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Probable observation of short-range-order effects in the specific heat of AgAu below 30 K

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By quenching an equiatomic AgAu alloy from 400°C and from 1000°C reproducible differences in specific heat have been obtained. The form of the difference is similar to that found between disordered and long-range ordered CuAu, but much smaller. The maximum difference (~0.8%) is seen at about 3 K. Other heat treatments produce intermediate results. It is postulated that the differences correspond to short-range ordering.

INTRODUCTION

At the absolute zero the entropy of an alloy is minimized by either long-range ordering (LRO) or segregation of the components. This may not occur because the temperature at which ordering or segregation becomes energetically favorable may be so low that atomic movement is not possible. However, there may be some tendency in this direction represented by short-range ordering (SRO) or clustering. The degree of SRO or clustering will depend on the thermal history of the sample. In the case of alloys showing LRO there is always significant SRO just above the order-disorder transition temperature. This SRO decreases with increasing temperature. It might therefore appear that a disordered sample should be produced by quenching from a very high temperature. However, it is found in practice that a partly ordered sample is obtained this way, presumably because the initial high equilibrium concentration of lattice vacancies facilitates atomic movement during and after the quench. To minimize this effect it may be best to produce a "disordered" sample by quenching from just above the order-disorder transition temperature when it is clear that the sample will show significant SRO.

The discussion in the previous paragraph shows that there are a large number of alloy systems where there is SRO and the degree of SRO depends on the thermal history. In turn this may result in uncertainty in the specific heat and entropy. The present work was undertaken to get some idea of the possible magnitude of these effects.

Recent work[1] has shown that LRO may have a surprisingly large effect on low-temperature specific heat. Consider the equiatomic alloy CuAu where there are two ordered phases, CuAu I and CuAu II, the latter a long-period superlattice. At temperatures below about 3 K the disordered sample has a lower specific heat than CuAu I. At higher temperatures (up at least to 30 K) the disordered phase has a higher specific heat than CuAu I, the maximum difference of about 20% occurring at about 8 K. The specific heat of the disordered sample exceeds that of CuAu II over the measurement range of 0.4–30 K. The maximum difference (~20%) occurs at about 5 K. As mentioned earlier, the disordered sample will show SRO.[2]

To investigate SRO it is best to choose an alloy system which shows no LRO. A suitable system is Ag-Au, where x-ray work[3] shows SRO. It has been estimated[4] that the LRO transition temperature for the equiatomic alloy is about 150 K but, owing to negligibly low atomic mobility here, the transition to LRO never occurs. It was decided to work with an approximately equiatomic alloy since the number of Ag-Au pairs is then a maximum and SRO effects might, as a result, be expected to be largest at this composition. This is confirmed by diffuse x-ray scattering experiments.[5] Previous work[6] had shown the Debye temperature (Θ_0^c) for this composition to be about 200 K, while that for disordered CuAu is 218 K.[1] If it is assumed that SRO affects the (lattice) specific heat in the same way as was observed[1] for the early stages of LRO and if it is assumed that the maximum effect occurs at a temperature proportional to Θ_0^c, then the SRO effect on specific heat would be expected to be a maximum at a temperature of ~5 K. Even if these assumptions are not strictly correct, it appeared likely that any effect should show a maximum within the 0.4–30 K temperature range of the experiments described in the present paper.

The other main problems to consider are whether samples can be prepared showing different degrees of SRO and whether the SRO is stable over time periods long enough for loading into a calorimeter. Information on the kinetics of SRO is available from electrical resistance measurements, but before considering these it is advisable to consider the possible mechanisms for SRO.

Two main models for SRO have been considered.[7] In homogeneous SRO the degree of SRO is uniform throughout the sample. In heterogeneous SRO there are small regions of SRO (or even LRO) in the disordered matrix. The size and number of the SRO regions and the degree of order in the ordered regions may vary with temperature in the latter model. Twin-process kinetics have been identified in Cu-Al supporting the latter model, but it is possible that other alloy systems might show homogeneous SRO.[8]

The electrical resistance work will now be discussed. The earliest significant work appears to be that of Schulze and Lücke.[9] They annealed Ag-Au alloy foils at a quenching temperature T_Q, then quenched to temperature $T_m = -40$°C and subsequently annealed several times at an intermediate temperature $T(T_Q > T > T_m)$. After each step the electrical resistance was measured at T_m in order to eliminate the effect of the thermal component of resistance. (The same procedure was followed in work to be cited later.) They observed an initial *increase* in resistance on annealing at T, which they attributed to an increase in SRO, followed by a decrease attributed to the annealing out of quenched-in lattice vacancies. The relative magnitude of these effects depended on the quenching temperature and sample composition. For the equiatomic alloy quenched from 450°C and annealed at 40°C, the lattice vacancy effect is negligibly small and the "half-life" of the resistance increase is about 500 min. For the same circumstances but quenching from 600°C the half-life is 30 min. The variation of half-life is simply explained by the number of equilibrium lattice vacancies at the quenching temperature. At first sight the *increase* of electrical resistivity with increase of SRO is rather surprising, but theory[10] shows that the sign of the dependence of resistivity on SRO depends primarily on the number of conduction electrons per atom in the system and that both signs are possible.

Results in disagreement with those of Ref. 9 were obtained by Giardina *et al.*,[11] who quenched a Au-15-at.%-Ag sample first into water and then immediately into liquid nitrogen. They performed isochronal annealing experiments and found an initial *decrease* of resistivity, complete by 0°C, which they attributed to the onset of SRO. At higher temperatures the resistivity gradually increased. This was attributed to scattering at the coherent phase boundaries gradually forming between ordered domains. Above about 100°C the resistivity falls again, this being attributed to the gradual coalescence of domains and consequent reduction of scattering at domain boundaries. Thus the results of this work are interpreted in terms of a heterogeneous SRO model.

Calorimetric and resistometric studies by Lang[12] supported the model and results of Ref. 9 and contradicted those of Ref. 11. In particular no abnormal thermal or resistive effects were observed below 0°C and the calorimetric measurements showed that disordering started on heating above ~100°C, contrary to the interpretation of Ref. 11. Lücke and Haas[13] attempted to duplicate as closely as possible the experiments of Ref. 11, even to the extent of using specimens from the same source. They performed isochronal annealing experiments in the same way as Ref. 11 but found no initial decrease of resistivity below 0°C. Above 0°C the resistance first increased, which they attributed to the onset of SRO, and then, above ~100°C [or lower for longer (~30 min) annealing periods] the resistance began to fall, corresponding to the falling equilibrium SRO. They also showed that the resistivity values attributed to equilibrium SRO were reversible with temperature change, as is required. (This reversibility had been demonstrated earlier by Radelaar.[14]) These results were confirmed by Lücke *et al.*[15] The reversibility in the equilibrium SRO region is difficult to reconcile with a literal interpretation of the domain-coalescence picture in this region proposed in Ref. 11. However, some results supporting the findings of Ref. 11 were obtained by Schüle and Crestoni.[16] In particular they observed the initial *decrease* of resistivity on isochronal annealing and produced evidence that there are two processes occurring in the alloy with rate constants differing by 10^5. They claim that the quenching procedures of Refs. 9, 12, and 13 were inadequate to observe the faster process.

It is clear that there is still considerable controversy regarding both the experimental and theoretical aspects of the electrical resistivity work. The data presented in Ref. 9 and the supporting work[12-15] is most useful in planning a specific-heat experiment. Thus in Ref. 13 it is shown that the resistivity assumed to correspond to equilibrium SRO falls as temperature increases but then goes through a minimum at ~400°C, so that it increases at higher temperatures. It will be recalled that the resistance is measured at a low reference temperature and the observed increase in resistance above about 400°C is thought to be due to the development of SRO during the quench (to the measuring temperature). This is facilitated by the increasing initial number of equilibrium lattice vacancies with increasing quench temperature. Thus quenching a sample from ~400°C might result in minimum SRO. Conversely, quenching from a high temperature (~1000°C) could result in considerable SRO because of the high initial concentration of lattice vacancies. In fact this might be the best way to obtain high degrees of SRO as it avoids the very long equilibrium times associated with low-temperature heat treatment.

TABLE I. Sequence of heat treatments and measurements.

Temperature	Cooling method	Time at room temp. before start of cool for specific-heat run	Temperature range of specific-heat measurements	Symbol in figures
1000 °C	QW[a]	194 d	2.5–30 K	■
400 °C	QB[b]	1.7 h	2.5–30 K	□
		26 d	2.5–30 K	▽
1000 °C	QW	1 d	2.5–30 K	◆
400 °C	QB	2 h	2.5–30 K	◇
		4 d	2.5–30 K	△
100 °C	C[c]	1 d	2.5–30 K	◁
200 °C	C	1 d	2.5–30 K	▷
400 °C	QB	3 h	0.4– 3 K	○
		7 d	0.4– 3 K	*
1000 °C	QW	3.5 d	0.4– 3 K	×
		4.5 d	0.4– 3 K	+

[a] QW: quench in water.
[b] QB: quench in brine (~−8 °C).
[c] C: cool tube containing sample in still air.

For the specific-heat experiment in the available apparatus it was necessary to quench a relatively massive (~200 g) sample and then mount in the calorimeter at room temperature before cooling to the measurement temperatures. Previous experience with the apparatus showed that it was possible to assemble and start cooling within less than 2 h of the quench. The experiments of Ref. 9, described above, suggest that it should be possible to retain a significant degree of the quenched-in SRO over this time span if the quench temperature is ~400°C. The other problem to consider is whether the quench of the sample itself is fast enough. The quench rate can be calculated[17] on the assumption that the surface temperature of the sample is suddenly reduced to the quenching bath temperature. With this assumption, the center of the sample would cool 50% of the total temperature change in about 1.6 sec. The average temperature of the sample would be reduced 50% of the total temperature change in about 0.15 sec or 90% of the change in about 1 sec. Rough tests confirmed these figures for a water quench from 600°C. Experiment was necessary to determine whether this quench rate was sufficiently rapid.

EXPERIMENTAL

The specific-heat measurements were made in apparatuses described elsewhere.[18,19] Preliminary experiments were made with the equiatomic AgAu sample used in earlier work on the Ag-Au system.[6]

TABLE II. Polynomial coefficients representing specific heat $C_p=\sum a_n^{T^n}$. Units: cal/K g-atom (1 cal = 4.186 J). Error limits are 95% confidence limits for each coefficient from the statistical analysis. Each polynomial reproduces the smoothed specific heat to within 0.01%.

Quenched from 1000 °C	Quenched from 400 °C
$a_{-2} = +(0.707\,790\,91 \pm 0.048) \times 10^{-6}$	$a_{-2} = +(0.642\,548\,2 \pm 0.047) \times 10^{-6}$
$a_1 = +(0.155\,674\,62 \pm 0.000\,41) \times 10^{-3}$	$a_1 = +(0.155\,149\,5 \pm 0.000\,40) \times 10^{-3}$
$a_3 = +(0.590\,844\,11 \pm 0.002\,1) \times 10^{-4}$	$a_3 = +(0.599\,292\,5 \pm 0.002\,0) \times 10^{-4}$
$a_5 = -(0.319\,607\,10 \pm 0.17) \times 10^{-7}$	$a_5 = -(0.534\,767\,9 \pm 0.16) \times 10^{-7}$
$a_7 = +(0.173\,198\,40 \pm 0.041) \times 10^{-8}$	$a_7 = +(0.205\,019\,5 \pm 0.039) \times 10^{-8}$
$a_9 = -(0.125\,896\,94 \pm 0.044) \times 10^{-10}$	$a_9 = -(0.150\,145\,0 \pm 0.041) \times 10^{-10}$
$a_{11} = +(0.461\,572\,18 \pm 0.25) \times 10^{-13}$	$a_{11} = +(0.566\,567\,6 \pm 0.22) \times 10^{-13}$
$a_{13} = -(0.103\,246\,35 \pm 0.082) \times 10^{-15}$	$a_{13} = -(0.130\,509\,3 \pm 0.070) \times 10^{-15}$
$a_{15} = +(0.145\,818\,75 \pm 0.16) \times 10^{-18}$	$a_{15} = +(0.188\,902\,9 \pm 0.13) \times 10^{-18}$
$a_{17} = -(0.126\,477\,93 \pm 0.18) \times 10^{-21}$	$a_{17} = -(0.166\,930\,5 \pm 0.14) \times 10^{-21}$
$a_{19} = +(0.061\,298\,398 \pm 0.11) \times 10^{-24}$	$a_{19} = +(0.819\,830\,1 \pm 0.85) \times 10^{-25}$
$a_{21} = -(0.126\,687\,39 \pm 0.27) \times 10^{-28}$	$a_{21} = -(0.170\,931\,4 \pm 0.21) \times 10^{-28}$
Symbol in figures × + ■ ◆	○ * □ ◇

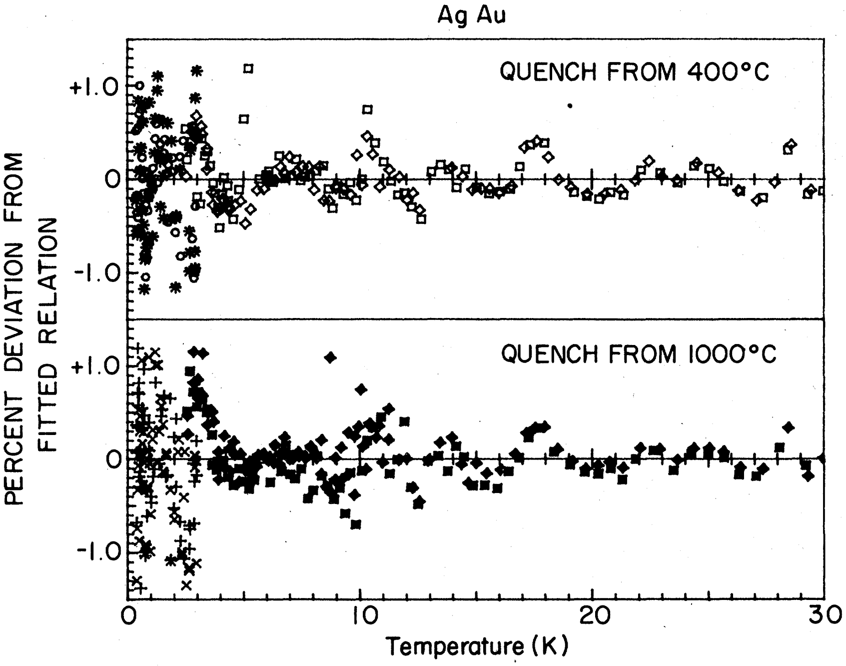

FIG. 1. Percentage deviation of the raw data from the fitted relations given in Table II.

Heat treatment produced differences of the same magnitude as in the later work, described below, but the differences were not satisfactorily reproducible. Two possible reasons were identified. The first was increasingly severe radio frequency heating problems associated with the proliferation of high-powered local radio transmitters. It seemed possible that this might have resulted in some irreproducibility of results. This problem was overcome by moving the apparatus to another location where the signal strengths of local transmitters were about 30 dB down. The second possible reason for reproducibility problems was slight variations in the quenching rate. This had been identified by others as a possible problem.[20] In order to minimize this problem it appeared advisable to cut the massive specific-heat sample into a number of pieces. Rather than cut up the sample mentioned above, which was required for other work, it was decided to use another sample of nominally equiatomic composition. This had been prepared for the earlier work[6] on the thermal parameters of the Ag-Au system as a function of concentration but was not considered sufficiently

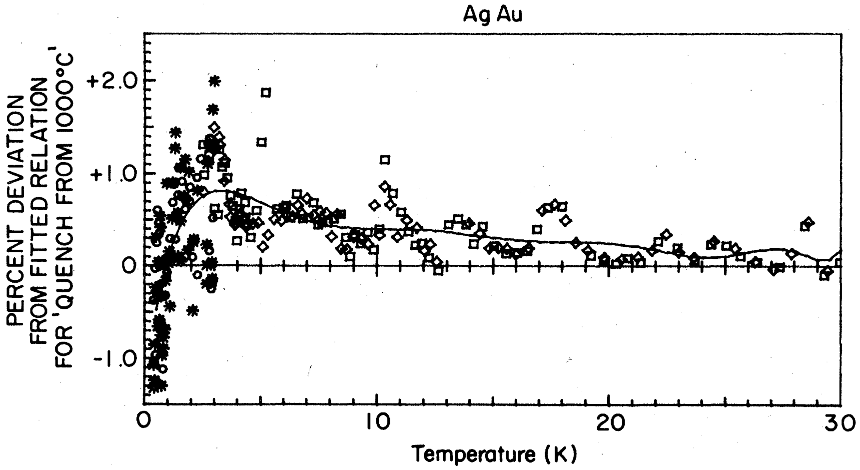

FIG. 2. Percentage deviation of the raw data for the quench-from-400°C heat treatments from the fitted relation for the quench-from-1000°C heat treatments.

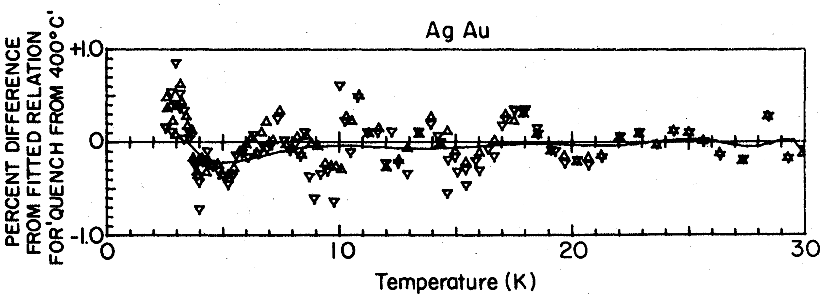

FIG. 3. Effect of a room-temperature anneal after a quench from 400°C. △, about 1 week after the quench; ▽, about 1 month after the quench.

homogeneous to use.[21] However, it was a very pure sample and appeared quite suitable for an investigation of the effects of heat treatment. The sample was made from Consolidated Mining and Smelting Co. of Canada (COMINCO) 99.9999% pure pellets of gold and silver. These were induction melted under high vacuum and chill cast into a heavy copper mould. The sample was then sealed up, under vacuum, in quartz and held at 1000°C for 16 d in an attempt to homogenize. Pieces were then taken from the top and bottom for analysis. The gold content was 53.58 at.% at one end and 49.41 at.% at the other. Assuming a linear composition gradient (not necessarily correct) the average composition is 51.50 at.% gold and average atomic weight 153.75. The impurity analysis results (all ppm by weight) were Fe 0.40 and 0.54, Mn 0.027 and 0.039 (both by the quantitative spectrographic method); Mg 0.01–0.1 and 0.01–0.1, Si 0.01–3.0 and 0.03–0.3, Cu 0.1–1.0 and 0.1–1.0 (qualitative spectrographic method). In order to facilitate rapid quenching the sample was cut into six wedge-shaped pieces by making three cuts along the axis with a spark cutter.

The sample was carefully cleaned, as described elsewhere,[22] before each heat treatment. For the "quench-from-1000°C" heat treatments the sample, resting on a piece of alumina crucible with alumina spacers between the six pieces, was sealed, under vacuum, in quartz and held at 1000°C about 6 h before quenching into distilled water (the quartz tube breaks as soon as it is immersed). The procedure for quench from 400°C was similar except that the sample container was Pyrex and the sample was held about 18 h at 400 °C before quenching into brine at about −8 °C. (A brine quench gives more rapid cooling than a water quench. The latter was used in the quench from 1000 °C to give a little more time for the attainment of equilibrium SRO during the cool.) For the other heat treatments the sample was sealed, under vacuum, in Pyrex and allowed to cool slowly outside the furnace after the heat treatment. The sample weight was 216.19 g at the start of the experiments and 214.55 g at the end.

RESULTS

The sequence of heat treatments and specific-heat measurements is shown in Table I. The 2.5–30 K runs following the two independent quenches from 1000°C were curve fitted with the two 0.4–3 K runs following a single quench from 1000°C. The result is shown in Fig. 1 as a plot of the percentage differences of the raw data from the coefficients listed in Table II. This is taken as the quench-from-1000°C result. The quench-from-400 °C result (Fig. 1 and Table II) is obtained

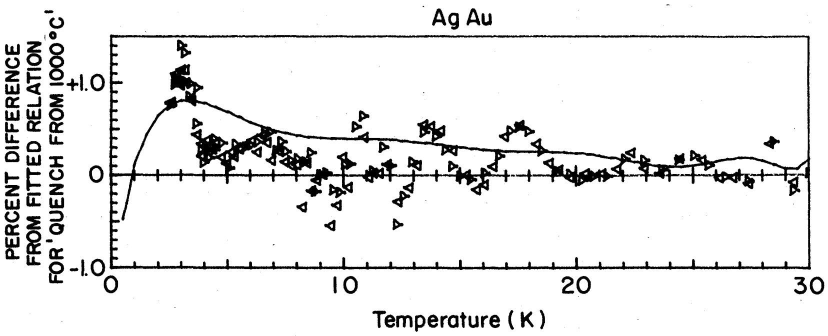

FIG. 4. Effect of low-temperature heat treatment following a quench from 400°C. ◁, about $2\frac{1}{2}$ days at 100°C; ▷, about $2\frac{1}{2}$ days at 200°C. The curved line represents the smoothed values for the quench-from-400°C condition.

from a similar set of four runs. The quench-from-400°C raw data are plotted as percentage differences from the quench-from-1000°C result in Fig. 2. The line is the smoothed value for the quench-from-400°C state. The two runs made after room-temperature storage, following a quench from 400°C, are shown in Fig. 3 as percentage differences from the quench-from-400°C result. Finally, Fig. 4 shows the effect of the 64 h at 100°C and 60 h at 200°C heat treatments plotted as a percentage difference from the quench-from-1000°C result. The line in this plot represents the quench-from-400°C result.

DISCUSSION

It will be observed (Fig. 1) that the results show systematic deviations about the smoothed value. This is a consequence of small errors in the temperature scale used, probably a combination of small errors in gas thermometry with limitations of the procedure used to fit the calibration data. Reference to Fig. 1 shows that the reproducibility of results is generally much better than the magnitude of the deviations (except possibly at the lowest temperatures). Thus the significance of differences must be based on the reproducibility rather than the magnitude of the deviation. [Low-temperature scales have been in a state of flux for a long time and our "local" temperature scale has been retained to facilitate comparison of results obtained at different times in this laboratory. It is known that the smoothed values agree well with those obtained elsewhere (e.g., comparison measurements on pure copper[23]). There has been criticism[24] regarding the premature adoption of "improved" temperature scales which finally appear worse than the discarded scale. For recently established errors in IPTS68 in the region of the present work see Ref. 25.]

The reproducibility of results obtained with several quenches from the same temperature will be clear from Fig. 1. Note in particular that a long storage time at room temperature has had little or no effect on the quench-from-1000°C state. The difference in specific heat between the quench-from-400°C and quench-from-1000°C states is clear from Fig. 2. and appears well established. The maximum difference is about 0.8% at about 3 K. The quench from 1000°C is expected to produce a maximum of SRO, while the quench from 400°C is expected to produce a minimum (see the Introduction). The form of the difference in specific heat produced by the two heat treatments is similar to that observed in long-range ordering (see Fig. 6 of Ref. 1) but the magnitude is much smaller. The results in Fig. 3 show that storage at room temperature after a quench from 400°C has little effect on the specific heat. Perhaps the results for the longer storage time (~1 month) have moved down significantly, consistent with the hypothesis of an increase of SRO. The curve is a fit to these latter results but is not strictly comparable with the other curve fits because results below 2.5 K were not available for the alloy in this state. Finally Fig. 4 shows that annealing at 100°C or 200°C lowers the specific heat more than short-term room temperature storage. There is little difference between the results obtained with the 100°C and 200°C anneals. Further experiments would be necessary to explore this in more detail, but it can be explained as the result of two processes. The first is that when the sample temperature is raised it takes a finite time for the equilibrium SRO at that temperature to become established.[26] Secondly, as the annealing temperature is raised the equilibrium SRO is decreased and the specific heat is expected to increase. Thus the annealing time at 100°C may not have been long enough to obtain the equilibrium SRO value, while at 200°C the equilibrium SRO value is lower and specific heat higher.

From Fig. 2 it is clear that the heat treatment has affected the specific heat at the lowest temperatures quite considerably. The parameters obtained from the specific-heat results are listed in Table II. There is no significant change in the nuclear specific-heat coefficient (a_{-2}) or electronic specific-heat coefficient (a_1). However, the change in the leading term of the lattice specific heat (a_3) is nearly 1.5% and more than double the sum of the 95% confidence limits. Thus, within the precision of the present work, heat treatment has had a signficant effect only in the lattice specific heat. [Comparing the results in Table II with those for the equiatomic alloy used in our earlier work[6] it will be seen that there is a significant difference in the value obtained for the electronic specific-heat coefficient (a_1). This may reflect several factors, e.g., (a) an error in the average atomic weight of the sample used in the present work which was based on the assumption of a linear concentration gradient in the inhomogeneous sample, (b) inhomogeneity in the sample tends to increase a_1, and (c) slight changes in the ^{3}He cryostat temperature scale[19] since the previous work. Clearly these factors do not affect the comparisons made in the present paper, where all measurements were made on the same sample.]

It will be recalled that the electrical resistance studies of Refs. 9 and 12–15 were used in planning the present work and it appears that the specific-heat results are consistent with these data and an interpretation based on the homogeneous SRO model. However, the present specific-heat results would probably also be consistent with a heterogeneous SRO model. In this case no observation would have been made of any process with a very short time constant.

Thus the present work appears not to clarify the controversy regarding the mechanism of short-range ordering, but is has shown that specific-heat variations of the order of 1% may be produced by various heat treatments—and these variations are most probably associated with different degrees of SRO. In no case would a completely disordered sample have been obtained and nonideal quenches would reduce possible differences. Hence the total possible change of specific heat associated with SRO would be greater than that observed in the present work.

In conclusion it should be mentioned that a significant dependence of the electronic specific-heat coefficient (γ) of Pd-rich Cu-Pd alloys was initially attributed[27] to short-range order but in a later publication[28] to clustering. The direction of the variation of γ with heat treatment is the same as that observed[29] in a Cu-Ni alloy for which clustering behavior has been proved very convincingly. In any case, the Cu-Pd system shows LRO at other compositions, so the results would be more ambiguous than in the case of the Ag-Au system considered in present work.

CONCLUSION

The specific heat of an equiatomic AgAu alloy has been varied by a maximum of nearly 1% by different heat treatments. The form of the variation and the instabilities observed after certain heat treatments are consistent with the differences being associated with different degrees of short-range order.

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