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THE EFFECT OF ORDERING ON LATTICE HEAT CAPACITIES:
ORDERED AND DISORDERED AuCu^{*}

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* Paper based on a thesis submitted by Donald T. Hawkins to the University of California, Berkeley, in partial fulfillment of the requirements for the degree Doctor of Philosophy.

ABSTRACT

Heat capacities of pure gold and AuCu in both the ordered and disordered states have been measured between 20 and 298 K by isothermal calorimetry. Values for pure gold agree well with previous data except in the temperature range 70-150 K, where they are 0.5-1.0 percent higher. Combination of the heat capacity data for AuCu obtained in this study with existing high-temperature data yields the configurational entropy of the disordered state:

$S^{\circ}(0\text{K, disordered}) = (1.195 \pm 0.1) \text{ cal g-atom}^{-1} \text{ K}^{-1}$. This value is somewhat lower than the theoretical value of $1.38 \text{ cal g-atom}^{-1} \text{ K}^{-1}$ expected for a completely disordered alloy of this composition. The difference is attributed to short-range order, the existence of which is confirmed by heat of formation measurements.

Ordered and disordered states both show a slight positive deviation from Kopp's Law up to about 175 K; then the deviations become slightly negative. The heat capacity of the disordered state is higher than that for the ordered state to 100 K, above which it becomes slightly lower. In agreement with previous data on AuCu₃ below 4.2 K, little change of Cp on ordering was observed.

1. INTRODUCTION

The low-temperature lattice heat capacity of binary metallic alloys has not been studied extensively. Of 141 alloy systems presented in the unpublished supplement to the compilation by Hultgren, Orr, Anderson, and Kelley,⁽¹⁾ 63 have low-temperature heat capacity data, and only 20 of these 63 systems have data extending above 20 K. Kopp's Law, stating that the heat capacity of an alloy equals the sum of the heat capacities of the constituent elements, is usually applied in the absence of data; whereas large deviations from Kopp's Law can exist, especially in the temperature range where C_p is rising rapidly. No study has been made of the effect of ordering on the lattice heat capacity of an alloy. Heat capacities of ordered Cd-Mg alloys have been measured;^(2, 3) C_p values were very close to Kopp's Law, but no measurements were made on the disordered alloys.

This study was undertaken to observe the effect of ordering on the lattice heat capacity of AuCu and to attempt to calculate ΔS° (0 K), the zero point entropy of the "disordered" alloy. The Au-Cu system was chosen for this work because much previous work at high temperatures has been done on this system,⁽¹⁾ making the extrapolation of C_p to 0 K less uncertain, and also because preparation of the sample does not pose any special difficulties. The heat capacities of both the ordered state and the disordered state were measured by isothermal calorimetry. The degree of short-range order remaining in the disordered sample after quenching was estimated by heat of solution

measurements. In addition to the measurements on the alloys, the C_p of pure gold also was measured.

2. EXPERIMENTAL

Apparatus

The sample holder (calorimeter), shown in figure 1 is made of copper, 0.015 inch thick, and is $5\frac{1}{4}$ inches long and $1\frac{1}{4}$ inches in diameter. A small well for insertion of the calorimeter thermocouple, also of copper, is soldered to the bottom of the can. The upper end of the can, and the $\frac{1}{2}$ inch diameter "chimney", are made of Monel. The lid is soft soldered into place after insertion of the sample. A small pinhole in the lid allows for evacuation and backfilling with ~ 1 atm of helium before final sealing. The outer surface of the can is covered with several thin layers of G. E. 7031 Formvar varnish, wound with 612 turns of silk-wrapped No. 40 (B & S) gold wire, and covered with 0.0025 inch platinum foil. The gold wire serves both as a resistance thermometer and heater during the measurements.

The entire sample holder is placed in a high-vacuum system, shown in figure 2. The sample holder is surrounded by a heavy copper jacket, into the upper portion of which is cast 2500 grams of lead. The jacket serves as a nearly constant temperature shield around the calorimeter. The calorimeter-jacket assembly is suspended inside an outer Monel can, which is connected to a diffusion pump and mechanical forepump, through a liquid nitrogen trap. A vacuum of better than 5×10^{-6} torr was maintained during the measurements.

Cooling was accomplished by submerging the outer can and jacket assembly in a Pyrex dewar vessel containing the coolant. Liquid hydrogen, liquid nitrogen, a dry ice-acetone slurry, and an ice-water mixture were used as coolants. A small amount of helium admitted to the high-vacuum system during cooling provided heat exchange between the system and coolant. The helium was pumped out before commencing measurements.

With this arrangement, measurements could be made between 20 K and room temperature. Facilities were available in the apparatus to reduce the pressure over the liquid hydrogen coolant, thereby making it possible to attain temperatures as low as 15 K, but the extra time and effort needed to gain this small reduction in temperature were judged unnecessary in this study, since the extrapolation of the C_p values to 0 K introduces only a negligible uncertainty in the entropy.

Electrical measurements to the nearest 0.1 microvolt were made using a White double potentiometer. Power was supplied to the resistance thermometer by two, 2 volt, low-discharge cells connected in series. The thermometer current was maintained at approximately 250 microamperes. The resistance of the thermometer was determined by measurements of the current through, and the voltage drop across, the gold resistance wire.

Before a measurement, the temperature of the jacket was adjusted so as to be 1 or 2 degrees above the temperature of the

calorimeter. A small upward, linear, drift in the resistance was observed due to heat transfer. After this drift rate had been satisfactorily established, heating was initiated. During the heating interval, the current from the resistance thermometer battery was directed through a series of "dummy" resistors which had been previously matched to the value of the actual resistance thermometer, thus maintaining a constant, steady discharge of the thermometer battery. During the heating interval, power was supplied to the calorimeter by two 12 volt storage batteries connected in series. Measurements of the voltage and current were made at intervals during this period, in order to determine the power input to the calorimeter. Heating was continued until the temperature of the calorimeter was approximately 1 or 2 degrees above that of the jacket. The length of the heating interval was measured by a timer graduated in divisions of 0.001 minute, and connected to a 110 VAC, 60 hertz tuning fork. The timer was connected in such a way that it was automatically started and stopped simultaneously with the power. After heating ceased, measurements of the resistance were made as before the run, until the final drift rate and temperature were established.

From measurements of the power input, which was calculated from the voltage and current readings by the method described by Gibson and Giauque⁽⁴⁾, and from the temperature rise of the calorimeter, the total heat capacity was calculated. Small

corrections were made to the results to account for power losses in the connecting wires, Newton's law heat transfer, and the fact that the surface temperature of the calorimeter, as measured by the resistance thermometer, is slightly higher than the temperature of the sample because heat is not distributed instantaneously during heating.

A series of measurements on the empty calorimeter provided values for its heat capacity, which were subtracted from the total measured Cp values, with minor corrections for the Cp of the helium gas in the calorimeter, and the varying amounts of solder used to seal the lid, to obtain the Cp of the sample.

During the measurements, the resistance thermometer was routinely calibrated against the copper-constantan calorimeter thermocouple, which had been calibrated against a Pt resistance thermometer standardized by the U.S. National Bureau of Standards.

A complete description of the calorimeter and the method of operation is given in Reference (5), with an earlier description in Reference (6).

Materials

99.999+% Au was obtained from Cominco American, Inc., and 99.999+% Cu was obtained from American Smelting and Refining Company. For both metals, all impurities were below the 1 ppm level, except that the copper had 2 ppm Te impurity.

After the measurements on pure Au were completed, the AuCu alloy was prepared. The pure metals, weighed to the proper composition, were melted together in a graphite crucible under helium in an induction furnace at 1200°C, then poured into a chilled copper mold to form an ingot 1 inch in diameter and 6 inches long. X-ray diffraction showed a single face-centered-cubic phase with a lattice parameter compatible with the composition $x_{\text{Au}} = 0.50$.

The ingot was slightly cold worked, then sealed into an evacuated quartz tube, homogenized at 590°C for 12 days, and quenched into an ice-brine bath. After quenching, the ingot was sawed into rods $\frac{1}{4}$ inch square by 5 inches long. The rods were given an ordering anneal by resealing them under vacuum into a quartz tube, holding them at 365°C for 5 days, and then slowly cooling them to about 200°C over a period of 4 days, reducing the furnace temperature about 25°C every 12 hours. The x-ray diffraction pattern of the rods showed sharp superlattice lines with a well defined, simple tetragonal structure, indicating that the sample was well ordered.

After measuring the C_p of the ordered samples, the rods were again resealed into evacuated quartz tubes. To insure rapidity of quenching, each rod was individually sealed into its own tube. Five small pellets suitable for enthalpy of formation measurements were also prepared and placed into five of the sample tubes, so that the

pellets were given the same heat treatment and quench as the rods. All tubes were then heated to $(475 \pm 2)^\circ\text{C}$ for 9 days and quenched one by one into an ice-brine bath. The tubes shattered on contact with the brine solution, so that quenching was very rapid. The x-ray pattern of the quenched samples showed no evidence of superlattice lines, indicating the absence of long-range order.

However, enthalpy of formation measurements by a liquid tin solution calorimetry showed that short-range order was present. For equilibrium alloys of this composition, Orr⁽¹⁰⁾ found $\Delta H^\circ(320\text{ K}) = -2150\text{ cal} \cdot \text{g-atom}^{-1}$ and $\Delta H^\circ(720\text{ K}) = -1230\text{ cal} \cdot \text{g-atom}^{-1}$. At 320 K, the sample is highly ordered; at 720 K, it is mainly disordered. The difference between the two ΔH° values, $920\text{ cal} \cdot \text{g-atom}^{-1}$, is nearly all due to ordering. For a sample quenched from 873 K, Orr found $\Delta H^\circ(320\text{ K}) = -1630\text{ cal} \cdot \text{g-atom}^{-1}$, so that, even though no long-range order was evidenced by the X-ray data, the sample had gained $400\text{ cal} \cdot \text{g-atom}^{-1}$ of energy during the quench. This energy is attributed to short-range order.

Enthalpy of formation measurements made in the same manner, on the samples used in this work gave $\Delta H^\circ(320\text{ K}) = -1365\text{ cal} \cdot \text{g-atom}^{-1}$, showing them to be highly disordered, but still possessing a short-range ordering energy of $135\text{ cal} \cdot \text{g-atom}^{-1}$.

* Throughout this paper, $\text{cal} = 4.184\text{J}$.

3. RESULTS

Seventy-two runs were made on pure gold. The experimental results are given in table 1, and the smoothed values in table 3. The results are also shown on figure 3, along with the values chosen by Hultgren, Orr, and Kelley⁽¹⁾. The present results agree well with the previous data of Franzosini⁽⁷⁾, Geballe and Giaouque⁽⁸⁾, and Clusius and Harteck⁽⁹⁾, except in the temperature range 70 - 150 K, where the present results are 0.5 to 1.0% higher. Integration of the values obtained in this study yields $S^\circ(298.15 \text{ K}) = 11.397 \text{ cal g-atom}^{-1} \text{ K}^{-1}$, of which $0.012 \text{ cal g-atom}^{-1} \text{ K}^{-1}$ are extrapolated below 20 K, and $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 1440 \text{ cal K}^{-1}$. Values of Hultgren, Orr, and Kelley⁽¹⁾ for the entropy and heat difference are, respectively, $(11.352 \pm 0.05) \text{ cal g-atom}^{-1} \text{ K}^{-1}$, and 1438 cal K^{-1} .

Very little scatter in the data is evident below 200 K. Above this temperature, there is a slight increase in the amount of scatter. The precision of the data is within 0.2% below 200 K, and within 0.5% thereafter. The same general trend was observed with all samples, and may be caused by moisture in the helium used to backfill the calorimeter.

Forty-nine runs were made on the ordered AuCu sample. Figure 4 shows the experimental values, the smoothed curve, and the Kopp's Law line for the ordered alloy. C_p values were smoothed by drawing a smooth curve on the ΔC_p plot, and were extrapolated by extrapolating the ΔC_p curve to 0 K. Integration

of the smoothed values gave $S^\circ(298.15 \text{ K}) - S^\circ(0 \text{ K}) = 9.791$
 $\text{cal g-atom}^{-1} \text{ K}^{-1}$, and $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 1325 \text{ cal g-atom}^{-1}$.

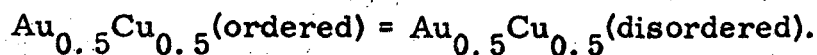
Forty-nine runs were made on the disordered AuCu sample. The Cp and ΔC_p data are shown on figure 5. Extrapolation to 0 K was done in the same manner as for the ordered alloy. Integration of the smooth curve gave $S^\circ(298.15 \text{ K}) - S^\circ(0 \text{ K}) = 9.886 \text{ e. u.}$, and $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K}) = 1323 \text{ cal g-atom}^{-1}$. Experimental results for both ordered and disordered AuCu are given in table 2. Smoothed Cp values, along with the deviations from Kopp's Law, expressed as ΔC_p values, are given in table 3.

With the aid of high-temperature data, the zero point entropy of AuCu can now be calculated. Combination of e.m.f. and entropy of formation measurements at $800 \text{ K}^{(1)}$ yields $\Delta S^\circ(800 \text{ K}) = 1.448$
 $\text{cal g-atom}^{-1} \text{ K}^{-1}$. In the absence of other data, it was assumed that the disordered alloy obeys Kopp's Law to 298.15 K, so that this same ΔS° value applies at that temperature. As shown in table 4, $\Delta S^\circ(0 \text{ K})$ can then be calculated, and is found to equal $1.195 \text{ cal g-atom}^{-1} \text{ K}^{-1}$. A small negative correction to ΔS° must be applied to account for the fact that Kopp's Law is obeyed only to 400 K, rather than to 298.15 K. (See table 3).

One can also calculate ΔS° from thermal data for the equilibrium alloy. ΔH° was measured as a function of temperature by Orr, Luciat-Labry, and Hultgren⁽¹¹⁾, and also by Hertz⁽¹²⁾. They show

a constant ΔH° from 298.15 K to 560 K, followed by a continuous increase in ΔH° from 560 K to 683 K, followed by a first-order transformation at 683 K, and then another slow increase in ΔH° to 800 K, above which ΔH° is constant. The constant regions are an excellent confirmation of Kopp's Law at those temperatures. The increase in ΔH° below the transformation temperature is attributed to the onset of disordering, while that above the transformation is attributed to the disappearance of short-range order. Slopes of the ΔH° versus T curve were taken, yielding ΔC_p values, which were then integrated to give entropies. Assuming that the ordered alloy is completely ordered at 0 K, i. e., that $\Delta S^\circ(0 \text{ K, ordered}) = 0.000 \text{ cal g-atom}^{-1} \text{ K}^{-1}$, the value $\Delta S^\circ(800 \text{ K}) = 1.445 \text{ cal g-atom}^{-1} \text{ K}^{-1}$ can be calculated from the C_p data as shown in table 5. This value is only $0.003 \text{ cal g-atom}^{-1} \text{ K}^{-1}$ lower than that obtained from the high-temperature ΔG° and ΔH° measurements, which is an excellent confirmation of the present data, the high-temperature measurements, and the assumption that the sample was nearly completely ordered. The uncertainty in ΔS° is estimated to be $\pm 0.05 \text{ cal g-atom}^{-1} \text{ K}^{-1}$.

Transferring the $\Delta S^\circ(0 \text{ K})$ value to 298.15 K using the C_p values measured in this work gives $\Delta S^\circ(298.15 \text{ K}) = (1.290 \pm 0.05) \text{ cal g-atom}^{-1} \text{ K}^{-1}$ for the reaction:



4. CONCLUSION

The value of the zero point entropy of AuCu is less than the theoretical value of $-R \ln 2$ for a completely disordered (random) 50-50 alloy, showing that some short-range order exists, although there is no evidence of order from the X-ray data. More rapid cooling rates, such as would be obtained by splat cooling methods, would probably yield a value of $\Delta S^\circ(0 \text{ K})$ closer to the theoretical value.

Ordering had little effect on the heat capacities. At low temperatures, the C_p of the disordered state is slightly higher than that for the ordered state, while at higher temperatures (above approximately 175 K for AuCu), C_p of the ordered state is slightly higher. The maximum C_p difference between the two states is less than $0.05 \text{ cal g-atom}^{-1} \text{ K}^{-1}$. The same general behavior has been observed in recent measurements on AuCu_3 ⁽¹³⁾. One would expect C_p (disordered) to be higher at low temperatures because in a disordered sample, with a less perfect lattice, there is a greater opportunity for low-frequency lattice vibrations to occur, thereby lowering the Debye temperature and raising the heat capacity. Previous work on AuCu_3 ^(14, 15) below 4.2 K also found little effect of ordering on C_p , while work on Ni_3Mn ⁽¹⁶⁾ and CuPt ⁽¹⁷⁾, also below 4.2 K, showed a large effect. It may be that in systems in which a large effect is observed, other effects, such as magnetic effects,

may be responsible. All these studies, however, confirmed the fact that C_p of the ordered state is lower than C_p for the disordered state. At higher temperatures, one would also expect the C_p of the ordered state to be higher, since as the temperature increases, the ordered state releases energy. However, the crossover of C_p (ordered) over C_p (disordered) cannot be attributed to the onset of disordering, since at the low temperatures of this study, diffusion rates of atoms in the alloy are so small as to be negligible. Enthalpy of formation measurements have shown that the disordering does not begin until the temperature is above 560 K.

Mr. Stanley E. Ross and Mr. Hong-il Yoon gave valuable assistance in the measurements. This work was conducted under the auspices of the U.S. Atomic Energy Commission.

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LIST OF FIGURE CAPTIONS

1. Calorimeter Can and Top.
2. Calorimeter Can and Jacket Assembly (High-Vacuum System).
3. Heat Capacity of Gold.
4. Heat Capacity of Ordered AuCu.
5. Heat Capacity of Disordered AuCu.

TABLE 1. Experimental Values for Pure Gold

<u>T/ K</u>	<u>Cp/cal g-atom⁻¹K⁻¹</u>	<u>T/ K</u>	<u>Cp/cal g-atom⁻¹K⁻¹</u>
19.68	0.656	111.61	5.323
21.61	0.876	116.56	5.428
24.22	1.182	121.40	5.439
27.36	1.602	127.02	5.474
27.50	1.624	131.67	5.534
30.88	2.013	136.23	5.563
31.34	2.035	143.29	5.627
35.48	2.365	153.05	5.667
42.69	2.934	158.48	5.709
49.70	3.446	163.78	5.732
58.75	3.985	168.95	5.729
68.54	4.414	176.95	5.785
73.89	4.616	181.89	5.753
78.45	4.675	187.49	5.795
80.79	4.824	191.47	5.785
82.86	4.878	198.57	5.818
85.32	4.931	202.64	5.833
91.14	5.057	202.69	5.836
96.06	5.125	206.74	5.811
101.38	5.195	210.51	5.914
106.55	5.273	210.84	5.867

TABLE 1. (Continued)

<u>T/K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>	<u>T/K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>
214.31	5.879	246.83	5.896
214.90	5.884	247.06	5.993
215.95	5.860	251.24	5.909
219.81	5.848	255.35	5.969
222.21	5.841	258.16	6.016
223.91	5.876	264.44	5.921
227.61	5.928	267.96	5.959
231.44	5.886	273.89	5.973
232.03	5.886	277.38	5.983
235.06	5.882	277.76	5.977
235.65	5.912	281.54	6.015
238.81	5.915	284.00	5.980
239.49	5.946	285.74	6.013
242.55	5.889	290.88	5.998
243.19	5.900	295.70	6.034

TABLE 2. Experimental Values for AuCu

DISORDERED			
<u>T/K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>	<u>T/K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>
25.08	0.784	133.05	5.090
26.97	0.921	138.74	5.182
30.22	1.216	144.72	5.247
33.63	1.462	150.92	5.313
40.36	1.898	156.87	5.325
44.06	2.146	162.75	5.357
48.20	2.450	168.79	5.478
52.05	2.672	174.81	5.427
57.49	2.995	181.55	5.487
64.25	3.379	187.10	5.511
69.59	3.619	193.09	5.586
75.40	3.861	197.93	5.538
80.74	4.083	203.94	5.578
85.50	4.249	209.91	5.654
94.65	4.456	216.37	5.653
100.60	4.579	220.05	5.693
106.60	4.695	227.87	5.736
112.75	4.733	233.96	5.751
118.81	4.916	240.08	5.721
124.64	4.982	246.00	5.779

TABLE 2. (Continued)

DISORDERED

<u>T/K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>
251.87	5.775
258.02	5.765
263.77	5.825
269.87	5.849
274.76	5.815
279.89	5.786
285.80	5.889
291.52	5.843
303.60	5.913

TABLE 2. (Continued)
ORDERED

<u>T/K</u>	<u>Cp/cal g-atom⁻¹K⁻¹</u>	<u>T/K</u>	<u>Cp/cal g-atom⁻¹K⁻¹</u>
24.66	0.678	122.09	4.951
26.31	0.837	128.30	5.059
28.42	1.025	134.03	5.185
31.43	1.248	140.01	5.279
35.12	1.507	145.94	5.271
40.08	1.719	152.04	5.342
46.73	2.264	157.87	5.379
51.49	2.608	163.88	5.358
55.41	2.843	170.28	5.443
60.20	3.114	176.13	5.503
65.83	3.410	187.92	5.579
71.91	3.652	194.15	5.583
77.75	3.947	199.87	5.633
80.30	3.992	203.94	5.628
84.42	4.179	207.82	5.642
91.84	4.264	212.79	5.663
97.94	4.371	216.75	5.684
103.76	4.643	220.97	5.715
109.77	4.775	233.11	5.765
115.77	4.911	238.85	5.748

TABLE 2. (Continued)

ORDERED

<u>T /K</u>	<u>Cp/cal g-atom⁻¹ K⁻¹</u>
245.04	5.829
251.50	5.825
256.14	5.802
262.35	5.824
268.04	5.831
280.18	5.882
286.07	5.899
292.10	5.905
295.98	5.926

TABLE 3. Smoothed Values

<u>T / K</u>	<u>PURE GOLD</u>	<u>DISORDERED AuCu</u>		<u>ORDERED AuCu</u>	
	<u>Cp/cal g-atom⁻¹K⁻¹</u>	<u>Cp</u> <u>cal g-atom⁻¹K⁻¹</u>	<u>ΔCp</u> <u>cal g-atom⁻¹K⁻¹</u>	<u>Cp</u> <u>cal g-atom⁻¹K⁻¹</u>	<u>ΔCp</u> <u>cal g-atom⁻¹K⁻¹</u>
20	0.700	0.496	0.073	0.453	0.030
25	1.230	0.817	0.078	0.779	0.040
30	1.781	1.173	0.087	1.140	0.054
35	2.273	1.535	0.096	1.508	0.069
40	2.712	1.896	0.092	1.854	0.050
45	3.119	2.231	0.085	2.185	0.039
50	3.474	2.554	0.084	2.507	0.037
55	3.783	2.858	0.088	2.815	0.045
60	4.056	3.142	0.105	3.100	0.063
65	4.287	3.413	0.130	3.361	0.078
70	4.481	3.650	0.145	3.600	0.095
75	4.646	3.852	0.142	3.807	0.097
80	4.784	4.030	0.131	3.992	0.093
85	4.902	4.184	0.115	4.158	0.089
90	5.008	4.325	0.101	4.309	0.085
95	5.100	4.455	0.090	4.446	0.081
100	5.181	4.570	0.080	4.566	0.076
110	5.317	4.762	0.060	4.770	0.068
120	5.425	4.927	0.042	4.944	0.059
130	5.513	5.071	0.025	5.090	0.050

TABLE 3. (Continued)

<u>T/K</u>	<u>PURE GOLD</u>	<u>DISORDERED AuCu</u>		<u>ORDERED AuCu</u>	
	<u>Cp/cal g-atom⁻¹K⁻¹</u>	<u>Cp</u>	<u>ΔCp</u>	<u>Cp</u>	<u>ΔCp</u>
		cal g-atom ⁻¹ K ⁻¹		cal g-atom ⁻¹ K ⁻¹	
140	5.588	5.180	0.011	5.211	0.042
150	5.649	5.276	-0.004	5.315	0.035
160	5.701	5.356	-0.015	5.397	0.026
170	5.746	5.424	-0.026	5.466	0.016
180	5.782	5.485	-0.034	5.527	0.008
190	5.813	5.540	-0.040	5.579	-0.001
200	5.839	5.585	-0.045	5.620	-0.010
210	5.861	5.632	-0.049	5.664	-0.017
220	5.882	5.673	-0.052	5.700	-0.025
230	5.900	5.712	-0.054	5.735	-0.029
240	5.919	5.743	-0.055	5.766	-0.032
250	5.937	5.774	-0.056	5.797	-0.033
260	5.955	5.801	-0.055	5.825	-0.031
270	5.973	5.828	-0.052	5.851	-0.029
280	5.993	5.854	-0.049	5.877	-0.026
290	6.012	5.879	-0.046	5.902	-0.023
298.15	6.027	5.895	-0.044	5.920	-0.019
300	6.029	5.903	-0.042	5.929	-0.016

TABLE 4

Calculation of ΔS° (0 K) for Disordered AuCu

<u>Reaction</u>		
(1)	$0.5\text{Au}(298\text{ K}) + 0.5\text{Cu}(298\text{ K}) = \text{Au}_{0.5}\text{Cu}_{0.5}(298\text{ K, disordered})$	$\Delta S^\circ = 1.448 \text{ calg-atom}^{-1}\text{K}^{-1}$
(2)	$\text{Au}_{0.5}\text{Cu}_{0.5}(298\text{ K, disordered}) = \text{Au}_{0.5}\text{Cu}_{0.5}(0\text{ K, disordered}) - [S^\circ(298\text{ K}) - S^\circ(0\text{ K})]$	$= -9.886 \text{ calg-atom}^{-1}\text{K}^{-1}$
(3)	$0.5\text{Cu}(0\text{ K}) = 0.5\text{Cu}(298\text{ K})$	$\frac{1}{2}[S^\circ(298\text{ K}) - S^\circ(0\text{ K})] = 3.962 \text{ calg-atom}^{-1}\text{K}^{-1}$
(4)	$0.5\text{Au}(0\text{ K}) = 0.5\text{Au}(298\text{ K})$	$\frac{1}{2}[S^\circ(298\text{ K}) - S^\circ(0\text{ K})] = 5.676 \text{ calg-atom}^{-1}\text{K}^{-1}$
(5)	Correction to disordered AuCu values between 298 and 400 K	$-0.005 \text{ calg-atom}^{-1}\text{K}^{-1}$
(6)	$0.5\text{Au}(0\text{ K}) + 0.5\text{Cu}(0\text{ K}) = \text{Au}_{0.5}\text{Cu}_{0.5}(0\text{ K, disordered})$	$\Delta S^\circ(0\text{ K}) = 1.195 \text{ calg-atom}^{-1}\text{K}^{-1}$

TABLE 5

Calculation of ΔS° (0 K) for Disordered AuCu Using Heat or Formation Data

<u>Reaction</u>			
(1)	$0.5\text{Au} (0 \text{ K}) + 0.5\text{Cu} (0 \text{ K}) = \text{Au}_{0.5}\text{Cu}_{0.5} (0 \text{ K, ordered})$	$\Delta S^\circ(0 \text{ K})$	$= 0.000 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(2)	$\text{Au}_{0.5}\text{Cu}_{0.5} (0 \text{ K, ordered}) = \text{Au}_{0.5}\text{Cu}_{0.5} (298 \text{ K, ordered})$	$[S^\circ(298 \text{ K}) - S^\circ(0 \text{ K})]$	$= 9.791 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(3)	$\text{Au}_{0.5}\text{Cu}_{0.5} (298 \text{ K, ordered}) = \text{Au}_{0.5}\text{Cu}_{0.5} (683 \text{ K, ordered})$	$[S^\circ(683 \text{ K}) - S^\circ(298 \text{ K})]$	$= 5.759 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(4)	$\text{Au}_{0.5}\text{Cu}_{0.5} (683 \text{ K, ordered}) = \text{Au}_{0.5}\text{Cu}_{0.5} (683 \text{ K, disordered})$	ΔS°	$= 0.490 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(5)	$\text{Au}_{0.5}\text{Cu}_{0.5} (683 \text{ K, disordered}) = \text{Au}_{0.5}\text{Cu}_{0.5} (800 \text{ K, disordered})$	$[S^\circ(800 \text{ K}) - S^\circ(683 \text{ K})]$	$= 1.191 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(6)	$0.5\text{Au} (800 \text{ K}) = 0.5 \text{ Au} (0 \text{ K})$	$-\frac{1}{2} [S^\circ(800 \text{ K}) - S^\circ(0 \text{ K})]$	$= -8.770 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(7)	$0.5\text{Cu} (800 \text{ K}) = 0.5 \text{ Cu} (0 \text{ K})$	$-\frac{1}{2} [S^\circ(800 \text{ K}) - S^\circ(0 \text{ K})]$	$= -7.015 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
(8)	Correction to ordered AuCu values between 298 K and 400 K		$= -0.001 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
<hr/>			
(9)	$0.5\text{Au} (800 \text{ K}) + 0.5\text{Cu} (800 \text{ K}) = \text{Au}_{0.5}\text{Cu}_{0.5} (800 \text{ K, disordered})$	$\Delta S^\circ(800 \text{ K})$	$= 1.445 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
	Experimental value	$\Delta S^\circ(800 \text{ K})$	$= 1.448 \text{ cal g-atom}^{-1} \text{ K}^{-1}$
	Difference		$= -0.003 \text{ cal g-atom}^{-1} \text{ K}^{-1}$

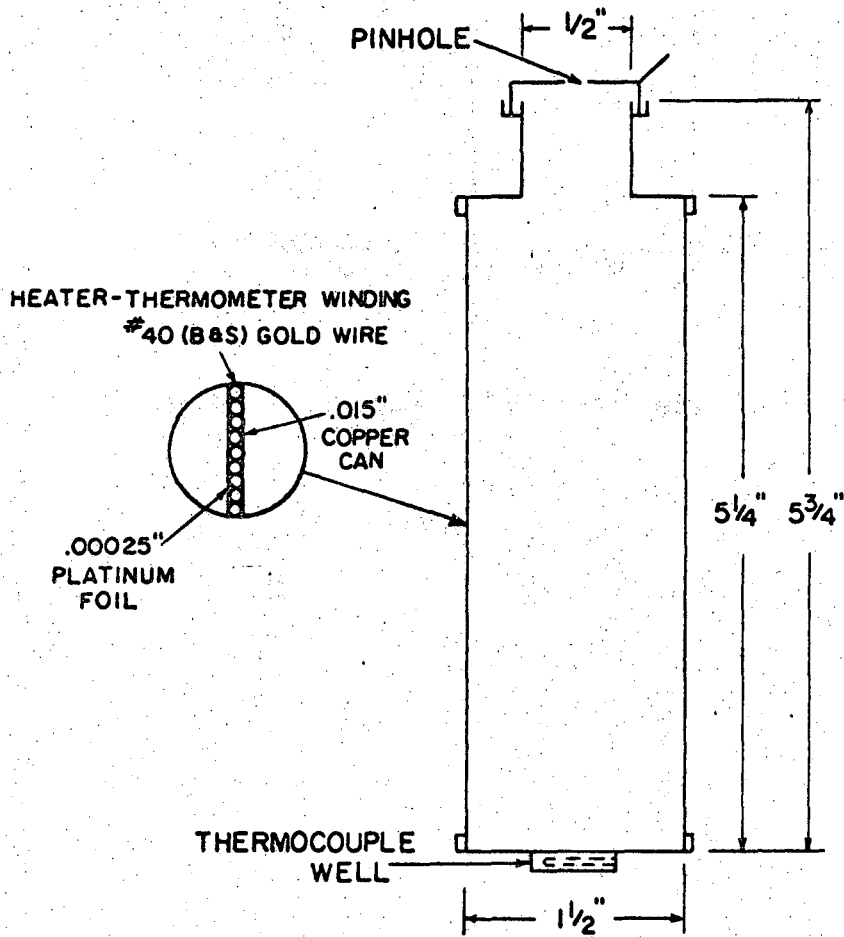


FIGURE 1. CALORIMETER CAN AND TOP.

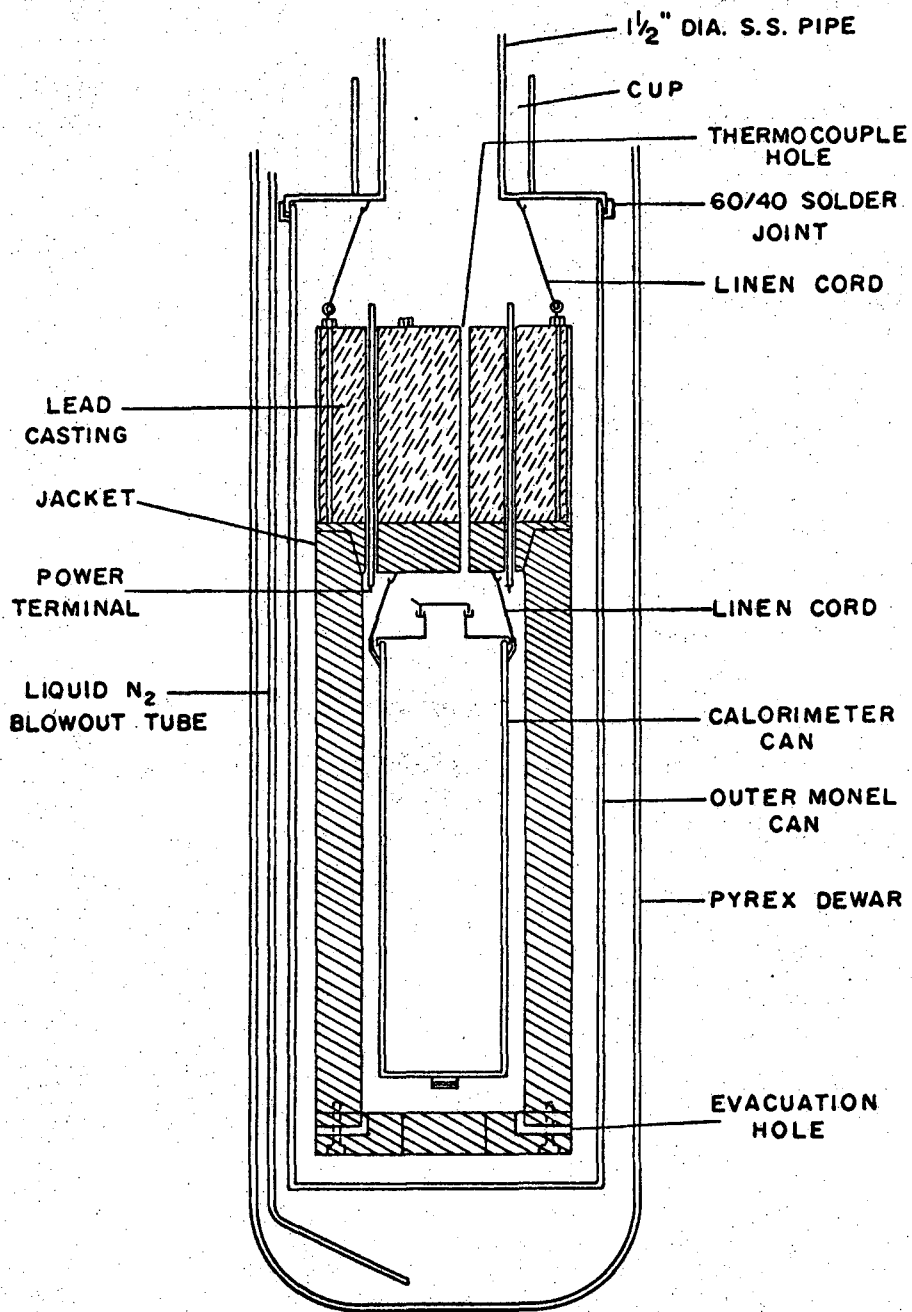


FIGURE 2. CALORIMETER CAN AND JACKET ASSEMBLY.
(HIGH-VACUUM SYSTEM)

XBL 6912-6631

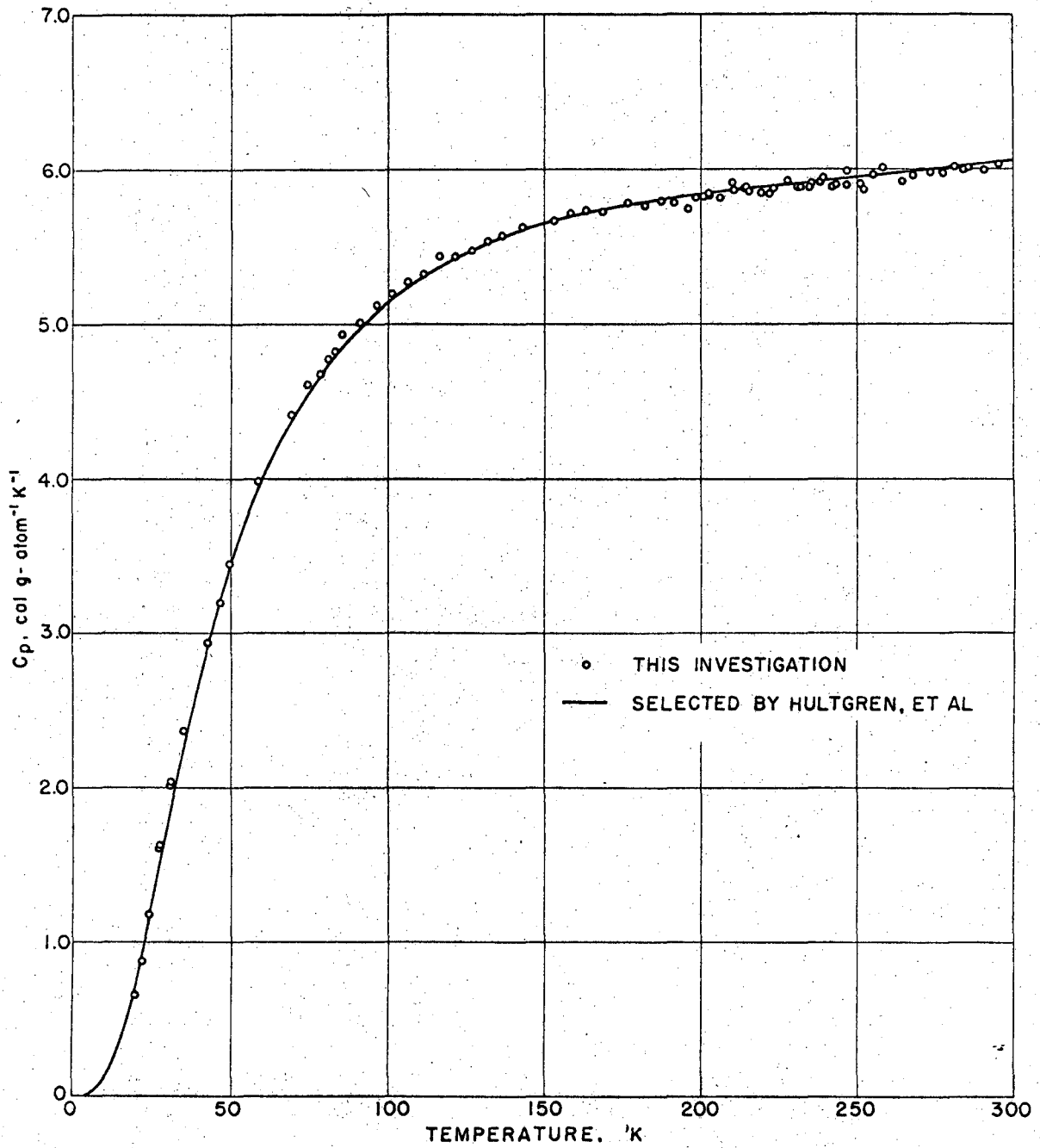


FIGURE 3 HEAT CAPACITY OF GOLD.

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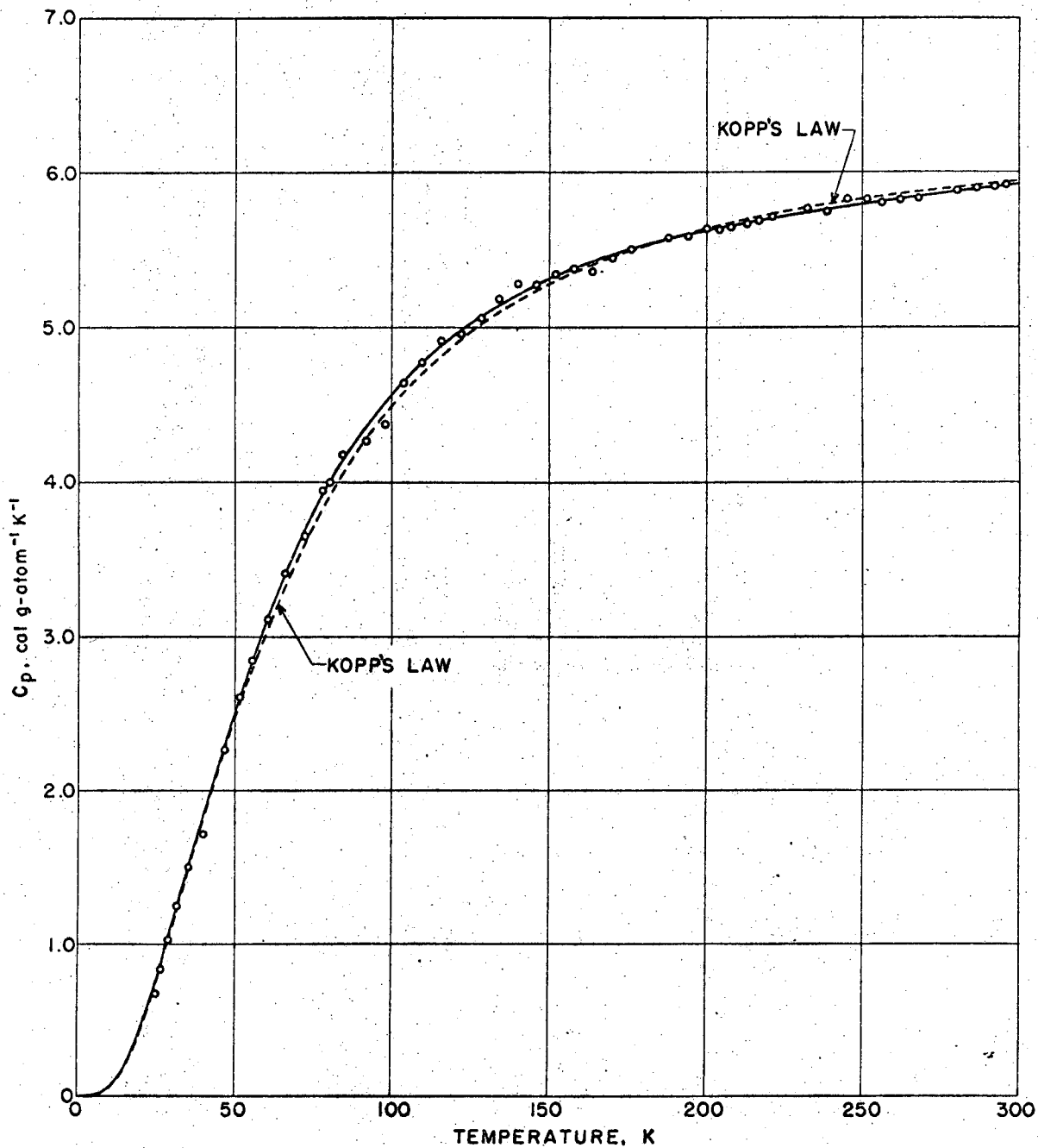


FIGURE 4 HEAT CAPACITY OF ORDERED AuCu.

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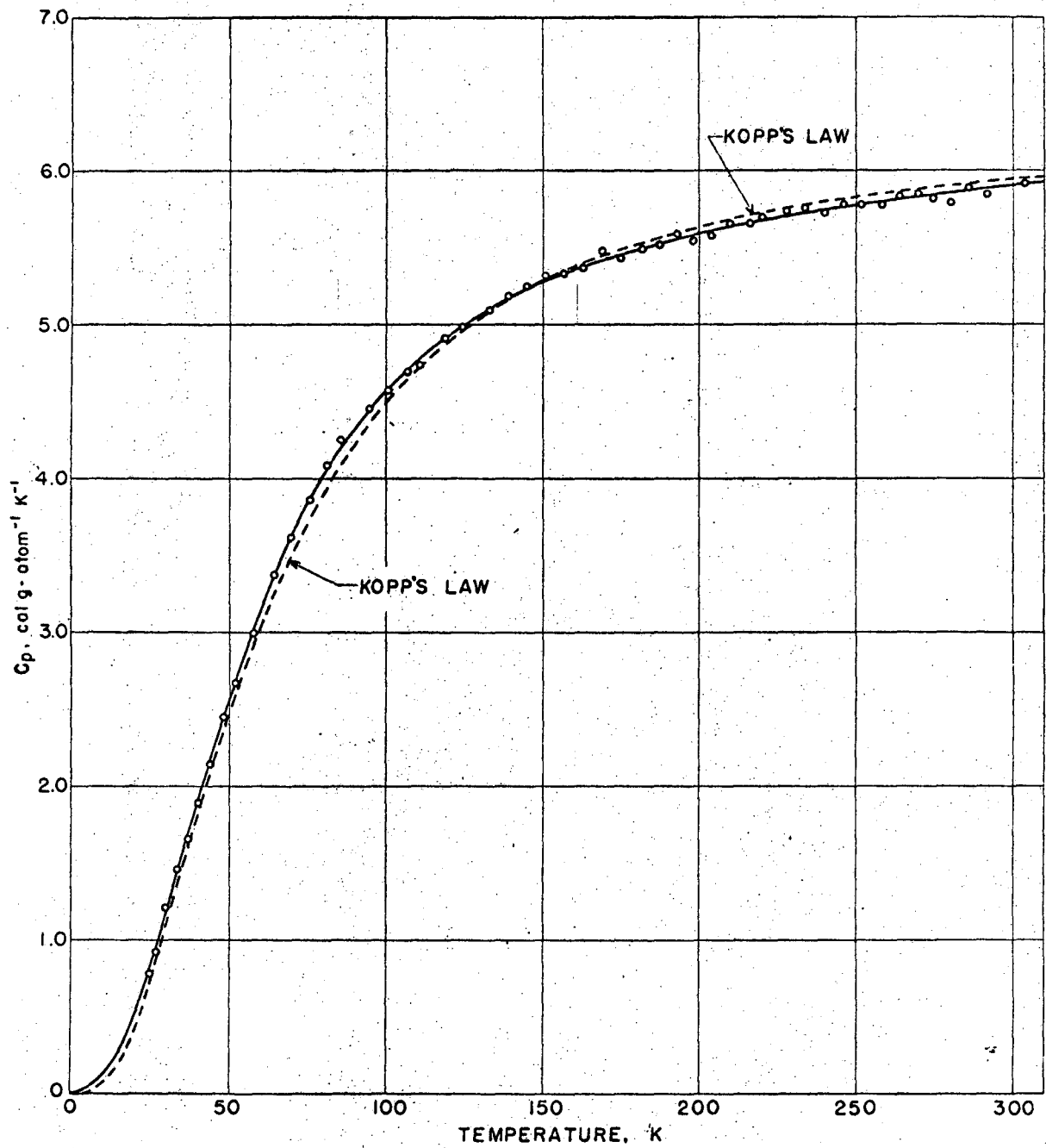


FIGURE 5 HEAT CAPACITY OF DISORDERED AuCu.

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