

Optical Absorption in Vapor-Quenched Aluminum

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An aluminum film formed by evaporation at 25 K onto a similar film previously deposited at room temperature displayed a featureless optical spectrum in the range 0.6–3.5 eV, the characteristic (200) peak being completely absent. A closer analysis showed the absorption to consist of a Drude term ($\hbar\omega_p = 7.45$ eV; $\tau = 3.4 \times 10^{-15}$ sec) and what is believed to be interband absorption, possibly associated with a residual (111) absorption band.

The Fermi surface of aluminum makes contact with the (111) and (200) Brillouin-zone boundaries, and on this account the interband optical spectrum is characterized by two absorption bands at approximately¹ 0.5 and 1.5 eV; the band at 0.5 eV is weak whereas that at 1.5 eV is strong and quite narrow, particularly when studied at low temperatures.² When aluminum mirrors are formed by evaporation onto cold substrates ($T < 200$ K), the characteristic absorption band at 1.5 eV is progressively reduced in intensity the lower the temperature of the substrate.² On the other hand, the breadth of the band is unaffected. The latter fact is significant because it implies that the sample is in a two-phase condition possessing regions of good crystal, with associated sharp Brillouin-zone boundaries, and other regions (e.g., grain boundaries) where the concepts of translational symmetry and Brillouin zones are inapplicable.³ The implication of earlier work is that if a low enough substrate temperature could be arranged, then the (200) absorption band would disappear completely and we might conjecture that the aluminum film had a structure analogous to that of the liquid for which interband absorption is known to be absent.⁴ We have realized the disappearance of the (200) peak by evaporating aluminum onto a substrate held at 25 K, but the resulting spectrum is complex; it does not resemble that of the liquid and poses new questions.

Optical data were obtained using an ellipsometer.² Aluminum mirrors were prepared and studied under conditions of ultrahigh vacuum, the base pressure being 10^{-10} Torr at room temperature (RT). A thick, opaque aluminum film was deposited onto a sapphire substrate at RT, optical data were taken, and the film then cooled to 25 K and new data recorded. The (200) peak observed at 25 K was sharp, Fig. 1, but not significantly sharper than earlier data obtained at 140 K.² A new thick film was then deposited on top of the first film while this was held at the low

temperature, ~ 25 K. New data were then taken and these are also shown in Fig. 1. Clearly they are very different from those found for the film formed at RT in that there is no indication whatsoever of the (200) absorption peak. The general appearance of the absorption is reminiscent of that found for the liquid,⁴ which is reasonably well described by the Drude equations for a free-electron gas.

A closer analysis of our low-temperature data shown in Fig. 1 clearly demonstrates however that the absorption is definitely not of Drude

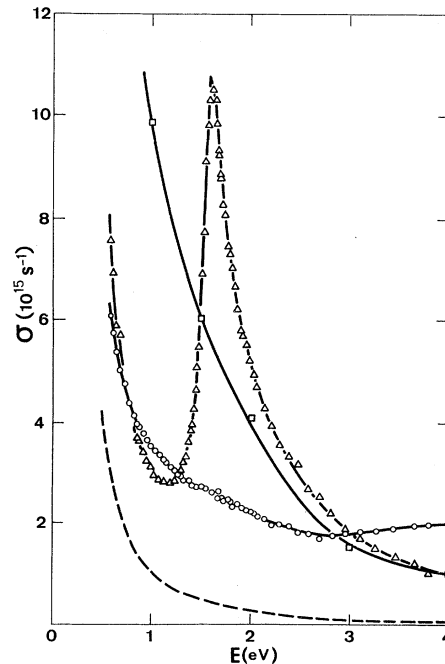


FIG. 1. Triangles, optical absorption at 25 K of an aluminum film deposited at RT. Circles, optical absorption at 25 K of an aluminum film deposited at 25 K; the slight kink at 1.6 eV is due to detector changeover, and the rise in absorption beyond 3 eV is attributed to scattering on account of surface roughness. Squares, optical absorption of liquid aluminum at 900°C (after Miller, Ref. 4). Dashed line, Drude absorption of crystalline aluminum, $m^* = 1.5$ and $\tau = 1.2 \times 10^{-14}$ sec.

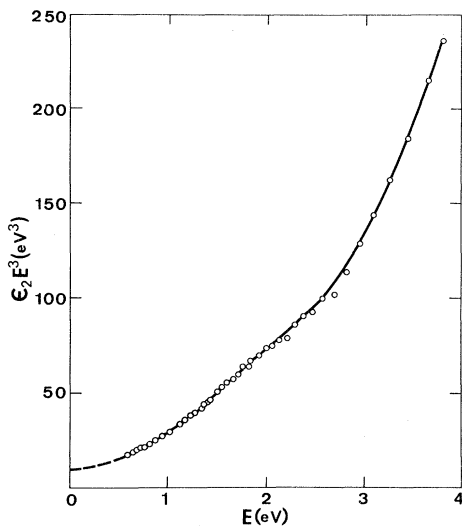


FIG. 2. $(\hbar\omega)^3\epsilon_2$ as a function of energy.

form. This is illustrated in Fig. 2 where $(\hbar\omega)^3\epsilon_2$ is plotted as a function of photon energy. The condition $\omega\tau \gg 1$ (τ being a Drude relaxation time) being valid, $(\hbar\omega)^3\epsilon_2$ should, for pure Drude behavior, be a constant quantity independent of ω . Clearly this is not the case as Fig. 2 shows, although there is no doubt that a Drude component is present in the measured absorption as indicated by the nonzero intercept of $\omega=0$. The film formed at 25 K was highly reflecting and clearly metallic; thus a Drude component is to be expected. It is not immediately obvious, however, how to separate the observed absorption into Drude and non-Drude components since we cannot decide from Fig. 2 alone whether the non-Drude component continues down to the lowest energies, or whether it exhibits a threshold at some finite frequency. The real part of the dielectric constant, ϵ_1 , also showed pronounced deviation from Drude behavior.

Ellipsometry presents us with independent measurements of ϵ_1 and ϵ_2 which, however, are inter-related through the dispersion relations. We have therefore used this advantage to attempt an approximate separation of the absorption into a Drude component ϵ_2^D and an additional component $\Delta\epsilon_2$ in the following manner: Working from Fig. 2 we assumed an ϵ_2^D , and this immediately established $\Delta\epsilon_2$. We could then, by Kramers-Kronig analysis of $\Delta\epsilon_2$, estimate the corresponding $\Delta\epsilon_1$, and this, when subtracted from the measured ϵ_1 , gave ϵ_1^D , which to be an acceptable Drude term required $1 - \epsilon_1^D$ to be linear in λ^2 . A least-squares fitting program was used to obtain

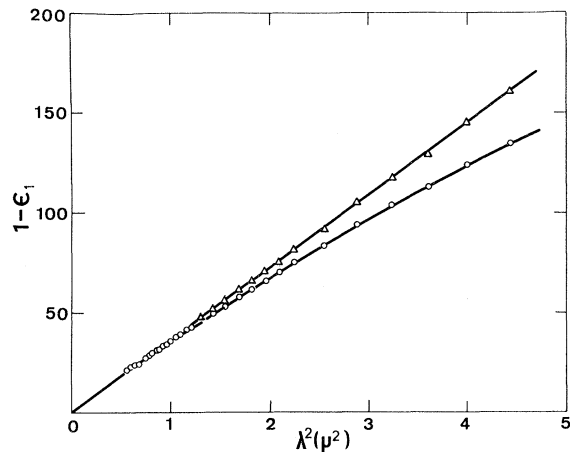


FIG. 3. $1 - \epsilon_1$ as a function of λ^2 . Triangles, derived Drude line; circles, measured $1 - \epsilon_1$ values.

a straight line through the derived $1 - \epsilon_1^D$ values, and the procedure was to obtain the best correlation coefficient for the line compatible with the least shift from the origin, Fig. 3.

Although the above procedure did not give a unique result, all the possible separations of the observed ϵ_2 into ϵ_2^D and $\Delta\epsilon_2$ had the same character in that they required $\Delta\epsilon_2$ to have a threshold at approximately 0.5 eV. Our preferred division is illustrated in Fig. 4. The chosen Drude components, ϵ_1^D and ϵ_2^D , imply a plasma energy of 7.45 eV and a relaxation time of 5.14 eV^{-1} (3.4×10^{-15} sec); these should be compared with those for crystalline aluminum, namely, 12.7 eV and

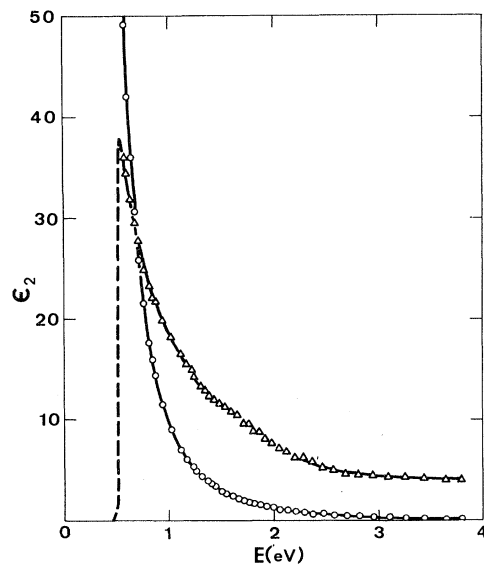


FIG. 4. ϵ_2 for an aluminum film deposited and studied at 25 K divided into a Drude component, circles, and a residual interband part, triangles.

18.3 eV⁻¹ (1.2×10^{-14} sec), respectively. If we assume that this Drude behavior stems primarily from a disordered structure, then we must associate the change in plasma energy with a decrease in the quantity n/m^* by some 30%, n being the volume density of electrons and m^* the effective mass. However, the present data do not allow us to assess individual changes in n and m^* .

We cannot associate the additional absorption denoted by $\Delta\epsilon_2$ with anything other than interband absorption, and it is noticeable that this absorption sets in at an energy very close to that of the (111) edge in crystalline aluminum, although the detailed shape of the deduced extra absorption does not have the same geometrical form as the crystalline edge. We shall call the observed extra absorption a pseudo (111) edge. On the other hand, we find it difficult to understand how the occurrence of a pseudo (111) edge, implying a well-defined (111) translational symmetry, can be reconciled with the complete absence of the stronger similar (200) edge. We might argue that the aluminum atoms condensing on a very cold, crystalline aluminum film tended to form close-packed planar clusters of very limited average diameter which did not join up laterally in an ordered manner, but which might have piled up in the thickness direction thereby maintaining

a large degree of the $ABCABCABC\dots$ pattern characterizing the (111) translational symmetry. Studies of the crystal structure of aluminum films condensed on cold substrates by Buckel⁵ do not substantiate the above contention since both the (111) and (200) diffraction peaks were clearly seen above a rather intense diffuse background [although the (200) peak appeared to be much weaker for films formed on cold substrates]. The observed optical absorption of aluminum could have been associated with another crystal modification but this is very unlikely, partly in view of the above mentioned diffraction experiments, partly because the (200) peak disappeared in a progressive manner and not discontinuously as the temperature of the substrate was lowered.

Clearly our optical data demonstrate a condition intermediate between the customary crystalline state and an amorphous state, but one that is not readily specified in detail.

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⁵⁵Mn NMR Study of Local-Moment Formation in CuMn

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NMR shifts and relaxation times are reported here for ⁵⁵Mn impurity nuclei in a series of liquid Al_{1-x}Cu_x:Mn alloys over the composition range $0 \leq x \leq 1$ and at temperatures from 1050 to 1425 K. Analysis of shifts and susceptibilities reveals abrupt changes in d -spin hyperfine field and orbital susceptibility at the Cu-rich end. A sharply increased value of the relaxation rate for $x \rightarrow 1$ is analyzed to give $J_{sd} = 0.82$ and 1.22 eV for the liquid and solid phases, respectively.

Nuclear magnetic resonance (NMR) in alloys containing dilute magnetic impurities has been employed extensively to investigate electronic structure and dynamics in the vicinity of the non-magnetic-host nuclear sites.¹ In this Letter we report NMR observations on the local-moment site itself in such a system: ⁵⁵Mn in solid and liquid CuMn. The nature of the impurity state and the process of moment formation were stud-

ied by measuring the ⁵⁵Mn frequency shifts and relaxation rates in liquid Al_{1-x}Cu_x host alloys for a series of Cu concentrations x varying from 0 to 1.² The Mn-impurity susceptibility (χ_{Mn}) in this liquid-alloy system has been found³⁻⁵ to change continuously from an increasing function of temperature for $x = 0$ (Al)^{4,5} to the T^{-1} behavior characteristic of a nearly free spin at $x = 1$ (Cu),³ while increasing in magnitude by a factor