SUPPRESSION OF THE NUCLEAR HEAT CAPACITY IN BISMUTH METAL BY VERY SLOW SPIN-LATTICE RELAXATION, AND A NEW VALUE FOR THE ELECTRONIC SPECIFIC HEAT*

H. K. Collan, M. Krusius, and G. R. Pickett
Department of Technical Physics, Technical University of Helsinki, Otaniemi, Finland
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The specific heat of metallic bismuth has been measured from 0.05 to 0.8 K. The nuclear-quadrupole heat capacity expected from NMR measurements is not observed, allowing a more accurate determination of the electronic specific heat than has been possible previously. A lower limit for the nuclear spin-lattice relaxation time is estimated.

While attempting to resolve by calorimetric measurement the discrepancy between the values of the nuclear-quadrupole coupling constant e^2qQ/h for metallic bismuth as measured by NMR (51 Mc/sec)[1] and calorimetrically (25 Mc/sec),[2] we have observed the complete suppression of the nuclear heat capacity due to extremely slow spin-lattice relaxation which effectively decouples the nuclear system from the lattice in terms of the time scale of the measurement.

Nuclear spin-lattice relaxation in metals takes place primarily through spin-flip processes involving a relaxing nucleus and an s-like conduction electron leading to the Korringa relation between the temperature T and the relaxation time T_1, $T_1T = \text{const}$. For normal metals T_1 varies considerably, ranging from about 0.06 sec for Tl^{205} to about 180 sec for Li^7 at 0.1 K,[3] being as a rule short for the heavier noncubic metals where static quadrupole hyperfine interactions are expected. Thus the thermal properties associated with the hf splitting are observable calorimetrically. In the special case of superconducting metals at temperatures well below T_c, the relaxation time is very long due to the small number of bogoliubons or "normal electrons" available for relaxation process, and nuclear heat capacities measurable in the normal state are not observed when the metal is superconducting.[4] The present measurement shows that bismuth, with an electron density of only some 10^{-5} per atom, behaves more like a superconductor than a normal metal in this respect.

A fortunate bonus of the absence of any nuclear heat capacity is that the electronic term γT can be separated from the large lattice contribution with some confidence. This is of importance as the coefficient γ is a measure of the electronic density of states at the Fermi level,

$$\gamma = \tfrac{1}{3}\pi^2 k^2 N(E_F), \qquad (1)$$

and can be directly related to the known properties of the Fermi surface. For bismuth existing values[2,5] for γ are widely at variance with the known Fermi-surface parameters. This inconsistency is largely removed by the present measurement.

A straightforward experimental arrangement was used in which a chrome alum slurry pill cooled the specimen to below 20 mK via a tin heat switch. Thermal contact to the sample was made by a copper foil tightly bound by terylene thread and the contacting surfaces wetted with an amalgam of Hg-In-Tl. The temperature was measured by a $\frac{1}{2}$-W 220-Ω Speer resistor greased into a hole drilled in the specimen. The resistance was measured with an ac bridge, the output of which was fed to a chart recorder through a lock-in amplifier. The thermometer was calibrated against the susceptibility of a spherical slurry of CMN powder, saturated solution, and glycerol, in turn calibrated against the vapor pressure of He^3 between 0.85 and 1.8 K using the T_{62} scale. The heater was a Pt-W wire wound directly on the specimen and thermally anchored with Apiezon-N grease.

As the nuclear-spin system was found to be much more loosely coupled to the lattice than we had expected, the effective specific heat at the lower temperatures was very small and on opening the heat switch the specimen rapidly warmed up, reaching 0.2 K in a few minutes. This made usual "heat-burst" measuring techniques impossible and two other methods were used. The heat-switch configuration allowed the length of switch in the normal state to be adjusted by varying the controlling field. The extraneous heat leak to the specimen could thus be compensated and the specimen stabilized at a desired temperature. In the first or integral method the temperature was stabilized and continuously recorded while a heating pulse, of duration 4 to 10 sec, was fed to the heater, warming the specimen through a temperature interval of up to several

times the starting temperature, and the drift back to equilibrium was followed. This procedure was repeated at different starting temperatures and the various determinations were fitted by an expression for the specific heat of the form

$$C_p = \gamma T + BT^3 + AT^{-2}, \quad (2)$$

using the definition

$$Q - \Delta Q = \int_{T_i}^{T_f} C_p dT, \quad (3)$$

where Q is the energy fed to the heater and T_i and T_f are the temperatures at the beginning and end of the heating pulse, respectively. The fraction of energy ΔQ lost to the surroundings during the heating period was accurately evaluated from the after drift. This process gave the parameters of (2) by many integrations over large temperature intervals rather than by fitting discrete points.

In the second or dynamic method the equilibrium temperature was again adjusted by the switch and the temperature drift followed as the heater power was suddenly changed. Assuming thermal equilibrium, as the power is changed from $\dot{Q}_1$ to $\dot{Q}_2$ the specific heat is given by

$$\dot{Q}_1 - \dot{Q}_2 = C(dT_1/dt - dT_2/dt), \quad (4)$$

where dT_1/dt and dT_2/dt are the before and after drift rates at the instant of change and all effects of the external heat leak cancel out. The thermal equilibrium criterion did not present any problems as the equilibrium time within the lattice was measured to be less than 0.1 sec. The drift curves were fitted by computer with a heuristic formula to give the instantaneous drift rates at the moment of change in $\dot{Q}$ more precisely.

The specimen, weighing 495 g, was of 99.9999% zone-refined grade material from Koch Light Laboratories cast in a high-purity graphite mold to a 24-mm-diam cylinder which consisted of a few large crystals. Subsequent analysis gave a final purity of better than 99.999%. The resistance ratio $R_{300}/R_{4.2}$ was 230.

The results are plotted in Fig. 1 with different symbols for the two methods. The specific heat at the lowest temperatures is extremely small and this is reflected in the scatter of the experimental points. Owing to the lower accuracy of the dynamic measurement only the integral determinations were used in calculating the specific-heat parameters. After correcting for the addenda, consisting mainly of 0.87 g of Cu and 2.2 g of nylon, the best fit gave $C_p = (8.5 \pm 2.5)T + (1120 \pm 50)T^3 + (0.0064 \pm 0.002)T^{-2}$ μJ/mole K. The errors quoted correspond to 95% confidence limits of the parameters.

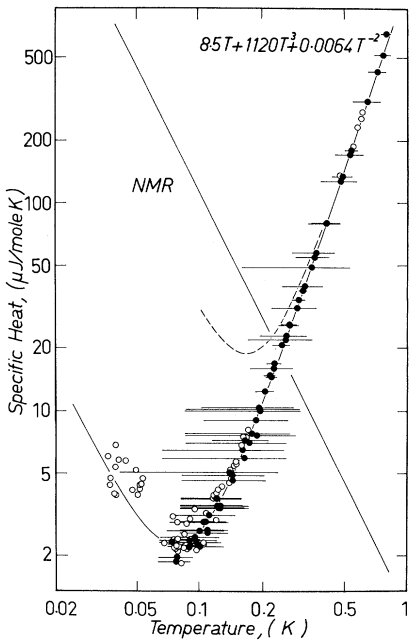

FIG. 1. Specific heat of bismuth. Open circles: points taken using the dynamic method (for measuring methods see text). Closed circles: determinations using the integral method, where the horizontal bar indicates the temperature interval of each measurement and the filled circle the measured specific heat reduced to the midpoint of the temperature interval by the relation $C_{\mathrm{meas}}(\bar{T}) = C_{\mathrm{calc}}(\bar{T}) Q_{\mathrm{meas}}(T_f - T_i)/Q_{\mathrm{calc}}(T_f - T_i)$ where Q_{meas} is defined by Eq. (3) and the calculated quantities are from the best-fit parameters. The broken curve is the measurement of Phillips (Ref. 2) and the full line labeled NMR is the equilibrium nuclear contribution calculated from the resonance measurements of Williams and Hewitt (Ref. 1).

As can be clearly seen, there is no evidence of the large nuclear heat capacity [(1.13 μJ K/mole)/T^2] expected from the quadrupole parameter measured by Williams and Hewitt by NMR.[1] The nuclear term [(0.28 μJ K/mole)/T^2] seen by Phillips[2] can be ascribed to contributions from the addenda as the measurement was made before the large nuclear heat capacity of Manganin heater wire was generally appreciated. The small "fast" T^{-2} component in the present measurement, seen most clearly in the dynamic points, we can also ascribe to the addenda and is probably due to transition-metal impurities, and to indium in the thermal-contact amalgam and in the heat-switch solder which has remained in the normal state after exposure to the demagnetizing field.

The lattice term, giving a Debye Θ of 120.3

± 1.5 K, is in excellent agreement with Phillips's value[2] and also agrees within the limits of accuracy with that of Kalinkina and Strelkov.[5]

The value for γ of 8.5 ± 2.5 μJ/mole K^2, although still somewhat uncertain due to the low value, is significantly less than the figures obtained by Kalinkina and Strelkov, 67 μJ/mole K^2, and Phillips, 21 μJ/mole K^2.

If we assume an ellipsoidal model for the Fermi surface then the density of states takes the particularly simple form

$$N(E_F)=\frac{1}{2}\left(\frac{n_e}{E_{eF}}+\frac{n_h}{E_{hF}}\right), \quad (5)$$

where n is the number of carriers, E_F is the Fermi energy, and subscripts e and h denote electrons and holes, respectively. In pure material we expect n_e and n_h to be equal. Figures for the Fermi energies and n vary somewhat but taking E_{eF} to be 27.6 meV and the band overlap $E_{eF}+E_{hF}$ to be 38.5 meV from Smith, Baraff, and Rowell,[6] and with $n_e = 4.4\times10^{17}$ cm^{-3} from the infrared absorption measurements of Boyle and Brailsford,[7] we obtain for γ a figure of 7.1 μJ/mole K^2. This is well within the limits of our experimental value and seems to rule out the necessity of assuming extra carriers with a high density of states as suggested by Lerner.[8] The result thus confirms the analysis of Balcombe and Forrest[9] and is also in agreement with a recent band-structure calculation of Ferreira.[10]

Although the measurement gives no information on the quadrupole-coupling constant, by careful study of the drift curves below 0.3 K we can estimate a lower limit for the spin-lattice relaxation time T_1. We assume that the nuclear spin system is describable by a spin temperature T_s, ascribing to it a heat capacity AT_s^{-2}, where the value of $A = 1.13$ μJ K/mole is calculated from the resonance result. Then, assuming the Korringa relation, we introduce a trial value for T_1T in the relaxation expression

$$d(1/T_s)/dt = (1/T_1)(1/T-1/T_s) \quad (6)$$

valid in the high-temperature approximation. By integration of (6) we obtain the spin temperature as a function of time $T_s(t)$ from the recorded lattice temperature $T(t)$. Using (6) and $T_s(t)$ and $T(t)$ we can then evaluate the rate of energy exchange between the lattice and the spin system, $AT_s^{-2}dT_s/dt$. Comparing this back with the observed drift rates we obtain a lower limit for T_1 of $100/T$ sec. This very long relaxation time is obviously a consequence of the small number of carriers.

The above value for T_1 shows that the quadrupole-coupling constant in pure bismuth cannot be measured calorimetrically. However, if the carrier density could be raised to the level of the similar semimetal antimony, where the nuclear heat capacity has been unambiguously observed,[11] the relaxation time should become short enough for the nuclear thermal anomaly to be measurable. Such an increase in carrier density can be achieved by doping with, for instance, 0.1 wt.% of tellurium,[12] at which low impurity level the destruction of the lattice symmetry by the solute should have almost no effect on the mean electric field gradient seen by the bismuth nuclei and thus the hyperfine parameter should not differ appreciably from that of the pure material.

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