Order-Disorder Transformation at the {100} Surface of Cu_3Au

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The long-range order parameter of the {100} surface of Cu_3Au has been determined as a function of temperature by low-energy electron diffraction. The order parameter of the surface, unlike the bulk order parameters, appears to be a continuous function of temperature, and the disordering process at the surface begins about 60°K below a common critical temperature. A Monte Carlo calculation of the order parameter in terms of a model incorporating nearest- and next-nearest-neighbor interactions reproduces the experimental results.

The characteristic parameters of the order-disorder transformation in the volume of the binary alloy Cu_3Au are well known.[1] The crystal structure is fcc in the disordered state, above the critical temperature $T_c = 390$°C. Below the critical temperature, in a perfectly ordered alloy, gold atoms can be assigned to the corners of a cubic unit cell and copper atoms to face-centered positions. If this arrangement of the ordered state is preserved near the free surface, diffracted beams of low-energy electrons associated with the superlattice should be observed in a low-energy electron-diffraction (LEED) pattern, and single-scattering theory predicts that the intensity of these beams is proportional to the square of the long-range order parameter.[2]

Experimental measurements were performed on the {100} surface of a Cu_3Au crystal. This crystal was used by Roy Kaplow of Massachusetts Institute of Technology to obtain much of the existing data on short-range order.[3] After repolishing and confirming the orientation of the {100} plane ($\pm\frac{1}{2}$°), the crystal was mounted in the LEED apparatus in front of a pyrolytic graphite heater. Temperature was monitored by a thermocouple embedded in the crystal.

Initial cleaning of the surface and subsequent removal of impurities collected in time from the ambient atmosphere (10^{-10} Torr) was effected by argon-ion bombardment and annealing at 750°C. Evidence that the surface was free of impurities, and that the *ratio* of copper to gold remained constant during protracted measurements and ion bombardment (followed by annealing to equilibrium), was obtained from Auger spectra which were collected at frequent intervals from the Cu_3Au crystal and from a pure-copper reference material located beside the crystal. It should also be noted here that the critical temperature, which is a function of composition, was unchanged after many cycles of bombardment and annealing, indicating a constant composition in equilibrium with the bulk crystal.

The time required at each temperature to obtain an equilibrium state of order and, presumably, surface-to-volume equilibrium also was defined by the results of an extensive x-ray study of ordering kinetics by Feder, Mooney, and Nowick.[4] The time ranged from 2 h at 350°C to 70 h at 230°C, below which no significant change could be observed.

Diffracted beams from the superlattice were indeed observed in LEED patterns, as shown and as indexed in Fig. 1. These beams disappear at a critical temperature of 390 ± 4°C, which corresponds to the critical temperature of the ordered state of the bulk lattice. A more precise measurement of the critical temperature at the surface is difficult to obtain because of the form of the temperature dependence of the intensity (see Fig. 2).

To evaluate the long-range order parameter S, as a function of temperature, intensity-voltage profiles (normalized to the incident beam current) for the $(0\bar{1})$ superlattice beam [Fig. 1(c)] were obtained at different temperatures in the range 300 to 648°K and are shown in Fig. 2. The arrows indicate the positions of Bragg maxima which are calculated on the basis of single-scattering theory.

In a single-scattering approximation, the intensity of a superlattice beam can be written as

$$I \propto S^2 e^{-2M}, \tag{1}$$

where S is the long-range order parameter in the binary system and $2M$ is the Debye-Waller factor.[5] Since S and M are functions of temperature, an independent measure of the Debye-Waller factor is required in order to evaluate the long-range order parameter. For this purpose the intensi-

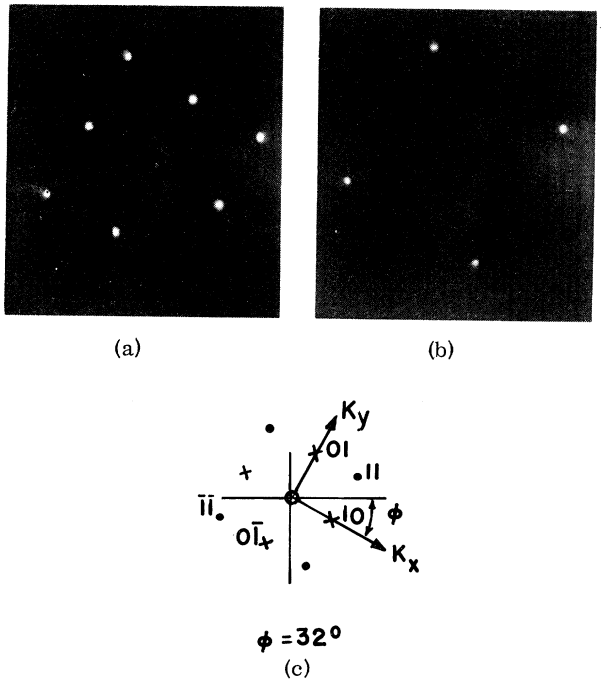

FIG. 1. Photographs and corresponding indices of LEED patterns from the {100} surface of ordered and disordered Cu_3Au at normal incidence and in incident energy of 70 eV. (a) The ordered state at room temperature (one beam is obscured by the crystal support). (b) The disordered state above the critical temperature. (c) Diagram showing indexing of diffracted beams. Crosses, superlattice beams; closed circles, fundamental beams.

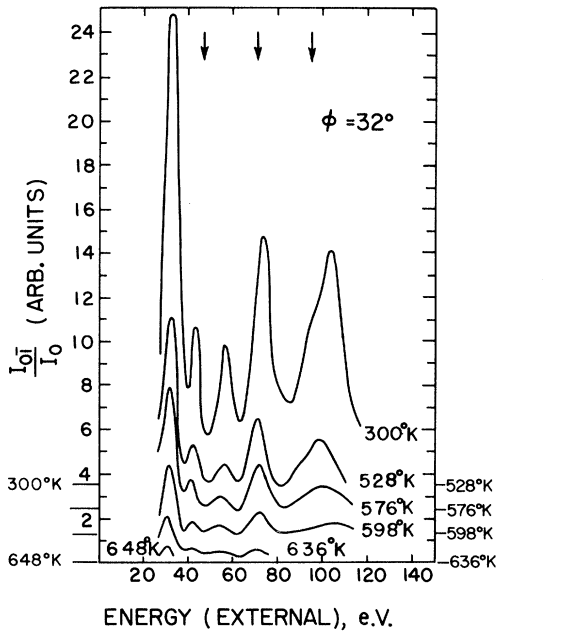

FIG. 2. Intensity profiles (normalized to incident current) for the $(0\bar{1})$ superlattice beam from the {100} surface of Cu_3Au at different temperatures from 300°K (uppermost curve) to 648°K (lowest curve). The origin of each spectrum is displaced, as indicated beside the ordinate scale.

ties of the specular beam (00) and one nonspecular beam $(\bar{1}\bar{1})$ were measured as functions of temperature from which it was determined that the respective (single-scattering) Debye temperatures were approximately equal (Fig. 3) at the same energy and angle of incidence. Accordingly, long-range order parameters were obtained from the intensity of the apparent Bragg maximum in the superlattice beam at 33 eV (external energy, Fig. 2) corrected by the Debye-Waller factor corresponding to Fig. 3, and normalized to the volume order parameter by assuming long-range order near the surface at 528°K to be the same as in the bulk ($S_B = 0.96$).

The validity of employing a single-scattering approximation for low-energy electron diffraction has been tested in a computer experiment by Jepsen, Marcus, and Jona[6] who found that a single-scattering formulation yields Debye temperatures at energies higher than 30 eV which are accurate to within 5% for the specular beam.

Values of the order parameter obtained from the superlattice beam are shown in Fig. 4, as a function of temperature, together with the bulk

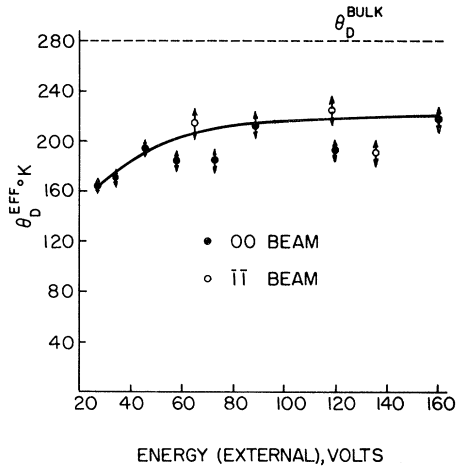

FIG. 3. Effective Debye temperatures for two beams computed from the slope of $\ln(I/I_0)$ *versus* temperature for prominent peaks in the intensity-energy profiles of the specular (00) and nonspecular $(\bar{1}\bar{1})$ beams. The error bars are estimated from the distribution of experimental data about the straight lines in plots of $\ln(I/I_0)$ *versus* temperature.

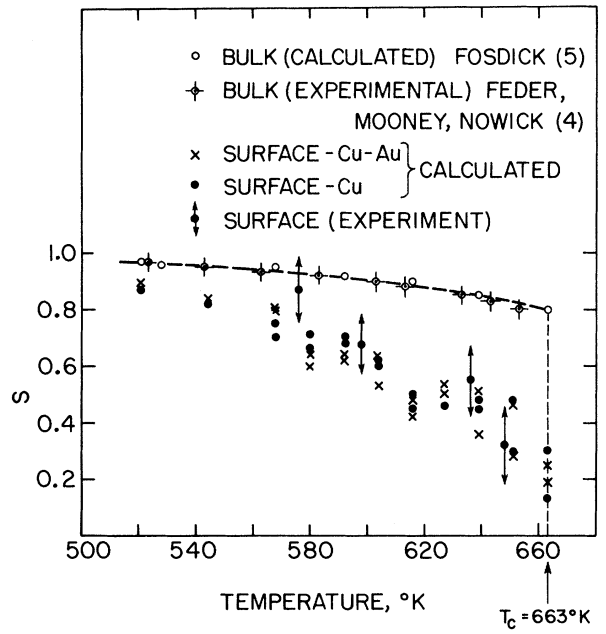

FIG. 4. Measured and computed long-range order parameters, as a function of temperature for the {100} surface of Cu_3Au, compared with calculated order in the bulk crystal. Closed circles without arrows correspond to model boundary conditions extrapolating to a Cu surface; crosses, to a Cu-Au surface. The scatter of the computed results for different boundary conditions provides a measure of the statistical uncertainty of the Monte Carlo averages. Open circles give calculated results for order in a model with bulk boundary conditions but with the same interaction as in the surface model. The computed parameters for the bulk crystal agree quite closely with measured values (Ref. 4) over the range shown. The experimentally measured order parameters for the surface are shown by the closed circles with error bars.

long-range order parameters obtained by x-ray measurements.[4] The "surface" long-range order parameter, unlike the bulk parameter, is a continuous function of temperature. The disordering process at the surface begins about 60°K below a common critical temperature.

The long-range order parameters near the surface layers were computed with a modification of the Monte Carlo technique previously applied to bulk Cu_3Au.[7] In the statistical computations, interactions between the atoms in Cu_3Au were represented by an Ising-like model Hamiltonian:

$$H = J_1 \sum_{\substack{\text{nn}\\ \text{pairs}}} \sigma_i\sigma_j + J_2 \sum_{\substack{\text{nnn}\\ \text{pairs}}} \sigma_i\sigma_j - \frac{\Delta\mu(T)}{2}\sum_i \sigma_i + \Delta E \sum_{\text{surface}} \sigma_i , \qquad (2)$$

where J_1 and J_2 are the nearest- and next-nearest-neighbor interaction constants. $\sigma_i = +1$ or -1, according as the site i is occupied by an atom of Cu or by an atom of Au. $\Delta\mu(T)/2$ is the difference in chemical potentials of Cu and Au for the bulk sample of Cu_3Au at a temperature T. The difference in chemical potentials was adjusted at each temperature so that the composition of a system corresponding to a bulk sample was that of Cu_3Au. The last term in (2) arises because of the lower coordination of atoms in the surface layer. Depending on the value of ΔE, which is the difference between Au-Au and Cu-Cu interaction energies, this term can lead to a segregation of Cu or Au in the surface layer. Since our Auger measurements indicate approximately constant average surface composition, we may suppose that ΔE is in a range for which there is little tendency for segregation.

Computations were performed with a cubic section of the lattice containing 500 lattice points. Since the presence of the surface destroys the translational symmetry of the solid normal to the surface (the z direction), periodic boundary conditions were applied only along x and y directions. Along the z direction, one boundary corresponding to the free surface was terminated by a simulated vacuum of two extra layers in which σ was set equal to zero; the other boundary was terminated in a simulated bulk by two layers disordered to the extent appropriate to the bulk at the temperature in question. The formulation was first tested by evaluating the long-range order parameter for bulk Cu_3Au with periodic boundary conditions in all three directions. Our results agree with those of Fosdick.[7]

In the calculation of long-range order in layers near the surface, an order parameter S_τ was defined for the τth layer as

$$S_\tau = (N_a - N_b)/N, \qquad (3)$$

where N_a and N_b are the numbers of gold atoms in the a and b sublattices of the τth layer and N is the number of atoms in a sublattice. Since ordering corresponds to alternating Cu and Cu-Au layers in the ⟨100⟩ direction, the order parameter has nonzero values (aside from fluctuations) only for alternate layers. Calculations were done for the two cases corresponding to boundary conditions which extrapolate to Cu and to Cu-Au surface layers. Because of steps in the {100} plane, the actual material surface most probably corresponds to an equal mixture of these two cases.

There are three parameters in Eq. (2) which determine the behavior of the model and these can, within limits, be determined without reference to surface order. We took J_2/J_1 as -0.2, quite close to the preferred value of -0.25 suggested in Ref. 7. To illustrate best the contrast between results from the bulk and from the surface, we adjusted J_1 so that the calculated points for the bulk order parameter agree with experiment[4] up to the experimental transformation temperature. This gave $J_1/k = 237°K$, a value about 7% higher than would have been obtained by the procedure of Ref. 7. Finally we let $\Delta E = 2.5J_1$, corresponding to a constant average surface composition.

In Fig. 4 we show the average of the order parameters for the two topmost Cu-Au layers, for the two boundary conditions of the surface model, together with the measured surface order and the calculated bulk order as a function of temperature. It appears from the figure that the difference between the observed behavior of the long-range order parameter at the surface and that in the bulk can be explained by a simple model involving only nearest- and next-nearest-neighbor interactions which are the same for both surface and bulk. Furthermore, it is evident from the analysis that consideration of a region of accommodation between surface and bulk is a necessary feature of any model meant to describe the phenomenon of long-range order at a crystal surface.

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[3]See, for example, *Local Atomic Arrangements Studied by X-Ray Diffraction*, edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach, New York, 1965).

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Polysulfur Nitride—a One-Dimensional Chain with a Metallic Ground State

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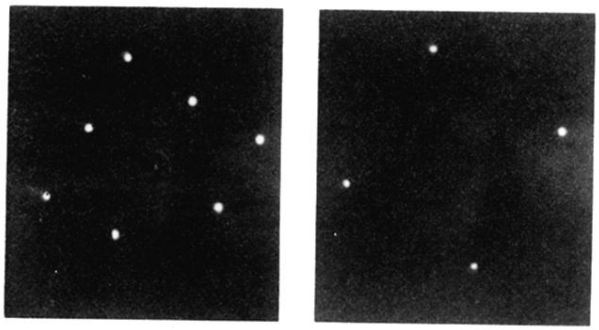
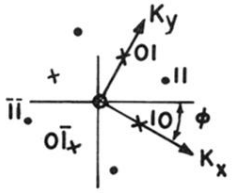
The temperature dependence of the electrical conductivity and Seebeck coefficient for the polymer chain system $(SN)_x$ has been measured along the chain axis from 4.2 to 300°K. The data show the system to be metallic over the entire temperature range studied, with a small conductivity maximum at ~33°K.

Considerable interest exists in examining the properties of both organic and inorganic structures which are highly anisotropic and can be visualized as containing one-dimensional chains—metallic "spines"—surrounded by a matrix whose properties are highly important in determining the transport properties of that system. The organic and inorganic systems of interest have, in the main, been the highly conducting charge-transfer salts of tetracyanoquinodimethane (TCNQ)[1] and the mixed-valence Pt chain complexes.[2] However, these compounds show "metal-insulator" transitions at temperatures varying from 60 to 250°K which have been interpreted in terms of



(a) (b)



$\phi = 32^{\circ}$

(c)

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