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# THE EFFECT OF ORDERING ON LATTICE HEAT CAPACITIES OF ORDERED AND DISORDERED $AuCu_3$

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# The Effect of Ordering on Lattice Heat Capacities of Ordered and Disordered $AuCu_3$*

by

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Short Title: The Effect of Ordering on Lattice Heat Capacities

## ABSTRACT

Heat capacities of the $AuCu_3$ alloy in both the ordered and disordered states have been measured between 20 and 298 K by isothermal calorimetry. At low temperatures the ordered state has a lower Cp by up to 6%. This is in accord with expectation that the stronger chemical bonds have a lower vibrational heat capacity. However, above 130°K, the ordered state has a slightly higher heat capacity. It is suggested that this may be due to a dilational contribution to Cp.

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[*] Paper based on a thesis submitted by Hong-il Yoon to the University of California, Berkeley, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

## 1. INTRODUCTION

The effect of the order-disorder transformation in alloys on the lattice vibrations of the atoms, in particular the lattice vibrational heat capacity has not been much investigated.

The specific heat of an oscillator of frequency $\omega$ is given by $Cv = k\,(Z / \sin h\, Z)^2$, where $Z = \hbar\omega / 2kT$. In an assembly of oscillators of different frequencies, all oscillators contribute the same amount to the heat capacities when the temperature is high, but when the temperature is low, only the oscillators of low frequencies give important contributions. One would expect that the disordered state has looser bonds and some irregular lattice arrangements which give low frequency vibrations, therefore lowering the Debye temperature and raising the heat capacity of the disordered alloy at low temperatures.

One study(1) on the composition AuCu showed the effect was small; below 100 K the disordered state had a Cp higher by 10 percent at 20 K, decreasing rapidly to 3 percent at 30 K to 0 percent at 100 K. Above 100 K to 300 K the Cp of the disordered state was lower by less than 1 percent.

It was decided to investigate further the effect of ordering on lattice heat capacity by a similar study of the ordered and disordered states of $AuCu_3$.

## 2. EXPERIMENTAL

The isothermal calorimeter previously described,(1) operating from liquid hydrogen to room temperatures, was used for this study. The alloy was made from 99.999 weight percent pure gold obtained from Cominco American, Inc. and 99.999 weight percent pure copper from the American Smelting and Refining Company. All detectable impurities were below the

1 ppm level except for 2 ppm Te in the copper.

About 1900 g of Au and Cu in the proportion $AuCu_3$ were melted together near 1473 K in a graphite crucible in an induction furnace and cast into a chilled copper mold under an atmosphere of helium. An ingot 2.5 cm in diameter and 15 cm long was formed. The top of the ingot was cut off, filings were taken from both ends, mixed, and given a short strain-anneal. Back-reflection x-ray diffraction lines from this sample were sharp, proving the sample was homogeneous. The ingot was sawed into square rods for placement in the calorimeter.

The rods were given an ordering heat treatment at 620 K for four days, slowly cooled to 400 K over a period of four days, then furnace cooled to room temperature. X-ray diffraction lines showed sharp superlattice lines of the ordered $AuCu_3$ structure.

The rods were placed in the calorimeter and Cp was measured by the usual isothermal calorimetry technique.(1) Results are shown in table 1.

The sample was then removed from the calorimeter and given a disordering heat treatment as follows. Each rod was individually sealed in an evacuated quartz tube and heated to 750 K for ten days. It was then quenched in ice water. An x-ray diffraction pattern showed the absence of superlattice lines. It was decided that the degree of short-range order in the sample could be most easily characterized by determining its heat of formation, which was measured by liquid tin solution calorimetry and found to be $\Delta H = -1150$ cal mole$^{-1}$. Orr(2) found $\Delta H = -1700$ cal mole$^{-1}$ for the completely ordered alloy, -1051 cal mole$^{-1}$,* for the equilibrium

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*Throughout this paper cal = 4.184 J.

(disordered) alloy, and -1180 cal $\text{mole}^{-1}$ for his quenched alloy. This shows the sample was mostly disordered; approximately the same degree of disorder was present as in Orr's quenched alloy.

The sample was again placed in the calorimeter and Cp values shown in table 2 were obtained. The smoothed Cp values of both states are shown in table 3 and figure 1, together with the deviation from Kopp's law.

## 3. DISCUSSION

The results are similar to those found for the effect of ordering at the composition AuCu.(1) The effect of ordering is not great. Below 130 K the ordered state has the lower Cp; above that temperature the reverse is true. The difference of Cp between two states is shown in figure 2.

In this system no magnetic or other anomalies are expected to add to the usual Cp contributions of the electronic, vibrational, and dilation terms.

Low-temperature Cp measurements by Rayne(3) and Martin(4) at liquid helium temperatures show there is substantially no change in the electronic contribution to heat capacity due to ordering of the samples. Both show that the contribution to the vibrational heat capacity is lower in the ordered state; they find the Debye temperature is increased by 7 and 16 K, respectively. This agrees qualitatively with the present results, which show the Debye temperature at 25 K is increased by 3 K, from 239 to 242 K.

Sufficient data are not available to evaluate the dilational contribution $Cp - Cv = 9\,\alpha^2 V T/\chi$ where $\alpha$ is the linear thermal expansion coefficient, V is the atomic volume and $\chi$ is the compressibility. The dilation term was estimated by Nernst-Lindemann(5) equation, $Cp - Cv = 0.0214\, Cp^2(T/T_m)$, where $T_m$ is the melting point of the alloy, 1250 K for $AuCu_3$. This value is negligible at low temperatures such as 25 K (0.00003 cal mole$^{-1}$ K$^{-1}$), but increases to about 3 percent at 298.15 K (0.176 cal mole$^{-1}$ K$^{-1}$).

If the dilation term were larger for the ordered state, it could account for the fact of the higher Cp of the ordered state above 130 K although the vibrational contribution to Cp is less.

Integration of the Cp data gives almost identical heat contents above 0 K for the ordered and disordered states, but the thermal entropy of the disordered state is greater. From these values, and the absolute entropies(6) of Au and Cu, one can calculate the differences of the entropies of formation of both states:

| | ordered | disordered |
|---|---|---|
| $\Delta S^\circ_{298.15} - \Delta S^\circ_0$ | 0.100<br>(±0.1) cal mole$^{-1}$K$^{-1}$ | 0.164<br>(±0.1) cal mole$^{-1}$K$^{-1}$ |

For the ordered state the entropy of formation at 298.15 K is given in the literature(6) as $\Delta S^\circ_{298.15} = \underset{(\pm 0.3)}{0.166}$ cal mole$^{-1}$ K$^{-1}$. This value was obtained from high-temperature measurements of ΔG, calorimetric determinations of ΔH, and Cp measurements above room temperature. From this and the previous value, one finds the entropy of formation of the ordered state at 0 K: $\Delta S^\circ_0 = \underset{(\pm 0.3)}{0.066}$ cal mole$^{-1}$ K$^{-1}$.

Great significance cannot be attached to this number in view of probable experimental error. However, it is just the magnitude to be expected for the configurational entropy of a well-ordered superlattice, which cannot be obtained in the completely ordered state.

For the disordered state the entropy of formation at 298.15 K has not been listed because Cp data in a certain temperature region are missing. At temperatures below the critical temperature of disordering, but high enough to allow diffusion, the Cp of the unstable disordered state cannot be measured by conventional techniques. However, by a reasonable interpolation of Cp between 298.15 K and high temperatures in the disordered region, we have arrived at the value $\Delta S^\circ_{298.15} = (1.126 \pm 0.3)$ cal mole$^{-1}$ K$^{-1}$. From this, as before, we find for disordered $Au_{0.25}Cu_{0.75}$: $\Delta S^\circ_0 = (0.981 \pm 0.3)$ cal mole$^{-1}$ K$^{-1}$. This is a very reasonable value for the configurational entropy of the incompletely disordered sample. The configurational entropy of a completely disordered sample of this composition is $\Delta S^\circ_0 = 1.117$ cal mole$^{-1}$ K$^{-1}$. The difference may be explained in terms of short-range order, the existence of which was confirmed by heat of formation measurements with tin solution calorimetry.

## ACKNOWLEDGMENTS

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Table 1. Experimental heat capacities for ordered $Au_{0.25}Cu_{0.75}$

| T, K | Cp cal mole$^{-1}$ K$^{-1}$ | T, K | Cp cal mole$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 25.54 | 0.508 | 154.03 | 5.187 |
| 27.06 | 0.597 | 160.02 | 5.205 |
| 28.30 | 0.668 | 166.09 | 5.259 |
| 29.54 | 0.753 | 171.85 | 5.325 |
| 31.06 | 0.805 | 177.85 | 5.363 |
| 33.37 | 0.982 | 183.86 | 5.372 |
| 36.62 | 1.166 | 189.80 | 5.419 |
| 39.97 | 1.397 | 197.42 | 5.432 |
| 44.68 | 1.649 | 202.26 | 5.489 |
| 49.75 | 1.992 | 206.12 | 5.492 |
| 55.07 | 2.336 | 209.58 | 5.505 |
| 61.22 | 2.689 | 213.74 | 5.520 |
| 67.04 | 3.003 | 217.92 | 5.538 |
| 73.07 | 3.323 | 222.05 | 5.558 |
| 78.95 | 3.546 | 226.61 | 5.547 |
| 84.08 | 3.723 | 231.10 | 5.622 |
| 87.41 | 3.858 | 235.32 | 5.628 |
| 91.43 | 3.991 | 240.26 | 5.653 |
| 95.99 | 4.119 | 250.05 | 5.682 |
| 101.60 | 4.284 | 258.74 | 5.736 |
| 107.74 | 4.404 | 262.04 | 5.725 |
| 113.82 | 4.505 | 266.76 | 5.760 |
| 119.83 | 4.649 | 271.62 | 5.772 |
| 126.08 | 4.780 | 277.54 | 5.800 |
| 132.14 | 4.847 | 283.97 | 5.805 |
| 136.41 | 4.972 | 289.64 | 5.804 |
| 142.11 | 5.027 | 295.65 | 5.832 |
| 148.01 | 5.087 | | |

Table 2. Experimental heat capacities for disordered $Au_{0.25}Cu_{0.75}$

| T, K | Cp cal $mole^{-1}$ $K^{-1}$ | T, K | Cp cal $mole^{-1}$ $K^{-1}$ |
|---|---|---|---|
| 23.65 | 0.459 | 143.59 | 5.026 |
| 25.68 | 0.554 | 149.82 | 5.097 |
| 27.02 | 0.630 | 155.85 | 5.186 |
| 28.36 | 0.707 | 161.62 | 5.213 |
| 29.77 | 0.803 | 167.45 | 5.232 |
| 31.68 | 0.919 | 169.90 | 5.276 |
| 33.90 | 1.058 | 173.67 | 5.292 |
| 40.00 | 1.400 | 179.85 | 5.338 |
| 45.72 | 1.765 | 184.39 | 5.352 |
| 51.63 | 2.143 | 192.19 | 5.382 |
| 58.45 | 2.565 | 198.22 | 5.454 |
| 63.78 | 2.816 | 205.86 | 5.486 |
| 69.59 | 3.128 | 211.57 | 5.503 |
| 75.92 | 3.455 | 215.66 | 5.547 |
| 81.51 | 3.596 | 221.48 | 5.564 |
| 80.20 | 3.664 | 225.50 | 5.613 |
| 83.51 | 3.703 | 229.99 | 5.614 |
| 87.34 | 3.870 | 235.73 | 5.648 |
| 91.51 | 4.008 | 241.82 | 5.636 |
| 95.65 | 4.159 | 247.81 | 5.683 |
| 101.59 | 4.286 | 253.65 | 5.678 |
| 107.45 | 4.395 | 259.65 | 5.685 |
| 110.93 | 4.530 | 265.97 | 5.710 |
| 114.32 | 4.580 | 271.74 | 5.730 |
| 119.59 | 4.652 | 279.46 | 5.796 |
| 126.04 | 4.757 | 286.39 | 5.786 |
| 131.55 | 4.859 | 289.42 | 5.804 |
| 137.63 | 4.926 | 295.51 | 5.795 |

Table 3. Smoothed heat capacity values for $Au_{0.25}Cu_{0.75}$.

| | ORDERED | | | DISORDERED | |
|---|---|---|---|---|---|
| T, K | Cp | ΔCp | T, K | Cp | ΔCp |
| | cal mole$^{-1}$ K$^{-1}$ | | | cal mole$^{-1}$ K$^{-1}$ | |
| 20 | 0.284 | 0.019 | 20 | 0.302 | 0.038 |
| 25 | 0.509 | 0.024 | 25 | 0.533 | 0.048 |
| 30 | 0.771 | 0.030 | 30 | 0.801 | 0.060 |
| 35 | 1.073 | 0.037 | 35 | 1.107 | 0.070 |
| 40 | 1.398 | 0.047 | 40 | 1.434 | 0.082 |
| 45 | 1.731 | 0.065 | 45 | 1.762 | 0.096 |
| 50 | 2.044 | 0.085 | 50 | 2.069 | 0.110 |
| 55 | 2.354 | 0.097 | 55 | 2.382 | 0.125 |
| 60 | 2.634 | 0.104 | 60 | 2.671 | 0.141 |
| 65 | 2.902 | 0.108 | 65 | 2.949 | 0.155 |
| 70 | 3.142 | 0.107 | 70 | 3.200 | 0.165 |
| 75 | 3.349 | 0.105 | 75 | 3.409 | 0.165 |
| 80 | 3.583 | 0.102 | 80 | 3.636 | 0.155 |
| 85 | 3.759 | 0.096 | 85 | 3.805 | 0.142 |
| 90 | 3.930 | 0.090 | 90 | 3.969 | 0.129 |
| 95 | 4.090 | 0.083 | 95 | 4.123 | 0.116 |
| 100 | 4.234 | 0.077 | 100 | 4.261 | 0.104 |
| 110 | 4.471 | 0.064 | 110 | 4.488 | 0.081 |
| 120 | 4.669 | 0.052 | 120 | 4.677 | 0.060 |
| 130 | 4.835 | 0.039 | 130 | 4.836 | 0.040 |
| 140 | 4.978 | 0.027 | 140 | 4.972 | 0.021 |
| 150 | 5.101 | 0.014 | 150 | 5.092 | 0.005 |
| 160 | 5.194 | 0.002 | 160 | 5.182 | -0.010 |
| 170 | 5.283 | -0.011 | 170 | 5.271 | -0.023 |
| 180 | 5.349 | -0.024 | 180 | 5.340 | -0.035 |
| 190 | 5.417 | -0.037 | 190 | 5.409 | -0.045 |
| 200 | 5.461 | -0.049 | 200 | 5.455 | -0.055 |
| 210 | 5.509 | -0.060 | 210 | 5.506 | -0.063 |
| 220 | 5.555 | -0.067 | 220 | 5.552 | -0.070 |
| 230 | 5.600 | -0.070 | 230 | 5.594 | -0.076 |
| 240 | 5.645 | -0.067 | 240 | 5.630 | -0.081 |
| 250 | 5.690 | -0.063 | 250 | 5.670 | -0.083 |
| 260 | 5.726 | -0.059 | 260 | 5.703 | -0.083 |
| 270 | 5.762 | -0.054 | 270 | 5.736 | -0.080 |
| 280 | 5.794 | -0.049 | 280 | 5.770 | -0.074 |
| 290 | 5.829 | -0.043 | 290 | 5.806 | -0.067 |
| 298.15 | 5.856 | -0.039 | 298.15 | 5.835 | -0.062 |
| 300 | 5.863 | -0.038 | 300 | 5.842 | -0.059 |

### Table 3. (Continued)

| ORDERED | DISORDERED |
|---|---|
| $S^\circ_{298.15} - S^\circ_0 = 8.880$ cal mole$^{-1}$ K$^{-1}$ (±0.1) | $S^\circ_{298.15} - S^\circ_0 = 8.945$ cal mole$^{-1}$ K$^{-1}$ (±0.1) |
| $H^\circ_{298.15} - H^\circ_0 = 1258$ cal mole$^{-1}$ (±15) | $H^\circ_{298.15} - H^\circ_0 = 1259$ cal mole$^{-1}$ (±15) |
| $\Delta S^\circ_{298.15} - \Delta S^\circ_0 = 0.100$ cal mole$^{-1}$ K$^{-1}$ (±0.1) | $\Delta S^\circ_{298.15} - \Delta S^\circ_0 = 0.165$ cal mole$^{-1}$ K$^{-1}$ (±0.1) |

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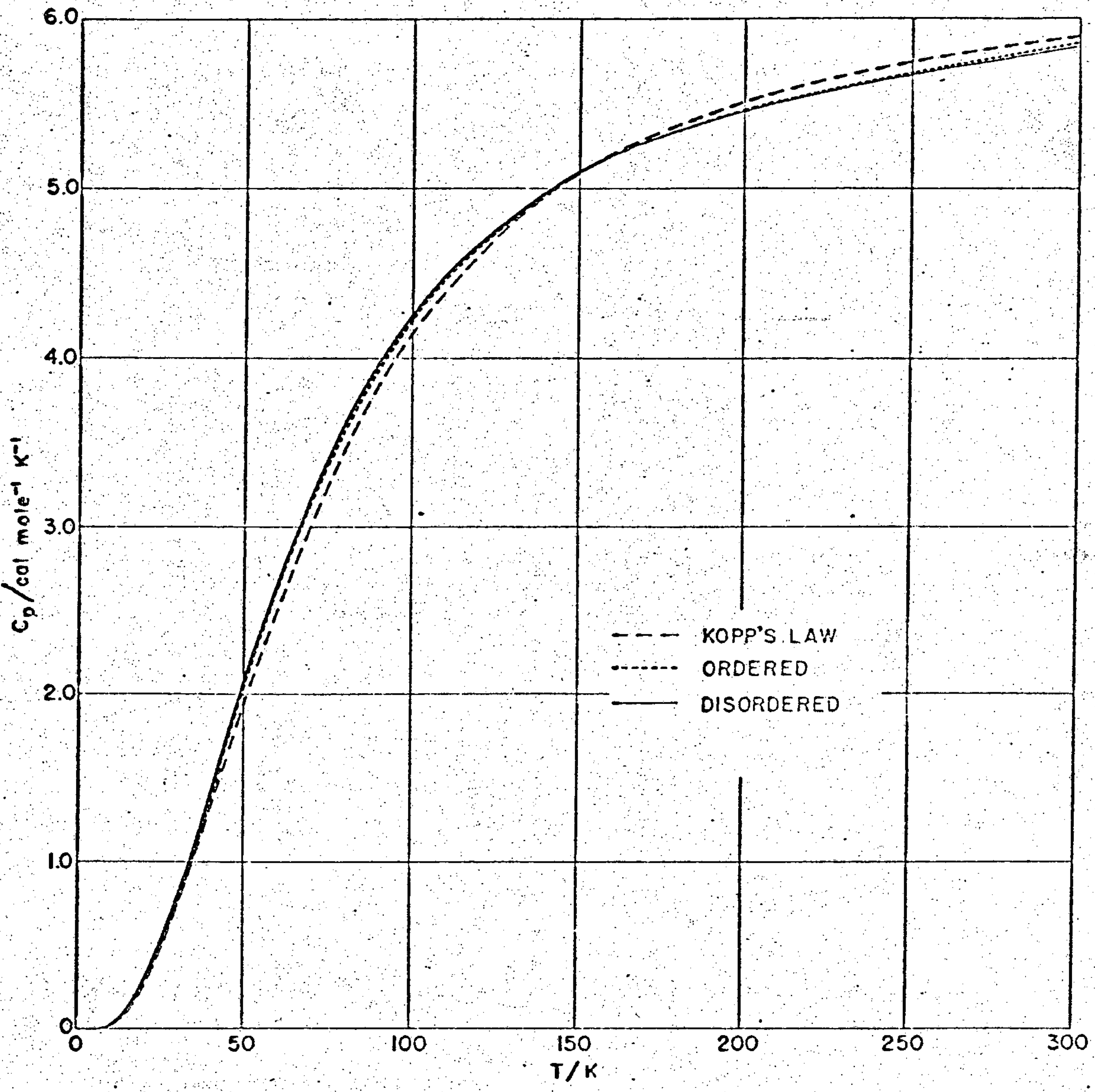

FIG. 1 HEAT CAPACITY OF ORDERED AND DISORDERED $Au_{0.25}Cu_{0.75}$

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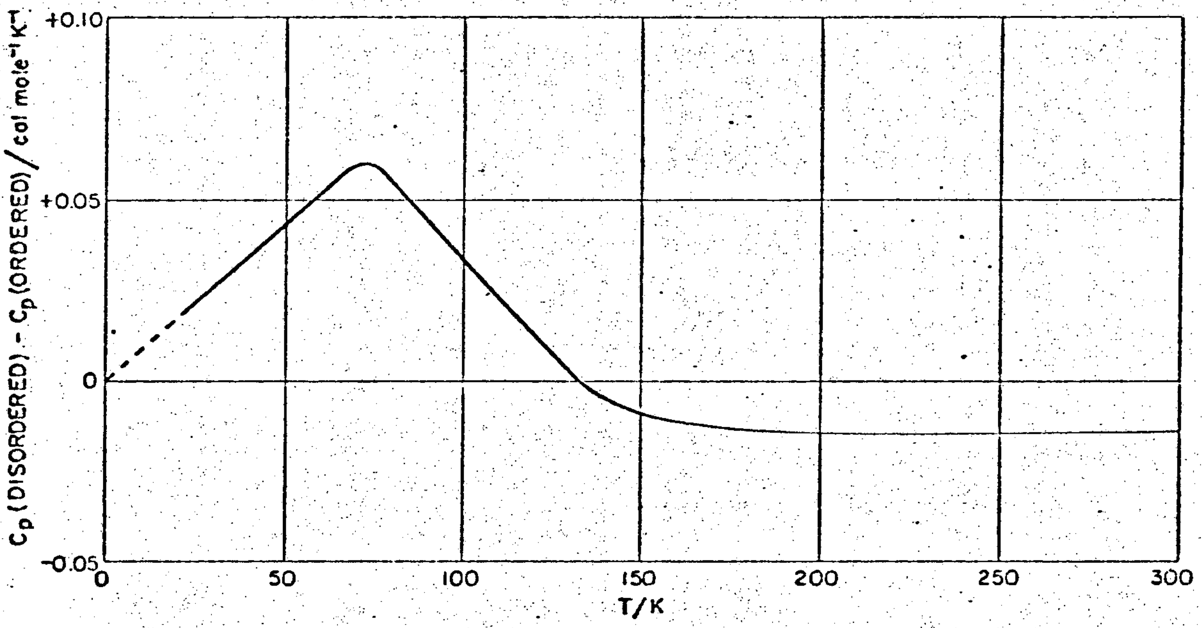

FIG. 2 HEAT CAPACITY DIFFERENCE BETWEEN THE TWO STATES OF $Au_{0.25}Cu_{0.75}$

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