

deduced from Shoenberg's⁷ de Haas-van Alphen data and Galt et al.⁸ (cyclotron resonance).

These results definitely indicate that the theoretical expression, Eq. (4) of the preceding paper, does not give a good fit. The curvature for the theoretical curves of energy versus magnetic field is much sharper than that indicated in Figs. 2 and 3. Extension of these measurements to higher magnetic fields will permit the study of the departure from parabolicity and the added resolution will allow the independent determination of the masses for the valence and conduction bands together with the g values associated with them.

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¹S. Zwerdling, B. Lax, L. M. Roth, and K. J. Button, Phys. Rev. **114**, 80 (1959).

²G. E. Smith, Phys. Rev. **115**, 1561 (1959).

³Measurements on this apparatus indicate that the temperature of the sample holder differed by no more than 2°K from the bath temperature using the liquid air refrigerant. The temperature of the sample was not measured when liquid helium was used, but it is believed that the sample was somewhat above 4°K.

⁴B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keyes, preceding Letter [Phys. Rev. Letters **5**, 241 (1960)].

⁵A crude attempt to estimate this gap was made by W. S. Boyle and K. F. Rodgers, Phys. Rev. Letters **2**, 338 (1959). They stated that the "edge at 20 microns would set the lower lying states at about 0.05 ev below the Fermi surface." If \mathcal{E}_F (≈ 0.018 ev) were subtracted this would give $\mathcal{E}_g \approx 0.03$ ev, which is too small.

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DIFFERENCE IN LATTICE SPECIFIC HEATS IN THE NORMAL AND SUPERCONDUCTING PHASES*

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A series of measurements of the heat capacity of annealed niobium in the normal and superconducting phases, carried out in this laboratory, was reported at the 1958 International Conference on the Electronic Properties of Metals at Low Temperatures.¹ One of the principal objectives of the investigation was the determination of the temperature dependence of the superconducting electronic specific heat C_{es} , and its comparison with the detailed predictions of the Bardeen, Cooper, Schrieffer² (BCS) theory. Although an exponential dependence of C_{es} with temperature was observed as required by the theory, it was not possible to make measurements below $0.2T_c$ and hence the predicted change to the lower temperature exponential³ could not be investigated. A new cryostat was therefore constructed for this and other investigations and the research on niobium was resumed.

According to current ideas, the determination

of C_{es} requires a measurement of C_n , the specific heat of the metal in the normal phase, and of C_s , the specific heat in the superconducting phase. Values of C_n were found to follow the relation:

$$C_n = \gamma T + A(T/\Theta)^3,$$

with $\gamma = 7.62$ millijoules/mole deg² and $\Theta = 231^\circ\text{K}$. Values of the normal lattice term, $A(T/\Theta)^3$, were subtracted from C_s at the same temperature to yield values of C_{es} which, down to 1.7°K , were found to satisfy the following relation:

$$C_{es} = \gamma T_c [10 \exp(-1.63T_c/T)],$$

with $T_c = 9.09^\circ\text{K}$. It should be pointed out that this procedure assumes that the superconducting specific heat consists of independent lattice and electron contributions and that the lattice specific heat is identical in the normal and superconducting phases.

The validity of this method for determining C_{eS} was discussed some time ago by Chester⁴ who pointed out that it could be proved only for those superconductors which obey the similarity rule for critical magnetic fields. Critical field studies of isotopic mixtures are limited, but where they have been made it has been found that the similarity principle holds. On the basis of this evidence it seems to have been assumed that the principle holds generally and that therefore the phonon spectrum in the normal and superconducting phases, at least for superconductors of several isotopes, is the same. Further, the current theoretical point of view as provided by the BCS theory presents no contradiction to these ideas.

The recent specific heat measurements of Bryant and Keesom⁵ on indium now indicate that the phonon spectrum in that superconductor at least is not the same in the normal and superconducting phases.

The purpose of this Letter is to present evidence that in niobium also the lattice specific heat is different in the two phases. When our measurements were taken at temperatures less than 1.7°K the total superconducting specific heat was found to be less than the corresponding lattice heat in the normal state as shown in Fig. 1. After another independent set of measurements had confirmed this result, a complete remeasurement of the superconducting and normal heat capacities was made using as a thermometer a 1-watt Allen-Bradley carbon resistor. This resistor was carefully recalibrated by comparing the resistance with (1) the vapor pressure of helium from 1.02°K to 4.2°K, (2) the transition temperature of a sample of very pure lead taken as 7.17°K,⁶ and (3) the triple point of normal hydrogen, 13.96°K. The results gave a complete confirmation of the 1958 measurements and also confirmed that C_S at the lowest temperatures was smaller than the normal lattice heat in the

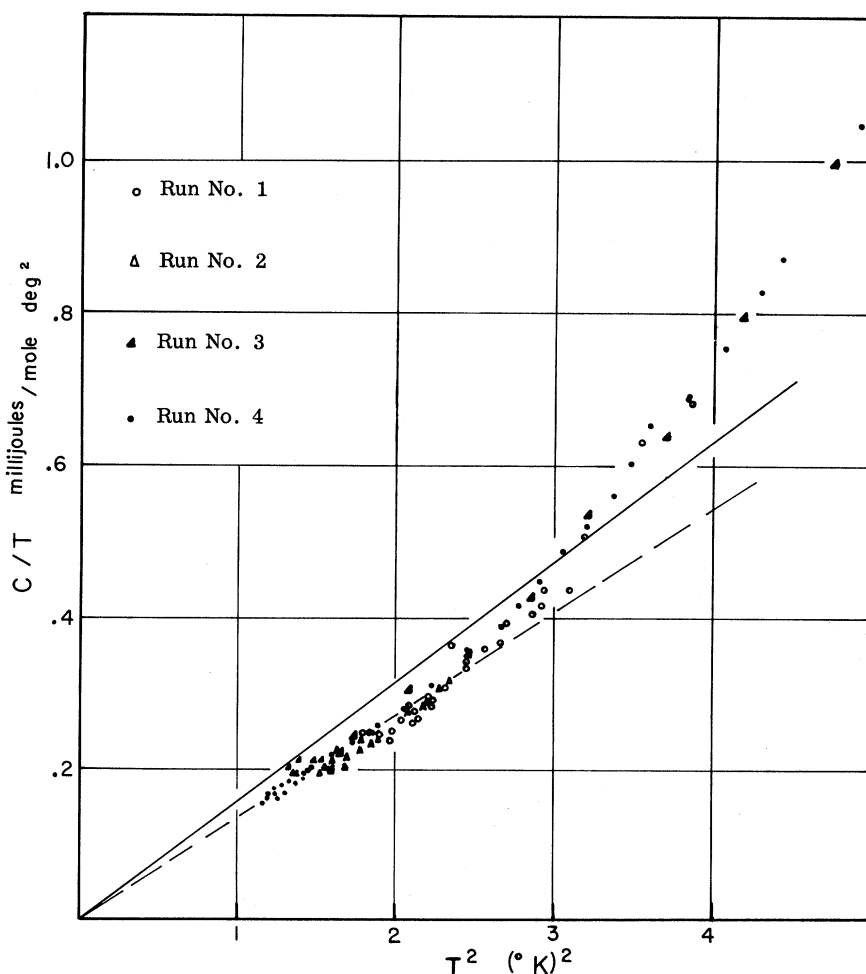


FIG. 1. Values of C/T vs T^2 for niobium in the superconducting phase at low reduced temperatures. The full line represents the lattice heat taken from the normal data. The dashed line is drawn to show the tentative assumption of a linear relation for C_S at the lowest temperatures.

same range. Figure 1 shows the results of the four separate measurements below $T^2 = 5.0$. If less weight is given to the first and less precise set of data represented by the open circles, then below $T^2 = 2.2$ ($T = 1.48^\circ\text{K} = 0.163T_c$) the individual determinations fall along a straight line which passes through the origin. A possible interpretation would be that the electronic specific heat at this temperature is inconsiderable in comparison with the superconducting lattice specific heat and that the latter can be represented by a T^3 term with an altered value of Θ which may be evaluated from the data as 243°K .

We regard this interpretation as provisional since a number of small corrections must be made to these data to account for the thermal capacities of the heater wires wound around the sample, for the Allen-Bradley carbon resistor, and for the glyptal adhesive. These corrections, now being investigated, would all be subtracted

and their influence, if significant, could only increase the discrepancy with the normal line. A detailed report of the measurements will be submitted in the near future.

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CHANGES IN SUPERCONDUCTING CRITICAL TEMPERATURE PRODUCED BY ELECTROSTATIC CHARGING*

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In the process of charging a parallel plate condenser, electrons are added to one plate and removed from the other one. Using a film 100 Å thick as one of the condenser plates, it is possible to add or subtract about one electron for each 10^4 atoms. The maximum charge that can be added is limited by the breakdown strength of dielectrics, typically on the order of 10^6 v/cm. The effect of electrostatic charging on the conductivity of a metal film has been investigated repeatedly over the last fifty years.¹⁻³ Recent measurements by Deubner and Rambke⁴ and by Bonfiglioli, Coen, and Malvano^{5,6} have shown that the normal-state conductivity of metals can be modified by electrostatic charging (field effect). Changes of relative conductivity on the order of one in 10^4 have been produced. The conductivity of the films can be increased or lowered depending on the sign of the added charge.

We have made measurements of the effect of charging on the normal-state conductivity of films of gold and have examined the effect on both the superconducting transition temperature and the normal-state conductivity of tin and in-

dium. Charging resulted in a change in the normal-state conductivity of all metals tried. It caused a change in the transition temperature of the superconducting materials.

Ruby (muscovite) mica substrates about 5μ thick were used for the experiments. A gold coating was evaporated onto the back side to serve as one plate of the condenser, and gold potential and current contact patches were placed on the front. The substrates were then placed in a vacuum system and the film to be studied was evaporated so as to form the second plate of the condenser. Charging voltages of 150 volts were applied giving a maximum electric field of 3×10^5 v/cm. The conductivity of the film was measured using a 1000-cycle bridge. Film thickness was estimated from the temperature-dependent part of the resistance.

Of the metals examined, gold would be expected to have the simplest conductivity mechanism. Our gold films were condensed at room temperature. Negative charging resulted in an increase in conductivity while positive charging caused a decrease. The relative change in conductivity was