solid solution, besides charge transfer in the crystal, are not very different, principally for the 300 K resistivity level : at this temperature the conduction electron coherent scattering by a regular stacking of Mn virtual bound states is lost because of thermal motion. If we further notice that local order is probably identical in i-phase and crystal /12/, with no Mn first-neighbours and consequently negligible d-d orbitals overlap, the virtual bound states description should be similar whatever their distribution is random, quasi-periodical or periodical, at least for high temperature transport properties. Our results support this view.

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(1) This result is strongly at variance with those of Parthasarathy et al. /11/, who observed a very large drop of resistivity upon crystallization under pressure of the i-phase in $\text{Al}_{78}\text{Mn}_{22}$ and $\text{Al}_{86}\text{Mn}_{14}$ (however extrapolation of their results at atmospheric pressure give much too small values for the crystals, with furthermore a decrease of resistivity with increasing Mn content !).

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