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Low-Temperature Specific Heats of *Ag*Sn Alloys*†

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The specific heats of pure Ag and *Ag*Sn alloys up to 8 at.% Sn have been measured between 2 and 4°K with a precision generally better than $\frac{1}{2}\%$. For pure Ag, the result is $\gamma=(0.646\pm0.005)$ mJ mol^{-1}°K,$^{-2}$ and the Debye temperature is (225.5 ± 0.5)°K, both in good agreement with one group of previous workers. The electronic coefficient γ varies linearly versus electron-per-atom ratio e/a at the rate $d(\ln\gamma)/d(e/a)=0.22\pm0.06$, in agreement with the *Ag*Cd data of Montgomery and Pells. The Debye temperature decreases on alloying, following a common curve versus e/a with the *Ag*Cd results. The calorimetric method is unusual; repeated measurements are made at 2, 3, and 4°K only, and considerable thermal conductance is allowed between the sample and a cold reservoir.

INTRODUCTION

THE study of the electronic specific-heat coefficients of dilute noble-metal alloys has given rise to an interesting puzzle about the band structure of the pure metals. Since it is well established that the Fermi surfaces of Cu, Ag, and Au touch the first Brillouin zone boundary, it is expected that the density of states at the Fermi level should decrease as the Fermi energy increases. (This assumes no overlap into the second zone.) However, it has also been established that the electronic specific-heat coefficient γ of copper increases when polyvalent nontransition metals are dissovled into (monovalent) copper.[1–3] One expects that the band structure of the alloy should not be much different from that of the pure metal (the so-called "rigid band model"), and that the polyvalent solute merely contributes electrons to the conduction band, swelling the Fermi surface, and thus leading to a decrease in the density of states, which should be proportional to γ. This does not happen.

It would be very interesting to see how the other noble metals behave in this respect. The *Ag*Cd system (italics denote the major constituent) has been investigated by Montgomery and Pells,[4] who find not only a positive slope but also a new value for the γ for pure silver which is close to that predicted by the free-electron model of silver.

There have been several attempts to account theoretically for the positive slopes of the γ versus concentration curves of these systems. One of the most interesting new ideas in this field[5,6] is that one must take into account the diffuseness of the Fermi surface in the alloys due to the reduced mean free path for the conduction electrons. The "thickness" of the Fermi surface for the alloys may be many times kT. The density of states must be averaged over this thickness to give the electronic specific-heat coefficient If the $E(k)$ relation were concave upward, this averaging would increase the γ value. Of greatest importance to us in this paper is the fact that such an increase should be proportional to the residual resistance per at.% of solute. According to Linde's rule[7] (as well as according to Linde's data for *Ag*Cd and *Ag*Sn) this contribution to the slope should be about nine times as great per at.% solute in *Ag*Sn as in *Ag*Cd, since the excess valence of Cd over Ag is 1, while that of Sn over Ag is 3.

We have now measured the low-temperature specific heats for the *Ag*Sn system up to 8 at.% Sn with a precision better than $\frac{1}{2}\%$. We confirm the near-free-electron value of γ for pure Ag and the increase of γ with solute concentration. Furthermore, the rate of increase is proportional to the *first* power of the excess valence of the solute with respect to Ag. In other terms, we find that the slope of γ versus *electron-per-atom ratio* is *independent* of the solute valence.

EXPERIMENTAL PROCEDURE

The experimental method is unusual in several respects: Measurements are made at only three temperatures, about 2, 3, and 4°K; ten or more measurements are made at each of these mean temperatures. The sample has more thermal contact with a cold reservoir than is usually allowed. An auxiliary heater is used to maintain a thermal steady state when the sample is at one of the average temperatures of measurement. The adjustment is made before each heating period.

The calorimeter is not unusual in its construction. It consists of an evacuated chamber (the "inner can") whose temperature is controlled by pumping on a 5-ml cavity in its top, which is filled with liquid helium from the bath. The inner can is surrounded by an evacuated "outer can" to shield it from the bath, which remains at 4.2°K at all times. Suspended inside the inner can

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[1] J. A. Rayne, Phys. Rev. **108**, 22 (1957).

[2] J. A. Rayne, Phys. Rev. **110**, 606 (1958).

[3] B. W. Veal and J. A. Rayne, Phys. Rev. **130**, 2156 (1963).

[4] H. Montgomery and G. P. Pells, Conference on "The Electronic Structure of Alloys," University of Sheffield, 1963.

[5] H. Jones, Phys. Rev. **134**, A958 (1964).

[6] Attributed to W. Lomer in Ref. 4.

[7] See N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 292.

by three No. 4 nylon screws, 2 cm long, is a small copper disk bearing the thermometer, the main and differential heaters, and a short, threaded stud onto which the sample is screwed. A little Apiezon J oil is used for thermal contact and lubrication. A mechanical thermal switch is used, consisting of a spring-loaded plunger whose indium-faced end presess on the sample holder when lowered and brings it into thermal contact with the 5-ml chamber through a copper braided strap.

Specific heats are determined by measuring the time required to heat between pre-chosen pairs of thermometer resistances. At least ten heats are made at each temperature. Since the variation in heating times is the principal source of randomness, the repetition of measurements between the same pairs of temperatures enables us to estimate the standard deviation of a specific-heat measurement. This may be used to test the linearity of C/T versus T^2 plots, to find the line parameters by weighted least squares, and to test the linearity of the final γ versus e/a plot. The standard error of the mean heating times was always less than 0.4%, and was usually about 0.15%.

The success of this method of specific-heat measurement depends on the use of a heating period which is much longer than the "internal" time constant of the sample and thermometer and yet is much shorter than the "external" time constant of the sample and the cold reservoir. To the extent that these conditions are satisfied, the sample and thermometer are always in thermal equilibrium and the sample is effectively insulated from the reservoir. Experimentally, we find that the internal time constant is considerably less than one second, which is about the reciprocal bandwidth of the thermometer bridge amplifier, and the external time constant is about 6000 sec at 3°K. The heating time is between 30 and 100 sec, being roughly the geometric mean of the two time constants. Error due to the finite internal time constant is further reduced by starting the measured heating period after a "running start" of 5 to 10 sec of application of heat. The temperature intervals were about 100 mdeg at 2 and 4°K and about 200 mdeg at 3°K. The correction for curvature of an assumed exponential heating curve at 3°K was negligible.

It is also assumed that the auxiliary heater power stays equal to the heat leak from sample to reservoir during the heating period. The calculable correction due to the failure of this assumption is negligible. The random fluctuations in heat leak are more serious. The heat balance was checked before and after each heating period. Only rarely was there a change as large as 0.02 μW.

In the error limits to be reported for the alloys of 1 through 7% Sn, there has been no allowance for the uncertainty of the thermometer calibration. This is because these seven runs were made consecutively with the same thermometer (a doped germanium thermometer, Radiation Research Corporation Model CG-1), for which the temperature intervals found from the respective calibrations varied by less than the expected uncertainty in the calibrations. The temperature intervals were thus averaged, and the same average values were used in the reduction of all seven of the runs. After these runs and before the runs on the 0 and 8% samples, the thermometer failed and was replaced by another whose calibration was not so well established as the first one. Thus the error limits set on the 8%-alloy results and on the pure-silver results are considerably larger than those on the 1 through 7% alloys. In analyzing the results, a weighted fit was made to the γ versus e/a curve, weighting by the inverse-squared standard deviations of the γ's. This has the effect of discounting the 0 and 8% results by a factor of about 3.

The thermometer resistance was determined in an 8 cps ac Wheatstone bridge, obtained by adaptation of a Liston-Becker Model 14 dc amplifier.[8] Thermometer power was kept below 10^{-8} W. The thermometer was calibrated after each run against the 1958 He^4 scale. During calibration the inner can was flooded with exchange gas. The 5-ml chamber served as a vapor pressure bulb.

The samples were prepared from 99.9999% Ag and 99.999% Sn[9] by melting in sealed silica tubes under argon. They were removed from the furnace while molten, shaken to insure mixing, brought to a temperature just above the liquidus, and then cooled rapildy by air blast to black heat. They were not cold worked, as is often done to promote uniformity, for fear of contamination by iron. They were annealed in air for several days, lightly machined to remove a surface layer, drilled and tapped for the mounting stud, and etched until no machining marks were visible. The samples in final form were cylinders about 2.5 cm in diameter and 5 cm long, being 1.5 to 2.0 moles of alloy.

Chemical analysis showed some inhomogeneity in the tin concentration. The largest variation was in the 6.8% sample which varied from inside to outside by ±0.14%. The observed rate of change in specific heat is so small that this variation in composition is not serious.

RESULTS

Table I contains the values of γ and θ_D found in this experiment. The results for γ, which are plotted in Fig. 1, follow the relation

$$\gamma=(0.646\pm0.005)+(0.144\pm0.041)(e/a-1)$$

in mJ $\text{mol}^{-1}\,{}^\circ\text{K}^{-2}$ with 95% confidence limits. The Debye temperatures, which are plotted in Fig. 2, decrease nonlinearly on alloying; a quadratic fit gives

$$\theta_D=225.5-21.0(e/a-1)-102(e/a-1)^2$$

in °K to within about 0.2°K average deviation.

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[8] B. A. Green, Jr., Rev. Sci. Instr. **32**, 364 (1961).

[9] Cominco Products Corporation, Spokane, Washington.

TABLE I. Values of γ and θ_D in $C/T=\gamma+\alpha T^2$ for dilute *Ag*Sn alloys, where $\alpha=(12\pi^4 R/5)\theta_D^{-3}$. Errors are one standard deviation.

Concentration (at.% Sn)	γ (mJ mol^{-1} °K^{-2})	θ_D (°K)
0.0	0.648 ± 0.008^a	225.1 ± 0.4^a
1.0	0.654 ± 0.004	225.3 ± 0.2
2.0	0.654 ± 0.002	225.0 ± 0.2
3.0	0.659 ± 0.005	223.1 ± 0.2
3.9	0.661 ± 0.004	221.5 ± 0.2
5.1	0.665 ± 0.004	220.1 ± 0.2
5.8	0.668 ± 0.006	218.2 ± 0.3
6.8	0.680 ± 0.004	217.2 ± 0.2
8.1	0.681 ± 0.008	214.6 ± 0.3

[a] Lower accuracy. See text. Recommended values for pure Ag are estimated by smoothing all data.

DISCUSSION

Electronic Heat Capacity

We shall discuss the value of and uncertainty in the slope of γ versus e/a separately from the intercept, since any undetected systematic error in the specific heats tends to cancel out in the slope.

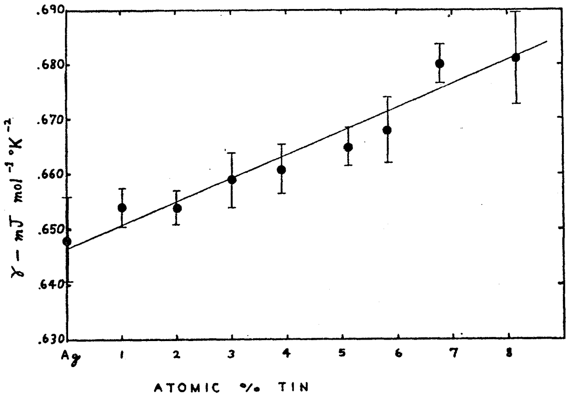

FIG. 1. The electronic specific heat of silver-tin alloys versus atomic fraction of Sn. Error bars are one st. dev.

It is useful to consider the logarithmic derivative of γ with respect to e/a, which may be compared with the value $\frac{1}{3}$ for a free-electron gas. We find for the *Ag*Sn system

$$d(\ln\gamma)/d(e/a)=0.22\pm0.06,$$

with 95% confidence limits. (All error limits quoted below are also 95% confidence limits.)

The greatest interest is attached to the comparison of this slope with that to be found in the system *Ag*Cd.[4] Montgomery and Pells have measured one alloy having 4.2 at.% Cd in Ag by a differential method relative to pure silver with the result

$$d(\ln\gamma)/d(e/a)=0.29\pm0.07.$$

The same authors have also measured 9 other alloys up to about 30 at.% Cd by more conventional means.

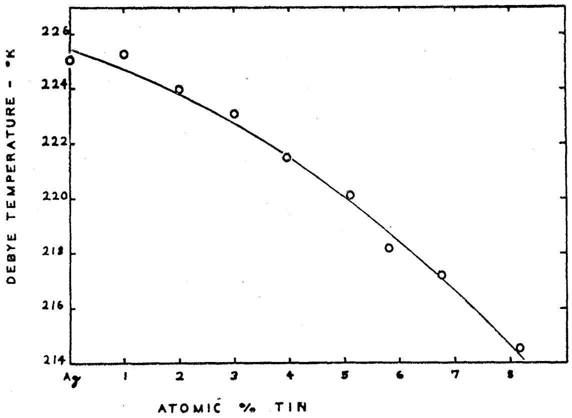

FIG. 2. The Debye temperature of silver-tin alloys versus atomic fraction of Sn.

The results are linear within experimental error, a least squares fit giving

$$d(\ln\gamma)/d(e/a)=0.22\pm0.08.$$

A combined estimate is then about 0.26 ± 0.05. Figure 3 shows the *Ag*Cd and the *Ag*Sn data plotted versus e/a.

It is safe to conclude that the slope for *Ag*Cd cannot be experimentally distinguished from that for *Ag*Sn. It is clear that the slopes do not differ by the large factor required by theories based on the effect of scattering. It may, of course, be that the scattering theory applies only to very low concentrations and that our pure-silver results are not accurate enough or our sample is not pure enough to pick up a rapid initial jump. From a comparison of the two available *Cu*Zn experiments,[1,3] however, it would appear that the initial jump is itself sometimes observed an artifact.

While the free-electron value 0.33 can be rejected in

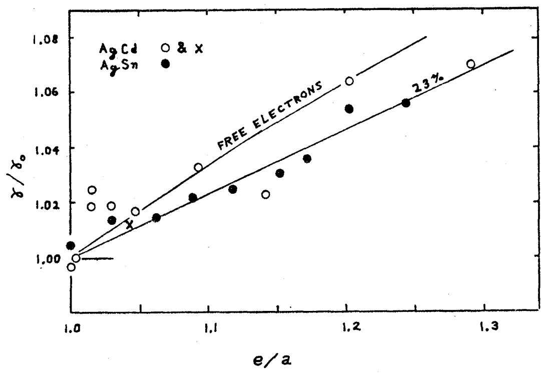

FIG. 3. Plot of the ratio of the electronic specific-heat coefficient γ for noble-metal alloys to its value for the pure metal γ_0 versus electron-per-atom ratio. The upper line is given by the free-electron theory, with initial slope 33% per unit e/a, and the second line has the slope 23% per unit e/a. The *Ag*Cd data are from Ref. 4, and the *Ag*Sn from the present work. For *Ag*Cd, the open circles represent data taken conventionally, while the cross represents the result of a differential measurement of claimed precision about six times that of the former.

the case of *Ag*Sn, it is still a better prediction than those given by rigid-band models which assume contact without overlap. The eight-cone model of Ziman,[10] for example, would give a negative value of about -0.8, while Jones' original theory[11] of free electrons with contact would give about -0.6.

The recent finding by Joseph and Thorsen[12] of a hitherto-undetected period in their de Haas–van Alphen study of silver is very interesting in regard to the + sign of these slopes. They suggest that the new period is due to caps of Fermi surface in the second Brillouin zone having diameters slightly less than the diameter of the necks. In the extended zone scheme, therefore, the Fermi surface of silver would be a sphere slightly distorted near the boundary of the first zone. It is quite likely that the effect of these additional pieces of Fermi surface would give a sufficeintly large positive contribution to the change in density of states with energy at the Fermi level to give a net positive slope not much less than that for free electrons. However, the cap interpretation of Joseph and Thoresen would require (on reasonable hypothesis) that the energy gap across the $\{111\}$ face of the first zone be only 0.22 eV. Other evidence[12a] seems to require a gap wider than 4 eV.

For the γ of pure Ag, we quote the intercept value of the γ versus *e/a* line, since we cannot reject the hypothesis of linearity, and since nine data give more confidence than one datum. This intercept for pure silver is

$$\gamma=(0.646\pm0.005)\text{mJ mol}^{-1}{}^{\circ}\text{K}^{-2}.$$

This γ value (and the θ_D value) are listed in Table II together with the results of previous measurements. There are two tight groups of three γ measurements each, closely clustered about 0.612 and 0.646 in the above units. The source of the difference was discussed by Filby and Martin,[13] who attributed it to two causes: the fact that all measurements of the 0.646 group (previous to ours) were made down to He^3 temperatures, and also that they used 99.9999% Ag instead of 99.99% Ag. Since our measurements were made between 2 and 4°K, and since our result closely confirms the 0.646 value, we conclude that this temperature range is low enough for silver. The 0.612 result is puzzling, since no one has yet explained how 0.1% or less of any impurity can *lower* the apparent γ value by 5%.

TABLE II. Comparison of recent specific-heat measurements on silver below 4.2°K.

	γ (mJ mol^{-1}°K^{-2})	θ_D (°K)	Purity
Keesom and Perlman[a]	0.66	225	99.98%
Corak *et al.*[b]	0.610 ± 0.005	225.3 ± 0.2	99.98%
Rayne[c]	0.613 ± 0.005	226.2 ± 0.3	99.99%
Filby and Martin[d]	0.646 ± 0.004[g]	226.2 ± 2[g]	99.9999%
Montgomery and Pells[e]	0.644 ± 0.012[g]	226.2 ± 0.2[g]	99.9999%
du Chatenier and de Nobel[f]	0.682	226.2	99.9999%
This work	0.646 ± 0.005[g]	225.5 ± 0.5[g]	99.9999%

[a] P. H. Keesom and N. Perlman, Phys. Rev. **98**, 548 (1955).
[b] W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **98**, 1699 (1955).
[c] J. A. Rayne, Proc. Phys. Soc. (London) **B69**, 482 (1956).
[d] J. D. Filby and D. L. Martin, Can. J. Phys. **40**, 791 (1962).
[e] H. Montgomery and G. P. Pells (private communication).
[f] F. J. du Chatenier and J. de Nobel, Physica **28**, 181 (1962).
[g] 95% confidence limits.

Debye Temperatures

It is interesting to note that the Debye temperatures decrease with alloying. If one compares the present results with those for *Ag*Cd,[4] one finds again that the Debye temperatures are a unique function of the electron-per-atom ratio. This behavior was also found in Cu-based alloys by Rayne[2] and in Sn-based alloys by Gayley, Lynton, and Serin.[14] It is consistent with the variation of the elastic constants on alloying as found by Bacon and Smith,[15] who investigated silver alloys at room temperature and found the results to be governed by the electron-per-atom ratio.

ACKNOWLEDGMENTS

Helpful discussions were held with J. A. Rayne, J. R. Clement, and J. K. Logan in the early stages of this work. The Union Carbide Metals Company, where one of us (B. A. G.) began this work several years ago, generously gave much of the equipment to the Western Reserve University. We thank H. Montgomery for a table of his data before their publication and for comments. Special thanks are due to T. J. Rowland, who suggested the problem, and to F. Slish, who helped in the early development of the calorimeter system.

Notes added in proof. (1) Two other *Ag*Sn specific heat experiments have been communicated to us. J. A. Birch and G. K. White find the same behavior on alloying that we do. However, T. B. Massalski and L. L. Isaacs find a rather different curve whose shape they interpret in terms of overlap into the second zone. Both groups confirm the 0.64+ value of γ for pure Ag, although Massalski and Isaacs find a pronounced T^5 term in C with which our data clearly disagree. We thank these authors for this information.

(2) Repeated measurements on our pure silver sample have confirmed $\gamma=(0.646\pm0.005)$ mJ mol^{-1} °K^{-2} and now give $\theta=(225.8\pm0.3)$°K with 95% confidence limits.

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[10] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[11] H. Jones, Proc. Phys. Soc. (London) **49**, 250 (1937).

[12] A. S. Joseph and A. C. Thorsen, Phys. Rev. Letters **13**, 9 (1964).

[12a] C. G. Berglund and W. E. Spicer, Phys. Rev. **136**, A1044 (1964), for example.

[13] J. D. Filby and D. L. Martin, Can. J. Phys. **40**, 791 (1962).

[14] R. I. Gayley, E. A. Lynton, and B. Serin, Phys. Rev. **126**, 43 (1962).

[15] R. Bacon and C. S. Smith, Acta Met. 4, 337 (1956).