

Letters to the Editor

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Theory of Superconductivity

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IN a previous note,¹ it was pointed out that a charged boson gas below its condensation point is a superconductor. This shows that a theory of superconductivity is established if it can be shown that in a metal at low temperatures charge-carrying bosons occur which condense at a critical temperature T_c . The purpose of this note is to point out that if the total interaction between electrons (Coulomb-interaction, interaction by lattice vibrations² and other effects) is such that it produces resonant states of electron pairs, then one should expect the onset of superconductivity.

In a rough way one might try to describe a resonant state as a bound state of two electrons with negative binding energy, i.e., ignore the width. Assuming such a state at an energy $\xi_0(1-\delta)$ per electron (ξ_0 being the Fermi energy of the free electron gas at absolute zero) the theory of chemical equilibrium applied to the equilibrium between electrons and these "bosons" yields qualitatively all the essential equilibrium features of superconductivity. At a critical temperature T_c given by

$$\delta = 6.54(kT_c/\xi_0)^{\frac{3}{2}} + 0.824(kT_c/\xi_0)^2 + O((kT_c/\xi_0)^4), \quad (1)$$

a transition of the second kind occurs with a discontinuity in the specific heat. Below T_c , the Meissner-Ochsenfeldt effect is exhibited; the number of superconducting (i.e., condensed) bosons at absolute zero is

$$n_{s0} = N \cdot \frac{3}{4} \delta. \quad (2)$$

(The penetration depth is determined by inserting (2) into London's theory³); the contribution of the non-condensed bosons can be neglected.

Quantitative agreement can, however, not be reached by this simple approach. The discontinuity in the specific heat is $\gamma\delta^2$; the difference in free energy between the normal and the superconducting state is of order $\xi_0\delta^2$. If δ is computed from formula (1) by using the experi-

mental T_c , both these quantities turn out to be much too small. Moreover, the trend of the specific heat curve below T_c is still essentially linear with almost the same slope as for the normal state.

Thus the description of the resonant state in terms of a single parameter δ is sufficient to give the qualitative features of superconductivity, but insufficient for quantitative purposes. In a quantitative treatment, the width of the resonance must play a crucial role. Furthermore, the problem has to be looked upon as a self-consistent one: the form of the resonance depends critically on the occupation of the electron states, and only in the vicinity of the Fermi surface can such resonances occur at all. At higher energies they will be too wide to have any effect; at low energies where all electron states are occupied, the resonances will be quenched by the Pauli principle. Qualitative considerations seem to indicate that the trend of these effects is indeed in the right direction for improving the agreement between theory and experiment.

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¹ M. R. Schafroth, *Phys. Rev.* **96**, 1141 (1954).

² H. Fröhlich, *Phys. Rev.* **79**, 845 (1950).

³ F. London, *Superfluids I*, (J. Wiley and Sons, Inc., New York, 1950).

Exponential Temperature Dependence of the Electronic Specific Heat of Superconducting Vanadium

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THE specific heat of a specimen of vanadium has been measured in the superconducting state from its transition temperature, 5.05°K, down to 1.2°K. Vanadium lends itself well to the study of the electronic specific heat of a superconductor because, in this metal, quite low values of T/T_c are easily attainable and the lattice contribution to the specific heat is small compared with the electronic contribution.

The specimen, a cylinder of mass 85 g, was prepared by arc-melting crystals of vanadium which had been made by the van Arkel iodide process. The specimen was annealed in vacuo ($p < 3 \times 10^{-6}$ mm) for 3 hours at 850°C and then cooled slowly at about 50°C per hour. No quantitative estimates of the purity of the specimen have been obtained yet, but for the purpose of comparing the present results with previous work¹ its hardness (121 ± 11 , diamond pyramid hardness) and its residual

resistivity (0.08 of its ice-point resistivity) are of interest. The breadth of the superconducting transition, shown by the present calorimetric measurements to be 0.10°K , is somewhat less than the value 0.15°K found by Worley, Zemansky, and Boorse² for each of two separate vanadium specimens.

The specific heat determinations were carried out in the conventional manner; in detail the experimental technique was identical with that to be described in a forthcoming paper on the specific heats of the noble metals.³ The uncertainties in the results for the specific heat of vanadium were largely attributable to the 1948 temperature scale in which, it was thought, the values of dT/dp might be in error by as much as 3 percent below 4.2°K and by a larger amount above 4.2°K .³⁻⁵ In the discussion of the present measurements the usual assumption is made that the electronic and lattice contributions to the specific heat are additive, with the latter taking the same values as in the normal state. In the absence, so far, of measurements on the present specimen in the normal state a value of the Debye θ of 298°K , the mean of the values for the two separate vanadium specimens measured by Worley, Zemansky, and Boorse,⁶ was assumed. The contribution of the lattice to the total specific heat ranged from 5 percent to 15 percent. Taking all the probable sources of error into consideration, including the probable error of 10 percent in the Debye θ , the probable error in the results for the electronic specific heat of vanadium is about 5 percent over the whole temperature range. The coefficient of the normal electronic specific heat, γ , was deduced from the entropy of the present specimen at 5.2°K , obtained from the present measurements, and from the above value of θ , by the application of the third law of thermodynamics. The resulting value, $\gamma = 21.5 \times 10^{-3} \text{ cal mole}^{-1} \text{ deg}^{-2}$, is in close agreement with the values 21.9, 21.4, and $21.1 \times 10^{-3} \text{ cal mole}^{-1} \text{ deg}^{-2}$ given by Worley, Zemansky, and Boorse.⁶

In Fig. 1 a representative selection of the present values of the reduced electronic specific heat, $C_{es}/\gamma T_c$, is plotted (open circles) logarithmically against the reciprocal, T_c/T , of the reduced temperature; the significance of plotting the results in this way will become clear later. In most previous calorimetric measurements on superconductors the results could be expressed in terms of an electronic specific heat given by

$$C_{es}/\gamma T_c = 3(T/T_c)^3, \quad (1)$$

the continuous curve in Fig. 1. It is clear that the present results show a marked departure from this equation, especially at the lowest temperatures. Agreement with the rather complicated expression for $C_{es}/\gamma T_c$ given by Koppe⁷ is somewhat better. However, it may be seen from Fig. 1 that the relation between $\log(C_{es}/\gamma T_c)$ and T_c/T for the present results is closely linear, suggesting an empirical equation of the form

$$C_{es}/\gamma T_c = ae^{-bT_c/T}. \quad (2)$$

The broken straight line in Fig. 1 represents this equation with $a=10.0$ and $b=1.52$ and, except for $T_c/T < 1.1$, it fits the experimental points to within the probable error of 5 percent over a temperature range in which C_{es} varies by a factor of more than 100. A detailed investigation of Koppe's expression for $C_{es}/\gamma T_c$ reveals that in this also the dominant term is of the form $\exp(-bT_c/T)$, where b is a constant of the order of unity. In vanadium the percentage correction to be applied to the total specific heat for the lattice contribution is smaller than in any other superconductor so far measured. It is therefore especially suited for investigating C_{es} . Moreover, the present measurements have been carried to larger values of T_c/T than any previous calorimetric measurements on a superconductor. The results suggest, for the first time, that the temperature

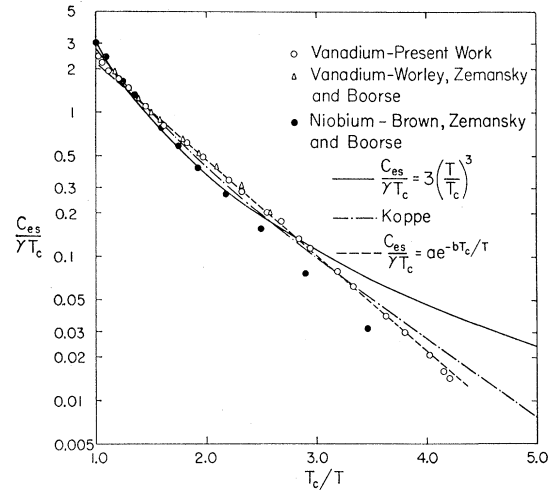


FIG. 1. Temperature dependence of the electronic specific heat of a superconductor.

dependence of C_{es} may be exponential, of the type represented by Eq. (2). It may be seen from Fig. 1 that the present results are in agreement in the limited overlapping temperature range with those obtained by Worley, Zemansky, and Boorse⁸ (open triangles) for a vanadium specimen with $T_c = 4.68^\circ\text{K}$.

Previously, the measurements of Brown, Zemansky, and Boorse^{9,10} on the electronic specific heat of superconducting niobium had been the first to suggest that there might be departures from Eq. (1). A selection of their smoothed values of $C_{es}/\gamma T_c$ has been plotted in Fig. 1 (solid circles). The differences between the result for niobium and those for vanadium may either be attributable to differences in experimental conditions or they may be genuine, representing a departure from a law of corresponding states among superconductors. Nevertheless, the results for niobium also can now be seen from Fig. 1 to be not inconsistent with an exponential temperature dependence of the type represented by Eq. (2). More indirect evidence for this type of temper-

ature dependence of C_{es} has been obtained from measurements by Goodman¹¹ on the thermal conductivity of superconducting tin below 1°K, which extended to values of T_c/T as large as 8. Here the electronic contribution to the thermal conductivity of the superconductor, which would be expected to be related to its electronic specific heat, also varied, over a wide range of temperature, in the exponential manner represented by Eq. (2).

On any single-electron model of a superconductor with a gap ϵ in the energy level spectrum, the expression for the specific heat would be expected to be dominated, at sufficiently low temperatures, by the term $\exp(-\epsilon/kT)$. The experimental evidence for vanadium, niobium, and tin discussed above supports the concept of such an energy gap; the magnitude of this energy gap, deduced from the experiments, is of the order of kT_c .

A full account of this work will appear in due course. The authors would like to acknowledge their gratitude to Dr. M. P. Garfunkel for his contribution to the experimental techniques used in this work.

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⁶ These results were reported at the Third International Conference on Low Temperature Physics and Chemistry, Houston Texas, 1953 (unpublished).

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¹⁰ Brown, Zemansky, and Boorse, Phys. Rev. **92**, 52 (1953).

¹¹ B. B. Goodman, Proc. Phys. Soc. (London) **A61**, 217 (1953).

X-Ray Diffraction Patterns from Liquid Helium*

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INTENSITY as a function of scattering angle for copper $K\alpha$ x-rays has been determined for liquid helium (mass 4) at temperatures above and below its lambda point. Proportional counter registration of the scattered x-ray intensity was used together with a Ross differential x-ray filter and a differential pulse height analyzer for monochromatization and for spurious background reduction. Scattering angles from 1.5° to 90° were covered. The helium sample was contained in a one quarter inch diameter, thin-walled beryllium tube in good thermal contact with, but separate from, a temperature regulating helium bath. The sample temperature was determined from its vapor pressure.

The collimating and observation slit systems both permitted a maximum horizontal crossfire of $\frac{1}{2}$ degree. The vertical divergence for each slit system for scattering angles $>5^\circ$ was about 7° and was decreased to about 2° for smaller angles. The scattering curves at 1.4°K and 4.2°K were repeated many times with a final estimated observational error in the curves of approximately ± 0.7 percent near the peak, ± 1 percent at 10° increasing to ± 4 percent at 1.5° and ± 1.5 percent at large angles. Only a small amount of data was taken at 2.2°K.

The resulting curves shown in Fig. 1 have been cor-

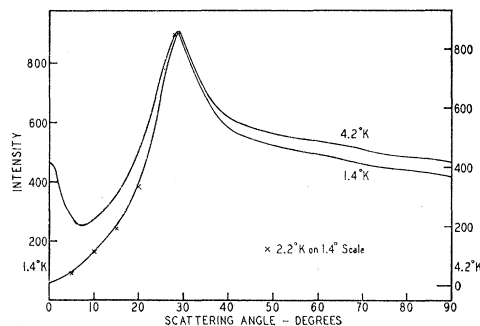


FIG. 1. Reduced scattering curves for liquid helium. The 1.4°K curve and the 2.2°K points follow the intensity scale, in arbitrary units, on the left while the scale on the right applies to the 4.2°K curve.

rected for polarization, absorption in the helium, and for change of scattering volume with angle. The 1.4°K and 2.2°K data have been corrected to correspond to the number density at 4.2°K. These data are apparently in general agreement with the results of Keesom and Taconis¹ and of Reekie and co-workers² who state that there is little difference in diffraction patterns above and below the lambda point for scattering angle $>12^\circ$. The diffraction peak at 1.4°K is shifted approximately 0.7° toward larger angles as might be expected for a density increase of 15 percent.

Two methods are available for reducing these corrected intensities to the liquid structure factors, $\mathcal{L}(\lambda, \theta, T)$ at each temperature. The conventional approach³ is that of determining the proportionality constant relating scattered intensities to the atomic scattering cross sections by assuming that at large scattering angles each atom scatters independently. Thus, the incoherently scattered portion can be subtracted using the computed incoherent cross section and the remaining coherently scattered intensity compared to the atomic structure factor. Because of the undulations observed near 90° this method is not entirely satisfactory here. Tweet⁴ has suggested an alternative method using a comparison to the scattering from a gas whose scattering cross section must also be known. Argon gas was used in the present experiment and by requiring analytically that both methods give identical results for \mathcal{L} it was possible to determine the above proportionality constant