Specific Heat of Dilute Alloys of Tin in Indium between 0.5 and 1.7 K*

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Specific-heat measurements were made on dilute alloys of tin in indium in the temperature range 0.5 to 1.7 K. For tin concentrations of 0, 0.8, 2.1, 4.9, and 9.7 at.%, γ (electronic specific heat) values of 1.66, 1.66, 1.74, 1.88, and 1.92 mJ/mole K^2 were found. This represents a more rapid increase in γ than would be predicted on the assumption of rigid parabolic bands, and may be due to filling of third-zone α arms. The variation of γ with concentration is different from that of the Knight shift.

INTRODUCTION

SPECIFIC-HEAT measurements on dilute alloys of tin in indium were undertaken to find out whether or not the electronic density of states at the Fermi surface, $N_0(E_F)$, would show the anomalous behavior observed by Anderson, Thatcher, and Hewitt[1] in their measurements of the ^{115}In isotropic Knight shift, K. They found a sharp dip of about 7% in K centered near 0.8 at.% tin. Magnetoacoustic measurements by Rayne,[2] orthogonalized-plane-wave (OPW) calculations by Gaspari and Das,[3] and more recently, pseudopotential band-structure calculations by Ashcroft and Lawrence[4] and Shaw and Smith[5] indicate that indium can be treated as a nearly-free-electron metal. To this approximation, both K and γ are proportional to $N_0(E_F)$.

EXPERIMENTAL PROCEDURE

Measurements were made in a helium-three cryostat described by Taylor,[6] using a discontinuous heating method. Data were taken from 0.5 to 1.7 K, a temperature range in which the electronic contribution is a fair fraction of the total specific heat. It was felt that extending the measurements to higher temperatures would not result in more accurate determination of γ values. The calibration of the germanium resistance thermometer used has been discussed by Taylor and McCollum.[7] Procedures were checked by measuring the specific heat of 99.999% pure copper, the results being within 1% of accepted values.[8] Normal-state measurements were made in fields ranging from 500 to 1000 G, produced by a room-temperature solenoid. All alloys but the 9.7% one gave identical results in 500 and in 1000 G fields. For the 9.7% alloy the results were not in agreement until the lower field was increased to about 800 G.

The effects of these fields on thermometer calibration were found to be negligible by additional specific heat measurements on copper. The addenda heat capacity amounted to about 1% of the total at 1 K and was measured separately. Alloys were obtained from Indium Corporation of America.[9] Elements used were 99.999% pure and tin concentrations were stated to be accurate to ± 0.1 at.%, which was later verified by wet chemical analysis. Spectroscopic analysis of the pure indium sample detected iron at a concentration less than 2 ppm. Each sample weighed about 200 G.

RESULTS AND DISCUSSION

It was assumed that the normal-state results for each alloy could be represented by $C=\alpha T^{-2}+\gamma T+\beta T^3+\delta T^5$, that is, a nuclear quadrupole term, an electronic term, and two lattice terms. An accurate determination of α could not be made from the data since the nuclear quadrupole term is only about 0.5% of the total specific heat at 0.5 K. From the resonance results of Anderson, Thatcher, and Hewitt a value for α was computed for each alloy, the values ranging from 0.0009 mJ K/mole for pure indium to 0.0016 mJ K/mole for the 9.7% alloy. It was decided to set $\alpha=0.001$ for all alloys, and a least-squares fit was made for each with the

TABLE I. Normal-state specific-heat coefficients for indium-tin alloys and RMS deviations as determined from a least-squares fit to $C=0.001T^{-2}+\gamma T+\beta T^3+\delta T^5$.

Sample	Concentration (at.% tin)	γ (mJ/mole K^2)	β (mJ/mole K^4)	δ (mJ/mole K^6)
I	0	1.66±0.003	1.37±0.006	0.065±0.002
II	0.8	1.66±0.01	1.37±0.01	0.055±0.01
III	2.1	1.74±0.003	1.35±0.005	0.065±0.002
IV	4.9	1.88±0.003	1.32±0.005	0.076±0.002
V	9.7	1.92±0.003	1.42±0.006	0.070±0.002

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[1] W. T. Anderson, Jr., F. C. Thatcher, and R. R. Hewitt, Phys. Rev. **171**, 541 (1968).
[2] J. A. Rayne, Phys. Rev. **129**, 652 (1963).
[3] G. D. Gaspari and T. P. Das, Phys. Rev. **167**, 660 (1968).
[4] N. W. Ashcroft and W. E. Lawrence, Phys. Rev. **175**, 938 (1968).
[5] R. W. Shaw, Jr., and N. V. Smith, Phys. Rev. **178**, 985 (1969).
[6] W. A. Taylor, thesis, University of California, Riverside (unpublished).
[7] W. A. Taylor and D. C. McCollum, Phys. Rev. **156**, 782 (1967).
[8] G. Ahlers, Rev. Sci. Instr. **37**, 477 (1966).
[9] Indium Corporation of America, Utica, N. Y.

results shown in Table I. $\gamma=1.66$ for pure indium may be compared to $\gamma=1.69$ obtained by O'Neal and Phillips[10] and $\gamma=1.59$, 1.61 obtained by Bryant and Keesom.[11] Possible explanations for the differences in γ values from different laboratories have been discussed by O'Neal and Phillips, and are believed to be due to variations in calibration procedures and in methods of data analysis. Figure 1 shows that the direction of the data points from the calculated specific heats is not greater than about 1%. The error bars in Figure 2, which show percent increase in γ versus concentration, have been drawn arbitrarily at $\pm 1\%$.

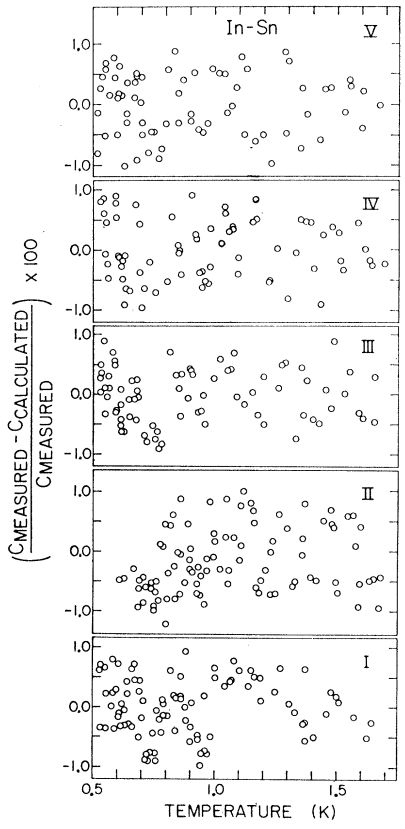

FIG. 1. Variation of specific-heat data from the least-squares polynomials given in Table I.

The rapid increase in γ beginning near 1% tin would not be predicted by the rigid-band model for which $N_0(E_F) \propto V^{2/3}Z^{1/3}$. The latter is shown as a dash-dot curve in Fig. 2 and was calculated by assuming indium to have three and tin to have four valence electrons.

The electron-phonon enhancement for indium has been calculated by Ashcroft and Lawrence. For the first and second zones they get 1.45, which is about 10% higher than the figure indicated by this work.

[10] H. R. O'Neal and N. E. Phillips, Phys. Rev. **137**, A748 (1965).
[11] C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961).

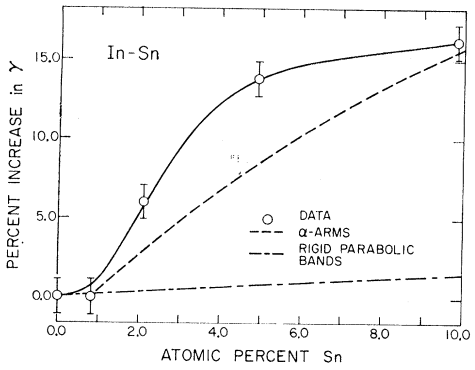

FIG. 2. Change in electronic specific heat γ with tin concentration.

Their calculation also gives a third-zone enhancement factor about 10% higher than that for the first two. The γ values for these alloys suggest a density-of-states curve for indium similar to that obtained by Ashcroft and Lawrence and labeled the $R_c=0.575$ Å model. R_c is a parameter describing the pseudopotential and is a measure of the range of the pseudopotential cancellation in the core region. They calculate densities of states using a free-electron model, an $R_c=0.715$ Å model, and an $R_c=0.575$ Å model. The important difference between the three is the location of the third-zone α arms. In the free-electron model they start to make a contribution to the density of states near $E/E_F=0.98$. In the $R_c=0.715$ Å model they lie at $E/E_F=1.04$ and thus would be completely empty at the highest tin concentrations used in this work. For the $R_c=0.575$ Å model they would begin to contribute somewhere near $E/E_F=0.99$. This model includes the first zone, the second-zone hole surface, and the third-zone β arms. All three models have flat density-of-state curves at E_F if the α arms are neglected. The $R_c=0.575$ Å model is shown as a dashed curve in Fig. 2, arbitrarily shifted so that the α arms begin to contribute at $E/E_F=1.002$.

Merriam[12] has found oscillations in the lattice parameters of indium-tin alloys near 8% tin and has attributed them to a Fermi-surface–zone-boundary interaction. Unfortunately, no sample measured in this work had a concentration near 8%, but such an interaction could not account for the increase below 6%. The concentrations were chosen by consideration of the Knight-shift data of Anderson, Thatcher, and Hewitt. The variation in γ bears little resemblance to that of K. Thatcher[13] has concluded that the dip in K near 0.8% tin, a dip also found in In-Cd, In-Tl, and In-Hg systems, is due to averaging of the anisotropic electron-electron interactions as a result of impurity scattering. Between 1 and 2% tin, both γ and K are rising, which could be due

[12] M. F. Merriam, Phys. Rev. Letters **11**, 321 (1963).
[13] F. C. Thatcher and R. R. Hewitt (to be published).

to an increase in $N_0(E_F)$. However, K is relatively constant between 2 and 6%.

CONCLUSIONS

The variation of the electronic specific heat γ with concentration does not follow that of the isotropic Knight shift. γ shows no dip but rather a rapid rise which may possibly be due to the contribution of third-zone α arms to the density of states.

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Magnetoacoustic Measurements of the Fermi Surface of Copper

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Oscillations in the attenuation of 600-MHz LA waves propagated along the principal symmetry direction of copper single crystals are examined as a function of magnetic field in a perpendicular plane. Frequencies of the magnetoacoustic oscillations are associated with the responsible electron-orbit groups on the Fermi surface and, from them, radial dimensions are derived. These dimensions are standardized by means of open-orbit resonances in terms of Brillouin-zone dimensions. This also gives an independent measurement of the velocity of sound at ultrahigh frequencies. A close correlation is found between measured dimensions and the Koringa-Kohn-Rostoker (KKR) calculation by Faulkner *et al.* A generally good fit of the measured dimensions to a recent synthesis of the copper Fermi surface by Halse and Shoenberg from de Haas–van Alphen (dHvA) data is also observed.

I. INTRODUCTION

THE attenuation of sound in pure metals at low temperatures is dominated by an electronic contribution. When the mean free path of the electrons is long compared to the wavelength, magnetoacoustic oscillations (transverse-field dimensional resonances) in the ultrasonic attenuation are observed when an applied magnetic field is varied. Such studies, performed on high-purity single crystals, can allow a projection of the Fermi surface on a plane perpendicular to the sound-wave direction to be directly delineated. Very adequate surveys of magnetoacoustic methods together with extensive references are available, e.g., by Tepley,[1] Gavenda,[2] Peverley,[3] and Roberts.[4] A semiclassical theoretical treatment of magnetoacoustic oscillations applicable to the present experimental conditions has been given for a spherical Fermi-surface model by Cohen, Harrison, and Harrison.[5] A comparable treatment of a cylindrical Fermi-surface model which incorporated open orbits and possibility of magnetic breakdown has been given by Sievert.[6]

An important application of accurate Fermi-surface dimensions obtained by the magnetoacoustic method is the evaluation of the assumptions made in band-structure calculations. The recent self-consistent augmented-plane-wave (APW) calculations for copper by Snow and Waber[7] and the Koringa-Kohn-Rostoker (KKR) calculations by Faulkner, Davis, and Joy[8] have made an accurate experimental study of copper appropriate. The direct Fermi radii such as are given by the magnetoacoustic method are best suited for this purpose. More accurate magnetoacoustic measurements are now possible because copper crystals having a long electron mean free path can be prepared and because the form of the Fermi surface is sufficiently simple that the identification of the many oscillation frequencies with electron orbits can be made unambiguously.

The magnetoacoustic effect supplements other methods of Fermi-surface study such as galvanomagnetic measurements, rf size effect, cyclotron resonance studies, and quantum oscillation effects. The basic requirement on specimen purity is that $ql \gg 1$. The quantity l is the electron mean free path and q is the magnitude of the sound-propagation vector, given by $2\pi/\lambda$, where λ is the sound wavelength. This is generally more severe than

[1] N. Tepley, Proc. IEEE **53**, 1586 (1965).
[2] J. D. Gavenda, in *Progress in Applied Materials Research* (Gordon and Breach, Science Publishers, Inc., New York, 1964), Vol. VI, p. 43.
[3] J. R. Peverley, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1966), Vol. IV, Part A, Chap. 9, p. 353.
[4] B. W. Roberts, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1968), Vol. IV, Part B, Chap. 10, p. 1.
[5] M. H. Cohen, M. J. Harrison, and W. A. Harrison, Phys. Rev. **117**, 937 (1960).
[6] P. R. Sievert, Phys. Rev. **161**, 637 (1967).
[7] E. C. Snow and J. T. Waber, Phys. Rev. **157**, 570 (1967).
[8] J. W. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. **161**, 656 (1967).