EVIDENCE FOR TWO ENERGY GAPS IN HIGH-PURITY SUPERCONDUCTING Nb, Ta, AND V†

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We have made heat-capacity measurements on zone-refined single-crystal samples of Nb, Ta, and V between 0.35 and 25°K. At temperatures below about $T_c/10$, the superconducting-state electronic heat capacity C_{es} is considerably larger than that predicted by the BCS theory,[1] and its temperature dependence differs from any reported previously. The data cannot be explained by energy-gap anisotropy of the usual magnitude. Suhl, Matthias, and Walker[2] have shown that inclusion of interband-scattering terms in the BCS Hamiltonian leads to two distinct energy gaps, and we believe our results demonstrate the existence of these two gaps.

The measurements were made in a calorimeter that permits measurements over the range 0.25 to 25°K, and which will be described in more detail elsewhere. All measurements were made with a sample holder that included a single germanium thermometer and a heater. Below 4.2°K and above 10°K the thermometer calibration was based on well-established procedures, but between 4.2 and 10°K it was based on an interpolation of the resistance-temperature relation for an Allen-Bradley radio resistor. In the latter region the data will be corrected when the germanium thermometer is calibrated accurately. Measurements on a copper sample suggest that the experimental error is less than 1% at all temperatures. The samples were screened from the earth's magnetic field with Mumetal, and were not exposed to other magnetic fields between the time of cooling below T_c and the start of the superconducting-state measurements. Thus, there can be no frozen-in flux during the superconducting-state measurements.

Figures 1 and 2 show the heat capacity of two Nb samples. Nb II ($T_c = 9.13$°K; residual resistivity ratio = 24) is a 99.9% polycrystalline sample of material similar to that from which the single crystal Nb I ($T_c = 9.26$°K; residual resistivity ratio = 110) was prepared by triple zone refining. Apart from a T^{-2} term associated with the interaction of the large (6.14 μ_N) nuclear moments with the external field, the normal-state heat capacity C_n is consistent

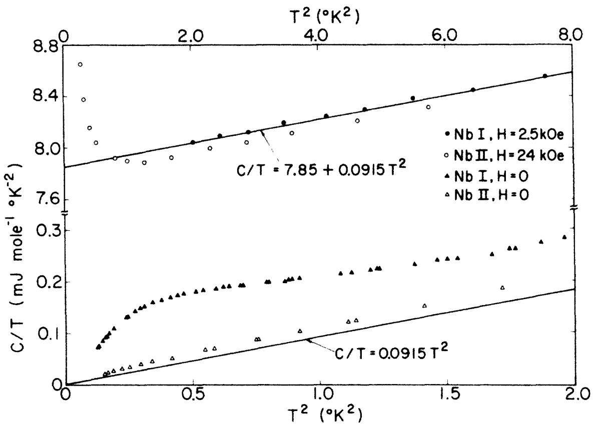

FIG. 1. The heat capacity of two samples of Nb. The straight line through the normal-state points of Nb I was chosen as the best representation of all normal state-state data for that simple at temperatures below 3°K.

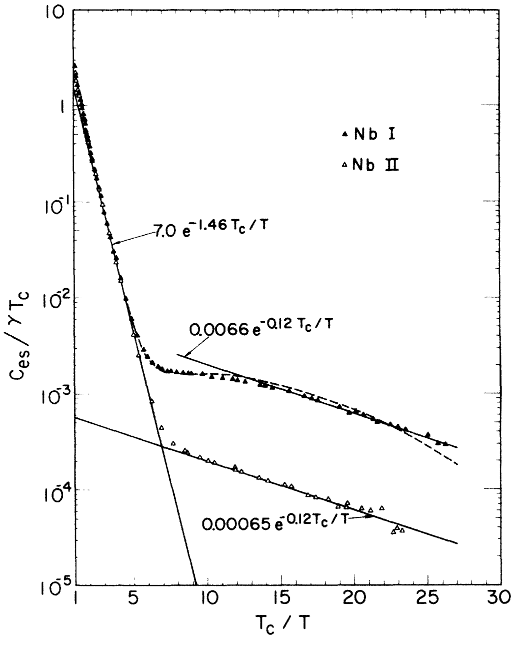

FIG. 2. The superconducting-state electronic heat capacity of two samples of Nb. The dashed curve represents the expression $C_{es}/T_c = 7.0\exp(-1.46T_c/T) + 0.0038(0.25T_c/T)^2\exp(0.25T_c/T)[1+\exp(0.25T_c/T)]^{-2}$.

with the usual analysis into electronic and lattice contributions, $C_n = \gamma T + (12/5)\pi^4 R(T/\Theta_0)^3$. For both samples, $\Theta_0 = 277°\mathrm{K}$, in agreement with the elastic constants[3] and other recent calorimetric data[4,5]; for Nb I, $\gamma = 7.85$ mJ mole^{-1} deg^{-2}; for Nb II, $\gamma = 7.79$ mJ mole^{-1} deg^{-2}. Between T_c and $T_c/6$, $C_{es}/\gamma T_c$ is approximately the same for both samples, and is given by $C_{es}/\gamma T_c = 7.0 \exp(-1.46 T_c/T)$ for $2 < T_c/T < 6$; for $T < T_c/14$, $C_{es}/\gamma T_c$ is proportional to $\exp(-0.12 T_c/T)$ for both samples, but with different proportionality constants; at intermediate temperatures $C_{es}/\gamma T_c$ is less than the sum of the corresponding exponential terms for both samples, but the discrepancy is particularly pronounced for Nb I.

Few measurements of C_{es} on metals with filled d bands extend to reduced temperatures low enough to compare with the data in Fig. 2. Some of the early measurements below 1°K showed positive deviations from exponential behavior at the lowest temperature reached, but different measurements on the same metals did not agree. Tin, for which deviations had been reported, is one of the more favorable examples for experimental investigation (high Θ_0 and T_c), and two recent measurements[6] on high-purity samples agree in showing a simple exponential temperature dependence of C_{es} down to $T \approx T_c/9$, below which C_{es} is lost in the lattice heat capacity.[7] The energy-gap anisotropy that has been observed by more direct methods in other superconductors is far too small to account for the two exponential terms in C_{es} of Nb, and we conclude tentatively that they reflect the presence of two distinct energy gaps produced by overlapping of the s and d bands at the Fermi surface.[2] The sensitivity of C_{es} to sample purity can be understood on the basis of Anderson's theory of "dirty" superconductors,[8] and explains why the deviation from a simple exponential has not been observed in earlier measurements.[9] The coefficients of T_c/T in the exponential terms suggest that, at 0°K, the larger gap $\Delta_1(0)$ and the gap in the "dirty" sample are both close to the BCS value $3.52kT_c$, and that the smaller gap $\Delta_2(0)$ is an order of magnitude smaller. If $\Delta_2(T)/\Delta_2(0)$ has a temperature dependence similar to that given by the BCS theory, kT becomes equal to $\Delta_2(T)$ at a temperature for which $\Delta_2(T)$ is still approximately equal to $\Delta_2(0)$. This situation is very different from that which occurs in a single-gap superconductor, and perhaps accounts for the marked deviation of C_{es} from the sum of two exponential terms. Figure 2 shows that a Schottky anomaly—which for $kT \lesssim \Delta_2(0)$ might be expected to approximate the contribution of the states just above the smaller gap to C_{es}—does represent $C_{es} - 7.0\gamma T_c \times \exp(-1.42 T_c/T)$ reasonably well. Another possibility, suggested by calculations for the case in which the interband-scattering contribution to the Hamiltonian is small,[2] is that the smaller gap (partially) collapses at a temperature well below T_c, producing a peak in C_{es}. We have not attempted a more detailed comparison with theory because it is quite possible that even Nb I does not exhibit "clean-sample" behavior.

We have also made measurements on two Ta samples with purities similar to those of Nb I and Nb II. They each show behavior similar to the corresponding Nb sample (but the measurements extend only to $T = T_c/12$). The purest V sample we have been able to obtain is similar in purity to Nb II, and also resembles that sample in the behavior of C_{es}.

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

[7] A T^3 term has been reported in C_{es} for Pb [B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. 137, A103 (1965)], but it is only 6% of the estimated lattice heat capacity, and this result is not in agreement with other measurements [N. E. Phillips, M. H. Lambert, and W. R. Gardner, Rev. Mod. Phys. 36, 131 (1964), and more recent measurements to be published].

[8] P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).

[9] For the Nb sample described in reference 4, C_{es} was apparently slightly larger than that of Nb II, but the authors attributed the excess over the lattice heat capacity to strains or impurities.

F^{19} NUCLEAR MAGNETIC RESONANCE LINE NARROWING IN LaF_3 AT 300°K

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The fluorine nuclear magnetic resonance (nmr) of a single crystal of lanthanum trifluoride, LaF_3, has been investigated at 16.00 Mc/sec in the temperature range from 173 to 573°K. The resonance line was observed to begin motionally narrowing at 300°K.[1,2] This is surprising since the melting point of LaF_3 is 1770°K. The purpose of this paper is to report the details of this observation.

Figure 1 shows the integrated spectra taken at three different temperatures with the magnetic field along the c axis of this hexagonal crystal.[3] Within the experimental accuracy the linewidth and line shape are the same along the c axis and perpendicular to the c axis. Below the 300°K the rigid-lattice line shape is squarer than a Gaussian. This is evident from Fig. 1. The measured ratio of the fourth moment to the second moment squared, $M_4/(M_2)^2$, for the rigid lattice is 2.3, which compares to 3.0 for Gaussian. As the temperature is raised above 300°K, the line narrows and becomes a composite of a broad and narrow line. In this temperature region the ratio $M_4/(M_2)^2$ reaches a peak value of 3.8. The frequencies of the two lines are shifted but never enough to be resolved by the Rayleigh criterion. As the temperature is raised still further, the two lines coalesce and the line stops narrowing.[4] In this high-temperature region $M_4/(M_2)^2$ decreases to a constant value of 3.2.

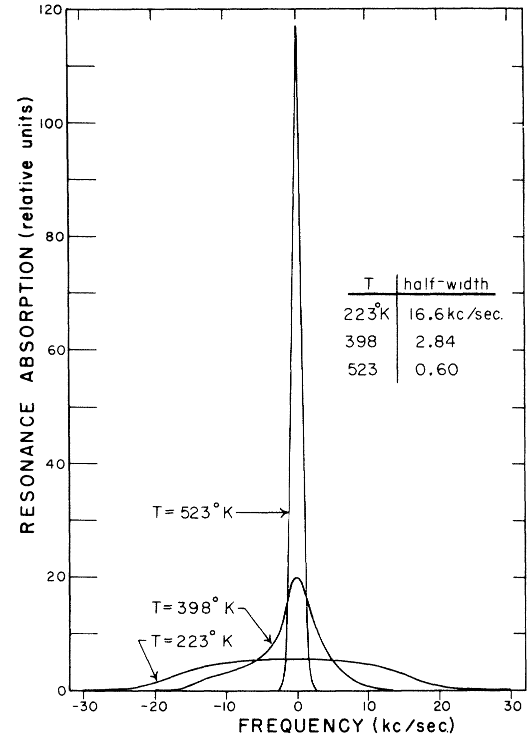

FIG. 1. Temperature dependence of F^{19} nmr absorption along the c axis. The half-width at half-intensity is given for the three temperatures.

The experimental measurements were performed on a Varian V-4200 nmr spectrometer operated at 16.00 Mc/sec. The temperature dependence was obtained using a Varian V-4540 variable temperature controller which controls and monitors the flow of cooled or heated dry nitrogen gas over the sample. The single crystal used was cylindrical with a diameter of $\frac{1}{4}$ in. and a length of $\frac{3}{8}$ in. In order to avoid distortions and saturation, the magnetic field scanning speed, the modulation frequency and amplitude, and the magnitude of the rf field were chosen at each temperature such that by decreasing their magnitudes still further no changes in the resonance line were observed. The spectrum at each temperature was scanned as many as 100 times and stored in a C-1024 time-averaging computer. This procedure improves the signal-to-noise ratio as the square root of the number of scans. The use of this procedure was necessary because below 300°K the line is so broad that a signal-to-noise ratio of unity was typical for a single passage through the resonance line. However, at high temperatures, the signal-to-noise is greatly enhanced because of