

Specific heat of ordered CuPt below 30 K

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Measurements were made on a sample containing 50.44-at. % Pt. The electronic specific heat γ is $248.5 \pm 0.5 \mu\text{cal/K}^2\text{g-at.}$ ($1.040 \pm 0.002 \text{ mJ/K}^2\text{g-at.}$) and the low-temperature limiting value of Debye temperature is $313.6 \pm 0.8 \text{ K}$, where the error limits are 95% confidence limits from the statistical analysis. These values correspond to a specific heat nearly double that previously reported for ordered CuPt in the 1–4 K range by Roessler and Rayne. The Debye temperature initially decreases with increasing temperature in the normal way. This behavior is contrasted with that of the ordered equiatomic alloy CuAu I where the Debye temperature initially strongly increases with increasing temperature. Both ordered lattices consist of alternating layers of light and heavy atoms (mass ratio ~ 3). The layers are in the (111) plane for CuPt and in the (100) plane for CuAu I. It had been suggested that the behavior of CuAu I might be evidence for some two-dimensional character in the low-frequency lattice vibrations.

I. INTRODUCTION

Recent specific-heat measurements¹ on the ordered equiatomic alloy CuAu I showed an unusual temperature variation of the Debye temperature which was found to initially increase strongly with increasing temperature. The CuAu I lattice consists of alternating layers of copper and gold atoms in the (100) plane. The mass ratio of the layers is about 3 and it was suggested¹ that the unusual temperature variation of the Debye temperature might be caused by some two-dimensional contributions to the specific heat. (The disordered equiatomic alloy and the ordered alloy CuAu II show a normal temperature variation of Debye temperature. In CuAu II the layered structure is broken up by a long-period superlattice.) To explore this idea further specific-heat measurements have been made on ordered equiatomic CuPt. The lattice consists² of alternating layers of copper and platinum atoms (mass ratio ~ 3) in the (111) plane. The temperature variation of the specific heat at low temperatures is found to be quite normal.

II. EXPERIMENTAL

The alloy was made from Sigmund-Cohn reference-grade platinum supplied as $\frac{1}{4}$ -in.-diam rod and American Smelting and Refining Co. pure copper (99.999%) supplied as $\frac{3}{8}$ -in.-diam rod. The solidus for the equiatomic alloy is about 1500 °C and the melting point of pure platinum is about 1769 °C.^{3,4} These were much higher temperatures than we had previously required in making specific-heat samples and some considerable experimentation was necessary in order to find the best way to prepare the sample. The requirements of high purity and good homo-

geneity were met by induction melting and chill casting. It would have been easy to melt in a graphite crucible but more than 1 wt % (>14 at. %) carbon may dissolve in platinum³ and it was therefore decided to use an alumina crucible. There was still the possibility that significant amounts of impurity⁵ or aluminum⁴ would leach out of the crucible into the molten alloy. With a water-cooled quartz tube between the crucible and induction furnace coil it was impossible to heat the sample sufficiently with the 10-kW power available. To overcome this problem a device of the "focus inductor"⁶ or "concentrator"⁷ type was employed. Initially a split graphite ring was tried but this reacted with the alumina at high temperatures.⁸ Success was achieved with a device constructed from a strip of 0.025-cm-thick molybdenum about 3 cm wide. The strip was bent to form almost a complete turn round, but spaced from, the crucible and was then bent back on itself to form an outer turn just inside the quartz tube. The outer turn was closed by heliarc welding the two ends together. The current induced in the outer turn flows through the inner turn and couples with the contents of the crucible. It was verified that the contents were being stirred by the induced currents. At the same time the molybdenum is heated by the current and forms a double-radiation shield. Melting was done in an atmosphere of helium gas at about atmospheric pressure to minimize evaporation of the copper. The temperature was measured by a thermocouple in an alumina tube (with closed end) passing through the crucible and closing a hole at the bottom. The sample was chill cast by raising this tube. Piping in the cast sample was minimized by using an arrangement similar to that described by Ekin and Deason⁹ in which the sample is cooled only from

the bottom by means of a water-cooled copper hearth. A graphite ring standing on the hearth serves to determine the shape of the sample.

After casting, it was found that some copper-colored material had condensed on the crucible sides and lid. The alloy material obtained weighed 0.6% less than the starting material. The sample was cleaned up by turning off the small pipe area and a region where it had adhered to the hearth. It was then etched in a mixture of equal quantities of concentrated hydrochloric and nitric acids. This left a dark surface which was dissolved away by diluting the acid mixture to about 50% strength with distilled water. The sample was washed in distilled water and then methanol. Some discolored areas were turned off and the cleaning repeated. The sample was then degassed by heating under vacuum while resting in a cleaned alumina crucible. The temperature was taken slowly up to 1200 °C and held here for about 1 h when the vacuum was 5×10^{-6} Torr and some evaporation was starting. The sample was then slowly cooled to room temperature under vacuum. Next the sample, resting in an alumina crucible, was sealed off in a quartz tube under high vacuum. The sample was heated to about 1100 °C for a month to homogenize. Then the ordering procedure started, the order-disorder transition temperature being about 815 °C.² The sample was cooled to about 750 °C and held 3 days, then 5 days at 650 °C, 2 days at 550 °C, 4 days at 450 °C, 3 days at 350 °C, 4 days at 300 °C, 7 days at 250 °C, finally furnace cooling at room temperature. The high-temperature soak should produce domain growth, while the long-range order within domains is improved² by holding at lower temperatures where diffusion is still reasonably fast. Pieces were then carefully cut off top and bottom of the sample for analysis and a flat was turned on the side for making thermal contact with the tray calorimeter. The sample was cleaned up again and weighed 107.54 g.

Quantitative spectrographic analysis by the carrier distillation method¹⁰ showed Fe: 2.7, 2.9; Al: 18.0, 16.6; Si: 1.7, 1.7; and Mo: 1, 1, where the figures are parts per million by weight and refer to each end of the sample. Semiquantitative analysis showed in addition less than 1-ppm Ag. The impurity analysis shows some pickup of Fe and Al from the alumina crucible and a trace of Mo from the inductor. Only the effect of the iron is likely to be seen in the specific-heat results and this will be discussed later. The wet analysis-composition determination gave 50.50- and 50.37-at. % Pt for the top and bottom, respectively. This is quite reasonable in view of the copper loss mentioned above and also shows the sample to be

homogeneous. The mean composition 50.44 at. % Pt leads to a "mean atomic weight" of 129.89 which has been used in the molar specific-heat determination.

The specific-heat measurements were made in two different apparatuses covering the range 0.4–3 and 3–30 K, respectively. For both apparatuses an automatic data acquisition system with on-line computer was used as described elsewhere.^{11,12}

III. RESULTS

Two runs with intermediate warm to room temperature were made in the lower-temperature apparatus. Least-squares fits were made to equations of the form

$$C_p = a_{-2}T^{-2} + \sum_{n=0}^{n=m} a_{2n+1}T^{2n+1}. \quad (1)$$

As described elsewhere^{11,12} points deviating by more than (standard deviation $\times 3$) were rejected as suspect and the process was repeated until no points exceeded the rejection criterion. A good fit with standard deviation of 0.66% was obtained for $m=2$ with three out of 110 points rejected. The coefficients obtained are given in Table I. Percentage deviations of the experimental data from this curve are shown in Fig. 1.

Three runs with intermediate warm to room

TABLE I. Polynomial coefficients representing specific heat $C_p = \sum a_n T^n$. Units cal/K g-at. 1 cal = 4.186 J. Error limits are 95% confidence limits for each coefficient from the statistical analysis. Atomic weight: 129.89.

Results for 0.4–3 K apparatus only. ^a	
a_{-2}	$(0.3 \pm 0.1) \times 10^{-6}$
a_1	$(0.2485 \pm 0.0010) \times 10^{-3}$
a_3	$(0.1452 \pm 0.0071) \times 10^{-4}$
a_5	$(0.17 \pm 0.09) \times 10^{-6}$
Results for both apparatuses. ^b	
a_{-2}	$(0.274453 \pm 0.071) \times 10^{-6}$
a_1	$(0.248482 \pm 0.00052) \times 10^{-3}$
a_3	$(0.150636 \pm 0.0012) \times 10^{-4}$
a_5	$(0.188423 \pm 0.039) \times 10^{-7}$
a_7	$(0.116421 \pm 0.044) \times 10^{-9}$
a_9	$(-0.525699 \pm 0.21) \times 10^{-12}$
a_{11}	$(0.864948 \pm 0.47) \times 10^{-15}$
a_{13}	$(-0.662961 \pm 0.50) \times 10^{-18}$
a_{15}	$(0.196087 \pm 0.20) \times 10^{-21}$

^a The coefficients represent the smoothed specific heat to 0.05%.

^b The coefficients represent the smoothed specific heat to 0.01%.

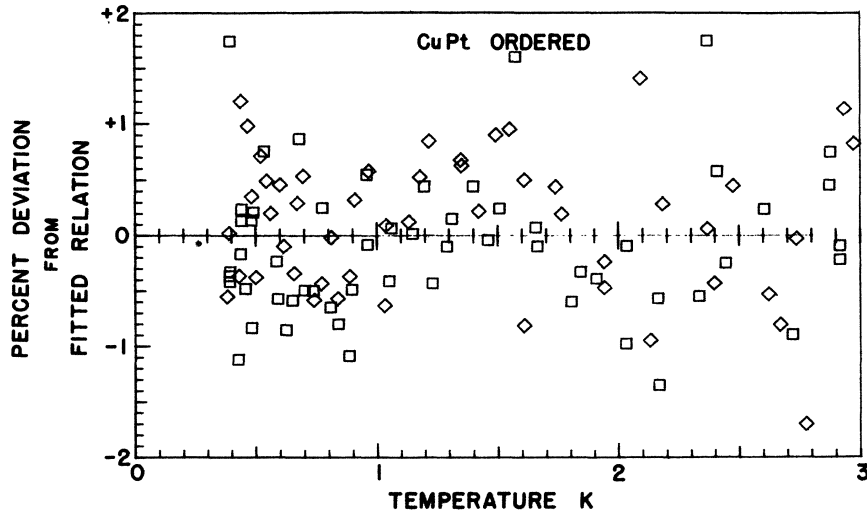


FIG. 1. Percentage deviations of the raw data from the fitted curve for results from the 0.4–3-K apparatus only (Table I).

temperature were made with the 3–30-K apparatus. On the first run there was an extraneous heating problem, probably rf heating, and the points below 10 K were discarded. On the second run there was a power failure when the apparatus had reached about 15 K. There were no problems in the final run. Data from these runs were combined with those from the lower-temperature apparatus and the best fit was obtained with $m=7$ when the standard deviation was 0.57%, and 17 out of 273 points were rejected as suspect. The coefficients obtained are shown in Table I and percentage deviations of the experimental data from this curve are shown in Fig. 2.

All the error limits shown are 95% confidence limits from the statistical analysis and do not include any allowance for systematic error.

IV. DISCUSSION

Comparing the coefficient set (Table I) obtained from the lower-temperature apparatus alone with that from all runs it is seen that the coefficients for the a_{-2} and a_1 terms agree well. The agreement for a_3 and a_5 is less good and the fit for all the runs taken together is preferred. The a_{-2} term probably represents two effects: (a) the nuclear specific heat resulting from the interaction of nuclear electric quadrupole moments with electric field gradients at nuclear sites.¹ Only copper has a quadrupole moment and this is rather small so the magnitude of this term is expected to be much less than in AuCu; and (b) the iron impurity probably carries a localized moment and is likely to contribute to this term via the Kondo or spin-glass

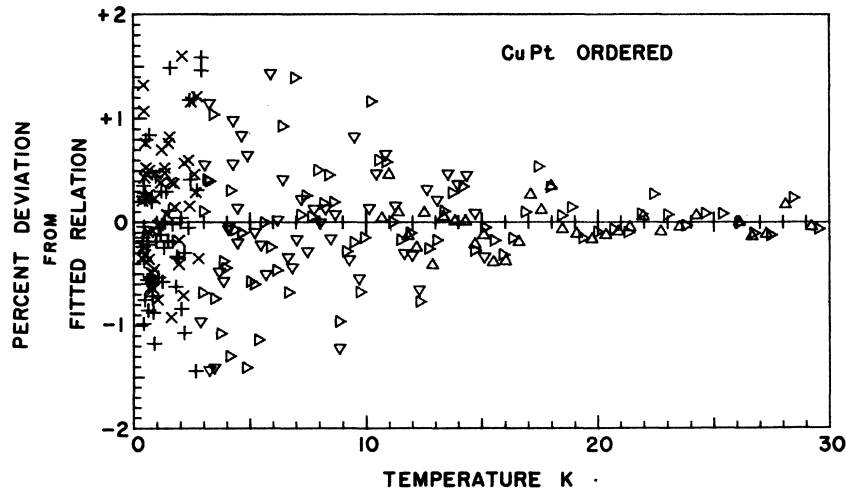


FIG. 2. Percentage deviation of the raw data from the fitted curve for results from both apparatuses (Table I).

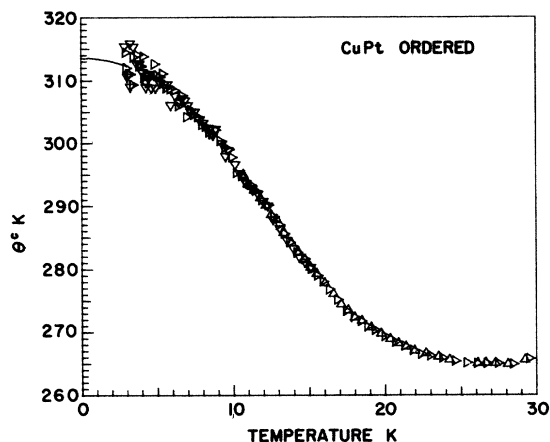


FIG. 3. Debye temperature plot. The experimental points are from the 3–30-K apparatus. Below 3 K the curve is extrapolated to zero using the coefficients for the fit of results from both apparatuses (Table I), but omitting the nuclear and electronic terms.

effects (see discussion in Ref. 13).

The a_1 term is the electronic specific-heat coefficient γ and the result $248.5 \pm 0.5 \mu\text{cal}/\text{K}^2 \text{g-at.}$ ($1.040 \pm 0.002 \text{ mJ}/\text{K}^2 \text{g-at.}$) is much closer to the value for copper¹⁴ than to that for platinum.¹³ This suggests that the electronic specific heat varies with composition in a similar way to that found for AgPd by Montgomery *et al.*,¹⁵ i.e., there is a rapid increase on the platinum side of the phase diagram. There are no ordered phases in the AgPd system and a crude explanation of the variation of γ with composition can be obtained on the rigid-band model, the Pd d band being progressively filled without change of shape as Ag is added. This and more sophisticated models are discussed by Montgomery *et al.*¹⁵ Probably a similar explanation is true for the CuPt system, the effect of ordering being only a small perturbation on the large variation of γ in going from pure Cu to pure Pt.

The a_3 term is related to the low-temperature limiting value of the Debye temperature, Θ_0° and the fit to all runs gives $\Theta_0^\circ = 313.6 \pm 0.8 \text{ K}$. This is much closer to the value for pure copper¹⁴ (344.5 K) than that for pure platinum¹³ (238.7 K). The remaining coefficients in Table I represent higher-order terms in the lattice-specific heat. The a_5 term is related to the initial temperature variation of Θ° . The positive value obtained corresponds to Θ° initially decreasing, and the variation of Θ° with temperature is shown in Fig. 3. This behavior is quite normal and should be contrasted with the initially rapidly increasing Θ° seen¹ in CuAu I. The equiatomic alloys CuAu I and CuPt both order with alternate layers of the light and

heavy atoms (mass ratio ~ 3 in both cases). In the former alloy the layers are in the (100) plane, whereas in the latter they are in the (111) plane. The disordered equiatomic alloy CuAu and the ordered alloy CuAu II (in which the layer structure of CuAu I is broken up by a long-period superlattice) both show¹ relatively normal variations of Θ° with temperature similar to that in Fig. 3 of the present paper. This leads to the suggestion¹ that the specific heat of CuAu I might show some two-dimensional effects (e.g., low-frequency modes in the heavy atom layers). It is clear that no such effect occurs in the CuPt alloy studied here. The composition is slightly (0.44 at.%) off the equiatomic value aimed at, but this is unlikely to completely change the properties. There is no report^{2,16,17} of a long-period superlattice at the equiatomic composition in CuPt (which could break up the layer structure). The original fcc lattice distorts tetragonally in CuAu I and rhombohedrally in ordered CuPt. Ignoring these distortions, the number of like nearest neighbors in CuAu I is four while the number of unlike nearest neighbors is eight. For CuPt the number of like and unlike nearest neighbors is unchanged and remains at six. The layers of different mass are rather further apart (in terms of nearest-neighbor distance) in CuPt than in CuAu I. Thus, on a naive "mass and restoring spring" model, it would have seemed more likely that two-dimensional effects would have been seen in CuPt than in CuAu I. The complete explanation undoubtedly requires a much more sophisticated model and may be related to the anomalous temperature variation of the specific heat of pure gold itself¹⁴ which is associated with positive dispersion in one branch of the lattice-vibration spectrum.¹⁸

Specific-heat measurements on both ordered and disordered equiatomic CuPt in the 1.4–4.2-K range have been reported by Roessler and Rayne.¹⁹ Their specific-heat values for the ordered phase are roughly half those obtained in the present work. The following may be the explanation of the difference. The ratio of the present and earlier γ values is 1.96 and the reciprocal of the ratio of the cube of the Θ_0° values (proportional to the leading term in the lattice-specific heat) is 1.85. Their sample weight is given as 93 g and the "average atomic weight" for CuPt is 129.315. Then $(129.315/93)^2 = 1.93$. The similarity of these three results suggests that an arithmetic error may have been made in Ref. 19 and the reciprocal of the ratio of atomic weight to sample weight was used in evaluating the atomic heat. Further evidence that the results of Ref. 19 are in error by a factor of about 2 can be obtained from the disordered-alloy results. The published Θ_0° value is

higher than the Θ_0° values of either of the components, whereas it is usually intermediate between these values in a single-phase system. Also, the γ value comparison in Table I of Ref. 19 shows it to be unusually low. It would be much more in line with the other alloys considered there if it was doubled.

It is also possible that there is a real difference between the specific-heat sample of Ref. 19 and that used in the present work. That of Ref. 19 was prepared in graphite and it is known³ that platinum can dissolve more than 1 wt% of carbon (>14 at. %). In investigations of pure platinum it was found²⁰ that most of the carbon is precipitated as graphite crystals but perhaps 5 at. % remains in the platinum lattice in atomic form. The author is not aware of any investigation of the properties of the CuPt-C system. However, the same crystal structure is obtained for CuPt samples melted in graphite² as for these prepared by arc¹⁶ and levitation¹⁷ methods.

No attempt was made to measure the disordered alloy in the present work because it was considered unlikely that a quench from above 800 °C

would retain disorder in a massive sample (See Ref. 1). Roessler and Rayne quenched from 887 °C into brine and x-ray examination of the surface showed no superlattice lines. Cooling rates inside the sample would have been less and it is quite likely that some ordering occurred. Mitchell *et al.*¹⁶ found that thin foils quenched from 1000 °C into brine showed distinct superlattice spots.

V. CONCLUSION

The specific heat below 30 K of ordered equi-atomic CuPt is quite normal in contrast to results for another mass-layered ordered lattice CuAu I.

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