

Heat Capacity of Pseudo-Copper below 4.2°K

G. L. GUTHRIE

*John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of
General Dynamics Corporation, San Diego, California*

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Heat-capacity measurements have been made on two face-centered-cubic alloys of the type $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$ at temperatures below 4.2°K for the values $x \approx 0.03$ and $x \approx 0.08$. The heat capacity has been found to obey a law of the type $C_v = \gamma T + (464.5/\theta_D^3) T^3$ cal/mole (°K). The Debye characteristic temperature θ_D is nearly the same as that for pure copper. For an alloy having $x \approx 0.03$, θ_D is approximately 1% higher than θ_D for pure copper. However, γ increases rapidly with increasing x , and is approximately 20% higher than the γ for pure copper when $x \approx 0.03$. The results are found to be incompatible with a rigid-band model approach to alloy theory.

INTRODUCTION

RIGID-BAND interpretations of properties of binary alloys have occasionally been advanced.¹⁻³ These interpretations have been applied to low-temperature heat-capacity measurements²⁻⁴ and to the results of magnetic moment and magnetic susceptibility measurements.^{5-7,9,10} The atomic moments of nickel alloys¹¹ containing small amounts of Mn, Fe, Co, Cu, Pd, Zn, Al, and Sn have been interpreted by this method,^{9,10} and the explanation of the atomic moment of the Cu-Ni alloys⁸⁻¹⁰ is regarded as one of the successes of this type of analysis. These explanations of the atomic moments of alloys involve the assumption that the nickel atoms and the solute atoms share a common set of bands, and that in the case of Cu and Zn doped into Ni, the 4s electrons of the solutes fill the holes in the nickel 3d band. The simplest interpretation of the low-temperature heat-capacity measurements of binary alloys involves the assumption that the addition of the heavier element fills electronic states in K space and shifts the position of the Fermi surface without changing the shape of the $N(E)$ versus E curve. If this is the case, and if we assume that γ is proportional to the density of states at the Fermi surface, then low-temperature heat-capacity measurements on alloys of the type $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$ should produce values of γ which are independent of x . This is so because the electron-to-atom ratio is independent of x , and the lattice spacing is almost independent of x .

EXPERIMENTAL PROCEDURE AND RESULTS

Two samples approximating the type $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$ were prepared, one with the value $x \approx 0.03$, and one with $x \approx 0.08$, hereafter referred to as the 3% and 8% samples. The 3% sample was melted in a sealed evacuated quartz tube. The tube was tipped repeatedly to ensure mixing, and was subsequently plunged into water while the mixture was molten. The 8% sample was melted in an alumina crucible under an argon atmosphere and was similarly water-chilled. Both samples received homogenizing heat treatment consisting of 48 hours of annealing at 900°C in sealed evacuated quartz tubes with a small amount of zinc powder enclosed to prevent dezincing of the surface.

Part of the 3% sample was polished, etched, and examined microscopically for evidence of coring. No such evidence was found. Both samples have been chemically analyzed and found to be nearly uniform in composition. The 3% sample was examined spectrographically and found to contain approximately 0.02% of solid impurities by weight. Chemical analysis showed that the Cu-Ni-Zn part of the sample consisted of 93.62% Cu, 3.17% Zn, 3.21% Ni at the top and 93.73% Cu, 3.03% Zn, 3.24% Ni at the bottom, percentage being atomic percent. The source of materials for the 8% sample was the same as that for the 3% sample, and it is therefore assumed that the impurities are the same. Chemical analysis at the top and bottom of the 8% sample showed that the Cu-Ni-Zn part of the sample consisted of 84.26% Cu, $7.73 \pm 0.03\%$ Ni, and $8.01 \pm 0.02\%$ Zn with the composition varying by the amount indicated over the length of the sample. The Cu-Ni-Zn compositions are given in atomic percent.

The two samples, weighing 402 and 363 grams for the 3% and 8% samples, respectively, were provided with carbon resistance thermometers and Manganin heaters, lacquered in place with Tuffernell baking varnish. They were placed in a standard liquid-helium calorimeter. The thermometers were calibrated and heat-capacity measurements were made. The thermometer calibrations consisted of 11 data points for the 3% sample and 8 data points for the 8% sample. These data were used to find least-squares values for

¹ Hoare, Matthews, and Walling, Proc. Roy. Soc. (London) **A216**, 502 (1953).

² F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42 (1957).

³ John A. Rayne, Phys. Rev. **108**, 22 (1957).

⁴ John A. Rayne, Phys. Rev. **110**, 606 (1958).

⁵ E. P. Wohlfarth, Proc. Roy. Soc. (London), **A195**, 434 (1949).

⁶ E. P. Wohlfarth, Proc. Leeds Phil. Lit. Soc. Sci. Sec. **5**, 89 (1949).

⁷ N. F. Mott, Proc. Roy. Soc. (London) **47**, 571 (1935).

⁸ E. C. Stoner, J. phys. radium **12**, 372 (1951).

⁹ Charles Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, pp. 329-337.

¹⁰ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 197.

¹¹ M. Alder, Ph.D. thesis, University of Zurich, 1916 (unpublished).

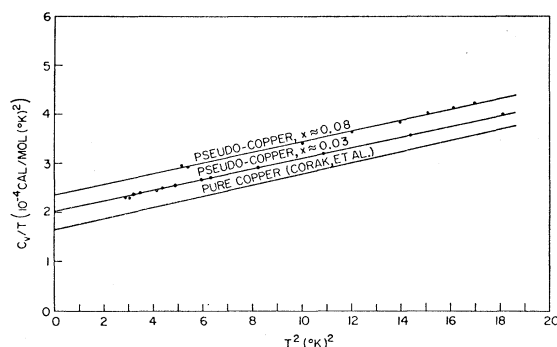


FIG. 1. C_v/T versus T^2 for two pseudo-copper alloys ($\text{Cu}_{1-2x}\text{Ni}_x\text{Zn}_x$) and for pure copper.

constants A , B , and C in the relationship

$$[(\log R)/T]^{\frac{1}{2}} = A + B \log R + C(\log R)^2.$$

This relation is a variation of the one suggested by Clement and Quinell.¹² The least-squares fit resulted in rms deviations of $\pm 0.00162^\circ\text{K}$ and $\pm 0.00246^\circ\text{K}$ for the 3% and 8% sample thermometer calibration curves. A series of heats was taken on each sample, and the data was processed by the IBM-650 computer, which was also used to produce a least-squares fit of $C_v/T = \gamma + (464.5/\theta_D^3)T^2$ cal/mole ($^\circ\text{K}$). Results are plotted in Fig. 1. The least-squares fit resulted in the values $\gamma = 2.029 \times 10^{-4}$ cal/mole ($^\circ\text{K}$)² for the 3% sample and $\gamma = 2.37 \times 10^{-4}$ cal/mole ($^\circ\text{K}$)² for the 8% sample. Pure copper¹³ has $\gamma = 1.65 \times 10^{-4}$ cal/mole ($^\circ\text{K}$)². The values for the Debye characteristic temperature θ_D were 349.1°K and 349.6°K for the 3% and 8% samples, respectively. This compares with the value $\theta_D = 344^\circ\text{K}$ for pure copper. The average deviation of the 3% sample from the law

$$C_v/T = \left[2.029 \times 10^{-4} \times \frac{464.5}{349.1^3} \frac{T^2}{(\text{°K})^2} \right] \text{ cal/mole } (\text{°K})^2$$

was 0.42%. The 8% sample data scattered about twice this much. Corrections for the Tuffernell, carbon resistor, and aluminum radiation shield would reduce the γ values by one or two percent.

DISCUSSION OF RESULTS

Alloys of the type $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$ have not only the same electron-to-atom ratio as pure copper, but also the same crystal type, and nearly the same lattice constant, melting point, and mass-to-atom ratio, for small values of x . Furthermore, for the values of x used in this work, they are not near any phase boundary.¹⁴ The Cu-Ni system is face-centered-cubic (fcc) in all proportions. The Cu-Zn system is fcc up to 32% Zn. The $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$ is fcc up to $x = 0.28$. Since Zn and

Ni are neighbors to copper in the periodic table, doping copper with Ni and Zn causes a minimum of perturbation in the potential which the copper lattice presents to the electrons.

The measured excess of the value of γ for the pseudo-copper above that for pure copper¹³ is incompatible with a rigid-band-model approach to alloy theory. It is impossible to attribute this increase in γ to a change in the lattice spacing. The nominal 3% sample has been found to be made up of fcc crystals with a lattice spacing of 3.584 ± 0.003 Å. This is about one percent smaller than the spacing for pure copper, which is also fcc. Such a decrease in the lattice spacing is usually regarded as being associated with a decrease in the density of states and therefore a decrease in γ . The present results show an increase in γ .

It may be noted that both the alloys used in these measurements deviate slightly from the ideal form $\text{Cu}_{1-2x}\text{Zn}_x\text{Ni}_x$. The nominal 3% alloy is slightly nickel rich, whereas the nominal 8% alloy is zinc rich. If we attempt to retain a rigid-band viewpoint, these deviations from the ideal do not explain the large increases in γ over the value for γ for pure copper. An alloy¹⁵ of 90% Cu, 10% Ni has the value $\gamma = 2.45 \times 10^{-4}$ cal/mole ($^\circ\text{K}$)². Interpolation shows that the nickel excess in the nominal 3% sample could be expected to cause an increase in γ of 0.016×10^{-4} cal/mole ($^\circ\text{K}$)² over the value for pure copper. The observed increase is approximately 20 times this amount. A similar attempt to keep a rigid-band viewpoint while explaining the results of the measurement on the nominal 8% sample leads to the same lack of success.

The observed increase in γ for the 3% alloy may be accounted for by attributing it to the zinc doping and nickel doping separately. This represents an abandonment of the rigid-band approach. Interpolating from the previously mentioned 90% Cu 10% Ni measurement, we find that the nickel concentration in the nominal 3% alloy causes an increase in γ amounting to 0.256×10^{-4} cal/mole ($^\circ\text{K}$)². Similarly, referring to the results of Rayne,³ we find that the zinc concentration can be expected to increase γ by 0.11×10^{-4} cal/mole ($^\circ\text{K}$)². If we add these increases to the γ for copper,¹³ we get a predicted total γ value of 2.016×10^{-4} cal/mole ($^\circ\text{K}$)², which compares to a measured value of 2.03×10^{-4} cal/mole ($^\circ\text{K}$)² for the nominal 3% sample. Corresponding calculation for the nominal 8% alloy shows a similar agreement between the calculated and measured values.

CONCLUSION

The usual rigid-band-theory explanations of the results of the measurements of the atomic moments of binary alloys of nickel are in conflict with the pseudo-copper heat-capacity measurements. The present results are most easily understood if it is assumed that there

¹² J. R. Clement and E. H. Quinell, Rev. Sci. Instr. **23**, 213 (1952).

¹³ W. S. Corak *et al.*, Phys. Rev. **98**, 1699 (1955).

¹⁴ *Metals Handbook* (American Society for Metals, Cleveland, Ohio, 1948).

¹⁵ Guthrie, Friedberg, and Goldman, Bull. Am. Phys. Soc. Ser. II, **1**, 147 (1956). Also, G. L. Guthrie, Ph.D. thesis, Carnegie Institute of Technology, 1957 (unpublished).

are unfilled states of $3d$ character in the alloys used in the present measurements. It is apparent that rigid-band interpretations of properties of binary alloy systems should be used with extreme care if at all. It is doubtful if low-temperature heat-capacity measurements of binary alloy systems can be used to construct density-of-states curves for pure metals.

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Optical Transmission of Heat-Treated Strontium Titanate†

H. W. GANDY

Electronics Laboratory, General Electric Company, Syracuse, New York

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The room-temperature optical transmission spectra of pure and doped SrTiO_3 crystals have been studied after heating them in oxygen and vacuum; spectral measurements were made in the quantum energy range from 0.1 to 3.4 eV.

A blue color, with strong attendant absorption in the infrared, can be induced in the pure crystals by heating them in vacuum with absorption maxima occurring at 0.9 and 2.9 eV. This induced absorption can be removed by heating the crystals in oxygen. Prolonged heatings of the pure, stoichiometric crystals in oxygen have failed to induce any measurable change in the transmission spectra in the aforementioned energy range.

Optical absorption can be induced in iron- and cobalt-doped SrTiO_3 crystal samples by heating them in oxygen; this absorption can be removed by heating the crystals in vacuum. The induced absorption occurs primarily at high quantum energies in the spectra of these doped crystals, with maxima occurring at 2.75 and 2.2 eV in the iron-doped samples, and at 3.0 and 2.6 eV in the cobalt-doped samples. It is suggested that the induced absorption observed in the doped crystals involves a controlled change in the valence states of these impurities.

INTRODUCTION

INVESTIGATIONS of the optical properties of single crystals of pure strontium titanate have been reported several times in recent years. These crystals are grown by the flame-fusion method using an oxygen-hydrogen flame in a Verneuil-type furnace at a temperature of about 2100°C; the purity of the SrTiO_3 furnace feed material and the details of the crystal-growing process may be found elsewhere.^{1,2} The structure of SrTiO_3 is that of a cubic perovskite, with one molecule per unit cell; strontium ions are located at the corners of the unit cell, oxygen ions at the centers of the cell faces, and a titanium ion at the center of the unit cell. These SrTiO_3 crystals have a high index of refraction (2.407 at 5893 Å), a low-frequency room-temperature dielectric constant at 310, and a dielectric loss tangent of 0.00025 when they are in the stoichiometric condition.^{2,3} The onset of fundamental electronic

absorption occurs at a quantum energy of about 3.2 eV,⁴ and the optical absorption coefficient rises to about 10^4 cm^{-1} at an energy of 3.5 eV as estimated from diffuse reflectance measurements made in this laboratory. The absorption coefficient of these crystals in the stoichiometric condition is less than 10^{-1} cm^{-1} over the energy range from 0.25 to 3.1 eV.^{2,4} Strong absorption occurs for energies less than 0.20 eV, the maximum being located at 0.075 eV.⁵

For the most part, the previous investigations of the pure SrTiO_3 crystals were performed on them in the stoichiometric state. The present work is concerned primarily with the transmission spectra of both pure and doped SrTiO_3 crystals which are not in the stoichiometric condition.

EXPERIMENTAL PROCEDURES

The pure and doped crystal samples used in this work were sawed from the boule form into slabs, ground to the desired thicknesses, while maintaining parallel faces, and then polished on a rotating wax lap using a

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² Levin, Field, Plock, and Merker, *J. Opt. Soc. Am.* **45**, 737 (1955).

³ A. Linz, *Phys. Rev.* **91**, 753 (1953).

⁴ J. A. Noland, *Phys. Rev.* **94**, 724 (1954).

⁵ J. T. Last, *Phys. Rev.* **105**, 1740 (1957).