PHYSICAL REVIEW B VOLUME 9, NUMBER 4 15 FEBRUARY 1974

Specific heat of silver-gold alloys below 30 °K

Douglas L. Martin
Division of Physics, National Research Council of Canada, Ottawa, Canada

(Received 26 September 1973)

The present measurements on six alloys cover the range 2.5–30 °K and are combined with earlier data below 3 °K on the same alloys for analysis. The anomalous maximum at about 8 °K in the Debye temperature of gold slowly decreases in magnitude and moves to lower temperatures as silver is added to gold. The alloy specific heats are compared with those calculated using the Kopp-Neumann rule (i.e., mixtures of the pure metals) and show negative percentage deviations of similar form for all alloys with the magnitude depending on composition and reaching a maximum for the equiatomic alloy. The nuclear entropy observed in the alloys but not in the pure metals is discussed in the context of the third law of thermodynamics and computation of the thermodynamic functions.

INTRODUCTION

The discovery[1] of the anomalous variation of the Debye temperature of gold with temperature (a maximum occurs at about 8 °K) and the probable normality of silver[2] prompted experiments in the 3–30 °K range on a number of silver-gold alloys. There is a continuous range of solubility in the silver-gold system with only a single phase. There is no sound evidence for any long-range ordering but short-range ordering probably occurs.[3] The results show that the anomalous maximum in Debye temperature gradually lessens and moves to lower temperatures as silver is added to gold. The question remains open whether there is still a slight maximum in silver which, combining with the normally falling Debye temperature, could account for the long T^3 region in the specific heat. The present results are also of interest in connection with the lattice specific heat of alloys generally and an analysis is made in terms of deviations from the Kopp-Neumann rule. Nuclear energy levels are not normally considered in calculating the thermodynamic functions[4] but have been considered again here because, while many ideal pure metals (e.g., silver and gold) show no nuclear specific heat, one may appear in an alloy owing, for example, to the disturbance of cubic symmetry.[5,6] It is concluded that the normal rules apply and the nuclear entropy should be ignored in calculating the thermodynamic functions.

EXPERIMENTAL

This work was started a number of years ago and measurements on nominally 95-at.%-Au–5-at.%-Ag, 90-at.%-Au–10-at.%-Ag, and 75-at.%-Au–25-at.%-Ag alloys were made in the apparatus of Ref. 2. Work was then suspended owing to problems in making homogenous silver-rich alloys and, although the alloys were made some years ago, it is only recently that work was resumed. In the meantime an automatic calorimeter had been developed[7] and the measurements on the remaining alloys were made with this apparatus. The pure silver and gold measurements were also made with this new apparatus and have been reported elsewhere.[8]

For all samples but one, two separate sets of measurements were made, warming the apparatus to room temperature between sets. The remaining sample (50-at.% Au) was only measured once because some measurements on the same nominal composition were available from the earlier work. However, it was later discovered that these earlier measurements were on a somewhat inhomogeneous sample which was afterwards discarded. Since the new measurements on the 50-at.%-Au sample fit in nicely with the other results it was not thought worthwhile to make another run.

All measurements are based[2] on the NBS-1955 provisional platinum temperature scale in the 20–30 °K range, on a gas-thermometer scale between 4 and 20 °K and on the 1958 ^{4}He vapor-pressure scale at lower temperatures.

The specific-heat samples are those described in Tables I and II of Ref. 6 and will be referred to in this paper by their nominal composition, although the average atomic weight obtained from wet analysis is again used in evaluating results.

RESULTS

The new results reported here are in the temperature range 2.5–30 °K and were combined with earlier results[6] in the 0.4–3.0 °K range for curve fitting. This is to minimise error in the overlap region where both apparatuses are probably subject to maximum experimental error.[7] The raw data were fitted by the least-squares method to the relation

$$C_p = \frac{H}{T^2} + \sum_{n=0}^{10} a_n T^{2n+1},$$

where the first term represents the leading term of the nuclear specific heat, the first term in the summation represents the electronic specific heat, and the remaining terms represent the lattice specific heat. In an attempt to remove erroneous points those deviating by more than three standard deviations were rejected and the curve fit repeated until no further points were rejected. The coefficients obtained, with their 95% confidence limits from the statistical analysis, are given in Table I. Deviations of the raw data from the fitted relation are given in Fig. 1. The deviations fit the same pattern for all the alloys as well as the pure metals[8] and represent slight errors in the temperature scale.

Using the electronic-specific-heat coefficients determined from the statistical analysis (i.e., a_1 in Table I) and converting C_p(lattice) to C_v(lattice) in the usual way,[9] Debye temperatures for the raw data were calculated and are plotted in Fig. 2.

DISCUSSION

In Table I the term a_{-2} is the coefficient of the leading term of the nuclear specific heat, thought to arise because the cubic symmetry is disturbed in these disordered cubic alloys and the resulting electric field gradients at nuclear sites split the levels associated with the electric quadrupole moment of the gold nucleus.[5,6] The term a_1 is the electronic-specific-heat coefficient γ, the term a_3 is related to the low-temperature limiting value of Debye temperature Θ_0^c and the term a_5—together perhaps with other terms—determines whether the Debye temperature will initially decrease or increase with increasing temperature. The values obtained for these quantities from the present analysis are compared in Table II with those given previously[6] from the measurements below 3 °K and those subsequently obtained by Davis and Rayne.[10] The error limits given in Table II for Ref. 6 include some allowance for possible systematic errors; the authors of Ref. 10 suggest that the stated error limits should be doubled to allow for possible systematic errors, and the error limits for the present results are the 95% confidence limits from the statistical analysis. It is thought[8] that, because the present analyses are on results over a wide temperature range, temperature-scale errors will be minimised. However, it is still possible that the error limits assigned to the present results should be increased to take account of possible systematic errors. Reference to Table II shows rather good agreement between the present and earlier[6] results on the same samples, in most cases within the combined error limits. Davis and Rayne's results[10] correspond to their specific-heat values being systematically higher for both the pure metals and alloys. However, the general trends are the same except that they find a deviation at the gold-rich end from a symmetrical relationship between γ and composition. (The point for the 95-at.% gold in the present work is high owing to a relatively high transition-metal impurity content.[6]) This could point to some errors in determining alloy composition. Davis and Rayne[10] have probably based their results on the weights of metal used in making the alloys whereas the present work is based on wet-analysis composition determinations which were found to give smoother results.[6]

In calculating the Debye temperatures (Fig. 2) it has been assumed that the electronic-specific-heat coefficients remain constant over the temperature range of measurement. This is not so because the electron-phonon enhancement of the electronic specific heat is a function of temperature.[11] However, it is unlikely that the probable variation will significantly affect the Debye temperatures because the electronic specific heat becomes rather a small fraction of the total and the electron-phonon mass enhancement itself is probably rather small.[11] Examining Fig. 2 shows that the anomalous maximum in the Debye temperature observed for gold is reduced in magnitude on alloying and moves to lower temperatures. It is a matter for speculation whether there is still a slight maximum in silver which could account for the long apparent T^3 region in the specific heat. The maximum in Debye temperature in gold has recently been identified with positive dispersion in the T_1 branch of the phonon spectrum as determined by coherent inelastic neutron scattering.[12] There may also be a small bump in the Debye-temperature plot for silver as determined from neutron scattering results.[13] Similar effects have been seen in aluminum[14] and solid helium.[15] The present and earlier[2] calorimetric result for pure gold has been qualitatively confirmed elsewhere.[16]

Single-impurity theories[17] show that when a heavy impurity is substituted isotopically (i.e., no force-constant change) in a light lattice a low-frequency resonance mode is formed and the specific heat will then initially increase more rapidly than does that of the parent lattice. Conversely, a light impurity results in modes at or above the high-frequency end of the spectrum. Specific-heat experiments[18] on dilute (~1%) alloys have qualitatively confirmed theoretical predictions for heavy impurities. Later experiments on KCl:TlCl showed that the temperature of the maximum of the low-frequency-resonance-mode contribution to the specific heat scarcely varied as the thallium contribution was increased from 1 to 5 at.%,[19] i.e., the single-impurity theory holds qualitatively for relatively concentrated alloys in this system. The earliest theory used the Debye approximation for the lattice vibration spectrum.

TABLE I. Polynomial coefficients representing specific heat $C=\Sigma\, a_n T^n$. Units cal/°K g atom. $J=4.186$. Error limits are 95% confidence limits for each coefficient from the statistical analysis. Each polynomial reproduces the smoothed specific heat to within 0.01% up to 30 °K (except for gold where two polynomials are used).

		Symbol in figures
Silver	Atomic weight 107.87	▶◀
	$a_1 = +(0.152\,796 \pm 0.00016)\times 10^{-3}$	
	$a_3 = +(0.399\,012 \pm 0.00091)\times 10^{-4}$	
	$a_5 = -(0.106\,099 \pm 0.059)\times 10^{-7}$	
	$a_7 = +(0.467\,857 \pm 0.12)\times 10^{-9}$	
	$a_9 = -(0.172\,020 \pm 0.11)\times 10^{-11}$	
	$a_{11} = +(0.176\,165 \pm 0.49)\times 10^{-14}$	
	$a_{13} = +(0.024\,7367 \pm 0.12)\times 10^{-16}$	
	$a_{15} = -(0.078\,9427 \pm 0.17)\times 10^{-19}$	
	$a_{17} = +(0.073\,1169 \pm 0.13)\times 10^{-22}$	
	$a_{19} = -(0.239\,793 \pm 0.38)\times 10^{-26}$	
90-at.% Ag–10-at.% Au	$a_{-2} = +(0.909\,412\,42 \pm 0.30)\times 10^{-7}$	▲ ▼
	$a_1 = +(0.152\,392\,55 \pm 0.00026)\times 10^{-3}$	
	$a_3 = +(0.434\,475\,00 \pm 0.0013)\times 10^{-4}$	
	$a_5 = -(0.466\,534\,04 \pm 0.10)\times 10^{-7}$	
	$a_7 = +(0.163\,401\,43 \pm 0.025)\times 10^{-8}$	
	$a_9 = -(0.135\,850\,01 \pm 0.027)\times 10^{-10}$	
	$a_{11} = +(0.631\,629\,82 \pm 0.16)\times 10^{-13}$	
	$a_{13} = -(0.182\,070\,36 \pm 0.054)\times 10^{-15}$	
	$a_{15} = +(0.326\,465\,51 \pm 0.11)\times 10^{-18}$	
	$a_{17} = -(0.352\,187\,10 \pm 0.12)\times 10^{-21}$	
	$a_{19} = +(0.208\,657\,14 \pm 0.078)\times 10^{-24}$	
	$a_{21} = -(0.520\,807\,23 \pm 0.21)\times 10^{-28}$	
75-at.% Ag–25-at.% Au	$a_{-2} = +(0.246\,860\,87 \pm 0.030)\times 10^{-6}$	■◆
	$a_1 = +(0.151\,935\,21 \pm 0.00027)\times 10^{-3}$	
	$a_3 = +(0.481\,198\,81 \pm 0.0014)\times 10^{-4}$	
	$a_5 = -(0.177\,905\,91 \pm 0.10)\times 10^{-7}$	
	$a_7 = +(0.137\,958\,78 \pm 0.024)\times 10^{-8}$	
	$a_9 = -(0.111\,691\,44 \pm 0.027)\times 10^{-10}$	
	$a_{11} = +(0.484\,882\,19 \pm 0.15)\times 10^{-13}$	
	$a_{13} = -(0.132\,437\,96 \pm 0.051)\times 10^{-15}$	
	$a_{15} = +(0.229\,662\,25 \pm 0.10)\times 10^{-18}$	
	$a_{17} = -(0.243\,200\,05 \pm 0.12)\times 10^{-21}$	
	$a_{19} = +(0.142\,749\,33 \pm 0.074)\times 10^{-24}$	
	$a_{21} = -(0.354\,928\,27 \pm 0.19)\times 10^{-28}$	
50-at.% Ag–50-at.% Au	$a_{-2} = +(0.744\,770\,39 \pm 0.035)\times 10^{-6}$	○
	$a_1 = +(0.152\,519\,85 \pm 0.00032)\times 10^{-3}$	
	$a_3 = +(0.588\,381\,09 \pm 0.0019)\times 10^{-4}$	
	$a_5 = -(0.619\,995\,71 \pm 0.17)\times 10^{-7}$	
	$a_7 = +(0.236\,091\,39 \pm 0.043)\times 10^{-8}$	
	$a_9 = -(0.187\,682\,54 \pm 0.048)\times 10^{-10}$	
	$a_{11} = +(0.792\,449\,89 \pm 0.29)\times 10^{-13}$	
	$a_{13} = -(0.207\,249\,76 \pm 0.096)\times 10^{-15}$	
	$a_{15} = +(0.342\,793\,90 \pm 0.19)\times 10^{-18}$	
	$a_{17} = -(0.347\,288\,84 \pm 0.22)\times 10^{-21}$	
	$a_{19} = +(0.196\,070\,16 \pm 0.14)\times 10^{-24}$	
	$a_{21} = -(0.471\,477\,43 \pm 0.36)\times 10^{-28}$	
25-at.% Ag–75-at.% Au	$a_{-2} = +(0.764\,035\,63 \pm 0.048)\times 10^{-6}$	◇□
	$a_1 = +(0.156\,972\,24 \pm 0.00040)\times 10^{-3}$	
	$a_3 = +(0.769\,000\,19 \pm 0.0026)\times 10^{-4}$	
	$a_5 = -(0.144\,666\,08 \pm 0.022)\times 10^{-6}$	
	$a_7 = +(0.368\,046\,14 \pm 0.057)\times 10^{-8}$	
	$a_9 = -(0.298\,829\,45 \pm 0.068)\times 10^{-10}$	
	$a_{11} = +(0.132\,461\,39 \pm 0.042)\times 10^{-12}$	
	$a_{13} = -(0.364\,521\,88 \pm 0.15)\times 10^{-15}$	
	$a_{15} = +(0.633\,361\,37 \pm 0.32)\times 10^{-18}$	
	$a_{17} = -(0.672\,682\,15 \pm 0.39)\times 10^{-21}$	
	$a_{19} = +(0.397\,479\,83 \pm 0.26)\times 10^{-24}$	
	$a_{21} = -(0.999\,182\,74 \pm 0.73)\times 10^{-28}$	

TABLE I. (*continued*)

10-at.% Ag–90-at.% Au	$a_{-2} = +(0.463\,484\,49 \pm 0.032) \times 10^{-6}$	△▽
	$a_1 = +(0.160\,917\,22 \pm 0.00031) \times 10^{-3}$	
	$a_3 = +(0.939\,894\,10 \pm 0.0020) \times 10^{-4}$	
	$a_5 = -(0.271\,069\,72 \pm 0.017) \times 10^{-6}$	
	$a_7 = +(0.517\,835\,66 \pm 0.042) \times 10^{-8}$	
	$a_9 = -(0.401\,103\,96 \pm 0.047) \times 10^{-10}$	
	$a_{11} = +(0.172\,668\,29 \pm 0.028) \times 10^{-12}$	
	$a_{13} = -(0.460\,340\,12 \pm 0.093) \times 10^{-15}$	
	$a_{15} = +(0.772\,936\,18 \pm 0.18) \times 10^{-18}$	
	$a_{17} = -(0.792\,586\,64 \pm 0.22) \times 10^{-21}$	
	$a_{19} = +(0.452\,177\,06 \pm 0.14) \times 10^{-24}$	
	$a_{21} = -(0.109\,784\,34 \pm 0.036) \times 10^{-27}$	
5-at.% Ag–95-at.% Au	$a_{-2} = +(0.592\,968\,02 \pm 0.056) \times 10^{-6}$	▷◁
	$a_1 = +(0.163\,384\,82 \pm 0.00043) \times 10^{-3}$	
	$a_3 = +(0.100\,348\,79 \pm 0.00028) \times 10^{-3}$	
	$a_5 = -(0.318\,007\,30 \pm 0.023) \times 10^{-6}$	
	$a_7 = +(0.570\,148\,52 \pm 0.060) \times 10^{-8}$	
	$a_9 = -(0.441\,448\,11 \pm 0.069) \times 10^{-10}$	
	$a_{11} = +(0.192\,626\,65 \pm 0.042) \times 10^{-12}$	
	$a_{13} = -(0.523\,589\,64 \pm 0.15) \times 10^{-15}$	
	$a_{15} = +(0.899\,097\,82 \pm 0.30) \times 10^{-18}$	
	$a_{17} = -(0.944\,563\,01 \pm 0.36) \times 10^{-21}$	
	$a_{19} = +(0.552\,697\,96 \pm 0.24) \times 10^{-24}$	
	$a_{21} = -(0.137\,732\,08 \pm 0.065) \times 10^{-27}$	
Gold	Atomic weight 196.967	
	Temperature below 17.5 °K	
	$a_1 = +(0.164\,661\,3 \pm 0.00027) \times 10^{-3}$	▶◀
	$a_3 = +(0.109\,577\,2 \pm 0.00033) \times 10^{-3}$	
	$a_5 = -(0.438\,692\,5 \pm 0.053) \times 10^{-6}$	
	$a_7 = +(0.699\,309\,8 \pm 0.28) \times 10^{-8}$	
	$a_9 = -(0.392\,164\,5 \pm 0.65) \times 10^{-10}$	
	$a_{11} = -(0.05\,604\,519 \pm 0.83) \times 10^{-12}$	
	$a_{13} = +(0.195\,780\,1 \pm 0.60) \times 10^{-14}$	
	$a_{15} = -(0.115\,075\,8 \pm 0.26) \times 10^{-16}$	
	$a_{17} = +(0.333\,032\,9 \pm 0.66) \times 10^{-19}$	
	$a_{19} = -(0.492\,041\,1 \pm 0.91) \times 10^{-22}$	
	$a_{21} = +(0.295\,844\,0 \pm 0.52) \times 10^{-25}$	
	Temperature above 17.5 °K	
	$a_0 = +0.116\,496\,8 \times 10^{+2}$	
	$a_1 = -0.328\,235\,9 \times 10^{+1}$	
	$a_2 = +0.377\,504\,6$	
	$a_3 = -0.226\,197\,6 \times 10^{-1}$	
	$a_4 = +0.759\,135\,2 \times 10^{-3}$	
	$a_5 = -0.134\,368\,9 \times 10^{-4}$	
	$a_6 = +0.976\,089\,9 \times 10^{-7}$	

Later theories have used the pure-metal spectrum as determined by neutron-scattering techniques and recently it has been shown that force-constant changes can improve the agreement between experiment and theory even further.[20]

The more dilute of the alloys measured in the present work will first be considered as they may offer a point of contact with the above "single impurity" theories and experiments. In Fig. 3 smoothed values for pure gold have been subtracted from the smoothed specific heat of the two gold-rich alloys and similarly the difference between the silver-rich alloy and pure silver is also shown, in all cases as a percentage difference of specific heat. The result for the silver-rich alloy (i.e., heavy impurity) is similar to those obtained for more dilute alloys with heavy impurities.[18] As far as the author is aware the case of light impurities has not been experimentally studied before. The gold-rich alloy results (Fig. 3) show the alloy specific heat to be less than that of the pure metal, as might be expected as there is a transfer of modes to the high-frequency end of the vibration spectrum. The difference is roughly proportional to the amount of silver added. The reason for the sharp minimum (in $\Delta C/C$) at about 4 °K is not known but it may be consistent with the phonon spectrum found by Mozer and Maradudin for a half-mass

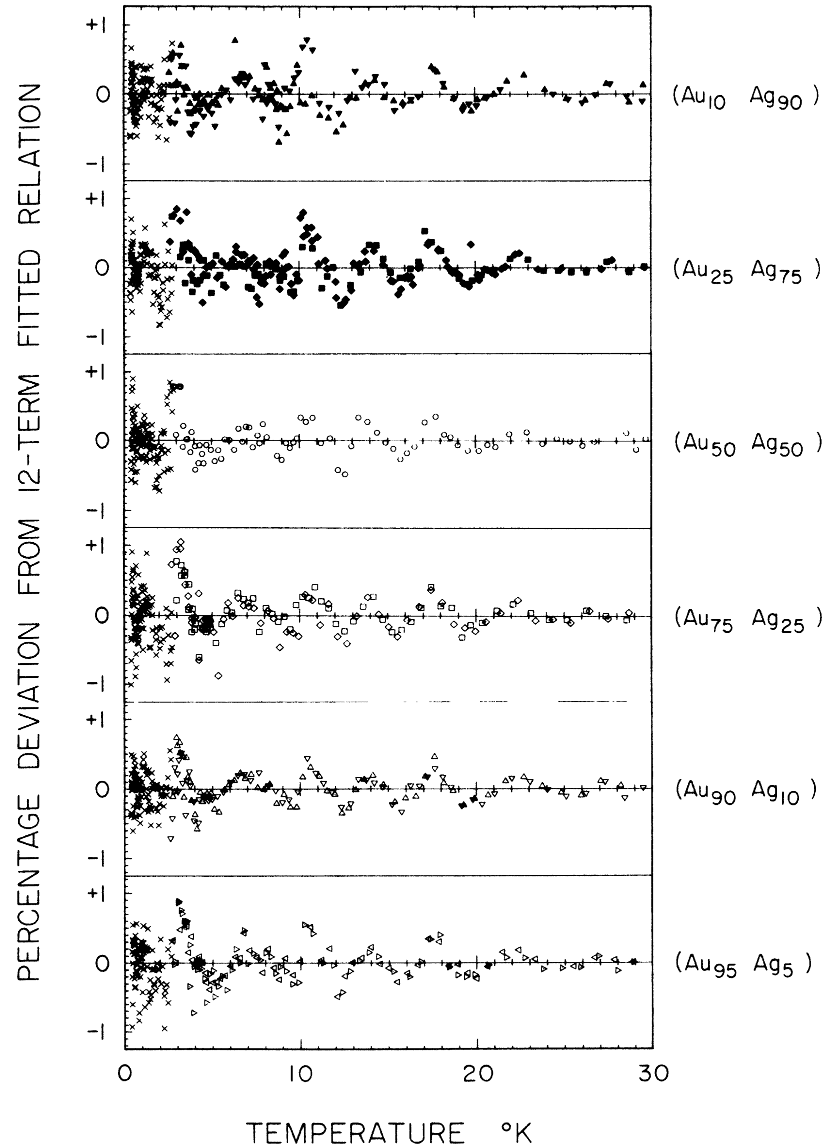

FIG. 1. Percentage deviation of raw specific-heat data from the fitted relation. See Table I for symbol key. Raw data from Ref. 6 are indicated by ×.

isotopic impurity in a fcc lattice (see Ref. 21, p. 494) which shows the depopulation of the pure-metal vibration spectrum to occur in the low-frequency half of the spectrum, the impurity band lying above the high-frequency end of the pure-metel spectrum.

Much theoretical work has been done on the problem of more concentrated alloys, the simple approaches retaining the "isotopic" approximation whereas later theories have taken account of both force-constant and volume changes on alloying. A good summary has been given by Maradudin, Montroll, Weiss, and Ipatova.[21] The culmination of this work (much of which, unfortunately, remains in a complicated analytic form not readily comparable with experiment) was, perhaps, the numerical evaluation of the vibration spectra of small three-dimensional crystals by Payton and Visscher.[22] Recent interest has been mainly concerned with the interpretation of inelastic neutron scattering results on particular alloys. Such an experiment, currently in progress on the silver-gold system,[13] should serve to explain some of the detail in the present specific heat results. It should be noted that the interpolation formula for Debye temperature as a function of composition given by Iosilevskii[23] for the isotopic impurity case predicts a deviation from linearity in the opposite direction to that observed in the present work for silver-gold alloys–suggesting that force constant changes are quite significant.

Figure 4 shows results for all the alloys where, instead of subtracting C_p for a pure metal, a mixture of pure silver and gold specific heats, as specified by the composition of the alloy, has

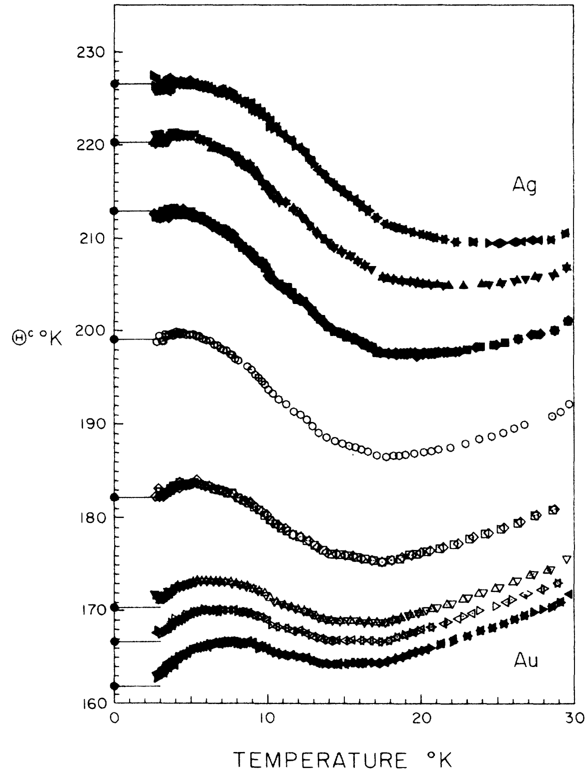

FIG. 2. Debye temperatures as a function of temperature. The solid circles are Θ_0^c values. See Table I for key to other symbols.

been subtracted (i.e., the Kopp-Neumann rule is used). In order to attempt to understand Fig. 4 it is necessary to consider both the lattice dynamics and thermodynamics of alloys. A crude picture of the lattice dynamics aspect has been sketched above. Thermodynamically an entropy of formation of the molten alloy may be experimentally determined. Part of this is accounted for by the entropy of mixing and any excess or deficit entropy will require that, after correction for nonperfect mixing (e.g., short-range order), the average specific heat of the alloy be raised or lowered with respect to the corresponding mixture of the pure metals. However, the lattice dynamics considerations, mentioned above, will modulate this general shift and both positive and negative deviations may be found. It is seen (Fig. 4) that all alloys exhibit a similar form of deviation from the Kopp-Neumann rule with the magnitude of the deviation depending on alloy composition. In all cases the deviation is similar to that shown for the "light impurity" in Fig. 3. Since the minima are smoothly decreasing as the alloys become more dilute it is thought that they are real and not the result of an experimental or numerical error. In any case it should be noted that the percentage difference is plotted in Fig. 4 and the clear minima there are not, in fact, minima in the absolute specific-heat difference between the alloy measurements and the Kopp-Neumann-rule estimates. The symmetry round the equiatomic composition is rather surprising and very similar to the symmetry seen in the excess entropy of mixing plot given by Kleppa[24] and also correlates in sign with the thermodynamic consequences of that plot. However, in Fig. 4 percentage differences have been plotted rather than absolute differences. Thus, the entropy differences are smaller (less negative) for the silver-rich alloys that for the gold-rich alloys and hence the symmetry is less good than Fig. 4 suggests. In fact, similarly nonsymmetric data have been obtained from the mean square vibration amplitudes deduced from an x-ray study of silver-gold alloys at 500 °C.[25] If the calorimetric and x-ray data are correct and if the larger entropy deficit for the gold-rich alloys persists over the whole temperature range, then one might conclude that short-range ordering was more likely in silver-rich alloys (from the observation[24] of a negative excess entropy of mixing symmetrical in composition).

It should be noted that in Figs. 3 and 4 the total specific heat has been used in computing the differences whereas the theories refer to lattice specific heat only. This was done because the electronic specific heat (Table II and Ref. 6) differs at most (at the equiatomic composition) by 4% from a linearly interpolated value and at 5 °K the electronic specific heat is about 13% of the total for silver and 6% of the total for gold.

The observed initial negative deviations for all alloy compositions (Fig. 4) are inevitable in view of the slight negative deviation of γ values from a linear interpolation combined with the slight positive deviation of Θ_0^c values from a linear interpolation (Table II and Ref. 6); however, the γ and Θ_0^c values alone are insufficient to account for the large specific-heat deviations seen in Fig. 4. Probably an explanation of the results must await the completion of the inelastic neutron scattering studies on silver-gold alloys which are currently in progress.[13]

Obviously, measurements to higher temperatures on this alloy system will be of interest and are being planned. However, results may be less clear-cut because the (C_p-C_v) correction will then become significant and lack of suitable data may necessitate approximations in calculating this term.

The discussion of entropy given above neglected consideration of the nuclear entropy which is normally ignored in computing thermodynamic functions[4] on the ground that the nuclear entropy is not

TABLE II. Comparison of results on silver-gold alloys. Units μcal/°Kg atom. $J=4.186$.

Composition	$H(T^{-2})$	$\gamma(T)$	Θ(°K)	$a_5(T^5)$	Ref.
Pure silver	•••	153.0 ± 0.3	226.7 ± 0.8	−0.06 ± 0.07	a
	•••	154.6 ± 0.5	225.2 ± 0.1	+0.01 ± 0.01	b
	•••	152.8 ± 0.2	226.6 ± 0.2	−0.01 ± 0.01	c
90-at.% Ag–10-at.% Au	0.05 ± 0.05	153.1 ± 0.6	221.9 ± 0.8	+0.14 ± 0.07	a
	•••	153.5 ± 0.6	219.8 ± 0.1	+0.02 ± 0.01	b
	0.09 ±0.03	152.4 ± 0.3	220.3 ± 0.2	−0.05 ± 0.01	c
80-at.% Ag–20-at.% Au	•••	153.4 ± 0.6	214.8 ± 0.1	+0.02 ± 0.01	b
75-at.% Ag–25-at.% Au	0.23 ± 0.05	152.2 ± 0.5	213.0 ± 0.7	−0.05 ± 0.07	a
	0.25 ± 0.03	151.9 ± 0.3	212.9 ± 0.2	−0.02 ± 0.01	c
70-at.% Ag–30-at.% Au	•••	153.3 ± 0.5	209.5 ± 0.1	+0.03 ± 0.02	b
50-at.% Ag–50-at.% Au	0.68 ± 0.04	153.4 ± 0.5	200.4 ± 0.5	+0.14 ± 0.07	a
	•••	154.5 ± 0.5	198.2 ± 0.1	+0.02 ± 0.01	b
	0.74 ± 0.04	152.5 ± 0.3	199.1 ± 0.2	−0.06 ± 0.02	c
25-at.% Ag–75-at.% Au	0.75 ± 0.06	157.1 ± 0.7	182.1 ± 0.5	−0.19 ± 0.11	a
	•••	158.9 ± 0.5	181.6 ± 0.1	−0.03 ± 0.02	b
	0.76 ± 0.05	157.0 ± 0.4	182.1 ± 0.2	−0.15 ± 0.02	c
17.5-at.% Ag–82.5-at.% Au	•••	162.6 ± 0.6	176.1 ± 0.1	−0.06 ± 0.03	b
10-at.% Ag–90-at.% Au	0.44 ± 0.05	161.4 ± 0.6	170.7 ± 0.4	−0.14 ± 0.12	a
	•••	165.2 ± 0.6	170.1 ± 0.1	−0.12 ± 0.06	b
	•••	164.9 ± 0.6	170.2 ± 0.1	−0.11 ± 0.06	b
	0.46 ± 0.03	160.9 ± 0.3	170.3 ± 0.1	−0.27 ± 0.02	c
5-at.% Ag–95-at.% Ag	0.51 ± 0.08	164.4 ± 0.8	167.3 ± 0.5	−0.16 ± 0.15	a
	•••	166.0 ± 0.6	165.7 ± 0.1	−0.17 ± 0.09	b
	0.59 ± 0.06	163.4 ± 0.4	166.6 ± 0.2	−0.32 ± 0.02	c
Pure gold	•••	165.1 ± 0.4	162.3 ± 0.3	−0.23 ± 0.11	a
	•••	166.9 ± 0.6	161.7 ± 0.1	−0.23 ± 0.10	b
	•••	164.7 ± 0.3	161.8 ± 0.2	−0.44 ± 0.05	c

[a] Reference 6. [b] Reference 10. [c] This work.

changed in chemical reactions. However, while no nuclear specific heat has been observed in pure silver and pure gold, a significant nuclear specific heat is observed in silver-gold alloys[5,6] (see Table I). If, in fact, the nuclear energy levels in the pure metals were degenerate, then account would have to be taken of the nuclear entropy of the alloys in calculating the thermodynamic functions. However, it seems probable that small perturbations (e.g., dislocations, zero-point motion) in the pure metals would cause a very small splitting of the nuclear levels. Then the nuclear entropy of an alloy would be the same as the sum of the nuclear entropies of pure metals and the nuclear entropy could be ignored in computing the thermodynamic functions as is usually the case. The Schotty anomaly arising in the pure metal would probably be at such a low temperature as to be unobservable by present day techniques. It might be noted here that a degenerate ground state (which can be realized in more than one way and hence has a residual entropy at the absolute zero) is not consistent with the third law of thermodynamics.[26]

A further problem arises in relation to the third law. A solid solution has an entropy of mixing which persists to the absolute zero. Presumably true equilibrium corresponds to either an ordered or unmixed condition which cannot be achieved owing to the very slow rate of diffusion in the solid at temperatures at which the ordered state

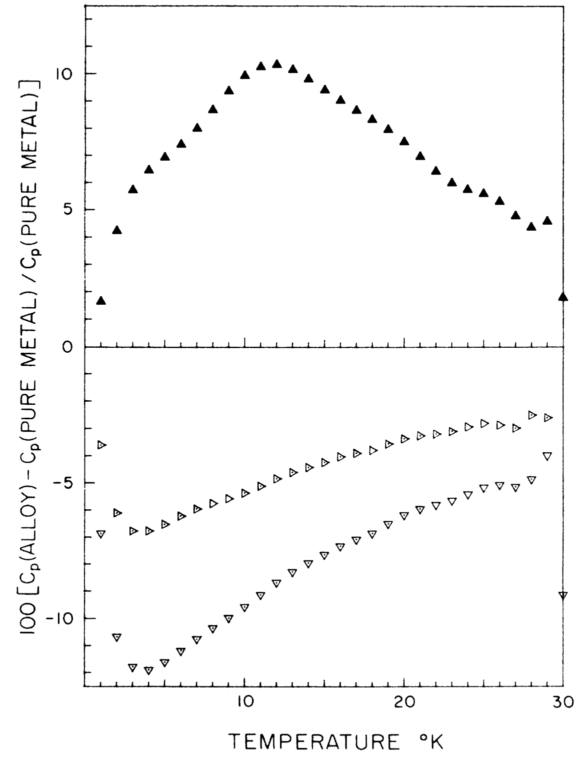

FIG. 3. Percentage deviation of specific heat of 90-at.%-Ag–10 at.%-Au alloy from that of pure silver and of 5-at.%-Ag-95-at.%-Au and 10-at.%-Ag-90-at.%-Au alloys from that of pure gold. Smoothed results at 1 °K intervals are plotted. See Table I for symbol key.

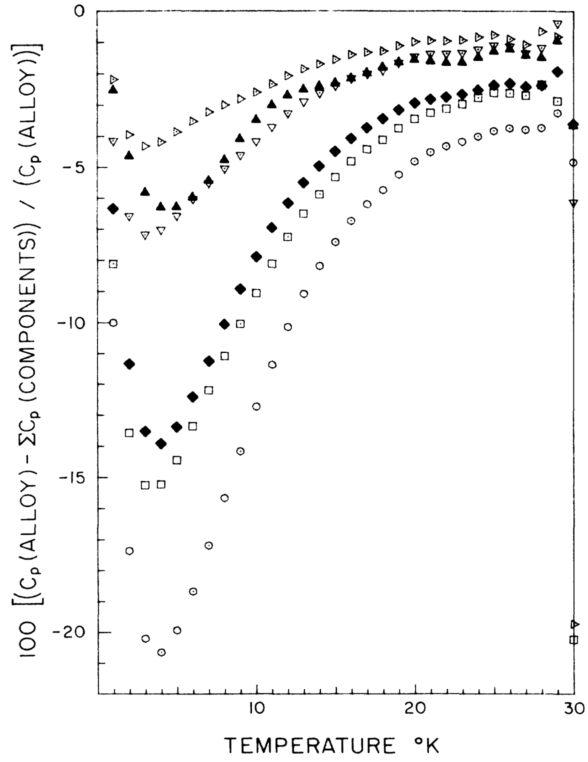

FIG. 4. Percentage deviation of the specific heats of silver-gold alloys from specific heats calculated by the Kopp-Neumann rule. Smoothed results at 1 °K intervals are plotted. See Table I for symbol key.

becomes the equilibrium state.[4] Thus a disordered solid solution does not violate the third law since the internal equilibrium condition has not been met.

CONCLUSIONS

As silver is alloyed to gold the clear anomalous maximum in the Debye temperature is reduced and moves to lower temperatures. There may still be a small maximum in silver. The specific heats of all the alloys lie below the Kopp-Neumann rule estimates as required by the earlier observation of a negative excess entropy of mixing in this system. A theoretical treatment of the lattice dynamics of the alloy system is required to explain *why* the alloy specific heats are below the Kopp-Neumann value. The observed deviations from the Kopp-Neumann Rule values become rather large in the region around 4°K. The entropy associated with the nuclear specific heat observed in the alloys should not be used in computing the thermodynamic functions.

ACKNOWLEDGMENTS

Information was kindly supplied by Dr. J. W. Lynn, Dr. H. G. Smith, and Dr. R. M. Nicklow on their neutron-scattering work. I am also indebted to Miss Maureen Leaver and R. L. Snowdon for their ready assistance, the former in preparing the results for publication and the latter with the experiments.

---

[1] D. L. Martin, Phys. Rev. Lett. 12, 723 (1964).

[2] D. L. Martin, Phys. Rev. 141, 576 (1966).

[3] E. Lang, Z. Metallkde 64, 56 (1973).

[4] See, for example, A. R. Ubbelohde, *An Introduction to Modern Thermodynamic Principles* (Oxford U. P., London, 1952).

[5] D. L. Martin, Phys. Rev. Lett. 18, 839 (1967).

[6] D. L. Martin, Phys. Rev. 176, 790 (1968).

[7] D. L. Martin, L. L. T. Bradley, W. Cazemier, and R. L. Snowdon, Rev. Sci. Instr. 44, 675 (1973).

[8] D. L. Martin, Phys. Rev. B (to be published).

[9] Below 30 °K the correction is almost negligible. For the alloys the parameters required in the correction equation were linearly interpolated between the values for pure silver and gold.

[10] T. H. Davis and J. A. Rayne, Phys. Rev. B 6, 2931 (1972).

[11] G. Grimvall, J. Phys. Chem. Solids 29, 1221 (1968); Phys. Kondens. Materie 11, 279 (1970).

[12] J. W. Lynn, H. G. Smith, and R. M. Nicklow, Phys. Rev. B. 8, 3493 (1973).

[13] J. W. Lynn (private communication).

[14] W. T. Berg, Phys. Rev. 167, 583 (1968). The behavior later observed in the specific heat of aluminum was predicted by G. Gilat and R. M. Nicklow [Phys. Rev. 143, 487 (1966] who fitted an eight-nearest-neighbor Born-von Karman force constant model to the phonon dispersion curves derived from neutron scattering measurements at 80 °K. The phonon spectrum and specific heat were then calculated. The cause of the anomalous maximum in Θ^c was not identified at the time but is now thought to be owing to positive dispersion in the $T2$ branch of the phonon spectrum. (Ref. 12).

[15] S. H. Castles and E. D. Adams, Phys. Rev. Lett. 30, 1125 (1973). The maximum in Θ^c is dependent on their present interpretation of the results which is not entirely satisfactory (e.g., it does not appear to lead to the required identity of elastic and thermal Debye temperatures in the low-temperature limit).

[16] B. M. Boerstoel, J. J. Zwart, and J. Hansen, Physica (Utr.) 54, 442 (1971).

[17] Ya M. Kagan and Ya A. Iosilevskii, Zh. Eksp. Teor. Fiz. 42, 259 (1962); [Sov. Phys.-JETP 15, 182 (1962)]; Zh Eksp. Teor. Fiz. 45, 819 (1963) [Sov. Phys.-JETP 18 , 562 (1964) ; G. W. Lehman and R. E. de Wames, Phys. Rev. 131, 1008 (1963).

[18] G. Kh. Panova and B. N. Samoilov, Zh. Eksp. Teor. Fiz. 49, 456 (1965) [Sov. Phys.-JETP 22, 320 (1966)]; J. A. Cape, G. W. Lehman, W. V. Johnston and R. E. de Wames, Phys. Rev. Lett. 16, 892 (1966); W. M. Hartman, H. V. Culbert, and R. P. Huebener, Phys. Rev. B. 1, 1486 (1970).

[19] A. V. Karlsson, Phys. Rev. B 2, 3332 (1970).

[20] M. D. Tiwari, K. M. Kesharwani, and B. K. Agrawal, Phys. Rev. B 7, 2378 (1973).

[21] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and

I. P. Ipatova, *Solid State Physics. Suppl.* 3, *Theory of Lattice Dynamics in the Harmonic Approximation*, 2nd ed. (Academic, New York, 1971).

[22] D. N. Payton and W. M. Visscher, Phys. Rev. 154, 802 (1967); Phys. Rev. 175, 1201 (1968).

[23] Ya. A. Iosilevskii, Fiz. Tverd. Tela 9, 2661 (1967) [Sov. Phys.-Solid State 9, 2090 (1968)].

[24] O. J. Kleppa, J. Phys. Radium 23, 763 (1962).

[25] V. Synecek, M. Simershu, and H. Chessin, Scripta Met. 3, 687 (1969).

[26] See, for example, F. E. Simon, 40*th Guthrie Lecture, Physical Society Yearbook* (Physical Society, London, 1956), p. 1.