CONTRIBUTION OF THE NUCLEUS TO THE SPECIFIC HEAT OF RHENIUM*

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Measurements of the heat capacity of a Re ingot[1] between 0.37 and 4.2°K show an anomalous contribution to the specific heat which is proportional to T^{-2}. This temperature dependence suggests that the contribution is the high-temperature part of a Schottky-type anomaly, arising from excitations among a set of discrete energy levels. Figure 1 shows the ratio of the total specific heat to the absolute temperature, C/T, plotted as a function of T. The specific heat of the Re measured in zero magnetic field can be expressed as

$$C_n = \gamma T + \alpha T^3 + A_0 T^{-2}, \quad T > 1.85°\text{K} \tag{1}$$

$$C_s = C_{es} + \alpha T^3 + A_0 T^{-2}, \quad T < 1°\text{K} \tag{2}$$

where γT is the electronic specific heat in the normal state, αT^3 is the specific heat of the lattice, and $A_0 T^{-2}$ is the anomalous contribution. C_{es} is the electronic specific heat which is expected, according to the Bardeen, Cooper, and Schrieffer theory of superconductivity,[2] to be given by

$$C_{es} = \gamma T_c\, a \exp(-bT_c/T), \quad T_c/T > 2. \tag{3}$$

Because αT^3 is small throughout and $A_0 T^{-2}$ is small at the higher temperatures, the constants can readily be adjusted by successive approximations to fit the data. Accepting the validity of Eq. (3), we find $A_0 = 0.052 \pm 0.002$ millijoule deg/mole. The other constants are $\gamma = 2.31 \pm 0.02$ millijoule/mole deg^2 and $\alpha = 0.026 \pm 0.002$ millijoule/mole deg^4, from which it follows that the Debye temperature $\theta_0 = 417 \pm 10$°K. With this choice of constants, the data appear to be consistent with the second law of thermodynamics, i.e., with

$$\left(\int_0^{T_c} C_{es} T^{-1} dT = \int_0^{T_c} \gamma dT\right)$$

within the limits of experimental accuracy. Setting $T_c = 1.70$°K in Eq. (3), we obtain $a = 8.5$ and $b = 1.46$.

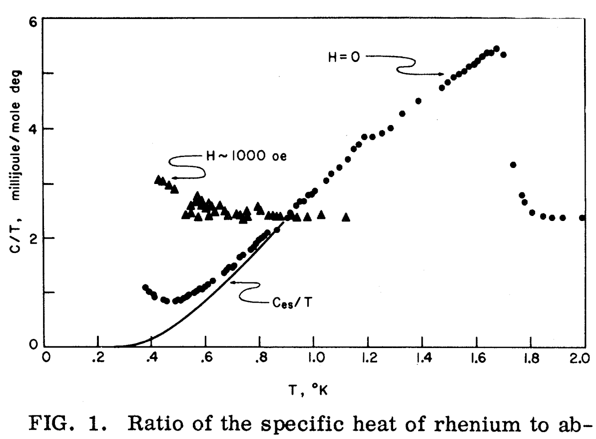

FIG. 1. Ratio of the specific heat of rhenium to absolute temperature as a function of temperature in zero magnetic field (●) and in 1000 oe (▲). The solid line is C_{es}/T vs T.

To quench the superconductivity and observe the magnetic field dependence of the anomaly, we remeasured in a field of about 1000 oersted. The resulting specific heat is also plotted in Fig. 1, and can be expressed as $\gamma T + \alpha T^3 + A_H T^{-2}$ with $A_H = 0.06 \pm 0.01$ millijoule deg/mole (because of fluctuations in the applied field, this measurement was less accurate). A_H does not appear significantly different from A_0, and we conclude that the anomaly is influenced by the applied field less than should be expected if it were caused by repopulation of electronic energy levels. For, since no deviation from the T^{-2} dependence of the anomaly is observed down to 0.37°K, the characteristic temperature of the zero-field splitting is certainly less than 0.37 deg. Calculations for a variety of splitting schemes, which involve interactions of the relatively large electronic magnetic moment with the field H, yield for $H = 1000$ oersted an anomaly about twice the magnitude of the one we observe in zero field.

There remains the possibility that the energy levels of the nucleus are separated sufficiently to produce the anomaly. This splitting can be produced by interaction between the nuclear electric quadrupole moment and the crystalline electric field.[3] Because the nuclear magnetic moment is much smaller than the electronic moment, its interaction with the magnetic field is much smaller than in the electronic case, and leads to a relatively weak dependence of the specific heat on H. The nuclei of the two stable Re isotopes have a spin of 5/2 and an average quadrupole moment $Q = 2.7 \times 10^{-24}$ cm^2. In the presence of an axially symmetric field gradient, whose maximum value we denote by eq, six degenerate energy levels of the Re nucleus will be split into three doubly degenerate pairs,[4] the separation of the lower two being $3e^2qQ/20$ and of the upper two, $6e^2qQ/20$. This splitting scheme leads to a specific heat $A_0T^{-2}=(14/9)Ra_0{}^2T^{-2}$ in the high-temperature limit $T \gg a_0$, where a_0 has been written for $3e^2qQ/20$. Comparing this result with the experimental value of A_0, we obtain $a_0 = 0.002$ deg and the maximum field gradient $eq = 0.14\times10^{16}$ esu. Since the ingot is polycrystalline and contains impurities, the value of eq may differ from that of a perfect crystal.

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[1] This ingot, furnished to us by Dr. M. P. Garfunkel, has a history similar to specimen 4C of J. K. Hulm and B. B. Goodman [Phys. Rev. 106, 659 (1957)], for which: T_C = 1.81°K with a transition breadth of 0.05 deg. The known impurities are Fe = 0.0011%, Si < 0.01%, and $W \sim 0.03\%$. We are grateful for the loan of this sample.

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

[3] See, for instance, M. H. Cohen and F. Reif, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 321.

[4] T. P. Das and E. L. Hahn, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Supplement 1.

NUCLEAR SPECIFIC HEAT OF GALLIUM AND ZINC

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Recently the specific heats of gallium[1] and zinc[1-3] have been measured in the superconducting state below 1°K. However the data have all been analyzed without concern of the possible effect of an interaction of the nuclear quadrupole moment with the gradient of the crystalline field. Now that such an effect has been shown to be of considerable importance for the specific heat of rhenium,[4] it becomes necessary to review the previous results.

Knight et al.[5] measured the pure quadrupole resonance spectra for Ga^{69} and Ga^{71} in the metallic state. From their results it becomes possible to calculate the quadrupole coupling constant for both isotopes and also the contribution of the nuclei to the specific heat of naturally occurring gallium (60.2% Ga^{69}, 39.8% Ga^{71}). This contribution is given by $C = 4.6/T^2$ ergs/mole deg when $T \gg 0.001$°K. It is only 5% of the specific heat of the conduction electrons at the lowest temperatures measured by us. Therefore we did not observe a departure of the electronic specific heat in the superconducting state from the expected exponential decrease with temperature:

$$C_{es} = \gamma T_C a \exp(-bT_C/T). \quad (1)$$

Recalculating our data, after subtracting this nuclear term, the constants for Ga in Eq. (1) change: a from 7.0 to 7.5 and b from 1.35 to 1.38. The fit of the experimental data and Eq. (1) is extended to somewhat higher temperatures: $T_C/T > 1.6$.

Zinc has a hexagonal crystal, and hence an appreciable field gradient can exist at the nuclei. However the single isotope which is magnetic, Zn^{67} (spin 5/2), has a natural abundance of only 4%. Phillips[2] noted deviations of the specific heat from the exponential temperature dependence, Eq. (1), outside the experimental error. It is reasonable to assume that these deviations are nuclear in origin and that they have a temperature dependence proportional to $1/T^2$. From his graph it follows that the additional term is then given by $C \sim 1.5/T^2$ erg/mole deg for naturally occurring zinc. Hence for Zn^{67}, $C \sim 37/T^2$ erg/mole deg and the nuclear quadrupole coupling constant for Zn^{67} is approximately 70 Mc/sec. If the additional term is subtracted from the specific heat data of Phillips, his constants of Eq. (1) change: a from 5.8 to 6.2 and b from 1.22 to 1.24 (using his values of γ and T_C). We reported values $a = 6.4$, and $b = 1.27$, which are only slightly higher. They were obtained at higher temperatures where this additional term can be neglected.

In the normal state, at the lowest temperatures Phillips notes a 5% deviation from the expected value of the heat capacity but allows the possibility of errors in his thermometers. However, this value of the deviation is to be expected if the splitting of nuclear energy levels of the Zn^{67} isotope contributes to the specific heat. It should be possible to substantiate our assumption by a quadrupole resonance experiment.

It is difficult to obtain data from Zavaritskii's[3] curves for zinc, but it appears that his results are not inconsistent with the above conclusions.

Zavaritskii[3] uses the relation $a = 4b^2$ for the