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Low-Temperature Specific Heats of α-*Cu*Sn and α-*Cu*Zn Alloys[*][†]

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The specific heats of copper, of five copper-tin alloys of up to 6.2 at.% tin in copper, and of one alloy of 2.7 at.% zinc in copper have been measured between 2°K and 4°K. The electronic specific-heat coefficient γ for the copper-tin alloys can be expressed as a function of electron-per-atom ratio e/a by the relation $\gamma = (0.700\pm0.003)+(0.17\pm0.04)\ (e/a\text{-}1)$ in units of mJ mole^{-1} °K^{-2}. The value of $\gamma = 0.705$ for the one *Cu*Zn alloy is consistent with the above relation. The value of $d(\ln\gamma)/d(e/a) = 0.24\pm0.06$ agrees with $d(\ln\gamma)/d(e/a) = 0.33\pm0.10$ calculated from earlier measurements on *Cu*Zn alloys by Veal and Rayne. Both of these results disagree with a value of $d(\ln\gamma)/d(e/a) = -0.94$ obtained from measurements on *Cu*Zn alloys by Massalski and Isaacs. The Debye temperature is a linearly decreasing function of e/a as expressed by the relation $\Theta_D = (344.7\pm0.8)$ °K$-(188\pm9)(e/a-1)$ °K. All errors are 95% confidence limits.

INTRODUCTION

Much effort has been expended to determine and understand the effect on the electronic specific heat of alloying polyvalent nontransition elements with the noble metals. It is easily shown that the electronic-specific-heat coefficient γ is directly proportional to the density of states at the Fermi surface. Therefore, a knowledge of γ should give direct knowledge about the Fermi surface. Rayne[1,2] measured γ for *Cu*Zn (italics indicate the major constituent—all alloys are understood to be in the alpha phase) and *Cu*Ge alloys and found γ to be an increasing function of electron per atom ratio e/a for both alloy systems. Therefore, it was concluded that the density of states was an increasing function of e/a. Based on Jones' rigid-band model, it followed that contact did not exist between the Fermi surface and the first Brillouin zone in copper. However, Shoenberg[3] soon found de Haas–van Alphen oscillations due to neck orbits in copper, indicating that contact does exist. Various review articles were written in which several hypotheses were put forth to explain these results with insufficient experimental results to verify or contradict them.[4–6] Specific-heat measurements were also made on two silver-based alloy systems, *Ag*Cd[7] and *Ag*Sn,[8] with γ again found to be an increasing function of e/a. Veal and Rayne[9] repeated Rayne's measurements on *Cu*Zn alloys after it had been discovered that small amounts of paramagnetic impurities have a large influence on specific heats. They found the change in γ to be much reduced but still positive. Thus, although the theoretical explanation of the results was not very clear, it seemed to be well established that γ does increase upon alloying copper and silver with polyvalent nontransition elements. However, recently Massalski and Isaacs[10] repeated the specific-heat measurements on *Cu*Zn alloys for a third time. They found the surprising result that γ decreases up to a concentration of approximately 3 at.% zinc in copper. This result was in close agreement with Jones' original rigid-band model but was inconsistent with all other experimental results on noble-metal alloys.

In the present research we have made specific-heat measurements on yet another series of copper alloys, *Cu*Sn. In addition, one *Cu*Zn alloy was measured for direct comparison with the conflicting results of Veal and Rayne and Massalski and Isaacs. We found γ to be an increasing function of e/a for the series of *Cu*Sn alloys. The one *Cu*Zn alloy is consistent with the *Cu*Sn results, and the results for both alloy systems are consistent with the results of Veal and Rayne.

No comparisons are made to the *Cu*Ge and *Cu*Zn data of Rayne[1,2] since the results of Veal and Rayne[9] indicate that the technique used in sample preparation introduced ferromagnetic impurities which enhanced the initial increase in γ.

EXPERIMENTAL DETAILS

Samples, approximately 2 mole in size, were prepared from 99.999% pure copper obtained from United Mineral and Chemical Corporation, 99.999% pure tin obtained from Cominco Products Corporation, and 99.999% pure zinc also obtained from Cominco. The samples were sealed in fused quartz tubes, the *Cu*Sn under vacuum and the *Cu*Zn under a reduced atmosphere of argon. They were heated approximately 100°C above their melting point in an electric furnace and mixed several times by removing them from the furnace and quickly inverting the quartz tubes. After lowering the temperature to just above the melting point, the

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[*] Supported in part by the U. S. Atomic Energy Commission.

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

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

[3] D. Shoenberg, Phil. Mag. **5**, 105 (1960).

[4] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

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

[6] V. Heine, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 279.

[7] H. Montgomery and G. P. Pells, Proceedings of a Conference on the Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).

[8] B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, A1168 (1965).

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

[10] T. B. Massalski and L. L. Isaacs, Phys. Rev. **138**, A139 (1965).

quartz tubes containing the molten alloy were immersed in cold water to promote sample uniformity, except for pure copper which was air cooled. After this the samples were drilled and tapped as required for attachment in the calorimeter. After thorough etching to remove any impurities left by the tool bits, all the samples were annealed at 800°C but for different times as indicated in Table I. For the 0.48% tin and 3.71% tin, annealing was terminated by turning off the furnace and allowing them to cool overnight. The others were terminated by quenching in water. These different heat treatments produced no difference in the trend of the results.

All samples were analyzed for paramagnetic impurities by an independent laboratory. The total amount in any one sample was found to be approximately 10 parts per million (ppm) except for the 6.21-at.% tin sample which contained 34 ppm.

The specific-heat measurements were made using the apparatus and technique developed by Green and Culbert[8] with slight modifications which have been described previously in a paper by Green and Valladares.[11] The technique is unusual in that the sample is in thermal contact with the low-temperature bulb through three No. 4 nylon screws about 2 cm long. The sample is then cooled using a mechanical heat switch and then heated through a preset temperature interval using an independent "differential heater." This temperature interval is approximately 5% of the equilibrium temperature.

An electric clock with a least count of 0.01 sec driven by a 60-cps tuning-fork power supply is automatically turned on and off as the sample temperature, as measured by a 0.1-W, 47-Ω, Ohmite resistor, in thermal contact with the sample, passes through the abovementioned preset temperature interval. The Ohmite resistor is calibrated against 1958 He^4 scale after each sample measurement. Specific heats are measured at seven temperatures equally spaced in T^2 with approximately 5 heats taken at each temperature. The differential heater powers are adjusted to keep the heating times between 30 and 70 sec. The heat capacity of the addenda, consisting of 20-g copper sample holder, etc., is determined by a separate measurement without a sample.

RESULTS

A least-squares fit of the data was made to each of the relations,

$$C/T=\gamma+\alpha T^2,$$

$$C/T=\gamma+AT^2+BT^4,$$

with the aid of a digital computer. The parameter B was found to vary randomly with a maximum value of 0.00011 mJ mole^{-1} °K^{-6}, approximately two standard deviations. Therefore it was assumed that B was insignificant and all reported parameters are the result of fit to the first equation. Table I gives the value of γ and of the Debye temperature Θ_D for each alloy. Figure 1 shows graphically the results for γ from the present data as well as that of Veal and Rayne[9] and Massalski and Isaacs.[10] Figure 2 shows the Debye temperatures taken from the corresponding papers.

TABLE I. γ and Θ_D, and annealing time for *Cu*Sn and *Cu*Zn alloys.

Solute concentration (at.%)	γ (mJ mole^{-1} °K^{-2})	Θ_D (°K)	Annealing time (hours)
Pure	0.702±0.002[a]	344.9±0.4	50
Pure[b]	0.696±0.002	344.1±0.4	50
0.48 Sn	0.702±0.001	341.5±0.3	504
0.93 Sn	0.707±0.002	340.3±0.3	168
1.95 Sn	0.711±0.001	333.7±0.3	50
3.71 Sn	0.718±0.002	324.3±0.4	504
6.21 Sn	0.731±0.002	309.3±0.3	168
2.67 Zn	0.705±0.002	342.7±0.3	65

[a] Errors shown are one standard deviation.
[b] Same sample remeasured.

A linear fit of the present *Cu*Sn data for γ gives

$$\gamma=(0.700\pm0.003)+(0.17\pm0.04)(e/a-1),$$

in units of mJ mole^{-1} °K^{-2}. The value of $\gamma=0.705$ for the one *Cu*Zn alloy measured during the present research is consistent with this relation. (All error limits are 95% confidence limits.)

It is useful to consider the logarithmic derivative of γ with respect to e/a which may be compared with the value of $\frac{1}{3}$ for free-electron gas. For the present *Cu*Sn data the initial value is

$$d(\ln\gamma)/d(e/a)=0.24\pm0.06.$$

A linear fit of the Debye temperature as a function of e/a gives the result

$$\Theta_D=(344.7\pm0.8)\text{°K}-(188\pm9)(e/a-1)\text{°K}.$$

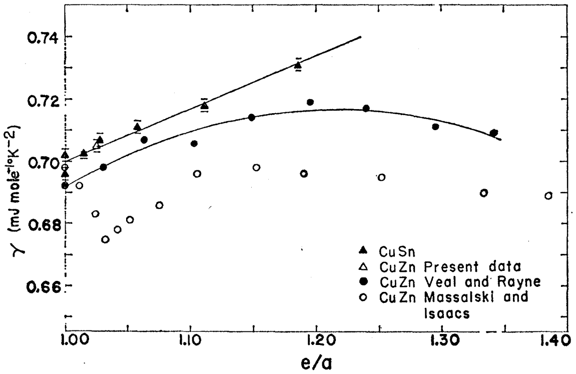

FIG. 1. The electronic-specific-heat coefficient versus electron-per-atom ratio for *Cu*Sn and *Cu*Zn alloys from the present work, Veal and Rayne (Ref. 9), and Massalski and Isaacs (Ref. 10). The curves shown correspond to $\gamma=0.700+0.17(e/a-1)$ and $\gamma=0.692+0.23(e/a-1)-0.5(e/a-1)^2$ in units of mJ mole^{-1} °K^{-2}, the results of least-squares fits of the present *Cu*Sn data and of the *Cu*Zn data of Veal and Rayne, respectively.

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[11] B. A. Green, Jr., and A. A. Valladares, Phys. Rev. **142**, 379 (1966).

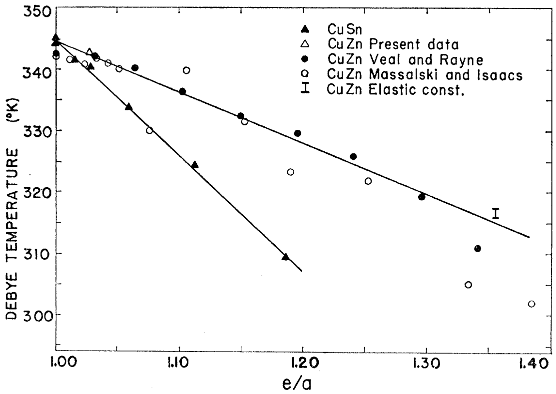

FIG. 2. The Debye temperature versus electron-per-atom ratio for *Cu*Sn and *Cu*Zn alloys from the present work, Veal and Rayne (Ref. 9), and Massalski and Isaacs (Ref. 10). The straight line through the *Cu*Sn data corresponds to $\Theta_D = 344.7\,°\mathrm{K} - 188(e/a-1)$ °K, the result of a least-squares fit. Curve I is calculated from elastic-constant data [J. A. Rayne, Phys. Rev. **115**, 63 (1959)].

DISCUSSION

Since we have measured one *Cu*Zn alloy with e/a of 1.027 and found its value of γ to be consistent with *Cu*Sn results, it is reasonable to compare the present results for alloys of low e/a (less than 1.03) with the conflicting results of Veal and Rayne and Massalski and Isaacs[10] on *Cu*Zn alloys. The present results are clearly inconsistent with the results of Massalski and Isaacs beyond experimental errors and indicate that γ does increase upon alloying copper with zinc or tin.

The reason for this discrepancy is not understood. The method used in the preparation of the one *Cu*Zn alloy was intended to duplicate the method of Massalski and Isaacs.[10] Furthermore, the wide variation in annealing time and terminal cooling of the *Cu*Sn samples indicated that such differences had no noticeable effect in the specific-heat results. Thus, if the results differ because of metallurgical technique, it must be a subtle difference. The measuring apparatus and techniques are slightly different, but any differences resulting therefrom are systematic and should not vary with Sn content.

The effect of paramagnetic impurities can also be discounted. As mentioned previously, the samples have been analyzed and found to have total paramagnetic impurities of approximately 10 ppm, except for the 6.21 at.% tin sample which contained 34 ppm. The actual analysis showed the Cu and *Cu*Sn samples, arranged in order of increasing tin concentration, to contain 4, 3, 6, 4, 8, and 26 ppm iron. The *Cu*Zn sample contained 4 ppm iron. The only other significant paramagnetic impurity was nickel, with manganese and cobalt impurities being less than 1 ppm. Experimental data on *Cu*Ni alloys[12] indicate that at least 100 ppm nickel would be necessary to produce an increase in γ of 0.002 mJ mole^{-1} °K^{-2}. Frank, Manchester, and Martin[13] have made specific-heat measurements on *Cu*Fe alloys with Fe concentrations down to 0.05% or 500 ppm. From their data, the increase in γ appears to be linear with a slope of 0.0008 mJ mole^{-1} °K^{-2} per ppm. Thus the increase from 4 to 8 ppm in iron impurities could produce a maximum change in γ of only 0.003 mJ mole^{-1} °K^{-2} except for the 6.21 at.% tin sample. This is much less than the increase of 0.018 mJ mole^{-1} °K^{-2} observed for the 3.71 at.% tin sample.

A direct comparison with the data of Massalski and Isaacs also excludes an explanation of the discrepancy on the basis of paramagnetic impurities. Analysis of their samples indicated total paramagnetic impurities of less than 2 ppm for zinc concentrations of less than 3 at.%. Thus at low concentrations our samples were less pure. However, our value of γ for pure copper is not significantly different from their value, whereas at an e/a of 1.03 the values of γ differ by approximately 0.030 mJ mole^{-1} °K^{-2} with no significant increase in the concentration of iron or total paramagnetic impurities in our samples.

It is interesting to make a quantitative comparison between the present results and those of Veal and Rayne.[6] A quadratic fit of their data gives the result

$$\gamma = (0.692 \pm 0.005) + (0.23 \pm 0.07)(e/a-1) - (0.5 \pm 0.2)(e/a-1)^2.$$

From this equation the initial value of the logarithmic derivative is calculated to be

$$d(\ln\gamma)d(e/a) = 0.33 \pm 0.10.$$

Thus our value of 0.24±0.06 agrees with their initial value of the logarithmic derivative within experimental error.

The rate of decrease of the Debye temperature as a function of e/a is much greater (by a factor of 2) for *Cu*Sn alloys than for *Cu*Zn alloys. The *Cu*Zn, *Cu*Ge, *Ag*Sn, and *Ag*Cd experiments, as well as similar measurements on tin-based alloys,[14] indicated the Debye temperature was a function of e/a independent of solute. The large separation between copper and tin in the periodic table no doubt accounts for the failure of this generalization in the present work, with the large mass difference probably being the most significant factor.

One further conclusion can be drawn from the fact that the γ curves for *Cu*Zn and *Cu*Sn agree while their Debye-temperature curves do not. It has been suggested that the initial increase in γ upon alloying arises from an increase in the enhancement factor in the density of states due to electron-phonon interaction. The present results show that if a Debye spectrum is a sufficient approximation, that is, if only the excited portion of the phonon spectrum is relevant, then such an explanation is not indicated. However, theorists differ about whether

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[12] G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, Phys. Rev. **113**, 45 (1959).

[13] J. R. Frank, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

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

virtual phonon processes can be neglected which involve phonons of higher frequency.

CONCLUSION

The electronic specific heat coefficient of copper increases when the copper is alloyed with Zn or Sn at the same rate per unit valence-electron concentration, namely about 28%. The Debye temperature decreases faster when copper is alloyed with Sn than when alloyed with Zn, indicating that the electron-phonon enhancement factor does not explain the increase in γ.

Low-Temperature Specific Heats of Silver-Zinc Alloys. The Effect of Lattice Dilatation*

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The specific heats of silver and six silver-zinc alloys covering the alpha phase were measured between 2 and 4°K with a relative precision of 0.2% or better. The purpose is to compare the effect of Zn as a solute with Cd and Sn, which have been shown to increase the electronic specific-heat coefficient γ for silver as a function of electron concentration e/a at the rate $d(\ln\gamma)/d(e/a)=0.2$ to 0.3 in spite of their considerable difference in valence. The comparison should reveal the effect of atomic volume, since Zn contracts silver upon alloying, while Cd and Sn expand it at a constant rate per unit e/a. The result for Zn in Ag is $d(\ln\gamma)/d(e/a)=0.65\pm0.17$ (95% limit). The volume effect, although opposite in sign from that expected on the free-electron model, is shown to be consistent with the rigid-band model including—indeed, requiring—contact between the Fermi surface and the first zone boundary, as is well established on other evidence. We conclude that the sign of the above derivatives and the observed volume effect are most simply explained if the density of states in silver is an increasing function of energy at the Fermi level in spite of this contact. These results imply that the electronic-thermal-expansion coefficient of pure silver is negative. Experimental test of this prediction will constitute a sensitive test of the rigid-band model. The Debye temperatures of the *Ag*Zn alloys do not differ from that of pure silver by more than 2°K, a slight negative trend being suggested. A significant T^5 component in the specific heat appears with Zn addition, growing from less than 0.0001 mJ mole^{-1} °K^{-6} in pure Ag to 0.0005 units at 32 at.% Zn.

INTRODUCTION

THE fact that the electronic specific-heat coefficient γ of pure silver is increased when the silver is alloyed with cadmium,[1] for example, has been considered paradoxical, for it is well known that the Fermi surface of silver is in contact with the first Brillouin zone boundary; thus expansion of the Fermi surface should reduce its free area, leading, it is argued, to a decrease in the density of states at the Fermi level. The argument rests fairly heavily upon the assumption that the band structure of silver is unchanged with alloying to a sufficient approximation (the rigid-band model). The effect of alloying with *B*-subgroup elements is considered merely to add electrons to the conduction band in proportion to the excess in valence of the solute over the solvent.[2]

Attempts to relax the assumption of rigid bands,[3] or to conceive of other contributions to the linear temperature term in the specific heat,[4] or to invoke the effects of electron scattering by the solute[5] have not provided predictive power for subsequent experiments. For example, alloying silver with Sn[6(a),6(b)] has about the same effect as alloying with Cd when scaled according to relative valence. This is most simply explained with the rigid-band model. The effect is not peculiar to silver; in fact, it was first seen in copper alloys.[7]

As part of an effort to unravel this mystery, we were led to consider the possibility of varying another important parameter of silver, its molar volume.

If a metal cube is compressed, (1) the momentum states of its conduction electrons are displaced in a uniform expansion, reducing the density of states in k space, (2) all Brillouin-zone boundaries are displaced outward, and (3) the Fermi surface, although it may be distorted somewhat from its initial shape, must expand so as to contain a volume inversely proportional to the

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[*] Supported in part by the U. S. Atomic Energy Commission.

[1] H. Montgomery and G. P. Pells, Proceedings of a Conference on The Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).

[2] For general background on the electronic structure of alloys and the history of attempts at understanding it, see W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (The Institute of Metals, London, 1962), 4th ed., especially pp. 41–45. See also J. Friedel, Advan. Phys. **3**, 446 (1954).

[3] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[4] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).

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

[6] (a) B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, A1168 (1965); (b) T. B. Massalski and L. L. Isaacs, *ibid.* **138**, A139 (1965).

[7] J. A. Rayne and W. R. G. Kemp, Australian J. Phys. **9**, 569 (1956); J. A. Rayne, Phys. Rev. **108**, 22 (1957); **110**, 606 (1958); B. W. Veal and J. A. Rayne, *ibid.* **130**, 2156 (1963); L. C. Clune and B. A. Green, Jr., preceding paper, Phys. Rev. **144**, 525 (1966). The results of L. L. Isaacs and T. B. Massalski, *ibid.* **138**, A134 (1965), show a decrease.