them to be good confirmation, at least for the body-centered cubic and face-centered cubic lattice. The series for the simple cubic lattice seems to be more irregular and the results converge more slowly, but we know of no reason why it should be qualitatively different from the body-centered cubic.

Our results depend on the hypotheses we have made concerning the nature of the functions studied. We detect no violation of the hypotheses, but, of course, we cannot prove them either. The results we obtain agree very well with those of Rushbrooke and Wood[12] for the bcc and sc and those of Domb and Sykes[9] for the fcc.

ACKNOWLEDGMENT

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Heat Capacity of Ordered and Disordered CuPt Below 4.2°K

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Heat-capacity measurements below 4.2°K on CuPt show that the electronic heat-capacity coefficient γ decreases from 0.825 mJ mole^{-1} deg^{-2} in the disordered condition to 0.530 in the ordered condition. The Debye temperature increases on ordering from 357 to 385°K. It is suggested that the observed changes can be explained either in terms of the alterations in the Brillouin zone structure which occur on ordering or by the possibility of a magnetic transition in the ordered condition.

THE order-disorder transformation in the CuPt system which occurs in the alloy of 50 at.% is unusual, since the number of unlike nearest neighbors in the ordered condition is the same as it is, on the average, in the random disordered condition.[1] Consequently, an explanation of the tendency toward ordering which is based on a decreased interaction energy for unlike nearest neighbors (quasichemical theory) is not applicable.

The effect of superlattice formation on the Brillouin zone structure of an alloy has been discussed by several authors.[2–5] When a superlattice forms in an alloy, the x-ray structure factor for certain planes is no longer equal to zero, as it is in the disordered condition. These extra superlattice reflections give rise to a reduction in the size of the basic Brillouin zone, which can lower the electronic energy of the alloy by interacting with the electrons near the Fermi surface. Since all of the electrons in the alloy partake of this interaction and since its existence does not require that the number of unlike nearest neighbors change, it is an attractive explanation for the tendency toward ordering in CuPt and has been elaborated upon in further detail by Nicholas.[6] Although it is difficult to predict in detail what effects the Brillouin zone–Fermi surface interface due to superlattice formation should have on the electronic structure, it is possible that the density of states curve could be changed. An earlier investigation of the low-temperature heat capacity of Cu_3Au[7] showed no difference in the electronic specific heat coefficient (proportional to the density of states at the Fermi surface) between the ordered and disordered conditions. It was felt, in view of the unusual nature of the transformation in CuPt, that a similar investigation in CuPt would be of interest.

EXPERIMENTAL

Copper of 99.999% purity (Asarco A-58) and platinum sponge of 99.999% (Johnson-Mathey 1010) in the appropriate amounts were induction melted in a high-purity graphite crucible under a protective atmosphere of helium. The resulting ingot was homogenized in the crucible by holding between 1250° and 1350°C for 5 h. Chemical analysis showed no significant composition difference between the top and bottom of the ingot; the mean concentration of copper was 24.51 wt%, the stoichiometric composition being 24.57 wt%. A spectroscopic analysis showed Fe to be present at less than 4 ppm, and Mn and Co both less than 1 ppm. A cylindrical specimen slightly less than

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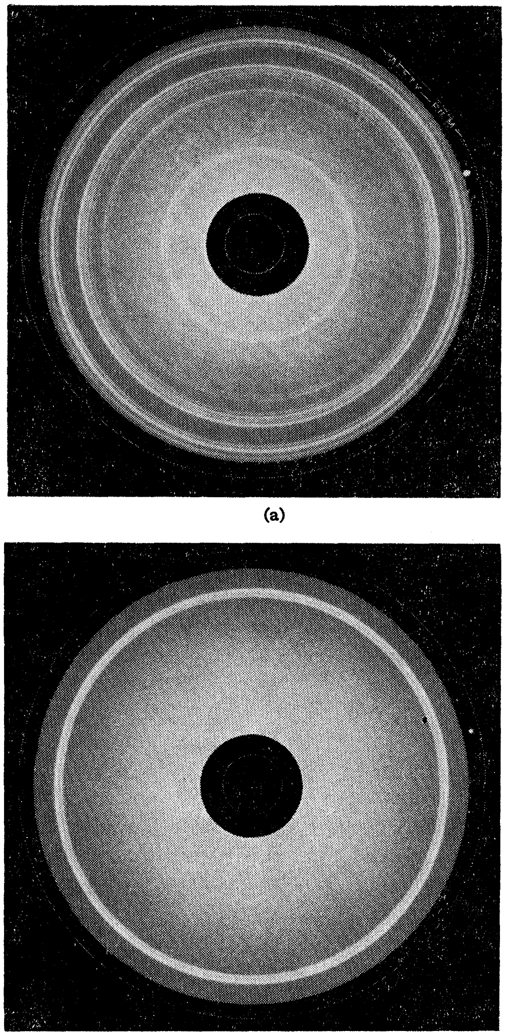

(a)

(b)

FIG. 1. X-ray back reflection photographs of (a) ordered and (b) disordered CuPt specimen used for heat capacity measurements.

an inch in diameter and weighing approximately 93 g was prepared for the calorimetric measurements. To produce long-range order the specimen, sealed in a Vycor tube under vacuum, was held for approximately 24 h at a series of temperatures starting at 850°C and decreasing approximately 50°C every 24 h down to 490°C. It was held for 4 days at 490°C, then cooled to 200°C in steps over the next two weeks and, finally, furnace cooled to room temperature. An x-ray back-reflection photograph using copper radiation and a nickel filter, Fig. 1(a), showed prominent superlattice lines and indicated the specimen to be well-ordered.[8] The specific heat of the ordered specimen was measured in the manner previously described.[9] The same specimen sealed under vacuum in a Vycor tube was then disordered by holding above the critical temperature for long-range order ($T_c = 815°C$) for 2.5 h and then quenching from 887°C into a NaCl brine at $-4°C$. An x-ray back-reflection photograph of the quenched specimen, Fig. 1(b), showed that the superlattice reflections had disappeared. In addition, a diffraction pattern of the quenched specimen was recorded on a Siemens diffractometer at a goniometer speed of $\frac{1}{8}$ degree 2θ per min using copper radiation and a nickel filter. No indication of superlattice lines could be seen, thus confirming that the specimen was disordered. (The term "disordered," used for the quenched condition, is intended to indicate the absence of long-range order; it should be recognized, however, that in the disordered condition the specimen contains short-range order.[8]) After completing the specfic heat measurements on the disordered specimen, a second sample was taken for spectroscopic analysis as a check that the specimen had not become contaminated by any of the treatments to which it had been subjected, i.e., the ordering heat treatment, quenching, cleaning, etc. This analysis showed that the impurities Fe, Co, and Mn, if present, were less than 4 ppm and most likely less than 1 ppm.

RESULTS AND DISCUSSION

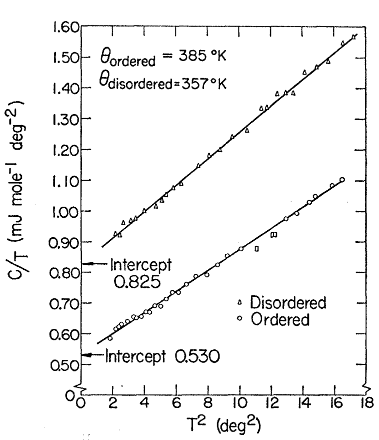
The results, Fig. 2, plotted in the usual form, viz., C/T *versus* T^2, give two straight lines. Thus, the low-temperature heat capacity is of the form

$$C = \gamma T + A(T/\theta)^3, \tag{1}$$

the first and second terms representing the electronic and the lattice heat capacity, respectively. The intercept γ and the Debye temperature θ for the ordered and disordered states, shown in Fig. 2, have been determined from a least-squares fit of a straight line to the data points.[10]

It is interesting to note the large decrease in the γ value of the ordered alloy relative to that of the disordered alloy. This behavior is to be contrasted with that observed for Cu_3Au[7] where the γ value remains unchanged on ordering. The observed increase in the

FIG. 2. Molar heat capacity divided by temperature C/T as a function of the temperature squared T^2 for disordered and ordered CuPt. Points shown as squares have been omitted in least-squares fitting of line.



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[10] The constant A in Eq. (1) is related to the Debye temperature by the relation $A = (12/5)\pi^4 R/\theta^3$, R being the gas constant.

Debye temperature on ordering is consistent with that observed in Cu_3Au.

It is of interest, in understanding the electronic structure of CuPt, to compare the relative change in the γ value which occurs on adding platinum to copper to that which occurs when palladium is added to silver[11] and when platinum is added to gold.[12] In order to make this comparison the γ values should be adjusted for the difference in lattice parameter between the pure solvent and the alloy. Accordingly, if we assume the rigid band model[13]

$$\gamma^* = \gamma_{\rm obs}(a/a_0)^2, \qquad (2)$$

where γ^* is the γ value which would be observed if the alloy had the same lattice parameter as the pure solvent, $\gamma_{\rm obs}$ is the value of γ measured for the alloy, and a and a_0 are the lattice parameter of the alloy and the pure solvent, respectively.

This comparison is made in Table I, which shows that the corrected electronic specific heat coefficient γ^* has increased relative to the value for the pure solvent γ_0 much more in AgPd and in AuPt than in disordered CuPt. (It should be pointed out, however, that the AuPt system is somewhat special in view of the existence of a two-phase region.[14]) The table shows that there is a very clear difference in the relative change in γ on alloying, whereas it would seem reasonable to expect these alloys to be quite similar in their electronic structures, since both palladium and platinum are known to have 0.6 holes in their d bands.[15] It is, of course, true that the comparison is complicated by the possible differences in short-range order in the alloys. In particular, it is known that considerable short-range order exists in quenched CuPt.[8] Since ordering decreases the γ value, the smaller relative increase in γ on alloying, noted in Table I, may be due to this effect.

TABLE I. The electronic specific heat coefficients in disordered CuPt, in AgPd, in AuPt and in pure Cu, Ag, and Au.

	$\gamma_{\rm obs}$[a]	γ^*	γ_0	Difference
CuPt Disordered	0.825	0.75	0.69	0.06
AgPd	1.69	1.80	0.64	1.16
AuPt	2.95	2.84	0.87	1.97

[a] See text for explanation of symbols.

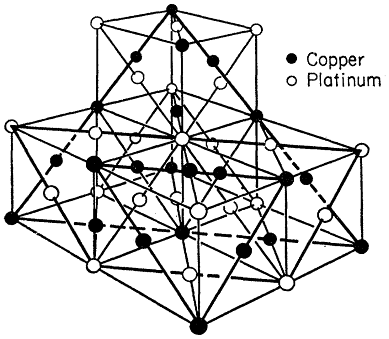

FIG. 3. The arrangement of atoms on a fcc lattice as in ordered CuPt. Rhombohedral distortion is not shown.

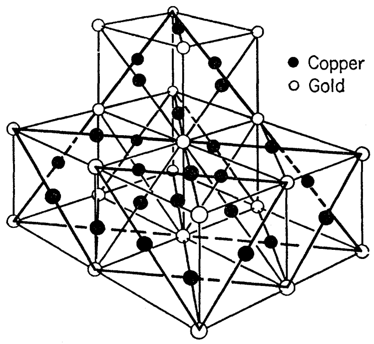

FIG. 4. The arrangement of atoms in the ordered Cu_3Au structure.

The rhombohedral ordered CuPt structure can be thought of as a stacking of close-packed planes alternately composed of either pure platinum or pure copper.[16] This arrangement is illustrated in Fig. 3; Fig. 1 shows the structure of Cu_3Au for comparison. It has been suggested[17] that with the CuPt arrangement an ordering of the spins of the platinum atoms could give rise to a magnetic transition. Although it is not known with any degree of certainty how such a transition might affect the electronic specific heat, it should be pointed out that in Ni_3Mn, for which the ordered state is ferromagnetic, the electronic specific heat decreases on going from the disordered to the ordered condition.[18] The decrease in γ observed in ordered CuPt may, then, be a similar effect due to magnetic ordering, either ferromagnetic or antiferromagnetic. There appears to be no data available to resolve this question.

It is, of course, also possible that the Fermi surface-Brillouin zone interaction is responsible for the decrease in γ which occurs on ordering. With our present understanding of the effects of ordering on the electronic structure of alloys, it is not possible to predict either the magnitude or sign of the expected change in γ on ordering.

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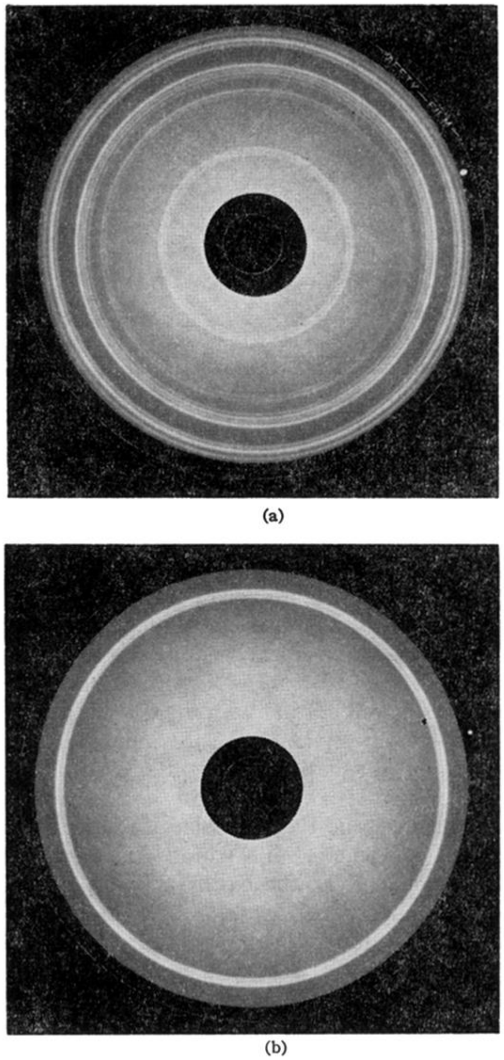

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