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Modulated Reflectivity Measurements on α-phase Cu-Zn, Cu-Al, Cu-Ga, and Cu-Ge Alloys

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The optical properties of copper-based alloys containing Zn, Al, Ga, or Ge were investigated using compositional modulation. This method enhances the structure in the spectral reflectivity of materials by measuring the difference in the reflectivities of two alloys. The energy of interband transitions between the *d* bands and the Fermi level remains approximately constant when up to 2-at.% Zn, Al, or Ga is alloyed to copper but increases for higher solute concentrations. For Cu-Zn, Cu-Al, and Cu-Ga alloys it was found that for a given solute concentration the transitional energy between *d* bands and the Fermi level is identical. The results are interpreted by assuming that the *d* bands, as well as the Fermi level, are raised by alloying. Cu-Ge alloys differ in many respects from the behavior of the aforementioned alloys.

I. INTRODUCTION

The optical properties of copper-based alloys have been investigated previously, mostly using conventional reflectivity or absorbtivity methods.[1-9] In a previous paper[6] we reported some preliminary results on α-phase copper-zinc alloys which were obtained using compositional modulation, a technique which enhances the structure in the spectral reflectivity of alloys and which provides, therefore, more accurate data of energies for optical interband transitions. In this paper, results are reported on copper-based alloys with additions of zinc, aluminum, gallium, or germanium which were obtained with a refined version of the differential reflectometer used previously.[6]

II. EXPERIMENTAL

The differential reflectometer can be used to measure the difference in the reflectivities (ΔR) of two alloys which vary only slightly in solute concentration. The alloys which are placed side by side are illuminated alternately with monochromatic light by means of an oscillating mirror, i.e., the light beam periodically scans from one sample to the other.[10] The output signal from a photomultiplier, which picks up the reflected light, is processed by a lock-in amplifier and a divider circuit which yields a value of $\Delta R/\bar{R}$, where $\bar{R}$ is the average of the reflectivities of the two specimens. The instrument therefore measures the normalized difference of the reflectivities between the two alloys, thus eliminating the fluctuations and structure of the light source and other instrumental components. The apparatus is capable of detecting differences in the reflectivities between two specimens of about 0.1%. The photon energy of a pronounced peak can be reproduced within ± 1 nm (i.e., within $\pm 3\times10^{-3}$ and $\pm 9\times10^{-3}$ eV depending on the wavelength). A typical "differential reflectogram," i.e., a plot of $\Delta R/\bar{R}$ versus the wavelength, scanned through the visible and near-uv region, is usually performed in less than 1 min. This minimizes errors due to changes of the surface conditions during the measurement.

The alloys were prepared from high-purity metals (typically 10-ppm impurity) encapsulated in Vycor glass tubes in a helium atmosphere and melted in an induction furnace. After cooling, the specimens were cold worked and then homogenized for about five days slightly below the solidus temperature. Next, two specimens having different compositions were cold-mounted side by side with essentially no gap in between, and mechanically polished using standard metallographic techniques down through 1-μm diamond compound. The reflectivity measurements were carried out within a few minutes after final polishing.

The composition and the homogeneity of the alloys were checked by microprobe analysis. The homogeneity of some specimens has also been tested with the differential reflectometer by scanning the full light beam across one sample only. Any inhomogeneity would produce a nonzero value or possibly structure in the differential reflectograms. It has been found that the above-mentioned heat treatment is sufficient to produce homogeneous alloys.

The advantage of differential reflectometry compared to conventional reflectance techniques is that the surface preparation as well as the environment in which the measurements are taken are not critical because the readings are taken on two samples which have similar compositions. Since the two specimens contained in one mount receive the same polishing simultaneously, any error due to surface deformation and oxidation is approximately the same. Even if the absolute values of the reflectivities are changed by surface effects, the normalized difference in their reflectivities is not affected significantly.

III. RESULTS

In Fig. 1 differential reflectograms of various copper-zinc alloys are presented. Figure 2 shows differential reflectograms of copper-based alloys containing an average composition $\bar{C}$ of 0.5-at.% solute where $\bar{C} = \frac{1}{2}(C_1 + C_2)$ and C_1 and C_2 are the compositions of the two alloys. In Fig. 3 the position of some characteristic peaks in the differential reflectograms are plotted versus the solute concentration. The following observations can be made.

(i) The differential reflectograms reveal three pronounced peaks labeled *A*, *B*, and *C* (Fig. 1).

(ii) With increasing solute concentration, peak *A* shifts to higher energies, broadens, and decreases in intensity per unit increase in composition, Fig. 1 (see also Refs. 3-6, 8, and 9).

(iii) Peaks *B* and *C* are shifted to lower energies, with increasing solute concentration, Fig. 1 (see also Refs. 3, 8, and 9).

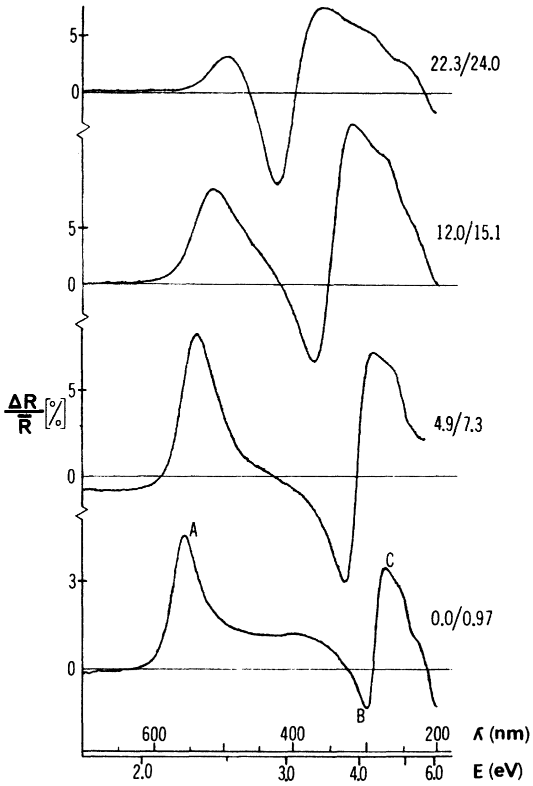

FIG. 1. Differential reflectograms ($\Delta R/\bar{R}$ vs photon energy) for various copper-zinc alloys. The numbers on each graph give the zinc concentration of the specimens in atomic percent.

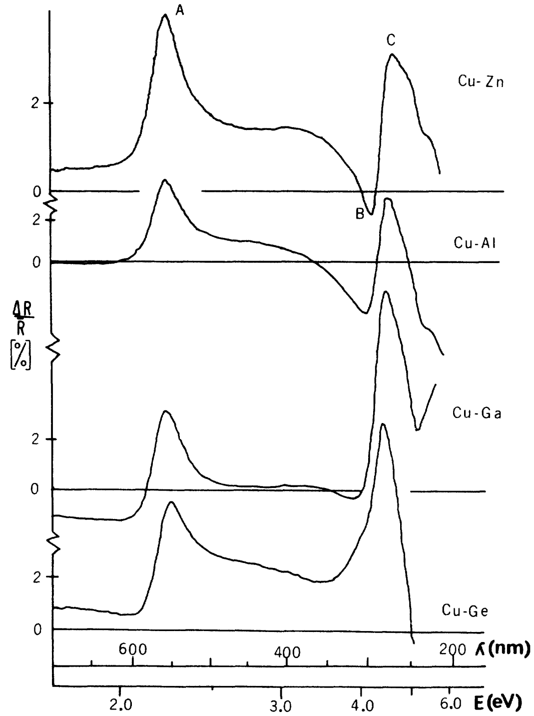

FIG. 2. Differential reflectograms for various copper-based alloys with an average composition of 0.5-at.% solute (one sample of each pair consists of pure Cu, the other of 1-at.% solute).

(iv) Peak *B* is not pronounced in Cu-Ga and does not show up at all for Cu-Ge alloys. Instead a broad minimum at smaller energies (around 3.4 eV) can be seen for the Cu-Ge alloys (Fig. 2).

(v) The differential reflectograms show some weak structure around 5.2 eV which is most pronounced in Cu-Ga (Fig. 2) and shifts to lower energies with increasing solute concentration (Fig. 1).

(vi) At low solute concentrations (up to about 2 at.%) peak *A* for Cu-Zn, Cu-Al, and Cu-Ga alloys remains at approximately the same energy and then increases almost linearly with increasing solute concentration. The change in energy of peak *A* increases at a slower rate beyond roughly 10-at.% solute (Fig. 3).

(vii) Special attention should be given to the fact that the transitional energies, *A*, are identical for a given solute concentration in Cu-Zn, Cu-Al, or Cu-Ga (Fig. 3).

(viii) The decrease of the energy of peak *B* with increasing solute concentration is larger for Cu-Ga alloys than for Cu-Zn alloys. This decrease seems to be identical for Cu-Ga and Cu-Al (Fig. 3).

(ix) The decrease of the energy of peak *C*, for most of the alloys investigated, is fairly small up to about 4-5-at.% solute followed by a steeper decrease and finally a less steep decrease. This

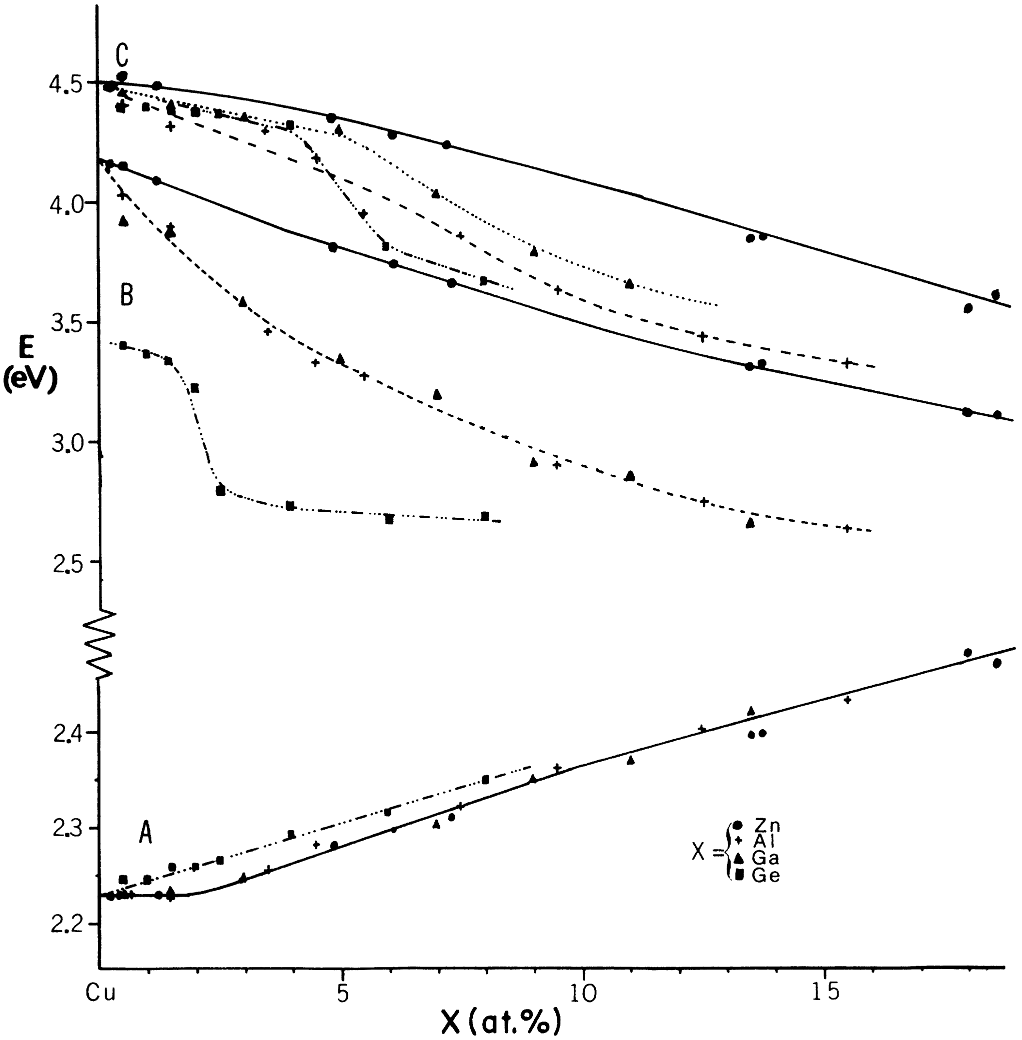

FIG. 3. Energy of peaks *A*, *B*, and *C* of Fig. 1 vs solute concentration for Cu-Zn, Cu-Al, Cu-Ga, and Cu-Ge alloys. (Note the enlarged scale for peaks *A* by a factor of 4.)

behavior is most pronounced in Cu-Ge and not present in Cu-Zn alloys (Fig. 3).

(x) The shallow minimum at about 3.4 eV (observed only in Cu-Ge alloys) varies in a manner similar to peak *C* (Fig. 3).

IV. DISCUSSION

We shall restrict the following discussion to transitions involving the *d* bands. The lowest energy peak (peak *A* in Figs. 1 and 2) can be ascribed to the threshold energy for optical interband transitions, in compositional modulation as well as in other modulation methods. In dilute copper-based alloys, transitions from the top of the *d* bands to empty states just above the Fermi level are responsible for this onset of interband transitions.

Observation (vi) above seems to indicate that the energy difference between *d* bands and the Fermi level is not altered substantially when up to 2-at.% Al, Ga, or Zn is added to copper. Friedel[11] predicts this behavior qualitatively and argues that when a small amount of a solute with an additional nuclear charge *Z* is introduced into a pure metal, the extra charge is screened by a rearrangement of the electrons. Thus, the Fermi level remains that of the pure metal as long as the impurities do not mutually interact. This mechanism does not seem to be universally valid, however, since germanium nuclei, which introduce three additional charges to copper, show an immediate increase in the energy of peak *A* with composition even at low solute concentrations. Using Friedel' s theory one could interpret this finding to indicate that these nuclei are not perfectly screened.

The transition energy between the d bands and the Fermi level (peak A) was observed to increase with increasing solute concentration [observation (ii) above]. The rigid-band model[12] can be used to predict this behavior by assuming that the shift of the main absorption edge, and thus peak A, is caused by an increase of the Fermi energy when a multivalent metal is alloyed with copper. (Here, the d bands are assumed to be unaffected by alloying.) Based on this theory[12] one would therefore expect that the slopes A in Fig. 3 should increase with increasing electron charge Z (or electron-to-atom ratio) of the solute. However, this was not observed [item (vii)]. In this context Friedel[11] predicts that dE/Z (where dE is the displacement of the Fermi level) is essentially only a function of the solute concentration. Also this relation was not found to hold in the present experiments. Our results suggest instead, that in Cu-Zn, Cu-Al, and Cu-Ga alloys dE (and not dE/Z) is a function of the solute concentration [item (vii)]. Friedel's theory as well as the rigid-band model (which arrive at similar conclusions in this respect) tend to focus their attention only upon displacements of the Fermi level. Since peak A is caused by the energy difference between the top of the d bands and the Fermi level one should, however, also consider changes in the d bands with increasing solute concentration which could compensate for some of the shift of the Fermi level. Our results seem to indicate that the d bands themselves are raised by alloying. Three different pieces of experimental evidence will be given which can be interpreted to support this statement.

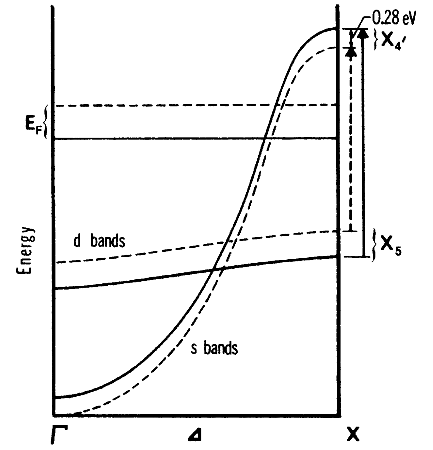

FIG. 4. Schematic representation of energy bands and Fermi level for pure copper (solid curves) and a Cu–10-at.%-Zn alloy (dashed curves). The arrows indicate the $X_5 \to X_4'$ transition.

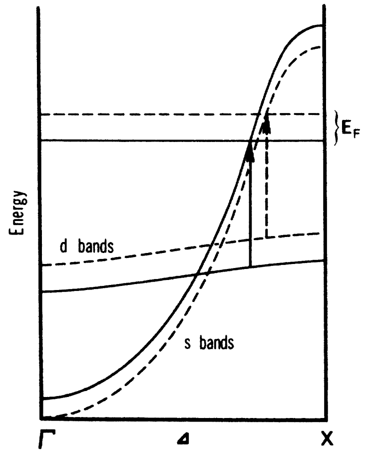

FIG. 5. Schematic representation of energy bands and Fermi level for two copper-based alloys containing the same amounts of a divalent or trivalent solute, respectively. Solid curve: Cu-Zn; dashed curve: Cu-Ga.

(a) Amar, Johnson, and Sommers[13] have calculated the increase of the Fermi level (E_F) with respect to the top of the d band for a Cu–30-at.% Zn alloy. They assumed for their calculation that the d bands would be unaffected by alloying. The increase of the Fermi energy was found, by them, to be 0.48 eV. For the same alloy we measured a total displacement of peak A of 0.32 eV.[9] Our results therefore indicate that the energy gap between the top of the d bands and the Fermi level is smaller than the calculation predicts. This discrepancy between experiment and calculation can be resolved by assuming that the d bands in the alloy are raised with respect to those for pure Cu.

(b) Amar *et al.*[13] and Pant and Joshi[14] have calculated the energy of the X_4' level for pure Cu and several Cu-Zn alloys. They found that for a Cu–10-at.%-Zn alloy this level was reduced by about 0.28 eV compared to that of pure copper (see Fig. 4). As mentioned above these authors assumed that the d bands remain unaffected by alloying.

Peak B in our differential reflectograms (Figs. 1 and 2) is probably in some way related to the $X_5 \to X_4'$ transition. (A rigorous relationship between the energy of this peak and the $X_5 \to X_4'$ transition cannot be given at this time.) A shift of peak B to lower energies with increasing solute concentrations (Fig. 3) could therefore imply a reduction of the $X_5 \to X_4'$ energy gap which is in accordance with the theory. For a Cu–10-at.%-Zn alloy we found that the energy of peak B was reduced by 0.7 eV compared to pure copper (Fig. 3 and Ref. 9). This value should be compared with the 0.28 eV which was found by calculation. We interpret this much larger experimentally observed reduction of the $X_5 \rightarrow X_4'$ gap to be due to an upward shift of the *d* bands of the alloy relative to those for pure copper (see Fig. 4).

(c) As mentioned above, one would expect that the slopes *A* in Fig. 3 would be larger for copper-based alloys with trivalent aluminum or gallium than for alloys with divalent zinc because of the greater e/a ratio of the former. However, these slopes as well as the energy difference between the *d* bands and the Fermi level are found to be identical for a given solute concentration [observation (vii)]. The situation can be best discussed by considering Fig. 5 in which the pertinent part of the band diagram for copper-based alloys containing a divalent and a trivalent solute is schematically presented. As implied in case (b) above, the *s* band is lowered with alloying, the effect being greater for a trivalent than for a divalent solute. Likewise the *d* band and the Fermi level are raised in the same manner.

It can be seen from Fig. 5 that in order that the transition energy between the *d* band and the Fermi level be identical for the two alloys, the *d* band of the "trivalent alloy" must be higher than that of the "divalent alloy."

The above-mentioned observations can only be partially explained with current theoretical models. It is hoped therefore that this paper stimulates further theoretical work on the electron theory of dilute alloys.

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