clearly very poor at low concentrations, as it cannot show the separate impurity band in the gap. It is instructive to consider how the present results would alter Shiba's work. For positive J the bound state and the impurity band are very close to the edge of the gap, and one might expect the AG[15] density of states to be a good approximation in this situation. For negative J smaller than g, on the other hand, one would expect the AG theory to be very poor, as the impurity band will appear deep in the gap. Thus our model accounts (in very qualitative fashion) for the tunneling results of Woolf and Reif.[16]

It is straightforward to extend the work of Sec. II to finite temperatures. One finds trajectories qualitatively similar to those for $T=0$ (compare the discussion in I). However, for finite concentrations the picture is slightly altered—increasing the temperature decreases the gap and thus the whole energy scale of the system, so the wave function of the localized state spreads out further and further. Thus overlap with other localized states becomes more significant, and for low impurity concentrations the initially narrow impurity band will spread (relative to the gap size) as the temperature approaches T_c. In this model gaplessness occurs when the impurity band spreads over the center of the gap.[5] This will happen for arbitrarily low impurity concentrations provided the temperature is close enough to T_c.

ACKNOWLEDGMENT

We wish to thank J. Zittartz for a letter (in reply to our earlier manuscript) describing some of his unpublished work on the bound-state problem, using an approach different from ours. The extension of our method described in Sec. IV was stimulated by the discrepancy between our classical result and his work for positive J.

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Specific Heat of Rhenium between 0.15 and 4.0 K*

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The specific heat of rhenium has been measured in the normal state between 0.15 and 4.0 K and in the superconducting state between 0.3 and 1.7 K. The specific heat in the normal state between 0.15 and 4.0 K was found to be $C_n=\gamma T+\alpha T^3+A/T^2$, where $\gamma=2290\pm20\ \mu$J/mole deg^2, $\alpha=27\pm2\ \mu$J/mole deg^4, and $A=49\pm2\ \mu$J deg/mole. Below $T_0=1.700$ K, the electronic contribution to the specific heat in the superconducting state was found to be $C_s=\gamma T_0 a e^{-bT_0/T}$, where $a=8.14$ and $b=1.413$. The above parameters were consistent with the vanishing of the entropy difference S_n-S_s at T_0. The value of the Debye temperature at absolute zero, $\Theta_0=416$ K, agrees with the value derived from measurement of elastic constants. The density of states at the Fermi level, $N(\zeta)$, derived from the measured value of γ, is 0.484 states of one spin per eV atom. The value for the superconducting energy gap derived from the value of b deduced in this work is $3.43kT_0$, compared to a value of $3.30kT_0$ deduced from thermal-conductivity measurements. The critical-field parameter H_0 was found to be 211 Oe, and the deviation of the critical-field curve from parabolic dependence was less than 3.7%. The resonant frequencies corresponding to the interaction between the nuclear quadrupole moment and the crystalline field are estimated to be 41 and 82 MHz.

1. INTRODUCTION

THE specific heat of rhenium has been measured previously by several workers[1–5] over various low-temperature ranges. Additional measurements of magnetic properties of this superconductor have been made,[6–11] which also yield some of the thermodynamic properties. Shepard and Smith[12] measured the elastic constants of rhenium single crystals down to 4.2 K,

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from which they derived a value for the Debye temperature at absolute zero, Θ_0, of 416.2 K.

For rhenium, the parameters a and b occurring in the expression for the superconducting electronic specific heat,

$$C_{es}/\gamma T_0 = ae^{-bT_0/T}, \quad 2 < T_0/T < 6 \tag{1}$$

have been deduced in only two investigations,[3,4] and the parameter A describing the high-temperature approximation of the nuclear contribution to the specific heat,

$$C_N = A/T^2, \tag{2}$$

has been measured in only one investigation.[3] The temperature range for these two investigations was not large enough to obtain the three parameters A, a, and b with great accuracy.

Using a dilution refrigerator recently built in this laboratory,[13] it was possible to cover a greater range of the parameter T_0/T occurring in Eq. (1). It was also possible to cover a greater portion of the high-temperature tail of the nuclear specific-heat contribution.

2. MEASUREMENT TECHNIQUES

The He^3 cryostat used for these measurements between 0.3 and 4.2 K has been described elsewhere.[14] The dilution refrigerator was constructed following essentially the description given by Wheatley, Vilches, and Abel,[15] and was used to measure the specific heat of the sample over the temperature range 0.15–0.5 K. This refrigerator reaches a low temperature of 0.03 K in the mixing chamber as indicated by the magnetic susceptibility of powdered cerium magnesium nitrate (CMN) immersed in the dilute solution in the mixer. No exchange gas was used to cool the specimen when specific-heat runs were to be made. The cooled dilute solution leaving the mixer flows through a sintered copper heat exchanger mounted below the mixer. This heat exchanger has a smooth gold-plated surface to which the sample holder is clamped, and is the heat sink to which heat from the sample can be conducted through a superconducting heat switch using a pure tin ribbon. In the He^3 cryostat the sample is cooled by direct mechanical contact with a plate which is always at the temperature of the He^3 bath.

The measurement of specific heat requires that the sample be isolated from its surroundings. Calibration of the sample thermometer, on the other hand, requires that the thermometer be in good thermal contact with the source of cooling. Because these requirements conflict with each other, the calibration was conducted separately from the specific-heat measurements.

A. Calibration

For measurements with the He^3 cryostat the sample thermometer was brought into thermal contact with the He^3 vessel through the use of exchange gas after the specific-heat measurements were completed. The thermometer used for temperature measurements in the range accessible to the He^3 cryostat was a 6-mg germanium resistance thermometer made in this laboratory and chosen for its small heat capacity. This thermometer was calibrated against the vapor pressure of He^4 and the vapor pressure of He^3. The paramagnetic susceptibility of a sphere of granulated ferric ammonium sulfate was calibrated between 0.5 and 1.2 K using a Curie-Weiss law, $\chi = C/T^*$, and a relation between the magnetic temperature T^* and the thermodynamic temperature T: $T^* = T + 0.00548/T$.[16] The susceptibility was extrapolated to lower temperatures for calibrating the resistance thermometer at temperatures below 0.5 K.

The thermometer used for measurements with the dilution refrigerator was an encapsulated germanium resistance thermometer made commercially.[17] On the basis of work done during this investigation and of other specific-heat work,[18] we concluded that this type of thermometer is stable against thermal cycling between room temperature and cryogenic temperatures. For calibration measurements with the dilution refrigerator the thermometer was remounted directly on the heat sink, in thermal contact with the CMN in the mixer.

The finely powdered CMN was shaped in the form of a cylinder whose diameter and height are 1.27 cm in length and bathed in the dilute solution in the mixer. Using the 1958 He^4 temperature scale above 1.2 K, the paramagnetic susceptibility of the CMN was calibrated between 1.2 and 4.2 K with a commercial mutual inductance bridge.[19] The measured susceptibility points were plotted against $1/T$ and a straight line was fitted to the points by a least-squares curve-fitting routine on a computer. The susceptibility of CMN follows a $1/T$ dependence to 0.006 K,[20] and was used to calibrate the commercial resistance thermometer for all temperatures below 1.2 K.

The temperatures for the calibration points were set by regulating the speed with which vapor was pumped from the still, or by heating one of the heat exchangers above the mixing chamber. About 1 h was required to reach a new steady-state condition of the refrigerator when moving from one calibration point to another.

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TABLE I. Specific heat of rhenium in normal (C_n) and superconductive (C_s) state. (C is in mJ/mole deg.)

T(K)	C_n	T(K)	C_s
0.1566	2.102	0.3264	0.512
0.1858	1.714	0.3385	0.458
0.2109	1.658	0.3504	0.438
0.2316	1.434	0.3700	0.398
0.2543	1.297	0.4012	0.381
0.2828	1.277	0.4367	0.389
0.3193	1.183	0.4684	0.412
0.3857	1.194	0.5411	0.537
0.4546	1.260	0.6049	0.699
0.5282	1.376	0.6505	0.897
0.6319	1.545	0.7197	1.000
0.7764	1.847	0.7531	1.354
0.9409	2.236	0.8514	1.924
1.176	2.766	0.9319	2.444
1.354	3.251	1.009	2.964
1.441	3.403	1.107	3.723
1.787	4.267	1.231	4.889
1.869	4.489	1.351	5.962
2.000	4.829	1.466	7.100
2.378	5.806	1.564	8.086
2.587	6.463	1.630	8.740
2.797	7.038	1.667	9.173
2.992	7.611		
3.250	8.491		
3.556	9.398		

In summary, the temperature scales are essentially the 1958 He^4 scale between 1.2 and 4.2 K and the 1962 He^3 scale between 0.5 and 1.2 K. Below 0.5 K the temperature scale is determined by the extrapolation of the temperature dependence of the susceptibility of the appropriate paramagnetic salt.

The relation between temperature and resistance was expressed by a formula:

$$\frac{1}{T}=\sum_{i=0}^{3} A_i(\log_{10}R)^i.$$

The calibration data were divided into several overlapping temperature regions, and a computer calculated the constants A_i for each temperature region.

B. Measurement of Specific Heat

The specific-heat measurements were made using a standard heat pulse method with heating periods of 10-sec duration. A Pt–9% W nylon-insulated wire was used as the sample heater.

Above 0.3 K the current through the sample thermometer was 0.1 μA, and below 0.3 K the current was 0.01 μA to minimize Joule heating in the thermometer. The currents were chosen so that the measured resistance at a given sample temperature was independent of current magnitude.

The apparent specific heat in the superconducting state below 0.25 K was much smaller than expected from extrapolation of the data measured at higher temperatures. This indicated that below 0.25 K the relaxation time between the nuclei and the lattice probably becomes far too long to extablish thermal equilibrium in a reasonable time. This effect has been reported for gallium,[21] indium,[22] and bismuth.[23] In the superconductive state the electrons in the sample are paired in the ground state and cannot mediate between the nuclear spins and the lattice. To shorten the nuclear spin-lattice relaxation time it was necessary to provide free electrons by driving the sample into the normal state, breaking up the electron pairs.

For measurement of the specific heat in the normal state below the transition temperature a magnetic field of 250 Oe was applied to the specimen, parallel to its long axis. This field strength affects the splitting of the nuclear energy levels so little as to be unobservable in the specific heat.

For specific-heat measurements in zero field, the magnetic field, was compensated to 0.05 Oe using a Helmholtz coil, whose field was applied above the transition temperature to avoid trapping of flux in the sample during the initial cooldown.

The addenda included the thermometer, heater wire, Glyptal, threads, copper leads, nickel tips of superconducting wires, and insulation. The ratio of addenda heat capacity to sample heat capacity was 4% at 4 K and decreased with temperature. The error in the calculated heat capacity of the addenda itself should not exceed 10%. At the low temperatures measured with the dilution refrigerator the total heat capacity of the addenda was negligible in comparison to that of the sample.

The systematic error in the measured heat capacity due to inaccuracies in the temperature scale and calibration is believed not to exceed 1% above 1 K, but may be about 3% at 0.3 K. Other systematic errors in heating current, heater resistance, timing, and correction for heat capacity of addenda added at most another 0.4% at 4 K, and decreased at lower temperatures. Graphical scatter in the data amounts to about 1%.

The specific-heat data measured by means of the He^3 cryostat agreed with the data measured with the dilution refrigerator, in the region of overlap, confirming, at least above 0.3 K, the assumption that the thermometer calibration does not change with thermal cycling.

3. RESULTS

From the earlier measurements on impure rhenium it follows that the specific heat for the normal state, C_n, is given by

$$C_n=C_l+C_N+C_{en}, \qquad (3)$$

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and that for the superconductive state C_s is given by

$$C_s=C_l+C_N+C_{es}, \tag{4}$$

where C_l, the lattice specific heat, is assumed to be the same for both the normal and superconducting states; C_N, the nuclear specific heat, is independent of field strength for applied fields less than 10^3 Oe, and

$$C_l=\alpha T^3+\beta T^5+\mu T^7+\dots, \tag{5}$$

$$C_N=A/T^2. \tag{6}$$

C_{en} and C_{es} are the electronic contributions to the specific heat in the normal and superconductive states, respectively, and can be expressed

$$C_{en}=\gamma T=\tfrac{1}{3}\pi^2k^2N(\zeta)T, \tag{7}$$

$$C_{es}=a\gamma T_0e^{-bT_0/T},\quad 2<T_0/T<6. \tag{8}$$

T_0 is the superconducting transition temperature in zero magnetic field, a and b are constants, and k is the Boltzmann constant.

The superconducting transition temperature T_0 was determined to be 1.700 K by observing the change in slope of the temperature-versus-time curve as the specimen heated or cooled slowly through the superconducting transition.

The rhenium specimen was a single crystal weighing 51.03 g, prepared by Westinghouse Electric Corp. from 99.995% purity metal powder using a zone melting technique. Its residual resistance ratio $\rho_{300}/\rho_{4.2}$ was measured and found to be 417.

Representative data comprising one-third of the specific-heat points for this rhenium specimen are listed in Table I and plotted as C_n/T versus T and C_s/T versus T in Fig. 1.

Analysis of data for $2<T<4$ K led to the conclusion that β and μ were vanishingly small for $T<4$ K. A further, iterative analysis used to determine the constants in Eqs. (5)–(8) was carried out using the following constraints:

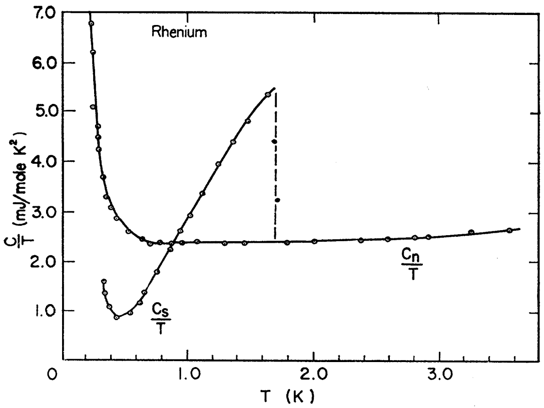

FIG. 1. Specific heat of rhenium in the normal (C_n) and superconducting (C_s) states, plotted as C/T.

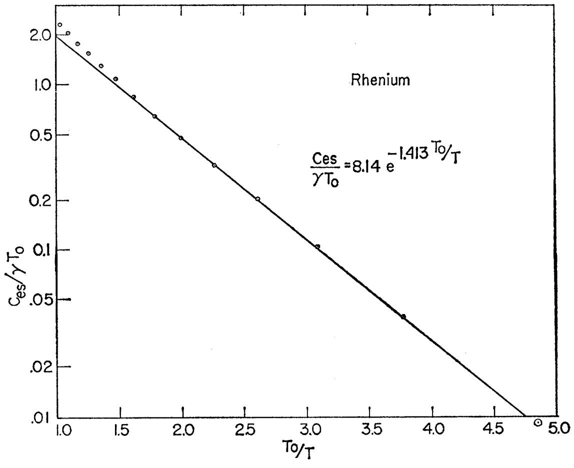

FIG. 2. Electronic specific heat of rhenium in the superconducting state, plotted as $C/\gamma T_0$.

(a) A semilogarithmic plot of $(C_s-A/T^2-\alpha T^3)/\gamma T_0$ versus T_0/T should fit a straight line for $2<T_0/T<6$. (See Fig. 2.)

(b) The entropies S_n and S_s for the normal and superconductive states, respectively, should be equal at T_0.

The constants obtained by analysis of the specific-heat data for this rhenium specimen are summarized as follows:

$T_0=1.700\pm0.002$ K, $a=8.14\pm0.06$,
$\gamma=2290\pm20$ μJ/mole deg^2, $b=1.413\pm0.005$,
$\alpha=27\pm2$ μJ/mole deg^4, $A=49\pm2$ μJ deg/mole,
$\theta_0=416\pm10$ K.

The value for the superconducting transition temperature T_0 is in excellent agreement with the results obtained by others.[3–5,7,9–11] The width of the superconducting transition, as indicated by the region over which the change in the slope of the heating curve took place, was 0.007 K. The value found for γ is in good agreement with that given by others,[1–4,10,11] and the value of the Debye temperature at absolute zero, Θ_0, is in excellent agreement with the value given by Shepard and Smith from their elastic constant data.[12]

The values of a and b given here should be better than those from previous measurements[3,4] since a greater range of T_0/T was covered and since the nuclear quadrupole moment contribution was accounted for in determining the electronic specific heat.

The magnitude of γ is related to the density of states at the Fermi level by Eq. (7), which gives $N(\zeta)=0.484$ states of one spin per eV atom. Mattheiss[24] gives a value of 0.37 from band-structure calculations using a relativistic augmented-plane-wave method. Using the renormalization factor due to enhancement

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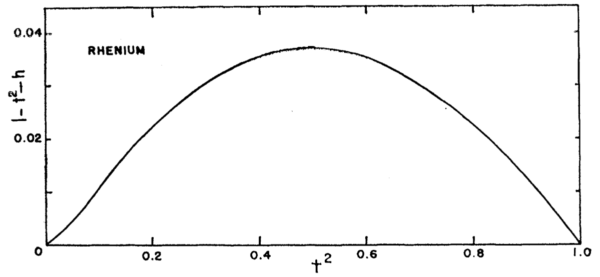

FIG. 3. Deviation of the critical field of rhenium from parabolic dependence on the reduced temperature.

of heat-capacity density of states by electron-phonon interactions, calculated by McMillan,[25] the value of $N(\zeta)$ predicted by theory becomes

$$N(\zeta)=N_{\mathrm{bs}}(1+\lambda)=0.54\,,$$

where N_{bs} is the band-structure density of states, and $1+\lambda$ is the renormalization factor. The coupling constant λ is 0.46 for rhenium.

The BCS theory[26] relates a value of $3.50kT_0$ for the energy gap in a superconductor at 0 K to a value of b equal to 1.44. Experimentally, $b=1.413$, for which the corresponding energy gap would be $3.43kT_0$. As yet no tunneling or infra-red data appear to exist to compare with this prediction. However, Sharma[27] has deduced a value for the superconducting energy gap, $2\epsilon(0)=3.30kT_0$, from measurement of the thermal conductivity of rhenium between 0.3 and 4.2 K.

The critical field $H_c(T)$ is thermodynamically related to the entropy difference S_n-S_s by the equation

$$H_c^2(T)=\frac{8\pi}{V_m}\int(S_n-S_s)dT\,,$$

where V_m is the molar volume, for which 8.84 cm³/mole[9] was used. The value of the critical field at 0 K was found to be

$$H_c(0)=H_0=211\text{ Oe}.$$

The deviation of the critical field from a simple parabolic dependence on the reduced temperature T/T_0 is

$$D=1-(T/T_0)^2-H(T)/H_0=1-t^2-h$$

and is plotted in Fig. 3. The maximum deviation is 3.7%, in good agreement with BCS theory.

The nuclear contribution to the specific heat is a Schottky-type specific-heat contribution due to the interaction of the electric quadrupole moment of the rhenium nucleus with the crystalline field,[3] which splits the sixfold degenerate energy level into three pairs separated by energies a_0k and $2a_0k$. Here k is the Boltzmann constant and a_0 has units of temperature. At temperatures much higher than the position of the maximum in the heat capacity due to the anomaly, the contribution is expressed by the relation

$$\Delta C=A/T^2=14Ra_0^2/9T^2\,,$$

where R is the gas constant, a_0k is equal to $3e^2qQ/20$, eq is the largest component of the electric-field-gradient tensor in the principal-axis system, Q is the scalar quadrupole moment of the nucleus, whose average value for rhenium is 2.66×10^{-24} cm², and e^2qQ is the quadrupole coupling constant. Using the experimentally determined value of A we find $a_0=1.95$ mK corresponding to $eq=0.14\times10^{16}$ esu. The resonant frequencies associated with these three pairs of levels should be 41 and 82 MHz.

4. CONCLUSIONS

The superconductive properties of rhenium, deduced from calorimetric measurements, are in good agreement with the properties of a weak-coupling superconductor calculated on the basis of the BCS theory of superconductivity.

Better values of the separations between the three pairs of nuclear energy levels are found and from these separations it is predicted that the NMR frequencies in zero field should be 41 and 82 MHz.

Note added in proof. Rockwood *et al.*[28] find for the coefficient of the nuclear contribution to the specific heat: $A=0.061$ mJ deg/mole.

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