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OPTICAL PROPERTIES OF Ag-Cu ALLOYS : EVIDENCE FOR d-VIRTUAL BOUND STATES ON Cu IMPURITIES (*)

J. RIVORY and M. L. THEYE

Laboratoire d'Optique des Solides (**), Université Paris VI,
 75230 Paris, Cedex 05, France

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Résumé. — Les propriétés optiques de solutions solides métastables Ag-Cu en toutes concentrations ont été déterminées et analysées entre 0,5 et 6 eV ; les résultats relatifs aux alliages riches en Ag sont interprétés en termes du modèle des niveaux liés virtuels.

Abstract. — The optical properties of metastable Ag-Cu solid solutions over the whole composition range have been determined and analyzed between 0.5 and 6 eV ; the results relative to Ag-rich alloys are interpreted in terms of the virtual bound state model.

The theory of the electronic structure of substitutionally disordered alloys, especially those which contain localized electronic states such as d-states, has been developed considerably in recent years [1-5]. The theoretical models still need to be tested against experimental results for representative alloys. Ag-Cu alloys are particularly interesting in this respect because of the small overlap of the d-bands of the pure constituents. As a result of experimental difficulties, they have been little investigated : in addition to differential measurements on very dilute alloys [6], only two studies, by optical absorption [7] and by high-energy photoemission [8] have been reported for concentrated alloys. We present the results of an optical investigation of Ag-Cu alloys over the whole concentration range and we interpret them according to the virtual bound state theory [1, 2].

As the solubility of Ag and Cu in each other is very small [9], only metastable solid solutions can exist in the non-dilute range. We tried to prepare such samples over the whole composition range in the form of thin films deposited by simultaneous evaporation of the two metals from the same tungsten crucible onto silica substrates, under a classical vacuum of 10^{-7} torr. The film structure and homogeneity were controlled by electron microscopy and electron diffraction performed on pieces of the same films stripped off the substrate. The film thickness (ranging from 100 to 400 Å) was determined by X-ray interferences with 1 % accuracy [10] and the

alloy composition by electron microprobe analysis with 1 % accuracy [11]. Homogeneous films could only be obtained by using very high deposition rates (flash evaporation) and by depositing the films on substrates held at low temperatures (~ 180 K) ; introduction of Ar in the vacuum chamber while the film was maintained at low temperature seemed to prevent atomic rearrangements leading to phase-separation when bringing the samples back to room temperature for optical studies. These films consisted of very small crystallites of about 15-20 Å (i.e. 3 or 4 atomic cells) ; truly amorphous films were obtained only when deposited at temperatures lower than 60 K. The diffraction diagrams, although very broad, were representative of real solid solutions. Annealing produced both recrystallization and phase-separation.

The complex dielectric constant $\tilde{\epsilon}$ was determined between 0.5 and 6 eV from the film reflectance and transmittance measured in air at room temperature, the film thickness being known [12] ; this method was supplemented in some cases by a Kramers-Kronig analysis of the reflectance data [13].

Figure 1 shows the imaginary part ϵ_2 of the dielectric constant versus energy between 2 and 6 eV, for a number of Ag-Cu alloys as well as for pure Ag and pure Cu. The modification of the ϵ_2 spectrum when going from Cu to Ag by alloying is strikingly different from what is observed for Ag-Au and Cu-Au alloys [14, 15, 16]. In these cases, the absorption edge moves continuously (although not linearly) and changes its shape smoothly from the edge of one pure constituent to the other, which is interpreted as being due to the shift and deformation of a common d-band. For the Ag-Cu alloys, there is no continuous modification of the spectrum and one must consider

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(**) Equipe de Recherche associée au C.N.R.S.

FIG. 1. — Imaginary part ε_2 of the dielectric constant versus energy for Ag-Cu alloys with different Cu concentrations, and for pure Ag and pure Cu.

separately the Cu-rich alloys, for which ε_2 is roughly Cu-like, and the Ag-rich alloys which present an original behavior to be discussed later.

For Cu-rich alloys, the ε_2 spectrum stays very similar to the pure Cu spectrum (up to $c_{\text{Cu}} = 0.55$). For small Ag concentrations, the absorption edge is very steep and located at the same energy as in pure Cu : 2.15 eV. When c_{Ag} increases, it is broadened but not shifted; the first maximum is rounded and shifted to higher energies (broadening effects may simply be due to disorder in these microcrystalline samples). Since the absorption edge in pure Cu, as for other noble metals, is mainly determined by transitions from the top of the d-band to the conduction band at the Fermi level, the upper part of the Cu partial d-band must be little affected by alloying with Ag. The second edge starting at 4 eV in pure Cu can still be seen at the same energy in the alloys, while the maximum centered at 4.8 eV decreases in intensity, becomes narrower and moves to lower energies. It is difficult to separate out the different contributions in this spectral range; the modification of the ε_2 curve around 5 eV is tentatively attributed to a perturbation of the bottom of the partial Cu d-band, due possibly to the presence of Ag d-states.

For Ag-rich alloys, the ε_2 spectrum shows two distinct parts : a high-energy portion which is very similar to the interband absorption in pure Ag, and a low-energy part which must represent the Cu impurity contribution. The absorption edge looks very much like the pure Ag edge, except for broadening effects; it has the same energy dependence and leads by extrapolation to the same onset for interband transitions from the top of the Ag partial d-band to the Fermi level : 3.85 eV. The upper part of that band is therefore not affected by alloying with Cu.

Between 2 and 4 eV, the impurity contribution shows up as a bump superimposed on the matrix intraband contribution to ε_2 ; its intensity increases with Cu concentration while it remains centered at

about 3.2 eV (even up to $c_{\text{Cu}} = 0.30$). This behavior is completely original in the noble metal alloys series but it looks very similar to the contribution of transition impurities in Ag, for example in Ag-Pd alloys [18, 19]. It may be inferred that, in Ag-Cu alloys, the Cu d-levels are in resonance with the continuum of conduction states and form virtual bound states localized on the Cu atoms, clearly distinct from the unperturbed d-band of the Ag matrix.

Theoretical expressions for the frequency-dependent optical absorption due to virtual bound state impurities have been derived by Caroli [20] and by Kjollerstrom [21]. We shall follow here the more intuitive treatment proposed by Beaglehole [22]. Absorption due to the presence of impurities takes place by two processes : resonant scattering of conduction electrons by the impurity d-states and excitation of impurity d-electrons to empty conduction states (and of host electrons to empty impurity states). The first process is accounted for by a generalized Drude formule :

$$\varepsilon_{2c} = \frac{\omega_p^2}{\omega \tau_a (\omega^2 + \tau_a^{-2})}$$

where ω_p is the plasma frequency of the matrix and τ_a , the relaxation time in the alloy, is given by :

$$\frac{1}{\tau_a} = \frac{1}{\tau_p} + \frac{c}{\tau_i}$$

τ_p is the relaxation time of the pure matrix (related to phonons, defects and other impurities) and τ_i the frequency dependent relaxation time due to scattering by the impurity with concentration c . If E_d and Δ are respectively the position with respect to the Fermi level and the half-width of the virtual bound state density, assumed to be Lorentzian, then τ_i is given by :

$$\frac{1}{\tau_i} = \frac{1}{\tau_i(0)} \frac{E_d^2 + \Delta^2}{2 \omega \Delta} \times \left[\tan^{-1} \left(\frac{\omega + E_d}{\Delta} \right) + \tan^{-1} \left(\frac{\omega - E_d}{\Delta} \right) \right]$$

The second process (interband transitions) gives a contribution :

$$\varepsilon_{2B} = c \left(\frac{\omega_d}{\omega} \right)^2 \times \left[\tan^{-1} \left(\frac{\omega + E_d}{\Delta} \right) + \tan^{-1} \left(\frac{\omega - E_d}{\Delta} \right) \right]$$

where ω_d is proportional to the matrix element characterizing these transitions (assumed to be constant).

In this model, the experimental ε_2 data below the onset of Ag interband transitions (i.e. between 0.5

and 3.5 eV) must be described by the expression :

$$\epsilon_2 = \epsilon_{2c} + \epsilon_{2B},$$

which allows one to determine by a least square method the four parameters characterizing the Cu d-virtual bound states in Ag : E_d , Δ , ω_d and $\tau_i(0)$. The parameters τ_p and ω_p , which correspond to the pure matrix, are difficult to choose : τ_p is strongly dependent on sample structure ($\hbar/\tau_p$ may vary from 0.025 to 0.05 eV for pure Ag films) and there remains some theoretical ambiguity concerning the value of ω_p in such treatments [23]. It was possible to determine simultaneously five parameters : E_d , Δ , ω_d , $\tau_i(0)$ and ω_p , τ_p^{-1} being fixed at different physically reasonable values; the results (especially the values of E_d and Δ) were not very sensitive to the choice of τ_p . The fitting was performed on the quantity $\omega\epsilon_2$, which gave more weight to the high energy values of ϵ_2 . Figure 2 shows these results for two

alloys with Cu concentrations 0.08 and 0.30; the two partial contributions ϵ_{2c} and ϵ_{2B} are indicated. The fitting is quite good for the dilute alloy, less good for the more concentrated one in which interactions of impurity atoms must already be large; however, the values of the parameters were the same in both cases. The main parameters E_d and Δ are determined with a few % accuracy, ω_d less accurately; $\tau_i(0)$ and ω_p were often strongly correlated, and their values are more scattered. Table I gives the values of E_d , Δ and ω_d for a few alloys, including the more concentrated one : the d-virtual bound states localized on Cu impurities in a Ag matrix are located at about 3.1 eV below the Fermi level and have a half-width of about 0.45 eV; the matrix element parameter for interband d-s transitions ω_d is about 4 eV.

TABLE I

Position with respect to the Fermi level E_d and half-width Δ of Cu d-virtual bound states in Ag, and coupling parameter for d-s transition ω_d deduced from the optical absorption as explained in the text for different Ag-rich alloys.

Cu concentration	E_d (eV)	Δ (eV)	ω_d (eV)
0.06	3.1 ± 0.1	0.56 ± 0.06	4.4
0.08	3.0 ± 0.1	0.4 ± 0.1	
0.09	3.15 ± 0.1	0.45 ± 0.1	3.6 - 4.0
0.10	3.1 ± 0.1	0.5 ± 0.1	4 - 5
0.30	3 ± 0.1	0.31 ± 0.05	3 - 4

In conclusion, we have succeeded in preparing true Ag-Cu solid solutions over the whole composition range by vacuum deposition on substrates at low temperature and we have measured and analyzed their optical properties. The optical absorption of Cu-rich alloys remain very similar to that of pure Cu, except for broadening effects at the edge and for changes at higher energies, probably related to the presence of the Ag partial d-state density in the vicinity of the bottom of the Cu partial d-band. In Ag-rich alloys, that part of the absorption spectrum due to the partial Ag d-band remains unchanged and the additional structure attributed to the Cu impurities can be interpreted in terms of the virtual bound state model. The observed non-modification of the upper part of the matrix d-band in the dilute cases, as well as the position and width of the d-virtual bound states on Cu impurities in Ag deduced from our data agree remarkably well with the results of high-energy photoemission experiments [9].

FIG. 2. — Results of the fitting procedure in the virtual bound state model for Ag-rich alloys, showing the experimental (..) and the calculated (o) ϵ_2 curves, as well as the theoretical intraband (*) and interband (+ +) contributions to ϵ_2 .

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