PHYSICAL REVIEW B VOLUME 16, NUMBER 10 15 NOVEMBER 1977

Optical properties and electronic structure of dilute Cu-Au, Cu-Zn, Cu-Al, Cu-Ga, Cu-Si, Cu-Ge, Cu-Sn, and Cu-As alloys*

R. J. Nastasi-Andrews† and R. E. Hummel

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

(Received 17 January 1977)

A systematic study of the optical properties of a large range of α-phase copper-based alloys was undertaken. The solutes were selected to include elements with one, two, three, four, and five valence electrons. The differential reflectometer, which is capable of determining within a hundredth of an electron volt the energy for interband transitions of electrons, was used for the investigations. Using a line-shape analysis, three different transitions could be identified: (i) A threshold energy for interband transitions around 2.2 eV which involves the upper *d* bands and the Fermi energy. This transitional energy does not change for solute concentrations up to approximately 1 at.%, confirming the theory by Friedel concerning screening of solute charges at low solute concentrations. Experimental evidence is given which suggests that both the *d* bands and the Fermi energy are raised by alloying. (ii) Lower *d*-band to Fermi energy transitions around 5 eV behave in many respects similar to the upper *d*-band to Fermi energy transitions, except that the lower *d* bands appear to be raised much less due to alloying. (iii) A conduction-band to conduction-band transition around 4 eV was observed to decrease in energy with alloying. Copper-gold alloys do not show any changes in the threshold energy due to solute additions. Additional broad structure around 3 eV indicates that transitions originating from gold *d* bands may be involved.

INTRODUCTION

The optical constants of copper have been studied in great detail.[1-11] Within the past ten years, this work has been supplemented to an increasing extent on copper alloys.[12-28] Unfortunately, a variety of techniques have been used to investigate the different alloy systems, making it rather difficult to perform reliable comparisons between the data. Likewise, disagreement between various types of band calculations, alloy theories, and results in number, location, and energy of the interband transitions for copper alloys has been of concern.

There is general agreement among various investigators that the structure observed in the spectral reflectivity of copper and its dilute alloys around 2.2 eV is due to upper *d*-band to Fermi energy transitions. There appears to be a rather wide range of energies (3.45–4.0 eV) where some investigators observed structure and assigned it to a transition from X_5 to $X_{4'}$ (Refs. 5, 6, 9, 10, 17, 18, and 22). The lack of agreement on the exact energy may be due to different types of experimental techniques and theoretical models used. It should be noted that this structure is weak and that the $X_5 \rightarrow X_{4'}$ transition does not show up in the calculated optical spectrum of copper.[7] It has been speculated therefore that the structure between 3.45 and 4.0 eV is due to volume effects[9] or to transitions from the Fermi energy to the upper L_1 band.[6,23]

The $L_{2'} \rightarrow L_1$ transition definitely appears both in experiments as well as in calculations. Structure assigned to this transition has been observed primarily between 4.2 and 4.8 eV; however, the exact energy is unknown (Refs. 5, 7, 9, 10, 17, 18, 23, and 27). Structure which is observed at energies around 5 eV is generally attributed to lower *d*-band to Fermi energy transitions.[7,16,20-23] (For more details, reference should be made to a literature review,[28] which includes the theoretical models governing interband transitions in copper and its alloys, and a compilation of the relevant experimental results.)

This paper presents a systematic and comprehensive study of the optical properties of a large range of α-phase copper-based alloys. The solutes were selected to include elements with one, two, three, four, and five valence electrons, including gold, zinc, aluminum, gallium, silicon, germanium, tin, and arsenic.

The investigations were performed using the differential reflectometer which is capable of determining within a hundredth of an electron volt the energy for interband transitions of electrons. The technique involves the modulation of the alloy composition within the same binary system.[29] In modulation spectroscopy an optical property of a material, such as the reflectivity, is measured as an oscillating perturbation, which modulates the band structure of the material, is applied to it. By observing the change in property, the derivative with respect to the perturbation is essentially obtained. Conventional spectral reflectance measurements of metals and alloys lack sharp structure due to the spreading of energy levels to energy bands. By using modulation techniques, such as compositional modulation,[29] sharp structure can be observed due to changes in the band structure which are caused by the change in alloy composition.

EXPERIMENTAL

A detailed description of the differential reflectometer was given by Holbrook and Hummel.[30] In the present study, an improved version of this instrument was used employing mirrors instead of lenses and a monochromator with a higher resolution and extended spectral range (8000–2000 Å). The sensitivity has been increased to observe differences in reflectivity up to 10^{-5}. Light, coming from a monochromator, is alternately scanned by a vibrating mirror on two alloys which are mounted side by side. The signal from a photomultiplier tube which picks up the reflected light from the specimens is electronically processed to obtain the normalized difference in reflectivities ($\Delta R/\overline{R}$).

The alloys (purity generally 99.999%) were melted under helium atmosphere in Vycor tubes. After cooling, the samples were cold rolled and subsequently homogenized slightly below the solidus temperature for 2 weeks under vacuum. The alloys were then cold rolled again and reannealed for one hour at 600 °C under vacuum to produce a uniform and fine grain size.

Two alloys with the same type solute but of slightly different composition (usually 1%–2% difference) were cold mounted side by side with virtually no gap in between. The samples were then mechanically polished using standard metallographic procedures (ending with 1-μm diamond polishing compound on felt cloth), rinsed with methanol, dried, and immediately transferred to the differential reflectometer. Since both alloys underwent identical preparation procedures at the same time, any possible changes of the metal surface, such as deformation, oxidation, etc., are nearly identical and subtract out due to the differential technique. The measurements can therefore be performed in air. Oxidation of the alloys decreases only the peak height but does not alter the energy of the peaks. This has been substantiated by comparing differential reflectograms obtained from specimens measured two minutes and several months after polishing.

RESULTS AND DISCUSSION

This study is a continuation of work done by Hummel and Andrews.[19] Some of the alloys used here have been on hand from earlier experiments. They have been remeasured, because of the change in equipment in order to eliminate the possibility of systematic errors.

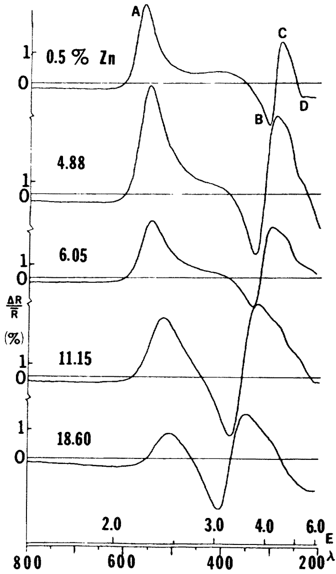

FIG. 1. Selected differential reflectograms for various copper-zinc alloys. The parameter is the average zinc content of the two alloys in at.%.

Some of the differential reflectograms of the alloys are presented in Figs. 1-4. Four distinct peaks can usually be observed, which will be designated as peaks *A–D*. The energies of these peaks for all alloys are presented in Tables I–III.

A legitimate question which arises immediately is the one about the correlation between a certain peak in a differential reflectogram and a specific interband transition. To assess this, one has to

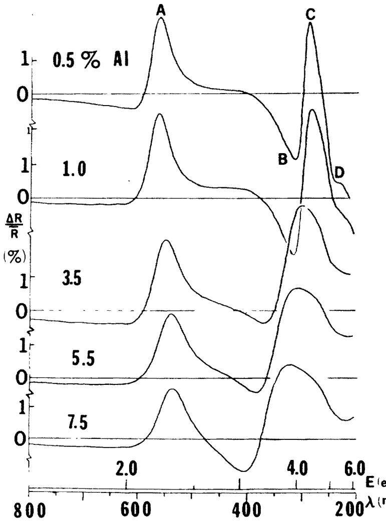

FIG. 2. Selected differential reflectograms for various copper-aluminum alloys. The parameter is the average aluminum content of the two alloys in at.%.

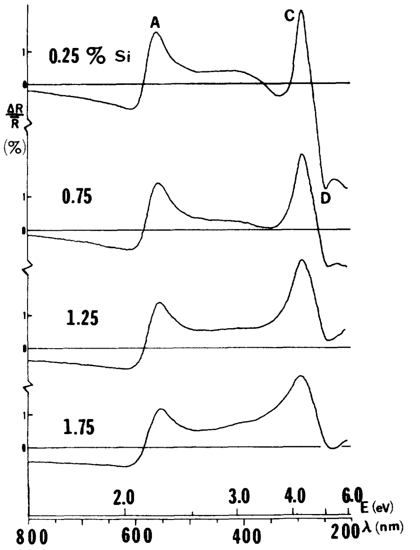

FIG. 3. Selected differential reflectograms for various copper-silicon alloys. The parameter is the average silicon content of the two alloys in at.%.

write a quantum-mechanical equation for the reflectivity, making several assumptions for a given interband transition, and to form the derivative of this reflectivity with respect to the modulated parameter, here, the composition X. By such a "line-shape analysis," a possible confirmation between theory and experiment can be obtained.

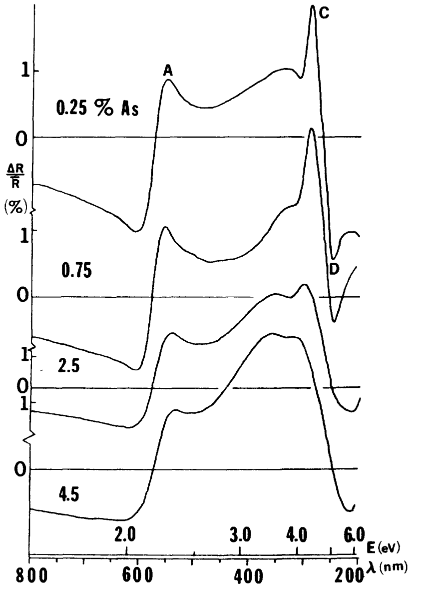

FIG. 4. Selected differential reflectograms for various copper-arsenic alloys. The parameter is the average arsenic content of the two alloys in at.%.

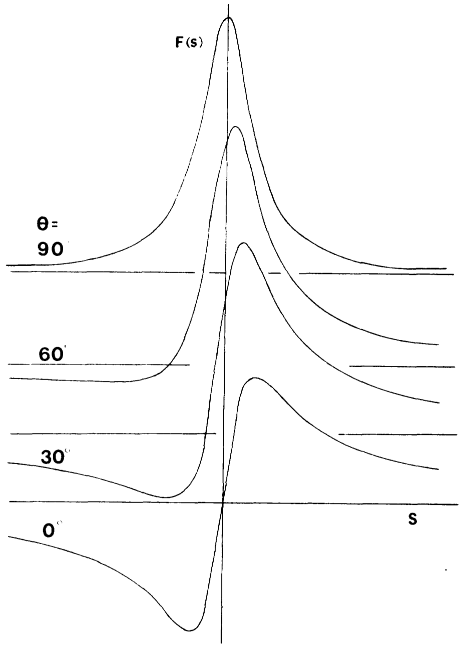

FIG. 5. Calculated $F(S)$ vs S diagrams for a d-band to Fermi-energy transition. $F(S)$ is essentially $\Delta R/\bar{R}$ and S is proportional to the photon energy. (Compare to the vicinity of peak A in the experimental differential reflectograms.)

Also, based on certain other parameters in the theory, the exact energy for the electron transitions (E_T) in the material can be obtained from the structure in the differential reflectogram. An analysis of this kind was recently done by Enderlein *et al.*[31] for a d-band to Fermi energy transition (e.g., peak A). The line-shape analysis yielded that $\Delta R/\bar{R}$ is proportional to a function $F(S) = \cos(\theta - \phi)\sin\phi$, where $\theta = \arctan(\beta/\alpha)$ (α and β are the "Seraphin coefficients,"[32] whose spectral dependence for copper is shown elsewhere[31]), and $\sin\phi = 1/(S^2+1)^{1/2}$, where S is proportional to the photon energy. Selected $F(S)$ functions for particular θ values are plotted in Fig. 5. For peak A, θ ranges from 0° to 90°. For $\theta = 90°$, $F(S)$ is symmetrical around $S = 0$ and the peak energy $E_{\max}$ is equal to the transition energy E_T. For $\theta = 0°$, $F(S)$ is asymmetrical about $S = 0$ and E_T lies in the middle between the minimum and maximum. For all other values of θ, the true transition energy E_T has to be found by curve fitting.[31] This has been done for our experimental data. The resulting transitional energies are listed in column 4 of Table I. By comparing columns 3 and 4, one notices that these corrections amount usually to a few hundredths of an electron volt, i.e., are generally very small.

We have shown elsewhere[31] that for the correct-

TABLE I. Maximum energy E_{max} and corrected transitional energy E_T for peak A as a function of composition for various copper-based alloys. Error limit for E_{max} is ±0.004 eV; for E_T ±0.007 eV.

Composition of alloys (at.%)	Average composition (at.%)	E_{max} (eV)	E_T (eV)
	copper-zinc		
0-0.5	0.25	2.198	2.180
0-1	0.5	2.199	2.182
0-2.5	1.25	2.210	2.187
2.45-7.3	4.88	2.255	2.227
4.8-7.3	6.05	2.269	2.240
9.8-12.5	11.15	2.378	2.343
17.36-18.09	17.73	2.435	2.416
18.2-19	18.60	2.439	2.413
	copper-aluminum		
0-0.1	0.05	2.219	2.187
0-0.5	0.25	2.214	2.189
0.5-0.25	0.375	2.227	2.176
0-1	0.5	2.207	2.185
0.1-1.5	0.8	2.208	2.188
0.5-1.5	1	2.204	2.183
1.5-2	1.75	2.233	2.198
2-3	2.5	2.237	2.208
3-4	3.5	2.263	2.231
4-5	4.5	2.273	2.249
5-6	5.5	2.293	2.267
6-7	6.5	2.309	2.279
7-8	7.5	2.316	2.290
8-10	9	2.344	2.329
	copper-gallium		
0-1	0.5	2.210	2.179
1-2	1.5	2.215	2.193
2-4	3	2.236	2.207
4-6	5	2.259	2.233
6-8	7	2.283	2.254
8-10	9	2.326	2.311
10-12	11	2.346	2.331

Composition of alloys (at.%)	Average composition (at.%)	E_{max} (eV)	E_T (eV)
	copper-silicon		
0-0.5	0.25	2.216	2.180
0.5-1	0.75	2.223	2.185
1-1.5	1.25	2.236	2.185
1.5-2	1.75	2.245	2.206
2-3	2.5	2.253	2.206
3-4	3.5	2.274	2.233
4-6	5	2.296	2.248
	copper-germanium		
0-1	0.5	2.221	2.178
0-2	1	2.232	2.187
1-2	1.5	2.235	2.190
1-3	2	2.245	2.195
2-3	2.5	2.251	2.210
3-5	4	2.277	2.229
5-7	6	2.299	2.242
7-9	8	2.343	2.274
	copper-tin		
0-0.5	0.25	2.219	2.178
0.5-1	0.75	2.226	2.178
1-1.5	1.25	2.231	2.189
1.5-2	1.75	2.246	2.198
2-3	2.5	2.256	2.211
3-4	3.5	2.272	2.226
4-6	5	2.289	2.238
	copper-arsenic		
0-0.5	0.25	2.246	
0-1	0.5	2.250	
0.5-1	0.75	2.245	
1-2	1.5	2.260	
2-3	2.5	2.289	
3-4	3.5	2.301	
4-5	4.5	2.319	

ly chosen θ value, a calculated $F(S)$ curve agrees quite well with an experimental differential reflectogram. One can therefore state with reasonable confidence that peak A and the substructure around this peak are caused by electron transitions from the upper d bands to the Fermi energy.

Threshold energy for interband transitions (peak A). In Fig. 6, the transitional energies E_T for peak A as a function of average composition X for copper-based alloys are plotted. (For Cu-As alloys no correction with reasonable accuracy could be obtained in the usual way[31] because E_{max} is distorted by structure at higher energies, Fig. 4.) The results can be seen to be qualitatively the same among the alloy systems investigated: Un-

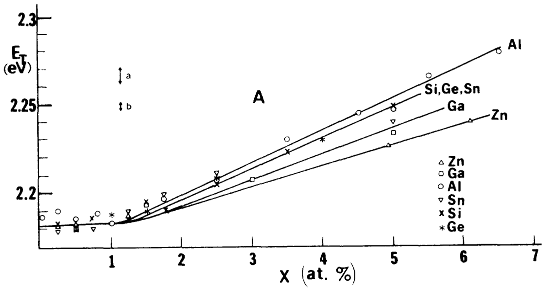

FIG. 6. Corrected transitional energies E_T for peak A as a function of solute concentration for Cu-Zn, Cu-Al, Cu-Ga, Cu-Ge, Cu-Si, and Cu-Sn alloys. a: possible error in marking maxima; b: possible error introduced by line-shape analysis.

TABLE II. Energy (E_{max}) of peak D and shift in energy (ΔE_{max}) compared to pure Cu as a function of composition for various copper-based alloys. Error limit for E_{max} is ±0.007 eV.

Average composition of alloy (at.%)	E_{max} (eV)	ΔE_{max} (eV)
copper-germanium		
0.5	5.06	0.03
1.0	5.06	0.03
1.5	5.16	0.13
copper-silicon		
0.25	5.03	0
0.75	5.08	0.04
1.25	5.09	0.06
1.75	5.30	0.27
3.5	5.57	0.54
copper-arsenic		
0.25	5.04	0.01
0.5	5.06	0.03
0.75	5.06	0.03
2.5	5.39	0.74
3.5	5.64	0.64
4.5	5.80	0.77

til slightly above 1 at.%, the solute additions do not vary the threshold energy appreciably from that of pure copper, as has been observed before by Hummel and Andrews.[19] Friedel[33] predicted this type of behavior and related it to "screening" effects. He argued that for the first few atomic-percent solute additions to copper, the additional charge from the higher valent solute is effectively screened and the copper matrix behaves as if the impurities were not present. The matrix remains unperturbed and it must thus have the same Fermi level as the pure metal. This remains true as long as the impurities do not interact.

After this initial flat portion, the E_T versus X curves show, in the present range, a linear increase in energy with increasing solute concentration (Fig. 6). The alloys presented behave very similarly, i.e., the difference in the threshold energies varies only within a few hundredths of an electron volt. A similar observation was made by Hummel and Andrews[19] on copper-based alloys with zinc, aluminum, or gallium, using the peak maxima E_{max} in the reflectograms as the basis for the transitional energy. (With the present improved differential reflectometer and its higher resolution, a larger separation of the E_{max} versus concentration behavior of the individual alloy systems can be observed, Fig. 7. However, when the small corrections are employed to E_{max}, as done

TABLE III. Energy (E_{max}) of peak B as a function of solute concentration for various copper-based alloys. Error limit for E_{max} is ±0.007 eV.

Average composition of alloys (at.%)	E_{max} (eV)
copppr-zinc	
0.25	4.319
0.5	4.036
1.25	3.972
4.88	3.716
6.05	3.651
11.15	3.250
copper-gallium	
0.5	3.834
1.5	3.760
3	3.526
5	3.292
7	3.176
9	2.876
11	2.756
copper-aluminum	
0.05	3.717
0.25	3.932
0.5	3.939
1	3.924
1.75	3.619
2.5	3.595
3.5	3.361
4.5	3.351
5.5	3.256
copper-tin	
0.25	3.794
0.75	3.620
1.25	3.535
1.75	3.377
2.5	3.274
3.5	3.103
5	2.819

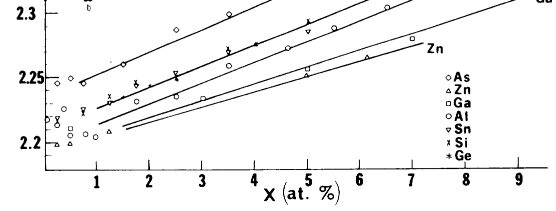

FIG. 7. Maximal energy for peak A as a function of solute concentration for Cu-Zn, Cu-Al, Cu-Ga, Cu-Ge, Cu-Si, Cu-Sn, and Cu-As alloys. a: possible error in marking maxima; b: possible error in alloy composition.

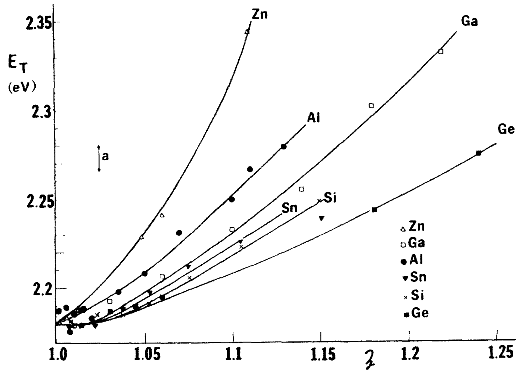

FIG. 8. Transitional energies for peak A as a function of $\mathfrak{z}$ for Cu-Zn, Cu-Al, Cu-Ga, Cu-Si, Cu-Sn, and Cu-As alloys ($\mathfrak{z}$ is the number of electrons per atom). a: possible error in marking maxima and introduced by line-shape analysis.

in Fig. 6, the separations become much smaller.)

If the Fermi energy were the only parameter in the band structure responding to solute additions, that is, to an increased number of electrons per atom (rigid-band model), then all alloy systems would be expected to behave alike in a $\mathfrak{z}$ versus E_T plot, where $\mathfrak{z}$ is the number of electrons per atom. That this is not the case (Fig. 8) can be interpreted by the assumption that the Fermi energy is raised much less than predicted by the rigid-band model and/or that with increasing solute additions, the d bands are proportionally raised in energy.

Recently, Bansil, Ehrenreich *et al.*[26] developed the concept of charge renormalization which arrives from a different point of view to a similar result. In this theory, it is postulated that when impurities are added to copper, the potential of the copper atoms is modified. In Figs. 9(a) and 9(b) the energy displacements from states for pure copper and pure zinc (assuming a hypothetical Zn crystal having an fcc structure and the same lattice constant as Cu) to a "neutral atom" configuration are shown. One notices a narrowing of the Cu d bands (which results from the reduction of Cu-Cu interactions with increasing Zn concentration), a downward shift of E_{Γ_1}, and a rise in Fermi energy E_F. The rise in E_F, which is due to the increase in the number of electrons per atom is lower than predicted by the rigid-band model because of the lowering of the bottom of the conduction band, E_{Γ_1}. Charge renormalization finally raises the Cu d bands. This results in a relatively small energy increase for the upper d-band to E_F transition with increasing X [see Fig. 9(c)]. Our experimental results agree with this finding.

It is interesting to speculate as to why all investigated copper alloys exhibit a similar increase in the transition energy with increasing composition: As shown above, the Fermi energy increases proportionally as the average number of electrons per atom increases. Despite a simultaneous lowering of E_{Γ_1}, it can be assumed that the Fermi energy still rises slightly more in, say, copper-silicon than in copper-aluminum. On the other hand, the amount of charge transfer from silicon to copper can be considered to be greater than that from aluminum to copper, thus raising the top of the d bands more for silicon than for aluminum. By a combination of the rising Fermi energy and the rising d bands due to charge transfer, it is possible to get similar transitional energies for different alloys of the same solute concentration. Possible reasons for not obtaining *exactly* the same transition energy could be due to various mechanisms such as influences of atomic diameter, effective mass, effective number of free electrons, change in lattice parameter, and others.

Transition around 5 eV. It is widely agreed in the literature[7,16,20-23] that absorption around 5 eV can be identified from the optical spectra involving transitions from the *lower* d bands to the Fermi energy. It seems therefore to be appropriate to employ a similar line-shape analysis, as for peak A, to the observed structure around 5 eV. One has to keep in mind, however, that in this energy region, α is negative and β positive,[31] so that the β/α ratio is negative (contrary to the condition around 2 eV where the β/α ratio is positive[31]). The negative β/α ratio should result in a line shape which is inverted compared to the one for peak A.[31] This can indeed be observed in the differential reflectograms at energies around 5 eV involving peaks C and D (Fig. 4). To investi-

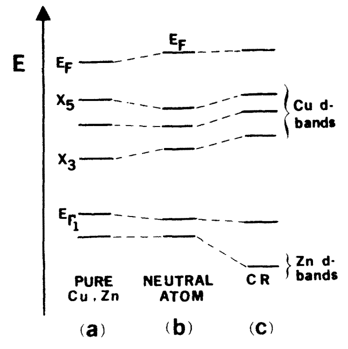

FIG. 9. Schematic energy-level diagrams for (a) pure copper and pure zinc (assuming both have fcc crystal structure), (b) α-copper–zinc alloys, neutral atom model, (c) α-copper–zinc alloys, charge renormalization (from Ref. 26).

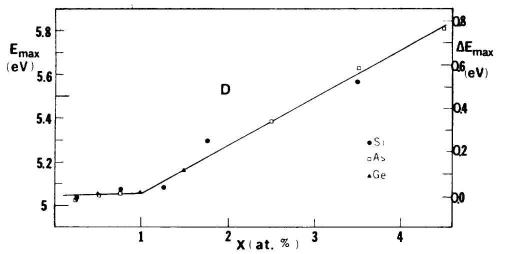

FIG. 10. Energy of peak D (E_{max}) and shift in energy (ΔE_{max}) compared to "pure copper" as a function of composition for various copper-based alloys.

gate this further, it is desirable to select an alloy system in which the 5-eV peak dominates over other structure in its vicinity. Pells and Montgomery,[16] using conventional optical techniques, have shown that this is the case for Cu-As and, to a certain extent, also for Cu-Ge. In these alloy systems, the "high-energy" peak[16] (around 5 eV) was observed to be much stronger than the so-called "low-energy" peak[16] around 4 eV.

By inspecting various differential reflectograms, e.g., Fig. 3 (Cu-Si) and Fig. 4 (Cu-As), a pronounced maximum C can be seen which is closely followed by a sharp minimum D. This type of behavior cannot be observed in the differential reflectograms for Cu-Zn (Fig. 1), for which alloys, according to Pells and Montgomery,[16] the peak around 4 eV is predominant. The differential reflectograms of these alloys confirm, therefore, qualitatively the observations which were obtained from conventional optical data.

In deducing information about the behavior of the structure around 5 eV from the differential reflectograms, one has to take into account that the location of the maximum C may be influenced by the close vicinity of a possible structure around 4 eV. Parallel to the reasoning in the previous section, one may argue that the basic information about the 5-eV peak is contained in the minimum D, and that similarly as for the 2-eV peak, a small correction has to be applied to obtain the correct transition energy. From the experience presented in the previous section, it can be assumed that the actual transition energy is a few hundredths of an electron volt smaller than the energy of peak D. Since we are basically interested in the energy shifts due to alloying, this minimum D and its shift compared to pure copper will only be considered in the following analysis. (The "pure copper" point was obtained by extrapolating the curve to $X = 0$.) Table II and Fig. 10 show that the energy difference increases with increasing solute concentration. This behavior is similar to that observed for the upper d-band to Fermi energy transition, and can be interpreted similarly by considering that the Fermi energy is raised with increasing solute concentration.

As for the threshold energy, practically no shift in energy can be observed up to about 1 at.% solute, which suggests that indeed, as for peak A, a d-band to Fermi energy transition is involved. Particular attention should be given to the fact that the threshold energy (upper d-band $\rightarrow E_F$ transition) rises as an average only 1.2×10^{-2} eV per at.% solute, whereas the present transition (lower d-band $\rightarrow E_F$) rises by about 16×10^{-2} eV per at.% solute, i.e., more than ten times as much. Since the rise in Fermi energy is, of course, the same in both cases, the difference can only be attributed to a difference in the behavior between the upper and lower d bands. Our results seem to indicate that the lower d bands are either not affected at all by alloying or move only small amounts.

Transition around 4 eV. It is widely assumed that the structure around 4 eV which is found in conventional as well as in modulated optical spectra is due to interband transitions between two "conduction bands," for example from $L_{2'}$ to L_1 (Refs. 5, 7, 9, 10, 17, 23, and 27). Therefore, a line-shape analysis, which uses as a basis d-band to Fermi energy transitions, cannot be utilized here.

Pells and Montgomery[16] infer from their experiments that in Cu-Zn alloys, the 4-eV transition is more pronounced than a possible 5-eV transition. This is confirmed by the differential reflectograms for these alloys (Fig. 1): peaks B and C are strongly pronounced, whereas peak D is only visible in the form of a small deviation from an otherwise smooth curve.

When the positions of peaks B and C are plotted versus solute concentration for Cu-Zn,[19,28] both curves run essentially parallel to each other. This suggests that the same information is contained in both peaks. Therefore, the information about the energy shift of the transition around 4 eV will be considered to be contained in peak B since for some alloy systems peak C may be influenced by higher-energy structure.

The energy change of peak B with respect to increasing alloy concentration for various copper alloys can be found in Table III and Fig. 11. It is shown there that the energy of peak B decreases sharply with increasing solute concentration, as observed before by several investigators for the transitions around 4 eV, and also predicted through several band calculations for the conduction-band to conduction-band transition $L_{2'} \rightarrow L_1$ (Refs. 14–16, 18, 19, 21, 24, and 26). The decrease in the transitional energy is largest in

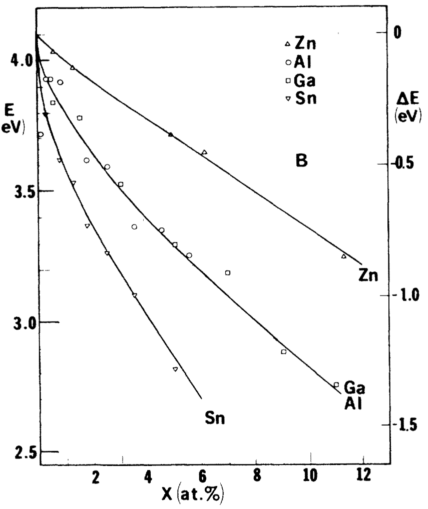

FIG. 11. Energy of peak B and shift in energy compared to "pure copper" as a function of composition for various copper-based alloys.

Cu-Sn and smallest in Cu-Zn with Cu-Ga and Cu-Al in between. It appears significant that the behavior is alike for both Cu-Ga and Cu-Al alloys which possess identical electron concentrations per atom, indicating that the shift of the energy is strongly influenced by the electron concentration of the solute. Further discussions have to await detailed band calculations which take into account the change in the conduction bands due to alloying.

Cu-Au ALLOYS

Upper d-band to Fermi energy transitions. The discussion of copper-gold alloys is treated separately because their differential reflectograms possess somewhat different features than those of the aforementioned alloy systems. The peaks are marked with lower-case letters to signify the difference (Fig. 12). The threshold energy for electron transitions from the top of the d bands to the Fermi energy can be taken, as before, from the structure in the differential reflectograms around 2 eV (peaks a and b), even though these peaks are less pronounced. The line shape is similar to the theoretical curves for $\theta = 330°$,[31] i.e., it has a flat tail toward higher energies, which makes corrections difficult.

In Fig. 13, the energy of peak b is plotted versus solute concentration for copper-gold alloys. It can be seen that, within the reading error of the maxima, the threshold energy for interband transitions is not changed. This behavior is expected since both copper and gold have the same valence electron concentration. Thus, by replacing Cu atoms with Au atoms, the difference between the Fermi energy and the top of the copper d bands apparently remains unchanged in accordance with the rigid-band model.

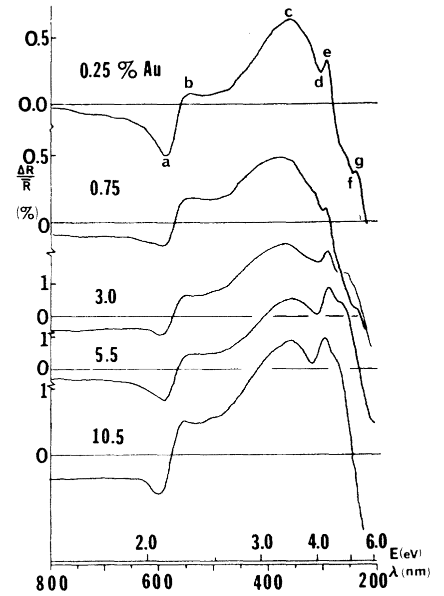

FIG. 12. Selected differential reflectograms for various copper-gold alloys.

Lower d-band to Fermi energy transitions. As before, an energy for the lower d-band to Fermi energy transition can be deduced from the differential reflectograms from peaks f and g (Fig. 12), which is, as before, around 5 eV. It seems to be significant that these transitions become weaker with increasing gold additions, as can be inferred from the disappearance of this structure at higher gold concentrations.

Conduction-band to conduction-band transitions. Structure around 4 eV which can be observed in Fig. 12 (peaks d and e) is similarly, as before, interpreted to be caused by conduction-band to conduction-band transitions. In Fig. 14, the shift in energy of this transition can be followed using the minima d. With increasing gold concentra-

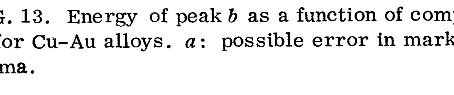

FIG. 13. Energy of peak b as a function of composition for Cu-Au alloys. a: possible error in marking maxima.

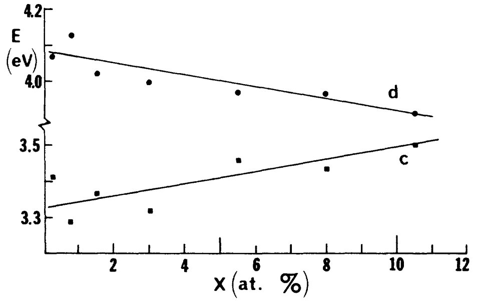

FIG. 14. Energy of peaks *c* and *d* as a function of composition for Cu-Au alloys.

tion, the transitional energy decreases. This shift is about one order of magnitude smaller (1.7×10^{-2} eV/at.% Au) than that observed for the same transition in Cu-Al and similar alloys (12.7×10^{-2} eV/at.% Al), suggesting only small changes in the conduction bands when gold is alloyed to copper.

Broad structure. The differential reflectograms (Fig. 12) show a broad structure around 3 eV. This structure can be considered to be the result of several closely spaced interband transitions which cannot be individually resolved. For their interpretation, it should be kept in mind that some of the gold *d* bands lie in the same energy interval as the copper *d* bands, so that additional interband transitions, originating from the Au *d* bands, are possible. In Fig. 14, the shift of the maximum of this structure is plotted. It can be seen that the maximum *c* increases with increasing gold concentration, suggesting a lowering of the gold *d* bands due to alloying. This seems to be similar to the lowering of the Zn *d* bands with increasing solute additions due to charge renormalization, as shown in Fig. 9.

Lifetime broadening. The initial and the final states of a given electron transition are not considered to be sharp, as is presented in a band diagram, but are somewhat broadened.[32] (This is a consequence of the limited time an electron stays at an excited energy level and of the uncertainty principle.) From the differential reflectograms, this "lifetime broadening" Γ can be obtained[31] by $\Gamma = |\omega_{\max} - \omega_T| \tan(\frac{1}{2}\theta + \frac{1}{4}\pi)$. The lifetime broadening, calculated from our data, has been found to increase steadily from 1.2×10^{14}/sec (for "pure" copper) to 1.9×10^{14}/sec for copper with about 9 at.% solute concentration.

CONCLUSIONS

The present results, in conjunction with recent theories, suggest that both the Fermi energy as well as the top of the *d* bands increase in energy with increasing solute concentration in a very specific way so that the threshold energies for interband transitions are identical within 1 or 2% for α-phase copper-based alloys having the same solute concentration. The results confirm the predictions of Friedel that up to a solute concentration of about 1 at.% the additional electrons are effectively screened so that essentially no change in the electronic configuration occurs in this concentration range.

A behavior similar to that involving transitions from the top of the *d* bands to the Fermi energy was found for the shift of a transition around 5 eV. This confirms theoretical considerations that at this energy, transitions from the lower *d* bands to the Fermi energy are involved. The larger shift of this 5-eV peak with increasing solute concentration compared to the threshold energy seems to indicate that the lower *d* bands are not affected as much as the upper *d* bands by alloying.

A further transition around 4 eV behaves in many respects differently than the aforementioned transitions and is observed to decrease in energy with increasing solute concentration. Conduction-band to conduction-band transitions are believed to be involved in this structure.

Copper-gold alloys do not show any change in the threshold energy due to solute additions, thus indicating that the Fermi energy as well as the copper *d* bands remain essentially unchanged with alloying. Additional structure between 2 and 5 eV indicates that transitions from the gold *d* bands may occur.

ACKNOWLEDGMENTS

We are indebted to the NSF and the University of Florida for financial support of this work. The assistance of Dr. J. B. Andrews in the experimental aspects of this study is gratefully acknowledged.

---

*Paper based in part on a thesis submitted by one of the authors (R. J. Nastasi-Andrews) in partial fulfillment of the requirements for the Ph.D. degree at the University of Florida.

†New address: University of Alabama in Birmingham, College of Engineering, Birmingham, Ala. 35294.

[1] B. Segall, Phys. Rev. 125, 109 (1962).

[2] H. Ehrenreich and H. R. Philipp, Phys. Rev. 128, 1622 (1962).

[3] B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. 138, A494 (1965).

[4] D. Beaglehole, Proc. Phys. Soc. Lond. 87, 461 (1966).

[5] U. Gerhardt, D. Beaglehole, and R. Sandrock, Phys. Rev. Lett. 19, 309 (1967).

[6] U. Gerhardt, Phys. Rev. 172, 651 (1968).

[7] F. M. Mueller and J. C. Phillips, Phys. Rev. 157, 600 (1967).

[8] G. Dresselhaus, Solid State Commun. 7, 419 (1969).

[9] C. Y. Fong, M. L. Cohen, R. R. L. Zucco, J. Stokes, and Y. R. Shen, Phys. Rev. Lett. 25, 1486 (1970).

[10] (a) A. R. Williams, J. F. Janak, and V. L. Moruzzi, Phys. Rev. Lett. 11, 671 (1972); (b) M. Welkowsky and R. Braunstein, Solid State Commun. 9, 2139 (1971).

[11] P. B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972).

[12] M. A. Biondi and J. A. Rayne, Phys. Rev. 115, 1522 (1959).

[13] M. M. Pant and S. K. Joshi, Phys. Rev. 180, 675 (1969).

[14] A. Lettington, Philos. Mag. 11, 863 (1965).

[15] H. Amar, K. H. Johnson, and C. B. Sommers, Phys. Rev. 153, 655 (1967).

[16] G. P. Pells and H. Montgomery, J. Phys. C Suppl. 3, 330 (1970).

[17] P. Soven, Phys. Rev. 151, 539 (1966).

[18] M. P. Das and S. K. Joshi, J. Phys. F 2, L42 (1972).

[19] R. E. Hummel and J. B. Andrews, Phys. Rev. B 8, 2449 (1973).

[20] A. S. DeReggi and R. S. Rea, Phys. Rev. Lett. 30, 549 (1973).

[21] R. S. Rea and A. S. DeReggi, Phys. Rev. B 9, 3285 (1974).

[22] R. Rosei and D. W. Lynch, Phys. Rev. B 5, 3883 (1972).

[23] D. Beaglehole and E. Erlbach, Phys. Rev. B 6, 1209 (1972).

[24] D. Beaglehole, Surf. Sci., 37, 708 (1973); D. Beaglehole and M. Wihl, Solid State Commun. 13, 427 (1973).

[25] T. Suzuki, M. Hasegawa, and M. Hirabayashi, Appl. Phys. 5, 269 (1974).

[26] A. Bansil, H. Ehrenreich, L. Schwartz, and R. E. Watson, Phys. Rev. B 9, 445 (1974).

[27] R. E. Hummel, J. A. Holbrook, and J. B. Andrews, Surf. Sci. 37, 717 (1973).

[28] R. J. Nastasi-Andrews, Thesis (University of Florida, 1976) (unpublished).

[29] R. E. Hummel, D. B. Dove, and J. A. Holbrook, Phys. Rev. Lett. 25, 290 (1970).

[30] J. A. Holbrook and R. E. Hummel, Rev. Sci. Instrum. 44, 463 (1973).

[31] R. Enderlein and R. E. Hummel (unpublished).

[32] B. O. Seraphin in *Optical Properties of Solids*, edited by F. Abelès (North-Holland, Amsterdam, 1972), pp. 164.

[33] J. Friedel, Proc. Phys. Soc. Lond B 65, 769 (1952).