

Optical investigations of short-range ordering of α -copper-aluminum alloys

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Differential reflectometry studies were performed on a Cu-17 at. % Al alloy. The differential reflectogram of a short-range ordered versus a disordered specimen shows a pronounced peak at 2.64 eV and a shoulder around 5 eV which is attributed to new structure in the ordered state. No such structure could be observed for a Cu-5 at. % Al alloy, confirming earlier reports in the literature that copper alloys containing less than 9 at. % aluminum undergo very little, if any, short-range ordering transformation. The new structure can be explained using the folding-band concept which yields additional interband transitions. Short-range ordering decreases the energy of one of the peaks in the differential reflectograms by 0.04 eV. This shift is equivalent to an increase in solute concentration amounting to one-half of a percent.

INTRODUCTION

Short-range ordering in copper-aluminum alloys has been extensively investigated in the past using mainly two groups of techniques. Firstly, the electrical resistivity and Hall constant were measured as a function of ordering.¹⁻¹⁰ Secondly, x-ray scattering¹¹⁻¹⁷ and electron microscopy¹⁸⁻²⁶ were applied to study the crystallographic structure of the ordered alloy. The emphasis of the interpretation of the various results has also been twofold. Köster and his group, by investigating systematically some binary-alloy systems, found that when short-range ordering takes place the Hall constant is altered in the same direction as it is varied by increasing additions of the solute.²⁷ Köster concluded from this that in the short-range ordered state the affinity between dissimilar atoms is slightly larger than for similar atoms. In other words, he suggested that in a short-range ordered alloy a given *A* atom is "surrounded" by more *B* atoms than one would statistically expect.

Electron microscopy studies by Gaudig and Warlimont²⁶ led to the conclusion that short-range ordering in α -copper-aluminum alloys could best be characterized by a microdomain model in which the domains are 10–20 Å in size and separated by diffuse boundaries which may be enriched in one constituent. The structure within the microdomain was assumed to be a two-dimensional antiphase-shift structure with nonuniform and irregular shift spacings, based on the $L1_2$ superlattice structure.

Recently, Epperson *et al.*¹⁷ analyzed short-range order coefficients (which they obtained from three-dimensional x-ray diffuse scattering investigations) in terms of the complete spectrum of nearest-neighbor atomic configurations. They found that these configurations bear a marked resemblance to the long-period antiphase-shift structures similar to the basic structural units of long-range ordered Cu_3Au .

Optical methods are capable of looking upon short-range ordering from a slightly different point of view. It has been convincingly demonstrated that the optical properties allow some direct conclusions upon the electron band structure of metals and alloys, particularly upon the energies of certain interband transitions around the Fermi surface.²⁸ Investigating short-range ordering by optical means is, however, not a trivial task. The expected variations, if any, of the band structure are so subtle that they are not likely to be discovered by comparing a reflectivity (or ϵ_2) spectrum of an ordered alloy with that of a disordered one. Differential reflectometry^{29,30} has a definite advantage over conventional optical methods. Here, one compares directly an ordered versus a disordered specimen of the same alloy at the same time by mounting them side by side, preparing the optical surfaces simultaneously, and analyzing the sample pair with an oscillating beam of monochromatic light of various frequencies. Electronic processing of the reflected signals yields the normalized difference in the reflectivities. It has been shown that structure in the spectral differential reflectivity curves is directly related to certain interband transitions.³¹

This paper reports studies of the order-disorder transformation in copper-17 at. % Al alloys using differential reflectometry. It will be shown that a weak but pronounced structure in differential reflectograms of ordered versus disordered copper-aluminum occurs, which suggests an additional interband transition in the short-range ordered alloy which is not present in the disordered alloy. It will also be shown that one of the characteristic energies for interband transitions is slightly shifted due to short-range ordering. This shift occurs in the same direction as can be observed when the solute concentration is increased. The results, therefore, consolidate both views mentioned above of looking upon short-range ordering.

EXPERIMENTAL PROCEDURE

Copper-aluminum alloys were prepared by melting 99.999% pure copper and 99.999% pure aluminum in a helium-filled quartz tube. The following combination of heat treatments and cold rolling was done to assure absolute homogeneity of the alloy composition across the samples and to obtain a fine grain. (Previous investigations have shown that, because of the high sensitivity of the differential reflectometer, even the smallest inhomogeneities will lead to structure in a differential reflectogram when the light beam is scanned across one sample.³²)

After melting in an induction furnace the alloys were solution heat treated at 800 °C for 10 days under helium atmosphere. One mm of the surface was removed by machining, and the samples were cold rolled by 70%. The alloys were again annealed at 800 °C for 9 days, the surface was mechanically cleaned, and the alloys were cold rolled by 40%. Recrystallization was done at 600 °C for one hour in helium atmosphere; the temperature was reduced to 400 °C and held there for 30 min with subsequent quenching of the sample into ice water. The alloys were then again rolled 50% to the final thickness of 1.5 mm. Two neighboring specimens 10×15 mm² in size were cut out from the strip utilizing a spark cutter and mounted side by side using a two-component mounting compound.³³ Their optical surfaces were prepared applying standard metallographic techniques utilizing 180–600 grit silicon carbide papers and microcut cloth³⁴ to remove possible silicon carbide embedding. Two openings were then cut through the back of the mount to facilitate removal of the specimens for heat treatment. Both samples were heat treated at 600 °C for 1 hour in helium atmosphere, quenched in ice brine, and stored at room temperature for approximately 42 h. (In one case storing was done for 1 yr.) One of the specimens was subsequently annealed at 290 °C for 1 h in helium atmosphere and also quenched into ice brine. Both specimens were inserted back into the previous mount and were given a final polish using 6 to 1 μ diamond polishing compound on polishing cloth. The samples were then washed with distilled water, rinsed with high purity methanol and swabbed with cotton to ensure that no oil film from the polishing liquid remained on the surface. The samples were dried in a clean air stream and immediately taken to the differential reflectometer. A differential reflectogram was obtained 3–5 min after polishing and about 20 min after quenching. The technique of reinserting the sample into the same holder had several advantages over casting a new mount after each

treatment: The mounting was faster (curing of the mount takes 40–60 min), the specimens were not heated during the curing process (about 70 °C), and the alloys needed only a fine polish after quenching. Mounting into a common sample holder is, however, necessary to provide equal treatment of both specimens and to assure that both specimens are situated in the same optical plane during measurement. The alloy compositions were checked by microprobe analysis and were found to be within ±0.1% of the nominal composition.

The differential reflectometer has been described elsewhere.^{29,30} An improved version has been used for this work that employs mirrors instead of lenses which allows one to measure a difference in reflectivity up to one hundredth of a percent. Briefly, an unpolarized monochromatic light beam (from a xenon source and a high-resolution double monochromator) is alternately scanned by a vibrating mirror (under near-normal incidence) across two specimens which are mounted side by side with virtually no gap in between. The total area scanned is about 2×4 mm². The signal from a photomultiplier tube (PMT) which picks up the reflected light from the specimens is electronically processed to obtain the normalized difference in reflectivity [$\Delta R/\bar{R}$ where $\bar{R} = \frac{1}{2}(R_1 + R_2)$]. The signal from the PMT is held constant by a PMT high voltage servo. An *xy* recorder plots $\Delta R/\bar{R}$ automatically as a function of wavelength. A scan between 200 and 800 nm (6.2 and 1.5 eV) requires about 3 min.

RESULTS AND DISCUSSION

Epperson *et al.*¹⁷ have measured the x-ray diffuse peak intensities for a Cu-14.76 at. % Al alloy as a function of its thermal history. They found that a high degree of short-range order (SRO) can be obtained by quenching this alloy from 600–650 °C in water at room temperature followed by a long-time storage at room temperature. They disordered this alloy by annealing it (after the quench from 600 °C) at temperatures up to 290 °C with subsequent quenching to room temperature. Our heat treatments were carried out (as described in the experimental section) in the same way. One Cu-17 at. % Al sample quenched from 600 °C and another one annealed at 290 °C after the 600 °C quench was analyzed by Epperson³⁵ with respect to their degree of short-range order. It was found that the diffuse peak for the sample quenched from 600 °C is more intense than for the one quenched from 290 °C, in accord with Epperson's earlier results.¹⁷ Consequently alloys quenched from 600 °C and "annealed" at room temperature will be labeled in this paper as "ordered,"

whereas alloys which underwent the additional 290 °C heat treatment with subsequent quenching will be called "disordered."

New interband transitions

Figure 1 shows a differential reflectogram of a sample pair consisting of a copper-17 at. % Al alloy. One of the specimens was in the ordered state, the other was disordered. Two pieces of structure can be detected: a fairly pronounced peak having a maximum at 469 nm (2.64 eV) and a broad shoulder around 250 nm (~5 eV). The features around the peak at 2.64 eV have a striking resemblance to that structure which we obtained for transitions between *d*- and *s*-band states just above the Fermi level.^{31,36,37} The difference between the reflectivities of the ordered and the disordered state is up to one-half of a percent, i.e., fairly small.

The transitional energies seen in Fig. 1 are different from those which are obtained by "compositional modulation."^{37,38} (In compositional modulation the light beam is scanned between two alloys having a slightly different solute concentration.) It has been shown³⁶ that in copper-based alloys the threshold energy for interband transitions (termed by us as peak "A" in Fig. 2, for example) occurs when electrons are excited by the photons from the upper *d* bands to the *s* state at the Fermi level. Peaks B and C are caused by the L'_2 to L_1 transition and peak D by transitions from the lower *d* band to the Fermi level.

The peak positions A through D for a Cu-17 at. % Al alloy are listed in Table I. It is evident from this table that the transitional energies at 2.64 eV and around 5 eV which were found for the order-disorder couple (Fig. 1) are not identical with any of the transitions A-D for compositional modulation.

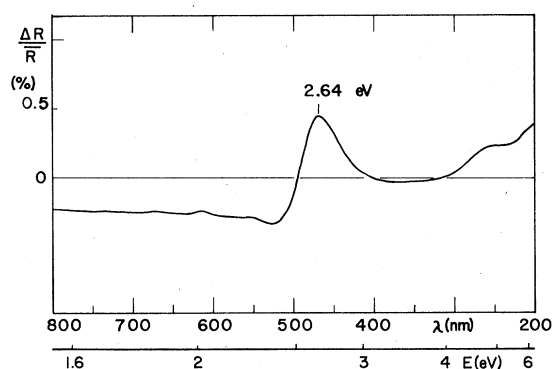


FIG. 1. Differential reflectogram ($\Delta R/\bar{R}$ vs λ) of ordered versus disordered Cu-17 at. % Al. (Heat treatment see caption of Fig. 3).

In other words, we have found two additional interband transitions for the ordered copper-aluminum alloy.

Before we attempt an explanation of these new peaks in Cu-17 at. % Al, it seems to be desirable to show that this structure is indeed caused by short-range ordering. It is known² that copper alloys containing less than 9 at. % Al undergo only very little SRO transformation if any. Epperson *et al.*¹⁷ observed extremely weak SRO diffuse scattering for these alloys. A sample pair having an aluminum concentration below 9 at. % and undergoing the same order-disorder heat treatment as above should show therefore a differential reflectogram which is essentially a horizontal line.

In order to test this hypothesis, a Cu-5 at. % Al alloy was prepared in a manner similar to the 17% Al alloy and heat treated and quenched simultaneously with the latter. Figure 3 shows a differential reflectogram of such a Cu-5 at. % Al pair, one sample quenched from 600 °C, the other annealed at 290 °C after the quench from 600 °C. The result is essentially a zero line. No ordering peaks can be observed in contrast to Fig. 1. The difference in reflectivity between the two samples is on the order of only $\pm 0.1\%$. Close inspection of Fig. 3 reveals that the largest deviations from the zero line are at the wavelengths of peaks A, B, and C (Fig. 2). In summary, it is reasonable to assume that the structure seen in Fig. 1 is caused by short-range ordering.

Comparison with existing theories

Additional interband transitions due to *long-range ordering* have been observed before in optical spectra. Particularly, the intermetallic phase Cu_3Au has been investigated repeatedly using conventional optical methods³⁹⁻⁴⁴ and also utilizing

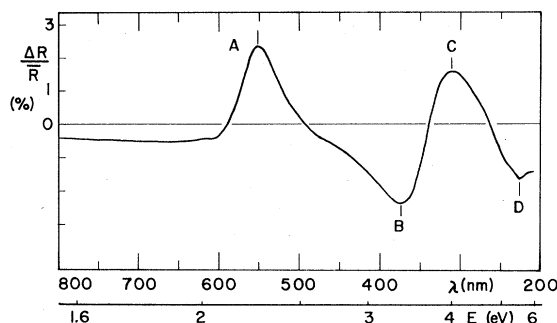


FIG. 2. Compositional modulation of a Cu-4 at. % Al versus a Cu-5 at. % Al alloy. The differential reflectogram is the equivalent of a Cu-4.5 at. % Al alloy [average composition (Ref. 36)]. The peak positions give approximately the transition energies for a Cu-4.5 at. % Al alloy (Ref. 31).

TABLE I. Peak positions of ordered Cu-16 at. % Al and Cu-17 at. % Al alloys. The peak positions for the 16 at. % Al alloy were obtained from Fig. 5 (average composition of a Cu-15 at. % Al and a copper 17 at. % Al alloy). Those of the 17 at. % Al alloy were calculated using the change in peak position per at. % listed in column 4 which are taken from Ref. 36.

Peak	Cu-16 at. % Al	Change in peak position per (at. %)Al	Cu-17 at. % Al
A	518 nm = 2.39 eV	+0.02 eV	514 nm = 2.41 eV
B	490 nm = 2.53 eV	-0.06 eV	502 nm = 2.47 eV
C	397 nm = 3.12 eV	-0.06 eV	405 nm = 3.06 eV
D	222 nm = 5.59 eV	+0.07 eV	219 nm = 5.66 eV

differential reflectance techniques.^{32,43} Nilsson and Norris⁴¹ interpreted the existence of a new ϵ_2 peak at 3.6 eV as the result of a band gap appearing across a new simple cubic Brillouin zone which appears when Cu₃Au orders (Fig. 4). Scott and Muldrew⁴³ examined the folding of energy bands into the simple cubic Brillouin zone accompanying the formation of the superlattice in Cu₃Au. They noticed that the Γ - X direction (Fig. 4) is bisected by the face of the inscribed simple cubic Brillouin zone at the point \bar{X} . The folding of the fcc Brillouin zone into the simple cubic zone about the point \bar{X} , with the point X being transferred to the point Γ , leads to a new transition from the d bands to the point X'_4 .

A similar consideration can be exercised for the case of copper-aluminum. Our previous studies^{36,38} have shown (confirmed by band calculations by Bansil *et al.*⁴⁵) that with increasing aluminum addition to copper the d bands are slightly raised and the s bands are lowered. The new Γ to Γ transition energy [probably from Γ_{12} to X'_4 (unfolded)] is therefore expected to be slightly larger than the threshold energy for interband transitions. This expectation is confirmed by our result. We found that the $d \rightarrow s(E_F)$ transition (peak A) requires a photon energy of 2.41 eV (Table I) whereas the new transition energy due to ordering

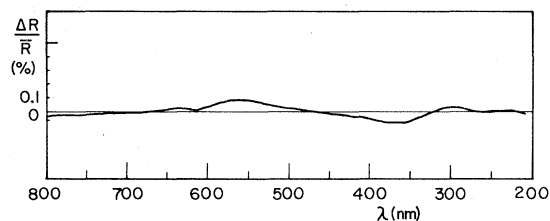


FIG. 3. Differential reflectogram of a sample pair consisting of a Cu-5 at. % Al alloy. One sample was quenched from 600°C with subsequent 42 h room temperature aging, the other was quenched from 290°C after the 600°C quench (identical treatment to that for specimens of Fig. 1).

was found to be 2.64 eV (Fig. 1).

The Γ - L vectors are identical for fcc and simple cubic Brillouin zones (Fig. 4) so that folding does not cause any new transitions. However, folding along the Γ - M - K direction is likely to produce an additional transition at higher energies which was indeed observed (Fig. 1). An alternate way of looking at the above would be to postulate local regions of copper-aluminum domains ("molecules" of sorts) which would have associated local transitions. Band calculations of ordered versus disordered copper-aluminum are needed to verify these interpretations.

Compositional modulation of ordered and disordered Cu-Al alloys

A sample pair suitable for compositional modulation^{36,38} consisting of a Cu-15 at. % Al and a Cu-17 at. % Al alloy was prepared. Both samples were brought simultaneously into the ordered state, mounted and polished together, and a differential reflectogram was taken (Fig. 5, lower

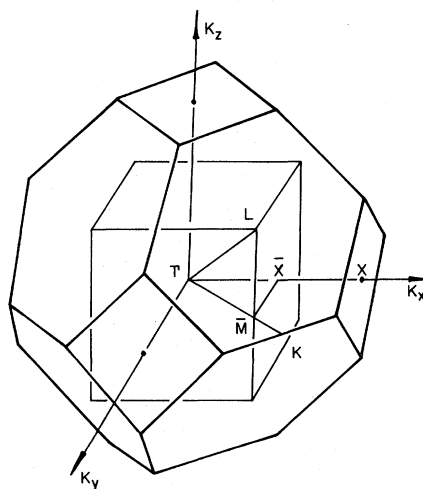


FIG. 4. First Brillouin zone of fcc lattice with inscribed Brillouin zone of cubic primitive superlattice.

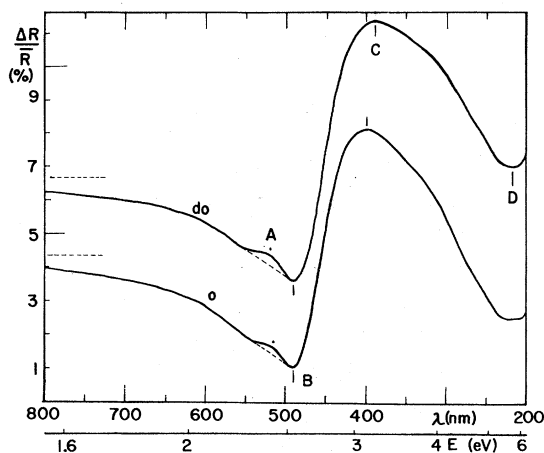


FIG. 5. Compositional modulation of Cu-15 at. % Al versus Cu-17 at. % Al alloys, ordered and disordered. The differential reflectograms are equivalent of a Cu-16 at. % Al alloy [average composition (Ref. 36)]. The two reflectograms are shifted for clarity. The respective zero points in $\Delta R/\bar{R}$ are indicated by the horizontal dashed lines.

curve). Subsequently the specimens were disordered and again studied using the differential reflectometer (Fig. 5, upper curve).

The reflectograms of the ordered as well as the one of the disordered alloys are relatively similar. The largest difference can be observed in the energies of peak C. The average of several measurements after identical heat treatments yielded for the ordered alloys a C peak at 397 ± 2 nm = 3.12 ± 0.02 eV and for the disordered alloys a C peak at 392 ± 1 nm = 3.16 ± 0.01 eV. This difference, as small as it may be, is important. It reveals that for the ordered state the energy of peak C is decreased by 0.04 eV.

Earlier studies have shown³⁶⁻³⁸ that peak C decreases in energy by increasing solute addition. Short-range ordering behaves therefore as if the solute concentration is increased. From the data of Table I one can deduce that ordering in Cu-17 at. % Al alloys is equivalent to an increase in solute concentration amounting to approximately one-half of a percent.

Köster²⁷ arrives, using Hall-constant measurements, at a similar result. He found, as mentioned in the Introduction, that when short range-ordering takes place, the Hall constant is altered in the same direction as it is varied by increasing additions of solute. He argues that the interaction of dissimilar atoms is larger in the ordered state in which the probability of finding a dissimilar atom as a neighbor is assumed to increase.

Further considerations

A word should be said on why the other peaks in Fig. 5 do not seem to shift due to ordering. In al-

loys with small solute concentrations (see, for example, Fig. 2) peaks A and B are distinctly separated. With increasing solute concentration peak A is shifted to higher and peak B to lower energies.³⁶⁻³⁸ In addition, peak A becomes less pronounced so that this peak position can be localized at high solute concentrations with only little accuracy.

The ordering peak which can be so elegantly observed in Fig. 1 is too small in magnitude (0.5% difference in R) to be distinguished as a variation of a strong signal which is more than one order of magnitude larger (Fig. 5). It demonstrates once more the power of the differential technique.

In light of this, it appears doubtful to us that Rea and DeReggi⁴⁶ have indeed observed short-range ordering in their unmodulated ϵ_2 spectra of a copper-10.2 at. % Al alloy. On one hand, these authors could not observe a change of the onset of interband absorption (feature A) with increasing solute concentration as we did.³⁶⁻³⁸ On the other hand, they observed a "drastic change" in the $(\epsilon_2)_{ib}$ spectra when they compared Cu-7.5 at. % Al with Cu-10.2 at. % Al, which they attributed to SRO. No attempt was made by these authors to compare ordered with disordered samples of the same alloy concentration.

CONCLUSIONS

Differential reflectometer studies have shown for the first time that new peaks can be obtained in short-range ordered copper-aluminum alloys. They are similar in character but much weaker in intensity than those observed for long-range ordered Cu_3Au . They can be explained by assuming the formation of a superlattice (in small domains) due to ordering and a folding of the energy bands into a simple cubic Brillouin zone. Thus, optical properties in conjunction with electron theory arrive at a similar general picture of short-range ordering as diffuse x-ray scattering and electron microscopy do, namely, to the suggestion of an existence of small areas which possess a periodic (superlattice) structure. On the other hand, our results also confirm the findings of Köster *et al.* that short-range ordering acts similarly to an increase in solute concentration.

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