Specific heat of copper-gold alloys below 30 K

Douglas L. Martin

Division of Physics, National Research Council of Canada, Ottawa, K1A 0R6, Canada (Received 17 February 1976)

Specific-heat measurements in the 0.4- to 30-K range on both ordered and disordered alloys containing 25, 50, and 75 at.% Au are reported and analyzed into nuclear, electronic, and lattice components. The disordered alloys containing 25 and 50 at.% Au are unstable at room temperature and slowly order with specific-heat "half-lives" of about 2000 and 100 days, respectively. No instability was observed for the 75-at.% Au alloy which has a lower order/disorder transition temperature ($\sim 200^{\circ}$ C) than the others ($\sim 400^{\circ}$ C). Order apparently improved in the long-period superlattice CuAu II when held at room temperature although CuAu I is the stable phase here. Results on CuAu₃ are consistent with the existence of a CuAu₃ II (long-period superlattice) ordered phase as well as the simple ordered structure CuAu₃ I. The above results suggest that antiphase domain boundaries cannot move at room temperature although long-range order can improve here. Also, that both random and periodic antiphase domain structures have similar effects on the specific heat. The lattice specific heats of the ordered phases CuAu I and CuAu₃ I were anomalous, both showing an initial increase (~ 10 and $\sim 5\%$, respectively) in Debye temperature as temperature is increased from zero. For CuAu I this could be a two-dimensional effect related to the layered structure. A similar explanation may be attempted for the case of CuAu₃ I.

I. INTRODUCTION

The Cu-Au system shows a continuous range of solid solubility. Apart from the disordered [facecentered-cubic(fcc)] phase a number of ordered phases are also formed. (Information on the phase diagram published up to 1964 is summarized in Ref. 1.) Around the compositions Cu_3Au and CuAu, fcc ordered phases are formed with order/ disorder transition temperatures of about 390 and 200 °C, respectively, at the stoichiometric compositions. These are designated Cu₂Au I and CuAu₃ I. A modification of the ordered Cu₃Au structure may be formed by introducing a onedimensional periodic antiphase domain boundary structure. This long-period superlattice form, designated Cu₃Au II, only occurs for alloys with Au contents significantly above stoichiometric. Until recently, information regarding the ordered phase of CuAu₃ was less certain because the lowtransition temperature makes the ordering very sluggish. However, it is now clear² that a longperiod superlattice (CuAu₃ II) may also be formed even at the stoichiometric composition. Around the equiatomic composition the ordered phase (formed below about 385 °C) consists of alternating planes of Cu and Au atoms, respectively, perpendicular to the c axis. This gives rise to a tetragonal distortion of the originally fcc lattice (c < a)and the structure is designated CuAu I. For ordering temperatures in the 385-410 °C range a onedimensional long-period superlattice is formed in a direction perpendicular to the c axis by introducing an antiphase boundary every five of the

original CuAu I unit cells. This gives rise to an orthorhombic lattice, designated CuAu II.

Earlier specific-heat measurements on Cu_3Au , CuAu, and $CuAu_3$ reported^{3,4} from this laboratory were in the 0.4–3-K temperature range and yielded results for the nuclear specific heat (a nuclear electric quadrupole effect), the electronic specific-heat coefficient (γ), and the low-temperature limiting value of Debye temperature (Θ_0^c). Apart from the disordered alloys, the phases Cu_3Au I, CuAu I, and CuAu II were also measured and significant effects of ordering on the various specific-heat components were observed. It was also found that the disordered equiatomic alloy was unstable and slowly ordered.

The present work was initially undertaken to examine the variation of lattice specific heat with temperature up to 30 K. Fortuitously there had been a time interval of several years between the earlier and present work and it was found that the disordered Cu₃Au alloy sample (stored at room temperature) had partly ordered in this time. An investigation of the secular variation of the specific heat of initially disordered Cu₂Au and CuAu was therefore undertaken to observe the ordering kinetics. It was also noted that the specific heat of the CuAu II sample had changed in a manner supporting an earlier observation⁵ that the long-range order improves on storage at room temperature although the equilibrum phase here is CuAu I. Finally, little work had been done previously on CuAu₃ and a more detailed investigation was therefore made.

Some aspects of this work have been reported briefly at two conferences.⁶

II. EXPERIMENTAL

The specific-heat measurements were made in two different apparatuses covering the ranges 0.4-3 K and 3-30 K, respectively. For both apparatuses an automatic data acquisition system with on-line computer was used as described elsewhere.^{7,8}

All but one of the specific-heat samples were those used previously^{3,4} and the earlier publications should be consulted for preparation and analysis data. The disordered CuAu₃, CuAu I (Sample 2 of Ref. 4), CuAu II and CuAu disordered (Sample 1 of Ref. 4), and ordered Cu_3Au samples were used without further heat treatment. The weights were unchanged from those previously reported^{3,4} except for the last mentioned which was reduced to 142.43 g after some pieces had been removed for analysis. The "disordered" Cu₃Au sample was redisordered twice (once for each apparatus) by sealing the cleaned⁹ sample, resting on an alumina crucible, in a Pyrex tube under vacuum, heating to about 410 °C for 15 h, and quenching into water (when the Pyrex breaks). The sample was then cleaned and dried under vacuum. The final weight of this sample was 157.84 g. A similar procedure was followed in redisordering the CuAu disordered (Sample 2 of Ref. 4) except that it was held at 500 °C for 16 h and then 421 °C for 2 h before quenching. Since this composition was known to be unstable, it was rapidly mounted on the calorimeter and cooling to liquid-nitrogen temperature began 1.63 h after the quench. The weight was 189.73 g. The earlier work⁴ had shown that there was no significant difference in the specific heats of freshly quenched CuAu samples of different mass and shape, thus indicating that the quenching procedure is satisfactory.

An additional sample of CuAu₃ was made to serve as the "ordered" sample. The starting materials and initial preparation were exactly as for the "disordered" sample.⁴ After casting, a porous "pipe" region was found and was drilled out with careful cleaning afterwards. The sample, supported on an alumina crucible, was then degassed under vacuum by heating to 750 $^\circ\!C$ and holding for 18 h and then heating to 850 °C for 3 h the final vacuum here being 4×10^{-6} mm Hg. The sample was then furnace cooled and, still supported on an alumina crucible, sealed under vacuum in a quartz tube and held for 37 d at 860 °C to homogenize. The sample was quenched from this temperature (quartz tube smashed). Samples for analysis were then taken from each end of the sample. [The composition analysis showed 25.01 and 25.02 at.% Cu, respectively, leading to an average atomic weight of 163.59. Quantitative spectrographic analysis

showed (ppm by wt.): Ni,0.042, 0.008; Fe, 0.57, 0.41; Si, 0.13, 0.11; Cr, 0.067, 0.057; Mn, 0.024, 0.025. Semiquantitative spectrographic analysis showed (ppm by wt.): Ag, 0.1 to 1.0, 0.1 to 1.2. (In each case the two figures refer to the two ends of the sample.)] The sample was then ordered. This was done by sealing under vacuum in Pyrex (sample resting on an alumina crucible) and heating to 150 $^{\circ}$ C, holding for 28 d, then cooling to 120 $^{\circ}$ C and holding 7 d, to 100 °C and holding 7 d, to 80 °C and holding 50 d, and finally cooling to room temperature. The prequenching and heat treatment is very similar to that recommended by Korevaar¹⁰ and, as shown by later work,² should produce longrange order without a long-period superlattice. The sample weighed 178.60 g.

As discussed previously,⁴ no x-ray examination of the specific-heat samples was made because information is only obtained on the surface of the samples and not the bulk which may be misleading in the case of a quenched sample. Also (see Sec. IV), x-ray results are much less sensitive to the early stages of ordering than is the specific heat.

When the CuAu disordered Sample 1 was being cleaned, after the specific-heat measurements reported here were completed, a small crystal fell out of the sample. Examination of this sample under a microscope showed many large cracks at grain boundaries. The CuAu disordered Sample 2 (about half the diameter of Sample 1) had no large cracks but either slight cracking or deep etching at some grain boundaries. The CuAu I Sample 1 was finely crystalline and appeared as the CuAu disordered Sample 2. However, the CuAu I Sample 2 was much more coarsely crystalline and had some large cracks. The CuAu II sample was also coarsely crystalline with some large cracks. There were no cracks in the Cu₃Au or CuAu, samples although one of these had been acid-cleaned many more times than most of the CuAu samples and some had very large crystals. Grain-boundary cracking at the equatomic composition has been observed by Syutkin, Syutkina, and Yakovleva¹¹ and, in agreement with the present observations, was found only to occur in large grained samples. The cause is strain following the formation of a noncubic lattice on ordering. Syntkin et al.¹¹ found that the boundaries between domains are undulating, which prevents failure. Stresses are therefore relieved by cracking at grain boundaries.

III. RESULTS

The new measurements presented here will be analyzed in conjunction with those published previously.^{3,4} The temperature scales employed below 3 K in the present and earlier work probably differ slightly giving rise to small differences in measured specific heat.⁸ In addition the standard deviation of the present results below 3 K may be worse than in the earlier^{3, 4} data because the automatic data-acquisition system is unable to directly identify errors caused by noise and relies on a statistical method to reject suspect data.⁸ As will be seen, this method only works well when the data being analyzed contain many experimental points. In the summary of results (Tables I and II) the number of points rejected and the number accepted for analysis are given. None of the rejected points are shown in the diagrams.

The raw experimental data will be shown as percentage deviation plots from least-squares fitted polynomial relations. The relation fitted to all the data is

$$C_{p} = HT^{-2} + \gamma T + \sum_{n=1}^{n=m} a_{2n+1}T^{2n+1}, \qquad (1)$$

where the first term represents the nuclear specific heat, the second the electronic specific heat, and the last the lattice specific heat. The first term in the lattice specific-heat expansion is connected to the low-temperature limiting value of the Debye temperature by the following:

$$a_3 = 464.3/(\Theta_0^c)^3,$$
 (2)

where the coefficient a_3 is in calorie units. The parameters from the least-squares fits to the data from the 0.4–3-K range apparatus are given in Table I which also contains a symbol key for some of the figures and a summary of the earlier results.^{3, 4}

The data from the 3-30-K range apparatus are analyzed together with the 0.4-3-K range results by least-squares fitting Eq. (1) to the combined data. In some cases the maximum value of m available on our computer (m = 10) was insufficient to get a good fit to the data over the whole temperature range and it was necessary to fit over a shorter range. An overlapping fit

$$C_{p} = \sum_{n=0}^{n=m} a_{n} T^{n}$$
(3)

was used to fit the remaining, higher-temperature, data. The nuclear, electronic, and lattice specific-heat values obtained from this analysis are given in Table II which also contains a symbol key for the percentage deviation plots. All the coefficients obtained from the fits of either Eq. (1) or Eq. (3) are given in Table III.

Note that all error limits are 95% confidence limits obtained from the statistical analysis and do not include any allowance for systematic error. For most samples two specific-heat runs were made with an intervening warm to room temperature as a check on reproducibility and stability.

Some notes on the course of measurements on each sample and the results obtained follow.

1. Cu₃Au disordered. The first series of measurements in the 3-30-K range did not join with the results below 3 K which had been obtained several years earlier. This suggested that the sample had partially ordered. The sample was therefore heat-treated to redisorder (see Sec. II) and the measurements repeated. Another run was made some 100 d later to check the course of ordering. The earlier³ measurements in the below 3 K region had been made some 30 d after the sample had been disordered and a significant change of heat capacity had probably occurred in this time. The sample was therefore heat-treated again to redisorder and fresh measurements were made in the below 3 K region. The results obtained for the freshly redisordered sample are summarized in Tables I-III and deviations are shown in Figs. 1 and 2.

2. Cu_3Au ordered. A single additional run was made below 3 K and curve fitted (Table I), the earlier³ runs on the same sample being shown as deviations from this fit (Fig. 1). Although the recent run has a bad scatter, the good agreement between 0.7 and 1.5 K, the most accurate temperature range of the earlier work,³ suggested no significant change of thermal capacity in the intervening years. Runs were therefore made in the 3–30-K range and curve fitted with all the below 3 K data, results being shown in Tables II and III and Fig. 2.

3. Cu_3Au partly ordered. Figure 3 is a plot of the differences of all the Cu_3Au results from the curve for the ordered alloy (Table III). The number attached to each curve gives the number of days since heat treatment.

4. CuAu disordered. The instability of this alloy had been detected in the earlier work⁴ and it was not considered necessary to make further measurements below 3 K. The new results above 3 K join well with the earlier data⁴ as seen in Fig. 4. The curve fit results are given in Tables II and III.

5. CuAu I ordered. The new results above 3 K join well with the earlier data⁴ below 3 K. See Fig. 4 and Tables II and III.

6. CuAu II ordered. The new results above 3 K did not join well with the earlier data⁴ below 3 K suggesting that the sample had undergone further ordering in the several-year interval between measurements. Results of two new runs below 3 K are given in Fig. 5 and Table I and the earlier data below 3 K are shown as differences from these results. The recent runs below and above 3 K were curve fitted together (see Fig. 4 and Tables II and III).

							QN	QN	Standard	Syml	ools Fios
	ш		μ cal	units			of points	of points	deviation	1.5.7	2-4
Sample	[Eq. (1)]	Н	λ	<i>a</i> ₃	a_5	θ ⁶ Κ	rejected	in fit	%		6,8,9
Cu ₃ Au disordered ^a	1	0.46 ± 0.04	162.4 ± 0.4	24.72 ± 0.12	•	265.8 ± 0.5	9	119	0.50	ΔQ	+
Cu ₃ Au disordered ^{b, c}	1	0.24 ± 0.04	161.8 ± 0.3	23.84 ± 0.12	:	269.1 ± 0.5	0	104	:	:	×
Cu ₃ Au ordered ^a	1	0.34 ± 0.11	155.2 ± 1.0	20.76 ± 0.30	:	281.7 ± 1.4	0	59	1.02	+	+
Cu ₃ Au ordered ^b	1	0.11 ± 0.05	156.1 ± 0.5	20.03 ± 0.17	:	285.1 ± 0.8	0	101	•	×	×
CuAu disordered ^d .e	2	1.59 ± 0.04	161.7 ± 0.4	43.75 ± 0.39	0.10 ± 0.06	219.8 ± 0.6	0	105	•	÷	×
CuAu I ^d .e	က	2.28 ± 0.06	173.9 ± 0.7	53.85 ± 0.98	-2.3 ± 0.3	205.1 ± 1.3	0	97	:	:	×
CuAu II ^a	2	2.28 ± 0.06	141.5 ± 0.6	32.31 ± 0.45	0.29 ± 0.06	243.1 ± 1.1	ę	120	0.53	0 *	+
CuAu II c.d	2	2.13 ± 0.03	142.2 ± 0.3	33.38 ± 0.25	0.28 ± 0.04	240.5 ± 0.6	0	196	•	×	×
CuAu ₃ disordered ^a	2	1.63 ± 0.20	162.0 ± 2.0	72.33 ± 1.67	0.16 ± 0.23	185.9 ± 1.5	0	59	0.93	0	+
CuAu ₃ disordered ^d	73	1.55 ± 0.03	163.3 ± 0.4	71.98 ± 0.34	0.14 ± 0.05	186.2 ± 0.3	0	201	:	×	×
CuAu ₃ ordered ^a	c,	2.27 ± 0.09	169.9 ± 1.1	75.81 ± 1.43	-2.85 ± 0.45	183.0 ± 1.2	5	119	0.48	$\nabla \Delta$	*
CuAu ₃ quenched ^d from 850 °C	73	1.81 ± 0.05	152.7 ± 0.5	59.83 ± 0.48	0.07 ± 0.07	198.0 ± 0.5	0	66	:	:	×
^a Present results.					^d Ref. 4.	No percentag	e standard d	eviation was	output by the	-moo	
^b Ref. 3. No percentag	e standard d	eviation was o	utput by the c	-mc	puter prog	ram used at tl	his time nor	were any po	ints rejected		
puter program used at th Now considered to be	ns time nor partly orden	were any poin red.	ts rejected.		Sample	.2					

TABLE I. Summary of experimental results in the 0.4 to 3 K range.

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Sample	m [Eq. (1)]	Range of fit	Н	μcal γ	units a3	a 5	6 ⁶ K	No. of points rejected	No. of points in fit	Standard deviation %	Figs. 2,3	Syml Figs. 4,6	ools Figs. 8,9	Fig. 13
Cu ₃ Au disordered Cu ₃ Au ordered	10	0-30 K 0-30 K	0.46 ± 0.04 0.17 ± 0.03	162.3 ± 0.3 155.6 ± 0.3	24.85 ± 0.15 20.54 ± 0.10	-0.02 ± 0.01 -0.03 ± 0.01	265.4 ± 0.5 282.8 ± 0.5	7 17	201 325	0.43 0.41	$\diamond^{\nabla}_{\Delta}$::	::	
CuAu disordered CuAu I CuAu II	10 10	0-25 K 0-15 K 0-22.5 K	1.63 ± 0.04 2.16 \pm 0.06 2.35 \pm 0.05	161.1 ± 0.3 175.9 ± 0.6 140.5 ± 0.4	$\begin{array}{c} 44.68 \pm 0.19 \\ 50.80 \pm 0.53 \\ 33.28 \pm 0.25 \end{array}$	-0.11 ± 0.02 -1.35 ± 0.11 $+1.16 \pm 0.03$	218.2 ± 0.3 209.1 ± 0.7 240.7 ± 0.6	5 3 11	207 205 260	0.31 0.38 0.47		⊳	:::	▶ □ 0
CuAu ₃ disordered CuAu ₃ ordered	10 10	0-25 K 0-15 K	1.59 ± 0.03 2.10 ± 0.08	162.8 ± 0.3 172.9 ± 0.8	72.60 ± 0.18 71.27 ± 0.81	$+0.02\pm0.02$ -1.45±0.18	185.6 ± 0.2 186.8 ± 0.7	34 8	413 229	0.31 0.51	::	::	$\Diamond \nabla$ $\Box \Delta$	+ x
	m [Eq. (3)]	Range of fit												
CuAu disordered CuAu I	2	20-30 K 10-30 K						00	22 72	0.08				
cuAu II CuAu ₃ disordered CuAu ₃ ordered	~ ~ 8	17.5-30 K 20-30 K 10-30 K						001	35 26 73	0.08 0.08 0.20				

7. CuAu partly ordered. All the data obtained on the CuAu alloys in the present work together with some of the data from Ref. 4 are shown in Fig. 6 as differences from the curve fit for CuAu I (Table III), the number on each curve being the number of days since heat treatment. The curve labeled 2327 is from measurements on CuAu disordered Sample 1 of Ref. 4, the curves 0, 19, and 109 are from measurements on disordered Sample 2 of Ref. 4.

8. $CuAu_3$ disordered. A single additional run was made below 3 K and curve fitted (Fig. 7 and Table I). The earlier results⁴ are shown as differences from this curve fit (Fig. 7) and suggest no significant change in sample state in the several years between measurements. The results above 3 K were fitted with all the below 3 K data and are illustrated in Fig. 8 as deviations from the fit given in Table III.

9. $CuAu_3$ ordered. This was a new sample. Results are shown in Figs. 7, 8 and Tables I-III.

10. $CuAu_3$ high-temperature quench. Figure 9 shows the difference of all results obtained for this composition from the fitted relation for the ordered alloy. The results⁴ obtained with a hightemperature quench are quite different from those labeled ordered and disordered. This will be discussed later.

IV. DISCUSSION

In an attempt to prevent ordering during or after the quench (facilitated by quenched-in lattice vacancies¹²), the "disordered" samples were quenched from a temperature just above the order/ disorder transition temperature where there is considerable short-range order. The "disordered" samples are therefore unlikely to be perfectly disordered. Similarly, the "ordered" samples are unlikely to be perfectly ordered because of the presence of antiphase domain boundaries, following nucleation and growth from many different points, and the fact that perfect order would only exist at very low temperatures where the chance of atomic movement is so slight as to inhibit its attainment.

Systematic deviation of all the measured points from the fitted curves, especially noticeable in the 3-30-K range, results from imperfections in the temperature scale used.⁷ Other deviations would correspond to the fitted function being a poor representation of the data. On some curves there is an increased scatter of points in the 12-K region. This corresponds to the area of minimum sensitivity of the germanium thermometer used and is where results are most likely to be influenced by zero shift in the ac Bridge.

TABLE II. Summary of experimental results in the 0.4 to 30 K range.

TABLE III. Polynomial coefficients representing specific heat $C_p = \sum a_n T^n$ units cal/K g atom. J = 4.186. Error limits are 95% confidence limits for each coefficient from the statistical analysis. Each polynomial represents the smoothed specific heat to within 0.01% up to 30 K unless a different range is specified.

Cu ₃ Au disordered	Cu_3Au ordered (Cu_3Au I)
$a_{-2} = (0.464035147\pm0.038)\times10^{-6}$ $a_1 = (0.162280881\pm0.00033)\times10^{-3}$ $a_3 = (0.248486843\pm0.0015)\times10^{-4}$ $a_5 = (-0.213604300\pm0.13)\times10^{-7}$ $a_7 = (0.165761249\pm0.033)\times10^{-8}$ $a_9 = (-0.154326809\pm0.038)\times10^{-10}$ $a_{11} = (0.738550366\pm0.23)\times10^{-13}$ $a_{13} = (-0.212525221\pm0.080)\times10^{-15}$ $a_{15} = (0.378080767\pm0.17)\times10^{-18}$ $a_{17} = (-0.405710770\pm0.20)\times10^{-21}$ $a_{19} = (0.240235049\pm0.13)\times10^{-24}$ $a_{21} = (-0.602098661\pm0.36)\times10^{-28}$	$\begin{array}{rl} a_{-2} &= (0.167\ 699\ 72\ \pm 0.030) \times 10^{-6} \\ a_1 &= (0.155\ 583\ 75\ \pm 0.000\ 25) \times 10^{-3} \\ a_3 &= (0.205\ 353\ 83\ \pm 0.0010) \times 10^{-4} \\ a_5 &= (-0.283\ 633\ 72\ \pm 0.075) \times 10^{-7} \\ a_7 &= (0.107\ 110\ 79\ \pm 0.018) \times 10^{-8} \\ a_9 &= (-0.779\ 936\ 14\ \pm 0.21) \times 10^{-11} \\ a_{11} &= (0.323\ 832\ 29\ \pm 0.12) \times 10^{-13} \\ a_{13} &= (-0.864\ 857\ 84\ \pm 0.41) \times 10^{-16} \\ a_{15} &= (0.148\ 166\ 36\ \pm 0.082) \times 10^{-18} \\ a_{17} &= (-0.155\ 786\ 56\ \pm 0.096) \times 10^{-21} \\ a_{19} &= (0.910\ 155\ 70\ \pm 0.61) \times 10^{-28} \end{array}$

CuAu disordered

(0 to 22.5 K)	(22.5 to 30 K)	
$a_{-2} = (0.16320905 \pm 0.0037) \times 10^{-5}$	$a_0 = (-0.239889450) \times 10^3$	
$a_1 = (0.16105381 \pm 0.00032) \times 10^{-3}$	$a_1 = (0.492416662) \times 10^2$	
$a_3 = (0.44675573 \pm 0.0019) \times 10^{-4}$	$a_2 = (-0.356778906) \times 10$	
$a_5 = (-0.107\ 676\ 57\ \pm 0.021) \times 10^{-6}$	$a_3 = (0.698\ 905\ 754) \times 10^{-1}$	
$a_7 = (0.74681023 \pm 0.073) \times 10^{-8}$	$a_4 = (0.437\ 105\ 889) \times 10^{-2}$	
$a_9 = (-0.89667111 \pm 0.11) \times 10^{-10}$	$a_5 = (-0.286445509) \times 10^{-3}$	
$a_{11} = (0.54417077\pm0.092)\times10^{-12}$	$a_6 = (0.634953655) \times 10^{-5}$	
$a_{13} = (-0.196\ 0.085\ 21\ \pm\ 0.043) \times 10^{-14}$	$a_7 = (-0.512597636) \times 10^{-7}$	
$a_{15} = (0.43531081 \pm 0.12) \times 10^{-17}$	•	
$a_{17} = (-0.584\ 079\ 11\ \pm 0.20) \times 10^{-20}$		
$a_{19} = (0.43439919 \pm 0.17) \times 10^{-23}$		
$a_{21} = (-0.13749012 \pm 0.063) \times 10^{-26}$		

CuAu I	CuAu II
$\begin{array}{l} (0 \text{ to } 12.5 \text{ K}) \\ a_{-2} = (0.215 682 86 \pm 0.0058) \times 10^{-5} \\ a_1 = (0.175 926 69 \pm 0.000 59) \times 10^{-3} \\ a_3 = (0.507 992 56 \pm 0.0053) \times 10^{-4} \\ a_5 = (-0.134 586 92 \pm 0.011) \times 10^{-5} \\ a_7 = (0.560 333 20 \pm 0.093) \times 10^{-7} \\ a_9 = (-0.119 039 12 \pm 0.038) \times 10^{-8} \\ a_{11} = (0.152 656 23 \pm 0.085) \times 10^{-10} \\ a_{13} = (-0.118 457 35 \pm 0.11) \times 10^{-12} \\ a_{15} = (0.535 337 74 \pm 0.90) \times 10^{-15} \\ a_{17} = (-0.126 237 51 \pm 0.42) \times 10^{-17} \\ a_{19} = (0.010 455 182 \pm 0.11) \times 10^{-12} \\ a_{21} = (0.005 025 914 8 \pm 0.12) \times 10^{-22} \\ (12.5 \text{ to } 30 \text{ K}) \\ a_0 = (-0.510 810 0) \\ a_1 = (0.204 278 1) \\ a_2 = (-0.331 334 2) \times 10^{-1} \\ a_3 = (0.277 409 9) \times 10^{-2} \\ a_4 = (-0.117 429 7) \times 10^{-3} \\ a_5 = (0.254 037 9) \times 10^{-5} \\ a_6 = (-0.223 042 8) \times 10^{-7} \end{array}$	(0 to 20 K) $a_{-2} = (0.235 379 00 \pm 0.0048) \times 10^{-5}$ $a_1 = (0.140 469 12 \pm 0.000 42) \times 10^{-3}$ $a_3 = (0.332 792 84 \pm 0.0025) \times 10^{-4}$ $a_5 = (0.162 475 10 \pm 0.031) \times 10^{-6}$ $a_7 = (0.033 320 123 \pm 0.13) \times 10^{-8}$ $a_9 = (0.174 335 24 \pm 0.25) \times 10^{-10}$ $a_{11} = (-0.367 335 32 \pm 0.26) \times 10^{-12}$ $a_{13} = (0.267 434 43 \pm 0.15) \times 10^{-14}$ $a_{15} = (-0.100 173 50 \pm 0.053) \times 10^{-16}$ $a_{19} = (-0.226 747 35 \pm 0.12) \times 10^{-22}$ $a_{21} = (0.101 957 85 \pm 0.056) \times 10^{-25}$ (20 to 30 K) $a_0 = (0.314 417 138) \times 10^3$ $a_1 = (-0.975 377 161) \times 10^2$ $a_2 = (0.129 145 650) \times 10^2$ $a_3 = (-0.946 025 130)$ $a_4 = (0.414 151 293) \times 10^{-1}$ $a_5 = (-0.108 332 413) \times 10^{-2}$ $a_6 = (0.156 762 135) \times 10^{-7}$
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CuAu ₃ disordered	$CuAu_3$ ordered ($CuAu_3$ I)	
(0 to 22.5 K)	(0 to 12.5 K)	
$a_{-2} = (0.1590301\pm0.0028)\times10^{-5}$	$a_{-2} = (0.2096820 \pm 0.0080) \times 10^{-5}$	
$a_1 = (0.1628342 \pm 0.00026) \times 10^{-3}$	$a_1 = (0.1728794 \pm 0.00084) \times 10^{-3}$	
$_{3}^{-} = (0.7260363 \pm 0.0018) \times 10^{-4}$	$a_3 = (0.7126537 \pm 0.0081) \times 10^{-4}$	
$f_5 = (0.217\ 121\ 7\ \pm 0.24) \times 10^{-7}$	$a_5 = (-0.1449104 \pm 0.018) \times 10^{-5}$	
$z_7 = (0.5139694 \pm 0.090) \times 10^{-8}$	$a_7 = (0.647\ 343\ 6\pm 0.15) \times 10^{-7}$	
$a_9 = (-0.6309735\pm0.15)\times10^{-10}$	$a_9 = (-0.1391479 \pm 0.061) \times 10^{-8}$	
$a_{11} = (0.3353241\pm0.13) \times 10^{-12}$	$a_{11} = (0.188\ 809\ 3\pm 0.14) \times 10^{-10}$	
$_{13} = (-0.9491346 \pm 0.66) \times 10^{-15}$	$a_{13} = (-0.1659207 \pm 0.18) \times 10^{-12}$	
$a_{15} = (0.1407337 \pm 0.20) \times 10^{-17}$	$a_{15} = (0.092\ 648\ 87\ \pm 0.14) \times 10^{-14}$	
$a_{17} = (-0.081\ 690\ 10\ \pm 0.34) \times 10^{-20}$	$a_{17} = (-0.314\ 923\ 9\pm 0.66) \times 10^{-17}$	
$t_{19} = (-0.02784081\pm0.32) \times 10^{-23}$	$a_{19} = (0.05919079 \pm 0.17) \times 10^{-19}$	
$_{21} = (0.039\ 597\ 67\ \pm 0.13) \times 10^{-26}$	$a_{21} = (-0.047\ 058\ 72\ \pm 0.18) \times 10^{-22}$	
22.5 to 30 K)	$(12.5 \text{ to } 30 \text{ K})^{\prime}$	
$_0 = (0.5524253765) \times 10^4$	$a_0 = (-0.54541110) \times 10$	
$a_1 = (-0.1610882487) \times 10^4$	$a_1 = (0.25197509) \times 10$	
$u_2 = (0.2007941023) \times 10^3$	$a_2 = (-0.49936920)$	
$_{3} = (-0.1386872190) \times 10^{2}$	$a_3 = (0.55459596) \times 10^{-1}$	
$_4 = (0.5732662368)$	$a_4 = (-0.37622910) \times 10^{-2}$	
$_{5} = (-0.1418099009) \times 10^{-1}$	$a_5 = (0.16087935) \times 10^{-3}$	
$x_6 = (0.194\ 385\ 161\ 5) \times 10^{-3}$	$a_6 = (-0.424\ 351\ 25) \times 10^{-5}$	
$r_7 = (-0.1139001250) \times 10^{-5}$	$a_7 = (0.631\ 807\ 68) \times 10^{-7}$	
	$a_8 = (-0.40678352) \times 10^{-5}$	

TABLE III (Continued)



FIG. 1. Results for Cu_3Au from the 0.4-3-K apparatus shown as percentage deviations from the fitted equation (1). See Table I for coefficient values and symbol key.

The results for each composition will now be discussed in turn and then some more general remarks will follow. In calculating Debye temperatures the γ values in Table II are used to obtain C_p (lattice) and the, almost negligible, C_p to C_v correction is made in the usual way. (For the alloys, the parameters required in the correction equation are linearly interpolated between the values



FIG. 2. Results for Cu_3Au in the 0.4-30-K range shown as percentage differences from the fitted equation (1). See Tables I and II for symbol key and Table III for coefficient values.

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FIG. 3. All results for Cu_3Au shown as percentage deviations from the fitted equation (1) for the ordered alloy. See Tables I and II for symbol key and Table III for coefficient values. Number on each curve refers to the number of days between final heat treatment and the day of measurement.



FIG. 4. Results for CuAu in the 0.4-30-K range shown as percentage differences from the fitted equations (1) and (3). See Tables I and II for symbol key and Table III for coefficient values.



FIG. 5. Results for CuAu from the 0.4 to 3 K apparatus shown as percentage deviations from the fitted equation (1). See Table I for coefficient values and symbol key.

for the pure metals.) Thus it is assumed that γ is not a function of temperature.

A. Cu₃Au

The results collected in Fig. 3 confirm our earlier observation of a very significant difference



FIG. 6. Most of the results for CuAu shown as percentage deviations from the fitted equations (1) and (3) for the alloy CuAu I. See Tables I and II for symbol key and Table III for coefficient values. Number on each curve refers to the number of days between final heat treatment and the day of measurement. (For clarity some of the partly ordered results below 3 K from Ref. 4 are not shown.)



FIG. 7. Results for CuAu₃ from the 0.4-3-K apparatus shown as percentage deviations from the fitted equation (1). See Table I for coefficient values and symbol key.

between the specific heats of the ordered and disordered phases. This difference was much larger than those observed previously¹³ and since.¹⁴ It was previously supposed³ that the disordered samples of Refs. 13 and 14 were partially ordered following a quench from high (~800 °C) temperatures of the relatively massive specific-heat sample. [The sample then has a high concentration (thermal equilibrium concentration) of lattice vacancies at the start of the quench which permits



FIG. 8. Results for CuAu₃ in the 0.4-30-K range shown as percentage deviations from the fitted equations (1) and (3). See Tables I and II for symbol key and Table III for coefficient values.

rapid atomic rearrangement as the sample cools below the order/disorder transformation temperature.¹²] It is now clear that storage at room temperature would also diminish the difference between the ordered and "disordered" samples. The slow ordering of Cu₃Au at room temperature will be discussed in detail in Sec. IVG.

The variation of Debye temperature with temperature for Cu_3Au is shown in Fig. 10. Both curves may show a very slight initial rise in Debye temperature as the temperature is increased from zero, the effect being more marked for the ordered alloy.

Above 20 K the present results overlap with those of Yoon and Hultgren¹⁵ whose smoothed values are systematically higher (5 to 10%). However, the two sets of results lead to the same sign and similar magnitude for the difference in specific heat of the ordered and disordered phases.

B. CuAu

The results collected in Fig. 6 confirm our earlier observations⁴ of large differences between the disordered and two ordered phases and also the rapid change in the specific heat of "disordered" CuAu stored at room temperature. As previously noted, the "disordered" alloy orders in the di-



FIG. 9. All results for $CuAu_3$ shown as percentage deviations from the fitted equations (1) and (3) for the ordered alloy. See Tables I and II for symbol key and Table III for coefficient values.



FIG. 10. Debye-temperature plots for disordered and ordered Cu_3Au . The experimental points are from the 3-30-K apparatus. Below 3 K the curve is extrapolated to zero using the results of the fit of Eq. (1) to results as specified in Table III.

rection of CuAu II rather than towards CuAu I which is the stable phase at room temperature. This is probably because ordering is a nucleation and growth process starting at many locations and resulting in many antiphase domain boundaries which are stable at room temperature (see next paragraph). Thus the long-range ordered structure of CuAu I cannot be produced and the result is more like CuAu II but with a random, rather than periodic, antiphase domain structure. The kinetics of this transformation will be discussed in Sec. IV G.

The latest measurements on CuAu II below 3 K showed that the specific heat had decreased slightly in the few years since the earlier measurements. This change is in a direction which increases the difference from CuAu I which is the stable phase at room temperature. It therefore appears that the CuAu II has become more CuAu-II-like, i.e., the order within the domains has improved but the antiphase domain boundaries have not moved. This observation and explanation are consistent with the finding of Hultgren and Tarnopol⁵ who noted that storage of CuAu II at room temperature results in the b/a lattice parameter ratio increasing; i.e., x-ray observations showed that the structure became more orthorhombic on storage at room



FIG. 11. Debye-temperature plots for the disordered and ordered phases of CuAu. Details as in legend to Fig. 10.

temperature.

The fact that the CuAu I sample specific heat has not changed significantly during several years at room temperature (cf. the disordered and CuAu II samples) suggests that the original heat treatment produced a high degree of long-range order. This would be consistent with the x-ray work of Gantois.¹⁶

The variation of Debye temperature with temperature for the three CuAu phases is shown in Fig. 11. The curves for the disordered alloy and CuAu II are normal but that for CuAu I shows a rapid initial increase of Θ^c as the temperature increases from zero. Some time ago it was found¹⁷ that pure gold had an initial increase of some 3% in Debye temperature as temperature was increased from absolute zero. More recently it has been shown¹⁸ that this corresponds to positive dispersion in one branch of the lattice vibration spectrum, possibly caused by electron screening effects. As gold is alloyed with silver (no longrange ordering seen in this system) the maximum in Θ^c slowly disappears.¹⁹ For equatomic AgAu the maximum is very small, similar to the present observation on disordered equiatomic CuAu.

The large initial increase of Debye temperature seen in CuAu I corresponds to the specific heat increasing less rapidly than T^3 . By plotting \log_{10} $(C_p - \gamma T) vs \log_{10} T$ a first linear region corresponding approximately to a $T^{2.8}$ variation is seen whereas the first linear region for the disordered CuAu corresponds to approximately T^3 . (In both cases the low-temperature limit is obscured by the nuclear specific heat.) It is possible that the layered tetragonal lattice might give some twodimensional character to the lattice vibration spectrum. For strongly layered materials, the specific heat initially increases as T^3 in the extreme low-temperature (elastic continuum) limit but a $\sim T^2$ region is then seen which would correspond to a two-dimensional solid. In the case of graphite (hexagonal, c/2a = 1.37) the T^3 region is followed by a $\sim T^{2\cdot 3}$ region.²⁰ The CuAu I case is somewhat different because the separation of atoms in adjacent layers is smaller than that of the atoms within a layer. Presumably the large mass ratio (3.1) of the atoms on alternate layers would be the dominating effect rather than the big difference in inter- and intralayer bonding forces which leads to the two-dimensional effects in graphite (and which causes the Debye temperature to increase steadily up to at least room temperature). There have been some theoretical speculations²¹ suggesting two-dimensional effects in layered lattices such as CuAu I.

Referring again to Fig. 11 it will be seen that the lattice specific heat of CuAu I is initially much greater (i.e., Θ_0^c less) than that of CuAu II. This corresponds to the presence of more low-frequency (two-dimensional ?) modes in CuAu I than in CuAu II. Above about 5 K the specific heats of both ordered phases are similar suggesting that the possible two-dimensional effects are being swamped by other lattice vibration modes. This two-dimensional hypothesis should be viewed with a degree of caution since a similar, but smaller, effect is observed in ordered CuAu₃. (However, even this structure might be considered, in some respects, as a layer lattice-see Sec. IVC.) Obviously, inelastic neutron scattering studies on CuAu I would be of great interest. The observed initial increase in Debye temperature of CuAu I is so large that it would scarcely be affected by possible changes in the value of the electronic specific-heat coefficient γ with temperature which results from electron-phonon interaction effects.²²

Noguchi, Kondo, and Mizutani,²³ apparently unaware of our earlier work,^{3, 4} published specificheat data on the three phases of CuAu in the 1.5– 3.5-K range. Their results appear to be in reasonable agreement with our present and earlier⁴ work but their derived values for γ and Θ_0^c , especially those for CuAu I, are affected by the limited range of their measurements.

Above 20 K the present results overlap with Hawkins and Hultgren²⁴ who measured CuAu I and disordered samples and whose smoothed values are systematically higher (5 to 8%). However, the two sets of results agree in the sign and magnitude of the difference in specific heat of CuAu I and the disordered phases. In Sec. IVA a similar disagreement with Yoon and Hultgren¹⁵ was found for Cu₃Au, suggesting that specific-heat results from Hultgren's laboratory are systematically high. However, in Ref. 24 results for pure gold are given which differ by up to 8% in the opposite direction from the present author's results.²⁵

C. CuAu₃

Relatively little work has been done with this composition because the low order/disorder transition temperature make the change rather slow and uncertain. In our earlier work⁴ a sample was quenched from two different temperatures and it appeared that a disordered sample had been obtained using a quench from just above the transition temperature. It was assumed that the quench from 850 °C had resulted in some ordering owing to the high quenched-in vacancy concentration facilitating atomic movement in the ordered region.¹² For the present work an "ordered" sample was made as described in Sec. II. Figure 9 shows the relationship of the various sets of results. The similarity with Fig. 6 is striking and it seems probably that the "quench from 850 $^{\circ}$ C" produced something similar to the long-period superlattice CuAu₃ II (see Sec. I). The situation may be similar to that seen in the ordering of CuAu at room temperature, i.e., a random antiphase-domain structure is produced owing to the start of ordering at many nuclei. The ordering probably takes place while the sample is cooling and proceeds relatively rapidly owing to the excess vacancy concentration. [Measurements on both disordered and ordered (CuAu₃ I) CuAu₃ show that the specific heat changes little, if at all, on sample storage at room temperature.] As already pointed out above, in the case of CuAu the specific heats of ordered samples with both random and periodic antiphase domain boundary structures are probably similar and are quite different from that of the CuAu I phase which has a layer structure of alternating planes of Cu and Au atoms.

Reference to the Debye Θ plot for CuAu₃ (Fig. 12) shows that the disordered phase is normal but the ordered phase has the same anomalous initial increase of Θ^c (as temperature is increased from zero) as does CuAu I. In the case of CuAu₃ the increase is about 5% compared with the 10% seen in CuAu. The similarity in the temperature variation of the lattice specific heats of CuAu I and CuAu₃ I raises the question whether any two-dimensional structure exists in the latter (cubic)



FIG. 12. Debye-temperature plots for disordered and ordered $CuAu_3$. Details as in legend to Fig. 10.

lattice. When viewed along any of the three axes the lattice is seen to consist of alternating planes of (a) all Au atoms and (b) an ordered array of equal numbers of Au and Cu atoms. Hence the lattice has some two-dimensional characteristics for vibration modes in certain directions. Furthermore, the Θ_0^c of the "quench from 850 °C" sample (Table I) is 198 K which, when compared with the Θ^c variation of the ordered (CuAu₃ I) sample (Fig. 12) shows that CuAu₃ I has an additional contribution to specific heat below about 5 K very similar to that observed in CuAu I.

D. Lattice specific heat

The Debye Θ plots (Figs. 10–12) show that the disordered alloy lattice specific heats vary in a relatively normal way with temperature. It is surprising that the disordered CuAu₃ sample does not show a small initial increase of Θ^c because this composition is intermediate between CuAu and pure gold, both of which show a small (~1%) initial in-

crease of Θ^c as the temperature increases from zero.

The ordered alloys CuAu I and CuAu₃ I both show a very marked increase of Θ^c as temperature is increased from zero and Cu₃Au I shows a much smaller increase. It has been suggested above that the marked increases may be two-dimensional effects related to the structure consisting of layers of different average mass. The same should then apply to the case of ordered Cu₃Au I. The data are collected in Table IV. It is clear that the mass ratios of the planes in CuAu and CuAu₃ scale with the observed increase of Θ^c but Cu_3Au does not fit this naive picture. A possible explanation is that the postulated "two-dimensional" effect is masked by the "resonance modes" appearing when a heavy impurity is introduced into a light lattice. The subject of resonance modes and "impurity modes" (high-frequency modes caused by light impurities) is reviewed briefly in Ref. 19 where references to the original work may be found.

The Kopp-Neumann rule states that the thermal capacity of an alloy equals the sum of the thermal capacities of its constituents. It is clear that the resonance and impurity modes discussed above will cause deviations from the rule. Another deviation may be related to the excess entropy of formation of the alloy tabulated by Hultgren $et \ al.^{26}$ (This is the difference between the entropy associated with the perfect mixing and that obtained from heat and Gibbs energy of formation measurements.) Part of any excess may be related to imperfect mixing (the configurational entropy) and part to the departure of the alloy from the Kopp-Neumann rule (the vibrational entropy, if the electronic contribution to specific heat is neglected). For the Cu-Au system the tabulated²⁶ excess entropy of formation at 800 K is slightly positive with a large error limit which would not preclude negative values. The γ and Θ_0^c values obtained for the disordered alloys in the present work (Table II) deviate from linear interpolations between the pure metals in ways which would have opposite effects on the specific heat. However, the lattice specific heat would be expected to dominate and result in the specific heat of disordered alloys being greater than the Kopp-Neumann rule values. This would correspond with the positive excess entropy of mixing actually ob-

TABLE IV. Layer structure in copper-gold alloys.

Alloy	Plane (a)	Plane (b)	Mass ratio Plane (a) /Plane (b)	Initial increase in ⊕°%
Cu ₃ Au I	Cu	CuAu	1:2	~0
CuĂu I	Cu	Au	1:3	10
CuAu ₃ I	Au	CuAu	1.5:1	5

served. X-ray measurements²⁷ show significant short-range order in CuAu as high as 800 K (the highest temperature at which measurements were made). Thus the vibrational contribution to the entropy of mixing is probably greater than the excess entropy tabulated by Hultgren *et al.*²⁶

Figure 13 shows the percentage deviation of the present results (smoothed values) from the Kopp-Neumann rule. The deviations depend on both the composition and state of order and exceed 50% for two of the ordered alloys. The result for the disordered alloys is quite different to that obtained for AgAu alloys 19 where the $\mathrm{Ag}_3\mathrm{Au}$ and AgAu_3 data were almost coincident. Presumably the dissimilar mass ratios in the two alloy systems must be a major factor in this difference. The deviations in Fig. 13 must largely reflect differences in the lattice specific heat. (Deviation of the electronic contribution to specific heat from a value linearly interpolated between pure copper and pure gold would only account for a maximum difference in Fig. 13 of 7.5% at 2 K; 3% at 4 K, and 0.5% at 10 K-all for CuAu II, the alloy for which the effect is greatest.)

Specific-heat measurements made elsewhere²⁸ on several copper-rich α -phase alloys (containing up to 10 at.% Au) give Θ_0^c results which fall on the curve **drawn** through the disordered alloy Θ_0^c re-



FIG. 13. Percentage deviations of the results from the Kopp-Neumann rule values. See Table II for symbol key.

sults from the present work and the Θ_0^c values for the pure metals.

The effect of ordering on the Θ_0^c values for Cu₃Au and CuAu alloys is qualitatively in agreement with the elastic modulus measurements (at room temperature and above) of Köster.²⁹ He did not investigate the composition CuAu₃. The effect of ordering on the low-temperature elastic constants of Cu₃Au was investigated by Flinn, McManus, and Rayne.³⁰ Their results for the ordered alloy lead to an elastic Θ_0^{el} value in excellent agreement with the Θ_0^c value from the present results but it seems that their "disordered" alloy was partly ordered, having been quenched from a high temperature.¹²

E. Electronic specific heat

All values of γ in Table II are closely similar to those reported earlier.^{3,4} The γ values for the disordered alloys show a slight negative deviation from a linear interpolation between pure copper and pure gold. This deviation is of a parabolic form consistent with Stern's charging theory.³¹ For a detailed comparison see Ref. 4. The ordered alloys Cu₃Au and CuAu II have γ values which are less than those of the corresponding disordered alloy (in agreement with all the systems tabulated by Kuentzler³²). However, the γ values of CuAu I and ordered CuAu₃ I are displaced in the opposite direction. As suggested above, under lattice specific heat, these latter two lattices can both be considered as being composed of alternating planes of two different compositions, i.e., there is some two-dimensional character as evidenced in the lattice specific heat. (The same might be expected of Cu₃Au, see Sec. IV D, but the lattice specific heat is relatively normal.) Reference to Table I shows that the "quenched from 850 °C" CuAu₃ fits in with Cu₃Au and CuAu II. It has been suggested above that this sample contains a nonperiodic antiphase domain structure effectively breaking the postulated two-dimensional character (cf. CuAu II). Table II of Ref. 4 shows that as CuAu spontaneously orders at room temperature, the γ value decreases, i.e., a nonperiodic antiphase domain structure reduces γ in qualitatively the same way as does a periodic antiphase domain structure (e.g., CuAu II).

The above observation of the similar effects of both (supposedly) random and periodic antiphase boundaries on the electronic specific heat appears to cast some doubt on explanations^{33, 34} of the γ difference between CuAu I and CuAu II being the result of the creation of new Brillouin-zone boundaries, making contact with the Fermi surface, as a result of the *periodicity* of the antiphase boundaries. (The reduction in electron energy accompanying the formation of the periodic antiphase boundaries is accompanied by an increase in domain boundary energy. The period is determined by the sum of these effects.) However, Jones³⁵ has argued that the anitphase boundaries might not be strictly periodic in CuAu II (thereby increasing the entropy-a possible explanation of the observed latent heat in going from CuAu I to CuAu II) without affecting the above explanation of γ difference. (That is, the overall long-range order of the superlattice with its definite period is maintained by the electrons but short-range order is not necessarily imposed.) It is quite possible that spontaneous ordering at room temperature could lead to a structure approximating these specifications but perhaps with a different average domain size. Jones's suggestion³⁵ has been incorporated in later theoretical work by Inglesfield.³⁶

The observed electronic specific-heat coefficient depends on both the electronic density of states at the Fermi surface and the electron-phonon interaction. It is possible that the difference in γ between the three phases of CuAu could arise from the latter term. However, this seems unlikely because Noguchi *et al.*²³ state that the magnetic susceptibility, not affected by the electron-phonon interaction, varies in the same way as γ between the three CuAu phases.

F. Nuclear specific heat

The coefficients, H, found for the nuclear specific-heat term (Table II) are close to those found earlier.^{3,4} As discussed in Ref. 4 the term is thought to arise from the interaction of electric field gradients with the nuclear electric quadrupole moments. Gold is expected to contribute an order of magnitude more than copper. There is nearest-neighbor symmetry round the gold sites in ordered Cu₂Au and the nuclear-specificheat term is therefore expected to decrease on ordering. For other compositions the asymmetry worsens on ordering and the nuclear term is expected to increase, as observed. For the disordered alloys the nuclear term initially increases as the gold content increases. If the terms are normalized to refer to one atom of gold the nuclear term is roughly symmetrical with composition, showing that the largest field gradients occur in the equiatomic alloy.

G. Disorder-order kinetics at room temperature

The observation of the change of specific heat with time of the disordered alloys Cu₃Au and CuAu when kept at room temperature was rather surprising. However, most previous ordering studies have been at high temperatures where the process takes place much more rapidly. At lower temperatures Sykes and Jones³⁷ found that ordering starts at 60 °C in Cu₃Au and Roessler has seen an unspecified change in the condition of disordered Cu₃Au at room temperature.³⁸

There is some dispute as to whether ordering takes place by a nucleation and growth process or whether it is a homogeneous reaction taking place over the whole volume of the sample.³⁹ Certainly in the first case and probably in the second case there is no mechanism to ensure that ordering starts on the right sublattice and an antiphase domain structure will be formed (in the first case after growth of nuclei until they touch). Then ordering can be divided into two further steps: (a) establishment of equilibrium order within a domain and (b) gradual coalescence of domains. The rate of atomic movement is largest just below the transition temperature but the equilibrium degree of long-range order increases as the temperature is lowered. Thus the ideal ordering procedure is to soak just below the order/disorder transition temperature to get large domains and then to cool slowly to improve the long-range order within the domains.

Despite the complexity of the ordering process, numerous authors have studied ordering rates as a function of temperature (generally above 200 °C where ordering is reasonably fast) and have been able to express their results in terms of relaxation time τ related to temperature Tas follows

$\tau = A e^{W/kT}$,

where k is Boltzmann's constant, A and W are constants, and τ is in seconds. Three typical experiments will now be described briefly. For AuCu, Dienes⁴⁰ studied the variation of electrical resistance with time for temperatures in the 250-360 °C range (on samples originally quenched from 600 °C and therefore, presumably, containing an excess of lattice vacancies). He found $A = 1.3 \times 10^{-9}$ and W to be 1.23 eV (1 eV = 1.602 $\times 10^{-12}$ ergs). These figures give τ as 17 min at 250 °C and 67 000 yr at 20 °C. For Cu₂Au, Sykes and Evans⁴¹ used samples quenched from 450°C and made measurements of electrical resistance versus time at temperatures in the 300-360 °C range. They found $A = 10^{-8.5}$ and W = 1.65 eV leading to a τ of 0.8 yr at 250 °C and 2.5×10¹² yr at 20°C. Also for Cu₃Au, Feder, Mooney and Nowick⁴² made precision lattice-parameter measurements as a function of time at temperatures in the 210 to 290 °C range for samples initially ordered at 368 °C. These were combined with other workers similar Young's modulus measurements at higher temperatures and gave $A = 2.78 \times 10^{-15}$ and W = 2.03

eV. At 250 °C the relaxation time is 1 d and at 20 °C it is 7.5×10^{12} yr. Comparing the two sets of figures for Cu₃Au it is seen that (a) the time for a change of long-range order is much less than that for the development of order at 250 °C, as expected, and (b) the extrapolation to 20 °C is not very accurate since the reverse result is obtained here. The specific-heat data of the present work correspond roughly to the conditions of the CuAu and first Cu₃Au experiments detailed immediately above.

Turning now to the present specific-heat results, it has been shown above that ordering at room temperature (~20°C) proceeds in CuAu with a half-life of ~100 d (as judged from the change of specific heat) and in Cu₃Au with a half-life of ~2000 d (judged similarly). Furthermore, the specific-heat results suggest that domain boundary movement does not occur at room temperature. (That is, it appears that individual atoms may change place to increase the order within a domain but insufficient energy is available for the cooperative movement of atoms required to shift a domain boundary.)

The big discrepancy between the half-life at room temperature extrapolated from high-temperature observations and that actually seen in the present work can probably be attributed to the following factors.

(i) The approximation in assigning a single halflife to the higher-temperature observations (see above).

(ii) The specific heat is much more sensitive to the early stages of ordering than other techniques.³⁷ For example, (a) x-ray observations, possible because a minimum size of domain of fair perfection is necessary to obtain superlattice lines and (b) electrical resistance measurements, because these are influenced by the number of domain boundaries, the degree of order within a domain, and the thermal component of resistance.

(iii) Quenched-in vacancies facilitate atomic movement as they move to sinks and have a profound effect on ordering rates.

(iv) The Arrhenius relation governing diffusion may break down at lower temperatures for a number of reasons: (a) vacancy clusters are more mobile than single vacancies.⁴³ (b) Dislocations may enhance diffusion rates.⁴⁴ (c) Zero-point phonons may enhance low-temperature diffusion.⁴⁵

The difference in the specific-heat half-life of Cu_3Au and CuAu may be related, in a naive fashion, to the fact that in ordering atoms have to move to the right point in the former but only the right plane in the latter. The disordered $CuAu_3$ alloy appeared quite stable compared with Cu_3Au and CuAu. This may be related in two ways to the lower order-disorder transition temperature (~473 vs ~673 K): (a) quenching was from a lower temperature considerably reducing the "excess" lattice vacancies present⁴⁶ and (b) room temperature is much closer to the disordering temperature for CuAu₃ than for the others and the driving force towards ordering is correspondingly less.

Recent theories of ordering kinetics limit themselves to the simple case of homogeneous changes in the degree of order. Dienes⁴⁷ treats the process as a chemical reaction between an A atom on a wrong site and a B atom on a wrong site reacting to form A and B atoms on the correct sites. The theory shows that ordering must start by fluctuations and the size of fluctuation required is much larger for an A_3B -type alloy than for an AB type. Also the ordering rate for AB is about 100 times faster than for A_3B . The sigmoid shape of the ordering curves are those expected in a nucleation and growth process although derived entirely from simple rate theory. Thus, Dienes's theory is in qualitative agreement with the present specific-heat work. A more fundamental theory,48 considering the possible diffusion mechanisms in a solid rather than a chemical reaction, leads to equations too complex for ready comparison with experiment. Dienes's theory has been shown,49 with some assumptions, to lead to Rothstein's equation

$$(\boldsymbol{P} - \boldsymbol{P}_0) / (\boldsymbol{P}_e - \boldsymbol{P}_0) = \coth(\alpha t + \beta), \tag{4}$$

where P is the instantaneous value of a physical property depending linearly on the long-range order parameter, P_0 is the equilibrium value for perfect long-range order, and P_e is the equilibrium value at that temperature. α and β are constants, t is the time, and the equation applies to a situation where the order in increasing. To make a crude comparison of the present specificheat data with this equation we make the assumption that P_e (at ~20 °C) differs by 1% from P_0 (perfect order) and rewrite Rothstein's equation (4) as

$$\operatorname{coth}^{-1}\left\{ \left[100(C_{p}^{t} - C_{p}^{0})/C_{p}^{0} \right] + 1 \right\} = \alpha t + \beta, \tag{5}$$

where C_p^t is the specific heat at time t after the start of ordering and C_p^0 is the ordered specific heat at the same temperature. It will be observed that the first term in the coth⁻¹ argument is exactly the ordinate in Figs. 3 and 6. By reading figures off these graphs in the region of the maximum difference between disordered and ordered samples (and taking the ordered sample as CuAu II in Fig. 6) the result shown in Fig. 14 has been obtained. Obviously more data would be needed



TIME (DAYS FROM QUENCH) FIG. 14. Illustrating a crude test of Rothstein's equation using the present specific-heat data (see text).

for a thorough comparison but it is clear that the fit is far from perfect. The fit is not improved by (i) doubling or halving the difference $(P_e - P_0)$, (ii) by making reasonable allowance for experimental error, or (iii) by eliminating the 2327-d

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point in the case of CuAu (where the difference $C_p^t - C_p^0$ is small). The discrepancy could indicate that the specific-heat change is not a linear function of the long-range order parameter or could be related to the numerous other assumptions implicit in the above equation (for instance,⁴⁹ that the change in order parameter is not large compared with unity—which corresponds to perfect order).

V. CONCLUSION

Cu₃Au and CuAu order spontaneously at room temperature and the order of CuAu II improves on storage at room temperature. The lattice specific heats of CuAu I and ordered CuAu₃ are anomalous at low temperatures, possibly a twodimensional effect. The difference in the properties of CuAu I and CuAu II may not depend on a strictly periodic antiphase domain structure.

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