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Optical properties and electronic structure of ordered and disordered Cu_3Au[†]

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We have carried out measurements of the reflectance spectrum from 1 to 13 eV on ordered and on disordered Cu_3Au. Optical constants were computed via Kramers-Kronig analyses. In addition, we used a sensitive comparison technique to measure directly the reflectance difference between ordered and disordered alloys. This is the first time that such a modulation technique has been applied to the optical study of an order-disorder transformation. As a result, spectral detail is observed which is not apparent in other measurements. Bulk samples were utilized for our studies of ordered and of quench disordered Cu_3Au. For the comparison technique, thin-film samples of ordered, disordered, and amorphous Cu_3Au of varying stoichiometry were prepared. We have found that the second principal maximum in ϵ_2 for ordered Cu_3Au is located at 3.28 eV, in contrast to 3.6 eV in the earlier measurements of Nilsson and Norris. They believe that this peak arises from a new gap upon ordering whereas we attribute it to new transitions in the same region of k space. Electron transitions involved with various optical features of the ordered alloys are based principally upon folding considerations applied to the copper and gold band structures.

INTRODUCTION

Much of the experimental data relating to the nature of disordered-alloy band structures comes from studies performed on dilute disordered alloys. Unfortunately, the interpretation of these data may often be ambiguous because many processes occur simultaneously on alloying. Four effects frequently important are (a) change in electron per atom ratio, (b) change in lattice constant, (c) addition of new local potentials, and (d) disruption of the periodic potential. Although it is possible to minimize certain of these effects through a proper choice of alloy system, it is impossible to eliminate any of the four effects entirely.

Here we will approach the problem of the disordered alloy by using optical techniques to study the order-disorder transition in Cu_3Au. Aside from a very small change in lattice constant the only effect occurring in an order-disorder transformation is the alteration of the periodic potential. Thus in a system undergoing such a transformation one may study effects of the breakdown of periodic potential independent of other parameters.

The alloy Cu_3Au is particularly suitable for such a study since it can be prepared either ordered or disordered at room temperature. Despite a good deal of effort expended on the theory of disordered alloys, no general, tractable method for computing band structures of disordered systems has yet been proposed. An early attempt to compute the band structure of a disordered system was a calculation of the band structure of α-brass by Amar, Johnson, and Sommers[1] (AJS) using the virtual-crystal model. In the virtual-crystal model the potential at each lattice site is replaced by a weighted average potential. As generally applied in this model, the disordered alloy has the same number of bands as the ordered alloy and one expects that these bands will shift smoothly on disordering. Because local-potential nearest-neighbor effects are not incorporated into the virtual-crystal model, one should not expect reliable predictions. Surprisingly, the results of the AJS calculation were in rather good agreement with the results of optical experiments. Pant and Joshi[2] have applied a similar technique to the band structure of Ag-In and have found results inconsistent with experiment.

A more general treatment of the problem of the disordered alloy is the coherent-potential approximation of Soven[3] and others. In this approximation the disordered alloy is treated as a problem in multiple scattering with the use of a modified-Green's-function technique. This technique allows for the introduction of states characteristic of the solute metal. Velicky *et al.*[4] have reviewed this method and shown that, within appropriate limits of concentration and solute-solvent bandwidth and separation, this model has characteristics of the virtual-crystal model and exhibits localized states of the tight-binding model. Although the coherent-potential model makes many qualitative predictions about the effects of alloying, there has been no successful attempt to apply it to real alloy systems.

EXPERIMENTAL PROCEDURE

A. Sample preparation

Thin-film alloy samples were deposited by flash evaporating powdered Cu_3Au onto clean quartz slides in a vacuum of 10^{-7} torr or better. The samples were raised to a temperature of 500 °C *in vacuo* and held there for 15 min. This treatment effected homogenization of the alloy film. Higher temperatures or longer anneal times were found to cloud the film surface due to excessive crystal growth. This effect has also been observed by Beaglehole and Hendrickson[5] in dilute gold-iron alloys. Cu_3Au films were ordered by annealing them for 24 h at 350 °C and slow cooling. This treatment produces a considerable amount of long-range order in the films. Sharpness of x-ray-diffraction superlattice lines was used as a criterion for determining the magnitude of long-range ordering. No quantitative measurement of long-range order in these films was carried out.

It was found that the evaporation of 1 at.% or less of gold or copper onto the surface of the Cu_3Au films before the 500 °C anneal significantly reduced the rate at which the sample subsequently ordered. It is believed that the excess metal was incorporated into the alloy during the first anneal, since the pure metal could not be detected by x-ray diffraction and since the visual color change which it had produced disappeared entirely after annealing. In addition, lattice-constant changes in the direction expected were observed for excess copper or gold.

Where bulk samples were used, reflecting surfaces were prepared by standard metallographic polishing techniques. Disordered samples were prepared by heating to 500 °C *in vacua* and quenching in water. This technique had no visual effect on the color of the reflecting surface; however, it did enhance the outline of grain boundaries on the polished surface (thermal etching). Coherent oxide layers, if present, were too thin to produce interference colors. Ordering of bulk samples was carried out by annealing *in vacua* at 350 °C for 48 h and slow cooling for 12 h. No change in color was detected by eye.

B. Apparatus

Monochromatic light was obtained using a modified McPherson model 350 monochromator. Three light sources were used to cover the spectrum from 10 000 to 900 Å. These were (1) a tungsten filament lamp usable between 10 000 and 3800 Å, (2) an Oriel Optics 1000-W xenon source usable between 6000 and 1900 Å and a McPherson open-end gas-discharge lamp using between 4000 and 900 Å depending on the gas used. Light from these sources was chopped at 400 Hz at the entrance slit to the monochromator. This allowed a lock-in amplifier to be used to extract a low-noise signal from the detected light. An EMI 6255-*S* phototube was used to detect light between 6000 and 2000 Å. With the aid of sodium salicylate phosphor this was extended to 900 Å in the uv. Infrared (ir) light was detected using an RCA 7102 phototube.

Reflectance measurements were made using a sample-in sample-out technique. During measurement samples were kept either *in vacua* or at positive pressure in an inert argon atmosphere.

A difference technique was developed for measuring the small differences in the reflectance of ordered and disordered Cu_3Au. The apparatus involved uses a tuning-fork tine to alternately place two samples in the beam of a reflectometer. These are thin-film samples which are deposited side by side on a quartz slide. The frequency of sample exchange is 100 Hz. The resulting modulated signal is fed to a lock-in amplifier which reads out a signal proportional to the difference in reflectance of the two samples. It should be noted that 400-Hz light chopping was not employed in this technique.

RESULTS

A. Ordered and disordered Cu_3Au

The first report on the difference in the optical constants of ordered and disordered Cu_3Au was published by Nilsson and Norris.[6] Figure 1 shows a plot of their results for the ϵ_2 spectra of ordered and disordered Cu_3Au in the region 2–5 eV. Spectra were computed using Kramers-Kronig transformations of reflectance data. Figure 1 shows that the ϵ_2 spectrum for ordered Cu_3Au has a maximum at 3.6 eV which is not present in the spectrum of the disordered alloy. In addition, it is seen that both ordered and disordered Cu_3Au have ϵ_2 peaks near 2.5 eV. The 2.4-eV peak in the disordered ϵ_2 spectrum rises and reaches a maximum at a lower energy than the peak in the ordered ϵ_2 spectrum. Other features which may be significant are an inflection point at 3.0 eV, a minimum at 3.7 eV and a maximum at 4.0 eV, all occurring in the spectrum of the disordered alloy. These features are absent in the ordered alloy spectrum probably because they are masked by the

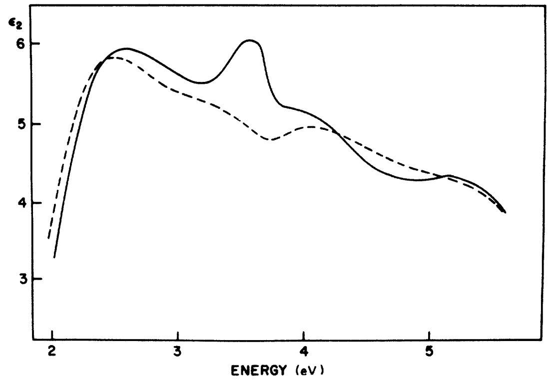

FIG. 1. ϵ_2 for ordered and disordered Cu_3Au obtained by Nilsson and Norris (Ref. 6).

relatively large peak at 3.6 eV.

Figures 2 and 3 show the authors' results for the ϵ_2 spectra of ordered and disordered Cu_3Au, respectively. These data were computed by performing Kramers-Kronig transformations on reflectance data taken between 1 and 13 eV. Reflectance data were taken at 0.2-eV intervals between 1 and 2.0 eV, 0.05-eV intervals from 2.0 to 6.0 eV, and approximately 0.5 eV intervals up to 13.0 eV. The reflectance measurements were performed on polished bulk samples. Again we see that a peak is present in the ordered ϵ_2 spectrum which is not present in that of the disordered alloy. This peak, occurring at 3.28 eV, is smaller than the peaks near 2.5 eV in both the ordered and disordered alloys. ϵ_2 in the disordered alloy spectrum rises rapidly and peaks at an energy lower than in the ordered alloy, 2.4 vs 2.6 eV.

Features worth noting in the disordered alloy spectrum are a small bump at 3.0 eV and a shoulder at 3.9 eV. The ordered ϵ_2 spectrum exhibits two features near the tail of the Drude region, a pronounced maximum at 1.3 eV and an inflection point at 1.9 eV. These structures are at most weakly present in the disordered alloy. It is difficult to account for the presence of these structures in either alloy and they may be artifacts of the measuring technique.

The principal feature noted in the results of Nilsson and Norris[6] and those reported here is the ϵ_2 maximum present in the ordered alloy but not in the disordered alloy. Our measurements indicate that this peak occurs at 3.28 eV while those of Nilsson and Norris place it at about 3.6 eV. We believe our result to be more accurate, since in the difference technique data below we give an independent confirmation of our direct reflectance results. In addition, the difference technique results will verify the presence of the small structure at 3.0 eV observed by both Nilsson and Norris and the authors.

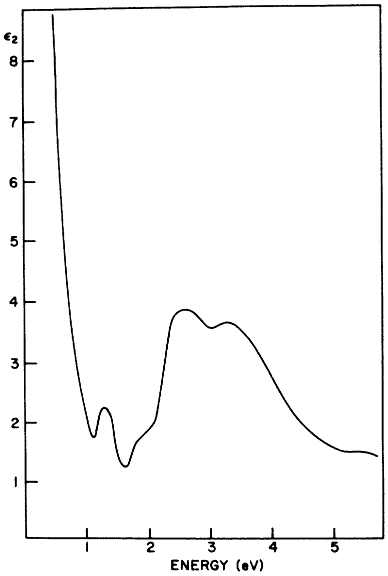

FIG. 2. ϵ_2 for ordered Cu_3Au (bulk specimen) obtained by us.

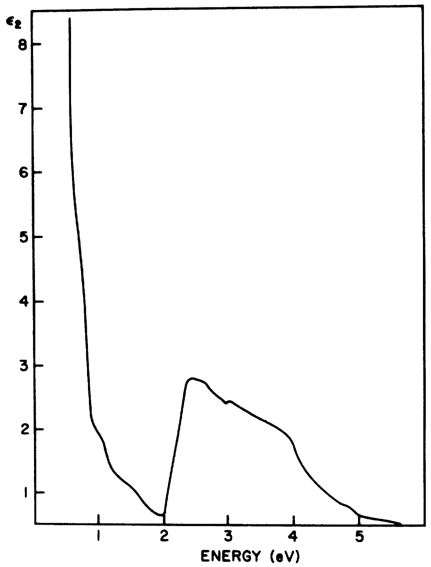

FIG. 3. ϵ_2 for disordered Cu_3Au (bulk specimen) obtained by us.

We may account for the difference of the observed position of the ordering peak by considering the manner in which the optical constant ϵ_2 was calculated. The Nilsson-Norris results were computed using a Kramers-Kronig transformation apparently on reflectance data taken in the spectral region 2.0–5.5 eV. Those presented here were taken over a spectral region 1.0–13.0 eV and are less sensitive to extrapolations used in Kramers-

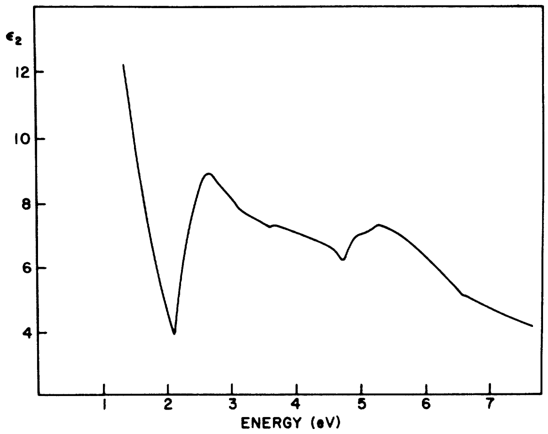

FIG. 4. ϵ_2 for copper obtained by us.

Kronig calculations. In the same way one can account for the fact that the shoulder present in our ϵ_2 data at 3.9 eV is washed out in the Nilsson-Norris data. Other smaller features in the optical spectra of ordered and disordered Cu_3Au are better examined with the aid of a variation technique.

As one would expect there is some qualitative resemblance between the optical structures seen in copper (Fig. 4) and gold (Fig. 5) and the structure in disordered Cu_3Au. Surprisingly, an especially strong similarity may be seen in the ϵ_2 spectra of gold and of ordered Cu_3Au; each has an onset just above 2.0 eV with a peak absorption near 3.0 eV. In addition, each has a second peak in the range 3.4–3.9 eV.

B. Results for difference technique

Experiments were performed which measured directly the reflectance differences between several samples in the Cu_3Au system in the spectral region 2–6 eV. Thin-film samples, approximately 2000 Å thick, were prepared in the manner described above and their compositions were checked by x-ray diffraction. Figure 6 shows the difference in ϵ_2 vs energy between the alloys ordered Cu_3Au and disordered $Cu_{74}Au_{26}$. Figure 7 shows the same type of plot for the alloys ordered Cu_3Au and disordered $Cu_{76}Au_{24}$.

It is seen that Figs. 6 and 7 have the following features in common: (i) a maximum near 2.2 eV, (ii) a small minimum and maximum near 3 eV, (iii) a dramatic minimum at 3.5 eV, (iv) a maximum around 3.8 eV, (v) a minimum near 4.1 eV, and (vi) a maximum near 4.5 eV. These points will be discussed below.

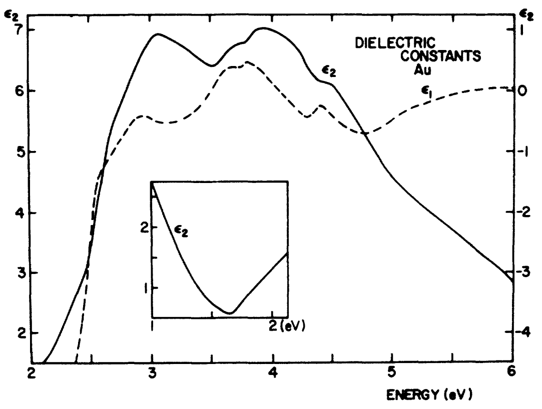

FIG. 5. ϵ_2 and ϵ_1 for gold obtained by Weiss (Ref. 13).

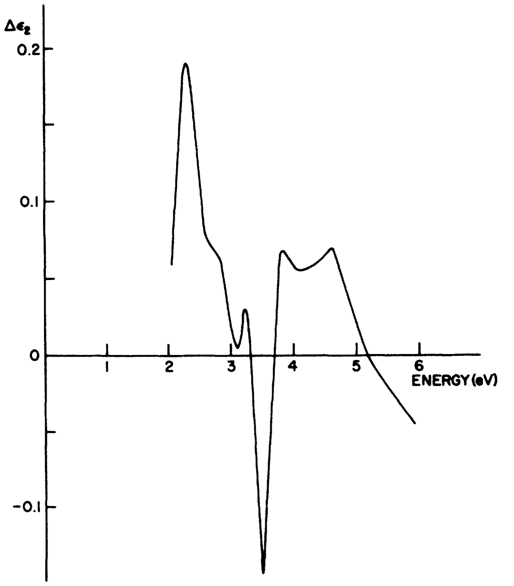

FIG. 6. Direct difference $\Delta\epsilon_2$: disordered $Cu_{74}Au_{26}$ − ordered $Cu_{75}Au_{25}$.

The values for ϵ_2 were computed from values of $\Delta R/R$ and values for the optical constants of disordered bulk Cu_3Au, using the expression

$$\Delta\epsilon_2 = [k(\epsilon_1 - 1) + n\epsilon_2](\tfrac{1}{2}\Delta R/R) - [n(\epsilon_1 - 1) - k\epsilon_2]\Delta\theta , \tag{1}$$

where

$$\Delta\theta = -\frac{E}{\pi}\int_0^\infty \frac{\Delta R/R}{(E')^2 - E^2}\, dE'$$

and values of optical constants refer to the reference sample. As a base line for the separation of ordering and compositional effects an experiment was carried out which measured the difference in

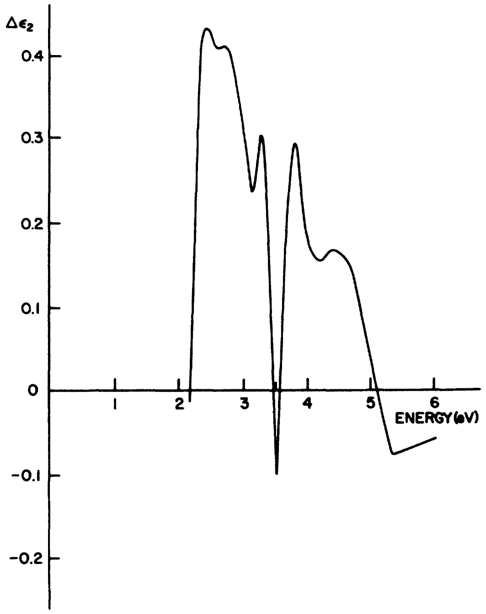

FIG. 7. Direct difference $\Delta\epsilon_2$: disordered $Cu_{76}Au_{24}$ − ordered $Cu_{75}Au_{25}$.

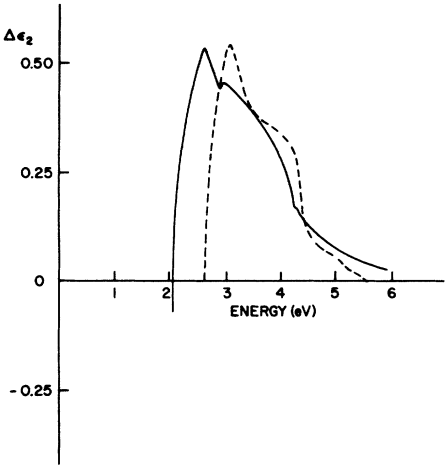

FIG. 8. Direct difference $\Delta\epsilon_2$: disordered $Cu_{76}Au_{24}$ − disordered $Cu_{74}Au_{26}$. Solid line, obtained from difference measurement; dashed line, obtained from data of Figs. 6 and 7.

ϵ_2 between disordered $Cu_{75}Au_{25}$ and disordered $Cu_{76}Au_{24}$. The results of this experiment are plotted in Fig. 8 (solid line) along with a normalized weighted difference taken from the curves in Figs. 6 and 7 (dashed line). A linear combination was used because of the difficulties in determining exact composition differences. If we let the value of $\Delta\epsilon_2$ in Fig. 6 be $\Delta\epsilon_{2a}$ and that of Fig. 7 be $\Delta\epsilon_{2b}$ then the dashed curve of Fig. 8 is given by:

$$\Delta\epsilon_2 = \tfrac{1}{3}(2\,\Delta\epsilon_{2a} - \Delta\epsilon_{2b}) \ . \qquad (2)$$

This combination was picked because it subtracted out resonances due to ordering near 3.3 eV.

We see that the two curves in Fig. 8 agree rather well except for the region near 2.5 eV. Several effects may be responsible for this discrepancy: (i) the 2.5-eV region may be too close to the limits of the integration; (ii) the effects of varying composition may be strongly coupled to the effects of varying order; and (iii) the effect of adding copper to stoichiometric Cu_3Au may not be merely the negative of the effect of adding gold.

Although both our results and those of Nilsson and Norris indicate that a maximum near 3.5 eV appears in the ϵ_2 spectrum of Cu_3Au when this alloy is ordered, there is some discrepancy as to the exact position of this peak. Our results place this maximum at 3.28 eV, while those of Nilsson and Norris place it at 3.6 eV.

As a check on our results for the position of this peak we utilized the expression

$$\epsilon_2(\text{ordered}) = \epsilon_2(\text{disordered}) - \Delta\epsilon_2 \qquad (3)$$

to reconstruct the ϵ_2 spectrum of the ordered alloy from the spectrum of the disordered alloy.

The energy of the peak position obtained in this way was 3.22 ± 0.05 eV. This result is not changed significantly even if the values of Nilsson and Norris for ϵ_2 disordered are substituted for those measured by the authors in expression (3).

C. Amorphous Cu_3Au

Measurements were made of the direct difference between the reflectances of thin films of disordered and amorphous Cu_3Au. The amorphous nature of the film was determined through x-ray diffraction. Diffraction patterns taken of the films exhibited no lines in the forward reflection region.

Films were prepared by slow flash evaporation of powdered Cu_3Au onto room temperature substrates. This mode of preparation makes it unlikely that the absence of diffraction lines is caused by fluctuations in composition. It is possible, however, that the films have a very small grain size of the order of 50 Å.

Figure 9 shows the $\Delta\epsilon_2$ spectrum [ϵ_2(disordered, Cu_3Au) − ϵ_2(amorphous, Cu_3Au)]. It was expected that the amorphous film would have optical properties which were a smeared out version of the disordered alloy. This is only partially true. The broad $\Delta\epsilon_2$ maximum at 4.2 eV could easily arise from a smearing out in the amorphous alloy of the shoulder at 3.9 eV observed in the disordered alloy. A small bump at 5.2 eV is also seen. In contrast, if we look at the data between 2.5 eV and 3.5 eV we see that there is more structure in the amorphous Cu_3Au than is expected. In addition we see a bump at 2.2 eV which is not expected. There is, therefore, an indication that amorphous substances can have unique band structures having

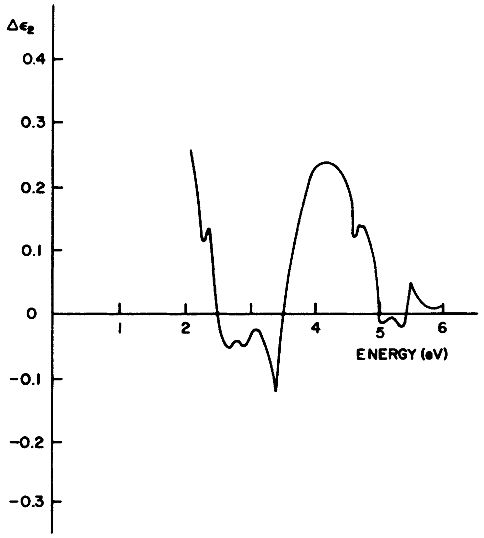

FIG. 9. Direct difference $\Delta\epsilon_2$: amorphous Cu_3Au − disordered Cu_3Au.

characteristics different from their crystalline counterparts.

DISCUSSION

A. Electronic structure of copper and gold

The two noble metals, copper[7] and gold,[8,9] have qualitatively similar band structures, as can be seen in Figs. 10 and 11. Both of these metals have high *d* bands approximately 2 to 3 eV below the Fermi surface. The *d* bands are strongly hybridized with the valence bands which are distorted in several regions of the Brillouin zone where bands overlap. This is in contrast with silver, the third noble metal, in which the *d* bands are low lying.

In the relativistic formulation of the band structure of gold, one has considerable spin-orbit splitting and this accounts for the differences in notation and number of bands between copper and gold. The difference in notation arises from the use of the double group for the gold lattice symmetry.

Optical properties provide a simple and direct means of studying electronic structure in metals. As would be expected, copper and gold have similar optical properties; both have minima near 2 eV in ϵ_2 marking the end of the Drude region. In both metals these minima are followed by overlapping maxima. However, in spite of these qualitative similarities in band structure and ϵ_2 spectrum, there is evidence of substantial differences in the origin of certain optical features.

Although a direct measurement of ϵ_2 indicates the joint density of states for transitions of a given energy, it does not give information relating to the bands from which the transitions originate. Such information can only be deduced from more difficult experiments such as piezoreflectance done on single crystals. Results of such experiments indicate that the first maximum at 2.6 eV in copper[10] is due principally to transitions $L_3 \rightarrow$ FS, (Fermi Surface) while in gold there are indications that transitions between sets of L bands and between sets of X bands both contribute to the first peak at 3.1 eV. From the band structure of Christensen and Seraphin,[8] we see that likely candidates for such transitions are $X_{7^+} \rightarrow X_{6^-}$ near X and $L_{4^+} \rightarrow$ FS near L. Piezoreflectance studies show both X and L contributions to this peak.[11] There is an abundance of possible transitions in gold due to relativistic splitting of bands and this makes peak identification impossible without piezoreflectance measurements.

Experiments with piezoreflectance indicate that the second ϵ_2 peak for copper (approximately 5 eV) results partially from transitions in the vicinity

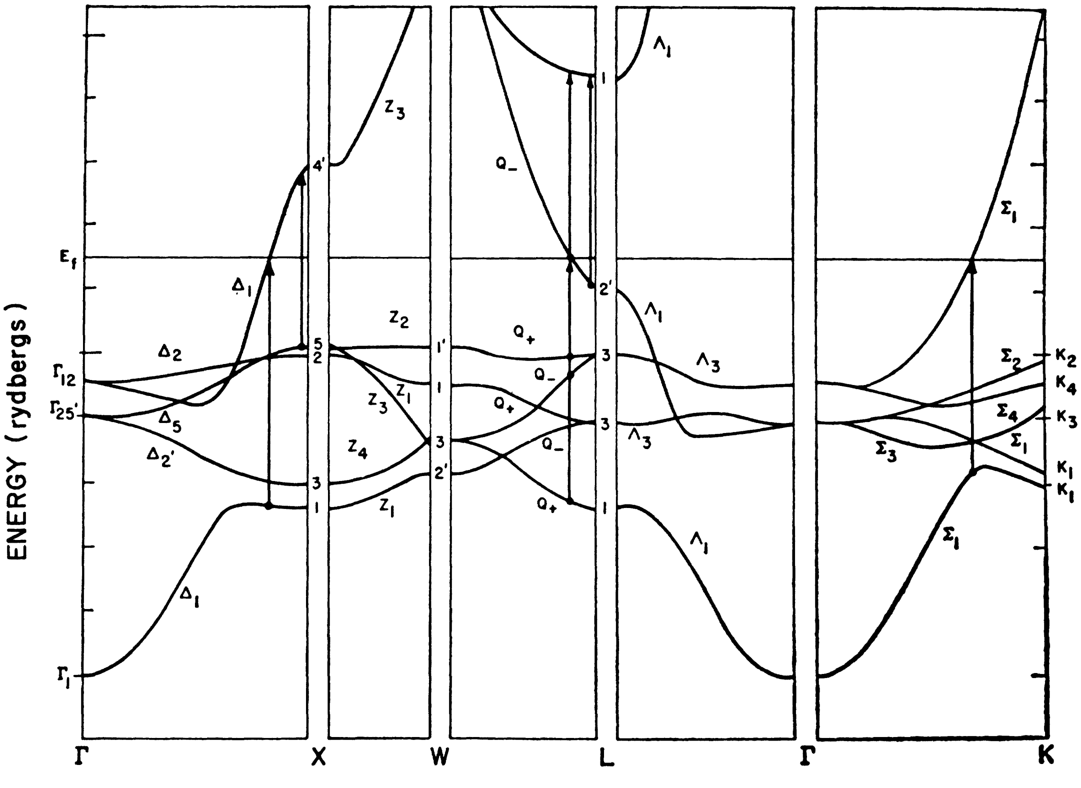

FIG. 10. Band structure of copper as given by Burdick (Ref. 7); results of Segall are similar.

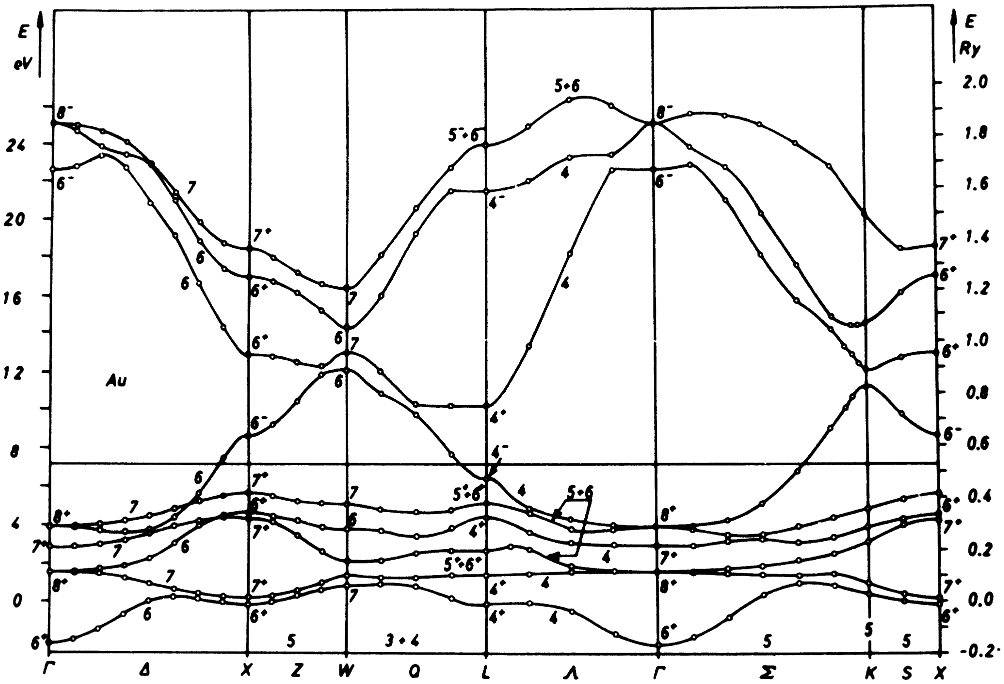

FIG. 11. Band structure of gold as given by Christensen and Seraphin (Ref. 8).

of L.[10] Both $L_{2'} \rightarrow L_1^u$ and $L_1 \rightarrow L_{2'}$ (FS) transitions can make contributions and apparently do so in roughly equal amounts; the lower-energy transition ($L_{2'} \rightarrow L_1^u$) is concentrated near the L critical point while the somewhat-higher-energy transition (d band → FS) occurs over extended regions of the Brillouin zone. This conclusion follows from band calculation results, piezoreflectance studies, and from changes in optical properties upon alloying.[12] This peak was originally believed to be caused by $X_5 \rightarrow X_{4'}$ transitions; however, it now seems more likely that X transitions contribute to the small features seen between 3 and 4 eV in the ϵ_2 spectrum of copper.

The ϵ_2 peaks in gold near 4 eV agree fairly well with $L_{4^-} \rightarrow L_{4^+}$ and $X_{6^+} \rightarrow X_{6^-}$ transitions as given by Connolly and Johnson.[9] Piezoreflectance studies[11] gave an X peak at 3.8 eV and an L peak at 4.6 eV. These assignments are consistent with the observations of Weiss and Muldawer,[13] who observed the insensitivity of these peaks to zinc additions to gold; neither transition involves the Fermi surface.

Some of the ϵ_2 structure in alloys as well as in pure metals probably occur over extended regions of the Brillouin zone and results from general interband transitions.

B. Disordered copper-gold alloys

There is some inconsistency in the literature regarding the effect of alloying on the bands in the disordered copper-gold alloys. Figure 12 summarizes the results of Nilsson, Persson, and Hagstrom,[14] Beaglehole and Erlbach,[15] and the authors on the movement of the first interband transition in the disordered copper-gold alloys on changing composition.

Both our limited results on peak shift and the results of Beaglehole and Erlbach on edge shift indicate that alloying of either pure copper or pure gold, each with the other, causes low-energy features in the ϵ_2 spectrum to shift to lower energy. The results of both our modulation data and our

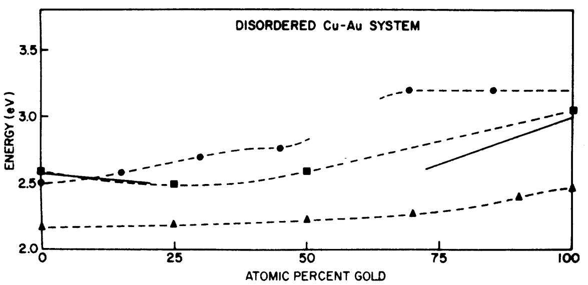

FIG. 12. Energy of the lowest-energy interband transition in the disordered Cu-Au system. ●, Peak of ϵ_2 as given in Fig. 2 of Nilsson (Ref. 14); ■, Peak of ϵ_2 as given by us; ▲, Absorption threshold as given by Nilsson, Persson, and Hagstrom (Ref. 14); Solid line-edge shift of Beaglehole and Erlbach (Ref. 15) (to which we have added 0.5 eV to produce correspondence with peak).

single sample optical data indicate that the position of these features reaches a minimum energy at Cu_3Au.

In contrast, the ϵ_2 peaks of Nilsson *et al.*[14] as plotted by the authors have a positive slope for increasing gold content in copper alloys containing small amounts of gold. For dilute copper alloys (small Cu), the energy vs composition curve has a nearly zero slope. Their results on the positions of interband thresholds have a closer agreement with our results on peak shift than do their results on peak shift, especially at high gold concentrations. At high copper concentrations however, the slope of their data is still opposite to ours.

Although it is difficult to account for the differences between ϵ_2 peak positions measured by the authors and those measured by Nilsson *et al.*, it is clear why one might expect some differences between the Beaglehole-Erlbach data on edge shift, data of Nilsson *et al.* on threshold shift, and our data on peak shift. In disordered alloys one would expect a general broadening and smearing of bands on alloying; hence the positions of onset edge and peak would tend to separate on alloying. Also the threshold measurements of Nilsson *et al.* may be somewhat suspect, since their data are taken over a limited energy range and the position of the threshold is very close to the region where extrapolated values must be placed in the Kramers-Kronig (KK) analysis. We have found that the position of onsets identified via KK processed data is very sensitive to both extrapolations and measured optical data in the low-energy region of the optical spectrum. For this reason we have not attempted to place the interband onset.

The interpretation of the observed shifts in ϵ_2 peaks is to some extent complicated by the fact that neither virtual-crystal nor coherent-potential calculations have been carried out on the alloy system. The latter calculation would prove quite formidable, and the former has been critized for its inability to predict the band structure of dilute Ag-In alloys. Beaglehole and Erlbach[15] have explained alloying effects qualitatively in both limits of dilute concentration in terms of changes in lattice constant (lattice expands when gold is added, contracts when copper is added) and the combining of the copper and gold *d* bands. The assumption in the Beaglehold-Erlbach argument is that the energies of the copper and gold *d* bands overlap in the alloy band structure and somehow recombine to form a *d* band of average energy. This explanation is consistent with known characteristics of the coherent-potential model. By contrast, in a tight-binding model these *d* bands would retain their identities. Soft-x-ray-emission spectra from Cu_3Au[16] gives some support for this possibility; the alloy spectrum may be obtained by simple addition of the spectra of the pure metals. In a virtual model a rigid *d* band or some other *ad hoc* contrivance must be assumed in order to properly place the *d* levels, and the success of such calculations is probably critically dependent on where these *d* bands are placed. Thus we may possibly account for the success of AJS in virtual-crystal calculations of the band structure of α-brass, contrasted with the difficulties encountered by Pant and Joshi[2] in predicting experimental results for Ag-In using a similar calculation.

The difficulty in determining the absolute positions of *d* bands with respect to the vacuum state is probably a considerable obstacle in attempts to determine *d* band overlap between alloy constituents. Photoemission studies are not helpful in such determinations since it is impossible at present to measure the surface contribution to the work function. Thus any measurements of photoelectric threshold for *d* electrons or even free electrons must be at best in error by a constant energy which is different for any given material.

C. Effect of ordering on Cu_3Au

The optical properties of ordered and disordered Cu_3Au were first explained[6] using the band structure of Gray and Brown[17] (GB) and a simplified virtual-crystal model. Our examination of the GB band structure revealed that it indicated the existence of a number of transitions at energies near which no features were observed in optical data. In addition the lack of a relativistic approach indicates that the GB band structure may not be very reliable.

Nilsson and Norris interpreted the appearance of an ϵ_2 peak at 3.6 eV on ordering as being the result of a band gap appearing across a new simple cubic Brillouin zone which appears when Cu_3Au orders. In the discussion below we indicate another possible explanation.

Figures 2 and 3 show the ϵ_2 vs E plots for ordered and disordered Cu_3Au. It has been noted that the principal difference between the ordered and disordered spectra is a maximum occurring near 3.5 eV in the ordered alloy. We will now discuss possible explanations for the difference seen between the ordered and disordered spectra.

First let us consider the virtual-crystal model. In this model the potential at each lattice site of a disordered or partially ordered alloy is replaced by an average atomic potential weighted according to the degree of long-range order in the alloy. Applying this model to Cu_3Au we derive a lattice with cubic symmetry for an alloy having any amount of long-range order and a face-centered-cubic symmetry for an alloy having no long-range order. This situation leads to several paradoxical conclusions in the limit of very small amounts of long-range order. Thus, one must take care with this model when applying it to systems in which order occurs.

Proceeding formally with the virtual-crystal model it is easily shown that, on ordering, the first-order approximation for the band gap at the new Brillouin zone is given by

$$\Delta E = 2F_{\text{cubic}}, \quad F = S(f_{\text{Au}} - f_{\text{Cu}}) , \tag{4}$$

where F_{cubic} is a structure factor for the potential corresponding to a new reciprocal lattice vector in the cubic Brillouin zone not present in the fcc Brillouin zone. S is the long-range order parameter and f_{Au} and f_{Cu} are Fourier coefficients of the potentials in the copper and gold sublattices, respectively.

In Fig. 13, we have a hypothetical portion of a band structure for an alloy undergoing an order-disorder transformation. Near the new Brillouin zone, an energy band gap is formed with magnitude $2\Delta E = 2S(f_{\text{Au}} - f_{\text{Cu}})$. Instead of transitions having an energy E_0, we have two sets of transitions of energy $E_0 + \Delta E$ and $E_0 - \Delta E$.

There are two reasons why this does not appear to be the mechanism leading to the alteration of the optical properties of Cu_3Au in its order-disorder transformation.

(i) The only peak available from which the ordering peak could have split off is the one at 2.4 eV. Part of the contributions to this peak comes from L states as in copper. Since the new Brillouin zone (BZ) does not cut the Γ-L band, there can be no new band gap; this does not preclude new gaps in the Γ-X band.

(ii) There is no evidence to indicate that the peak at 3.28 eV splits off from some other peak or is shifted significantly by variations in long-range order.

When the transition from disordered to ordered Cu_3Au occurs, many bands formerly occupying the higher k states in the fcc BZ are folded into the smaller ordered cubic BZ. This folding could produce certain changes in optical properties which are independent of the difference in the structure factors of copper and gold. These changes although not usually considered, may be very important in explaining the effect of order-disorder on optical properties as well as in explaining the stability of the ordered phase at low temperatures.

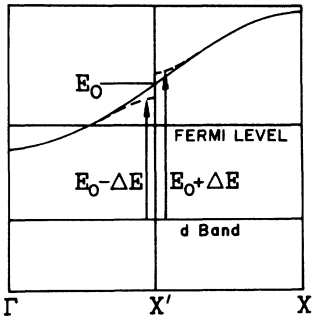

FIG. 13. Hypothetical band structure of disordered Cu_3Au (solid lines) and ordered Cu_3Au (dotted lines). A gap near X' occurs upon ordering.

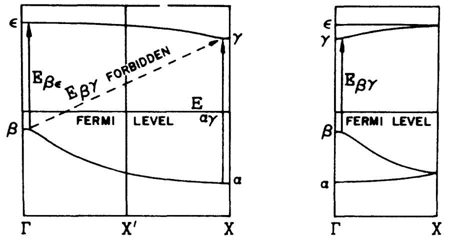

FIG. 14. (a) Hypothetical allowed transitions in the fcc Brillouin zone. (b) New allowed transition in the reduced sc zone for the ordered alloy.

Figure 14 shows a possible effect of folding energy bands on optical constants. It is seen that, after bands are folded, transitions having high joint density of states may be possible at energies which were previously forbidden. In order to determine what effects folding might have on the order-disorder transformation in Cu_3Au, we will try using the band structures of copper and gold as approximate models for disordered Cu_3Au.

Figure 15 shows the ordered simple cubic (sc) BZ enscribed in the fcc disordered BZ. We first note that the Γ-L vector lies entirely within the sc BZ; hence folding does not affect the L bands. The Γ-X direction is exactly bisected by the sc BZ at the point X'. If we reduce the fcc BZ to the sc BZ the Γ-X bands are folded in half about the point X', with the point X being transferred to the point Γ. In copper this results in new transitions to the point $X_{4'}$ from a somewhat lower set of d bands. These transitions would be about 0.1 Ry higher (1.36 eV) in energy than the X_5 to $X_{4'}$ transitions. This would probably be a Γ to Γ transition involving $\Gamma_{25'}$ to $X_{4'}$ (unfolded). A somewhat similar situation occurs in the gold band structure with the upper state being X_{6^-} and the initial gap being smaller. The Γ-K direction is particularly interesting in both copper and gold near the point M of the sc BZ. This cuts the bands along the Γ-K direction just beyond the point where the Γ_{8^+} band crosses the Fermi surface. In such situations the upper portion of the band may be drawn down toward the Fermi surface lowering the energy of the system.[18,19] This may account for the low-temperature stability of the ordered phase. At higher temperatures the Fermi surface is smeared to higher energy and there is no longer a large energetic

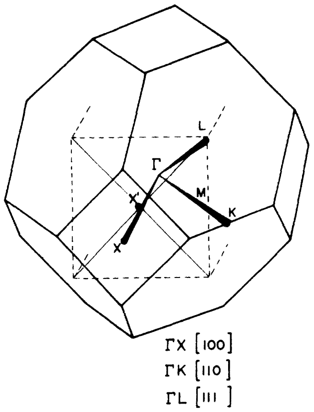

FIG. 15. Symmetry points and Brillouin zones for fcc and included sc lattices.

advantage to the sc state.

In addition to the new allowed transitions which can appear near the symmetry points on ordering, new general interband transitions are also possible. This may account for some of the structure seen in the $\Delta\epsilon_2$ data.

SUMMARY AND CONCLUSIONS

The above results and discussion have important implications relating to the nature of the band structure of the copper-gold disordered alloy system and the effect of ordering on the band structure of an alloy.

The results given here, as well as the results of Beaglehole *et al.*, indicate that the coherent-potential model is adequate to describe the behavior of the optical properties of the disordered copper-gold system. The lowering of the energy of the first interband transition on alloying in both copper and gold (this was first observed by Beaglehole and Erlbach) has been confirmed by the authors. The above results conflict with those of Nilsson *et al.*, who observed an increase in the energy of structure associated with the first interband transition on alloying of the copper rich Au-Cu alloys.

A peak observed by Nilsson and Norris at 3.6 eV in ϵ_2 data for Cu_3Au due to ordering has been confirmed; however, it was found to be at a somewhat lower energy (i.e., 3.28 eV).

The concept of a folded band structure has been introduced to explain the behavior of Cu_3Au on ordering. Although this concept does not appear to be restricted to any particular model it is consistent with a virtual-crystal model of ordering. There is, however, no indication that the ordering peak in Cu_3Au is related to the appearance of new band splittings which characterized the original Nilsson-Norris interpretation of ordering in this alloy.

It is anticipated that the folded band structure concept will be adequate to explain ordering effects in any system in which the over-all symmetry and lattice parameter remain nearly the same on ordering (e.g., in systems transforming bcc to sc). In addition this concept may be useful in explaining the stability of the ordered phase in such alloys.

Here we have also described the first use of a sensitive difference technique to study the effect of ordering on the optical properties of alloys. This proved to be a powerful technique for carefully studying subtle changes in optical constants not revealed in direct measurement techniques.

In addition we have reported the preparation of a material believed to be amorphous Cu_3Au. Our optical studies indicate that the amorphous phase of this alloy may have band structure characteristics which are significantly different from those of either ordered or disordered Cu_3Au.

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

[2] M. M. Pant and S. K. Joshi, Phys. Lett. A 28, 556 (1969).

[3] P. Soven, Phys. Rev. 156, 809 (1967); Phys. Rev. 178, 1136 (1969).

[4] B. Velicky, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968); B. Velicky and K. Levin, Phys. Rev. B 2, 938 (1970).

[5] D. Beaglehole and T. J. Hendrickson, Phys. Rev. Lett. 22, 133 (1969).

[6] P.-O. Nilsson and C. Norris, Phys. Lett. A 29, 22 (1969).

[7] B. Segall, Phys. Rev. 125, 109 (1962); G. A. Burdick, Phys. Rev. 129, 138 (1963).

[8] N. E. Christensen and B. O. Seraphin, Phys. Rev. B 4, 3321 (1971).

[9] J. W. D. Connolly and K. H. Johnson, MIT Solid State Mol. Theory Group Semi-Annual Prog. Rep. 72, 19 (1970).

[10] U. Gerhardt, D. Beaglehole, and R. Sandrock, Phys. Rev. Lett. 19, 309 (1967); U. Gerhardt, Phys. Rev. 172, 65 (1968).

[11] P. S. Szczepanek and D. Beaglehole, Bull. Am. Phys.

Soc. 16, 636 (1971).

[12] W. R. Scott and L. Muldawer, Bull. Am. Phys. Soc. 14, 321 (1969).

[13] D. Weiss, Ph.D. dissertation (Temple University, 1971) (unpublished); D. Weiss and L. Muldawer, Bull. Am. Phys. Soc. 17, 367 (1972).

[14] P.-O. Nilsson, A. Persson, and S. Hagstrom, Solid State Commun. 6, 297 (1968); P.-O. Nilsson, Phys. Kondens Mater. 11, 1 (1970).

[15] D. Beaglehole and E. Ehrlbach, Solid State Commun. 8, 225 (1969); Phys. Rev. B 6, 1209 (1972).

[16] J. A. Catterall and J. Trotter, Proc. Phys. Soc. Lond. 79, 691 (1962).

[17] D. Gray and E. Brown, Phys. Rev. 160, 567 (1967).

[18] J. C. Slater, Phys. Rev. 84, 179 (1951).

[19] J. F. Nicholas, Proc. R. Soc. A 66, 201 (1953).