PHYSICAL REVIEW VOLUME 108, NUMBER 3 NOVEMBER 1, 1957

Heat Capacity of Cu_3Au below 4.2°K

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(Received July 30, 1957)

Heat capacity measurements below 4.2°K have been made on Cu_3Au in both the disordered and ordered states. It is found that ordering increases the Debye temperature of the lattice but that it leaves the electronic heat capacity substantially unchanged at a value in excess of that for free electrons. An explanation of the latter observation is proposed in terms of the changes in Brillouin zone structure that are presumed to take place on ordering. The values of Debye temperature do not agree with those obtained from low-temperature resistance measurements, but are in good accord with the value computed from the room-temperature elastic constants of ordered Cu_3Au.

I. INTRODUCTION

BOTH Muto[1] and Slater[2] have considered theoretically the effect of ordering on the zone structure of an alloy. Thus, in going from the disordered to the ordered state, the structure factor for many of the planes in the reciprocal lattice space becomes nonzero, causing a reduction in the size of the basic Brillouin zone. It would thus be expected that in the ordered state there would be a considerable overlap of the Fermi surface into the higher subzones.

Muto has considered ordered Cu_3Au in some detail and concludes that susceptibility[3] and Hall effect[4] data are consistent with a scheme where the Fermi surface just overlaps into the third subzone. Since this situation should result in a marked reduction in the density of states, it was considered of interest to measure the low-temperature specific heat in order to see whether this reduction was in fact observed. In addition such measurements give an independent check on the Θ values for disordered and ordered Cu_3Au obtained by Bowen[5] from low-temperature resistance studies and the Θ value computed by Quimby[6] from the room-temperature elastic constants of ordered Cu_3Au.

II. EXPERIMENTAL

Measurements were carried out in the same manner as described in a previous paper.[7] The specimen of Cu_3Au was prepared by induction-melting appropriate quantities of high-purity copper and gold in a graphite crucible, care being taken to ensure adequate mixing of the components. Subsequent chemical analysis revealed an insignificant difference in the macroscopic chemical composition between the top and bottom of the ingot, the mean concentration of copper being 49.1% by weight, which figure is within the experimental error of the ideal composition, *viz.*, 49.15% by weight.

After casting, the ingot was hot worked to remove segregation and then homogenized at 800°C for 48 hours. The specimen was turned to size and water quenched from 800°C to produce a disordered condition. X-ray examination revealed no trace of superlattice lines, but from the work of Cowley[8] it must be expected that short-range order existed to a considerable degree in the specimen. Heat capacity measurements were made in the quenched condition, after which the specimen was ordered. To prevent oxidation of the specimen during this heat treatment, it was sealed under vacuum in a Pyrex tube. Following the procedure outlined by Jones and Sykes,[9] the alloy was held for an hour at 410°C and then cooled at 370°C. It was maintained at this temperature for 48 hours and then cooled at a rate of 20°C per hour down to 200°C. Subsequent x-ray analysis gave well-defined superlattice lines and measurement of the relative intensities of the various reflections in the usual fashion[10] gave a value of long-range order parameter $S\sim 1.0$, the uncertainty in this figure being due to difficulties in correcting for extinction, preferred orientation, and grain size in the specimen.

III. RESULTS AND DISCUSSION

When plotted in the usual form, *viz.*, C/T *versus* T^2, the data for the two samples give straight lines as shown in Figs. 1 and 2. Thus, the low-temperature capacity must be of the form

$$C=\gamma T+A(T/\Theta)^3, \qquad (1)$$

the first and second terms representing the electronic

TABLE I. Values of γ and Θ in the relation $C=\gamma T+A(T/\Theta)^3$ for disordered and ordered Cu_3Au.

Specimen state	γ (millijoule $mole^{-1}$ deg^{-2})	Θ (deg K)
Quenched from 800°C	0.66 ± 0.02	278 ± 2
Ordered	0.69 ± 0.02	285 ± 2

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[1] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **34**, 377 (1938).

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

[3] H. J. Seemann and E. Vogt, Ann. Physik **2**, 976 (1929).

[4] A. Komar and S. Sidorov, J. Tech. Phys. (U. S. S. R.) **11**, 711 (1941).

[5] D. B. Bowen, Acta Met. **2**, 573 (1954).

[6] S. L. Quimby, Phys. Rev. **95**, 916 (1954).

[7] J. A. Rayne, Phys. Rev. **107**, 669 (1957).

[8] J. M. Cowley, J. Appl. Phys. **21**, 24 (1950).

[9] F. W. Jones and E. Sykes, Proc. Roy. Soc. (London) **A166**, 376 (1938).

[10] D. T. Keating and B. E. Warren, J. Appl. Phys. **22**, 286 (1951).

and lattice heat capacity respectively. The corresponding values of γ and Θ are given in Table I, the quoted uncertainties representing both random errors estimated at the 99% confidence level and systematic errors assumed to be $\frac{1}{2}$%. It will be seen that the γ values in the disordered and ordered states agree to within experimental error, whereas the Debye temperatures differ by about 2.5%.

(a) Electronic Heat Capacity in the Disordered State

It might be expected that the γ value in the quenched condition could be computed from that of copper, utilizing the rigid band model of a binary alloy and making due allowance for lattice expansion. Thus, assuming that the density of states increases as the square of the lattice parameter for a fixed electron/atom ratio, we have

$$N'(E_0)=N(E_0)(a'/a)^2, \tag{2}$$

a, a' being the lattice parameters for the pure solvent and the alloy and $N(E_0)$, $N'(E_0)$ the corresponding densities of states. Since

$$\gamma=\tfrac{1}{3}\pi^2k^2N(E_0), \tag{3}$$

we have

$$\gamma'=\gamma(a'/a)^2. \tag{4}$$

Using the values $\gamma=0.687\times10^{-3}$ joule mole^{-1} deg^{-2}, $a=3.608$ kX and $a'=3.743$ kX, we find $\gamma'=0.738\times10^{-3}$ joule mole^{-1} deg^{-2}, which value is much greater than that observed. It is possible that the discrepancy is due to the existence of short-range order in the specimen and further experiments are planned on other copper-gold alloys to investigate this point.

(b) Electronic Heat Capacity in the Ordered State

In the ordered state the structure factor for the $\{100\}$ planes is nonzero and the first Brillouin zone becomes a cube containing $\frac{1}{2}$ electron per atom. Thus, since the alloy contains one electron per atom, the Fermi surface must almost certainly encompass the higher subzones in the ordered condition. Muto[1] has proposed that it just overlaps into the third zone as shown in Fig. 3. Now according to the Peierls[11] formula, such a situation causes an increase in the electron diamagnetism and this could produce the increased diamagnetism of ordered Cu_3Au as observed by Seemann and Vogt.[3] Such a scheme is also not inconsistent with the change in sign of the Hall coefficient on ordering, as observed by Komar and Sidorov.[4]

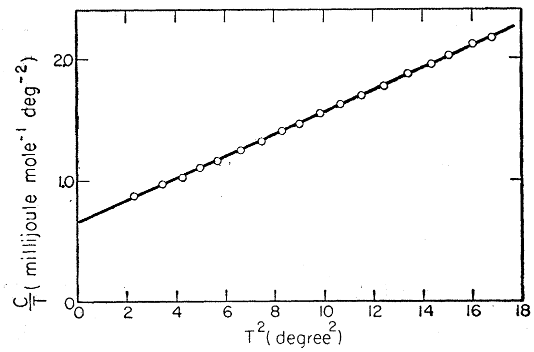

FIG. 1. Heat capacity of disordered Cu_3Au.

Clearly the results of the present work are not in accord with Muto's model, since this leads to a value of γ much smaller than that observed experimentally. It seems likely, therefore, that the Fermi surface extends much further into the third zone, and that the density of states curve for the ordered alloy is as shown schematically in Fig. 4. In this diagram the maxima at A, B, and C correspond to the beginning of contact between the Fermi surface and successive zone boundaries, so that it is here assumed almost to touch certain of the planes bounding the third zone, giving a γ value in excess of that for free electrons, *vide* dotted line in Fig. 4.

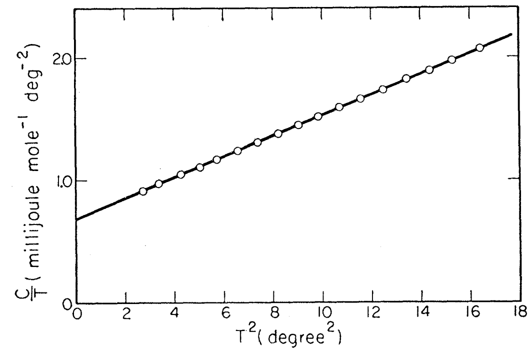

FIG. 2. Heat capacity of ordered Cu_3Au.

This situation could still give an increase in the diamagnetism of the conduction electrons, although one would expect the effect to be relatively small. Inasmuch as the experimental increase in diamagnetism is only 20%, the present overlap scheme must be considered reasonable from this viewpoint. Furthermore, such a band structure could still give a positive Hall coefficient owing to the presence of holes in the 2nd zone. Thus, referring to the general formula[12] for the Hall coefficient in an overlapping band scheme, *viz.*,

$$R=-\frac{1}{ec}\left(\frac{n_1\tau_1^2}{m_1^2}-\frac{n_2\tau_2^2}{m_2^2}\right)\Big/\left(\frac{n_1\tau_1}{m_1}+\frac{n_2\tau_2}{m_2}\right)^2, \tag{5}$$

we have, assuming $n_1=n_2=n$ and $\tau_1=\tau_2$,

$$R=\frac{1}{nec}\left(\frac{m_1-m_2}{m_1+m_2}\right), \tag{6}$$

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[11] R. Peierls, Z. Physik **80**, 786 (1933).

[12] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), second edition, p. 213.

where n is the number of electrons in band 1 and m_1, m_2 are the effective masses in bands 1 and 2 respectively. Clearly (6) can have a positive sign if $m_1 > m_2$ and it is not impossible that such a situation exists in ordered Cu_3Au.

(c) Lattice Heat Capacity

Reference to Table I shows that the Debye temperature for the ordered state is larger than that in the disordered state. This fact is in qualitative agreement with the observation that the elastic constants for Cu_3Au increase on ordering.

It is interesting that our values for the change in Θ on ordering and the magnitude of Θ in the disordered state differ greatly from the corresponding quantities obtained by Bowen[5] from low-temperature resistance measurements on Cu_3Au wires. According to his measurements $\Delta\Theta = 22°K$ and $\Theta_{disordered} = 175°K$ compared to our values of $\Delta\Theta = 7 \pm 4°K$ and $\Theta_{disordered} = 278 \pm 2°K$. Although the value of Θ obtained from resistance measurements seldom agrees exactly with that obtained from low-temperature heat capacity data, the discrepancy is not usually as large as that found here.

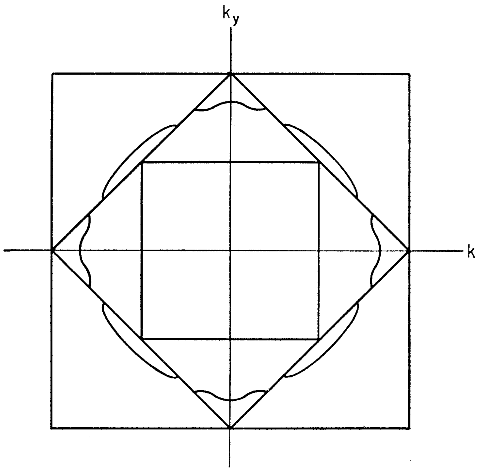

FIG. 3. Cross section of proposed zone structure for Cu_3Au.[1]

Using the data of Siegel[13] on the elastic constants of Cu_3Au, Quimby[6] has computed the values of Debye temperature for the alloy over the temperature range from 20°C to 450°C. At 20°C he finds $\Theta_{ordered} = 272°K$, while at the critical temperature the Debye temperature is found to drop from 249°K to 239°K. Since the Debye temperatures of both copper and gold increase slightly in going from room to liquid helium temperatures, it is not unlikely that a similar increase would occur in Cu_3Au. In the case of copper this increase is 30°K, so that assuming a similar figure for the alloy, we find from Quimby's data extrapolated to absolute zero

$$\Theta_{ordered} \simeq 300°K,$$

which agrees well with the figure obtained here. Assuming that the Θ *versus* T curves for the two states of Cu_3Au are similar, one would also expect a change in Debye temperature at the absolute zero equal to that found at the critical temperature. This gives $\Delta\Theta = 10°K$ in good agreement with our value.

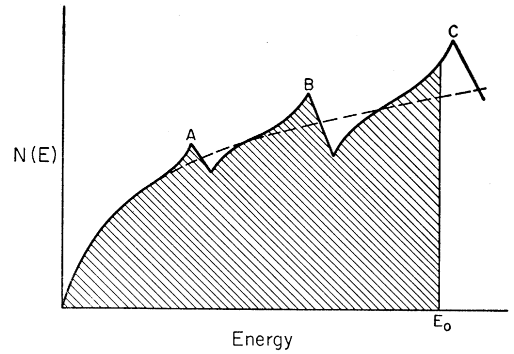

FIG. 4. Proposed density of states curve for ordered Cu_3Au.

IV. CONCLUSION

From studies of the electronic heat capacity, it is concluded that there must be considerable overlap into the third Brillouin zone for Cu_3Au in the ordered state. As expected, the Debye temperature was found to increase on ordering.

ACKNOWLEDGMENTS

Thanks are due to Mr. C. P. Mueller of the Technology Department for preparing the specimen of Cu_3Au used in this experiment. Particular thanks are due to Dr. P. Flinn for his efforts in obtaining x-ray diffraction patterns on the sample and also for many stimulating discussions.

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[13] S. Siegel, Phys. Rev. **57**, 537 (1940).