

PHYSICAL REVIEW LETTERS

VOLUME 2

FEBRUARY 15, 1959

NUMBER 4

MEASUREMENT OF THE TEMPERATURE VARIATION OF THE ENERGY GAP IN SUPERCONDUCTING ALUMINUM

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(Received January 23, 1959)

Direct evidence for the existence of a gap in the electron energy spectrum of superconductors¹ has been obtained from studies of the absorption of electromagnetic energy in the frequency range $h\nu \sim kT_C$ (the millimeter microwave and far infrared regions).²⁻⁵ By the extension of the measurements³ on superconducting aluminum ($T_C = 1.178^\circ\text{K}$) to lower temperatures ($T = 0.38^\circ\text{K}$) and to shorter wavelengths ($\lambda = 3.1 \text{ mm}$), we have been able to determine the value of the energy gap at absolute zero and to measure the variation of the gap with temperature.

The apparatus previously described⁶ has been modified in that the inner liquid helium Dewar now is filled with He³. Pumping on this bath reduces the temperature to $T = 0.35^\circ\text{K}$. The present measurements were made on a sample in which spurious absorption has been reduced to $< 1\%$ of the normal state value. Thus it is possible to determine unequivocally the photon energy which spans the gap at absolute zero (actually, at small reduced temperature values) by noting an abrupt rise in the absorption as a critical frequency is exceeded.

Examples of the absorption data, expressed as curves of surface resistance ratio $r \equiv R/R_n$ (R_n is the surface resistance in the normal state) versus reduced temperature $t \equiv T/T_C$ for several wavelengths, are shown in Fig. 1. It will be seen that for wavelengths longer than 3.96 mm ($h\nu < 3.08 kT_C$) the low-temperature values of r are less than 1%, suggesting that the intrinsic

absorptivity of the metal goes to zero at absolute zero. However, for wavelengths shorter than 3.36 mm ($h\nu > 3.63 kT_C$) the absorption remains appreciable as the temperature approaches zero. This abrupt increase in the absorptivity at absolute zero implies the existence of a forbidden energy gap which has been spanned by photons of these energies.

The curve at $h\nu = 0.64 kT_C$ exhibits the general features of absorption curves obtained at lower frequencies in that an abrupt decrease in absorption is noted as the temperature falls below T_C , and the curve tends to zero absorption at absolute zero. However, at higher frequencies, e.g., $h\nu = 3.08 kT_C$, the absorption curves no longer decrease abruptly just below T_C . In a previous paper³ this behavior was attributed to additional absorption, largely the result of induced transitions of electrons across the temperature-dependent energy gap, and a method was outlined for separating this effect from the

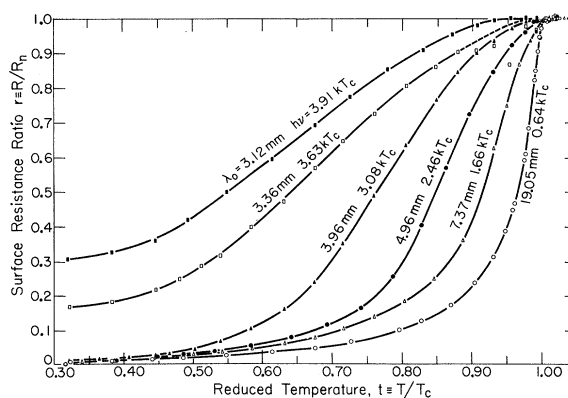


FIG. 1. Measured values of the surface resistance ratio, r , as a function of the reduced temperature, t , for superconducting aluminum. The wavelengths and corresponding photon energies are indicated on the curves.

normal electron absorption. In the present paper the larger temperature and frequency ranges covered permit us to determine directly the onset of additional absorption by examination of isotherms of surface resistance ratio versus photon energy.

Isotherms derived from our measured curves for a number of temperatures are given in Fig. 2. The curve labelled $t=0$ is determined by extrapolation of our r vs t curves to absolute zero. It will be seen that for temperatures substantially below the transition temperature the surface resistance ratio initially increases rather slowly with frequency. However, above a critical frequency (photon energy) the absorption rises much more rapidly. The effect becomes less pronounced on successive isotherms as $t \rightarrow 1$. To a first approximation we may take the energy at which the onset of this increased absorption occurs as the value of the energy gap for the particular temperature. This neglects the effect of the electromagnetic penetration depth, which is altered in the vicinity of an absorption edge.

The inferred values of the energy gap at each

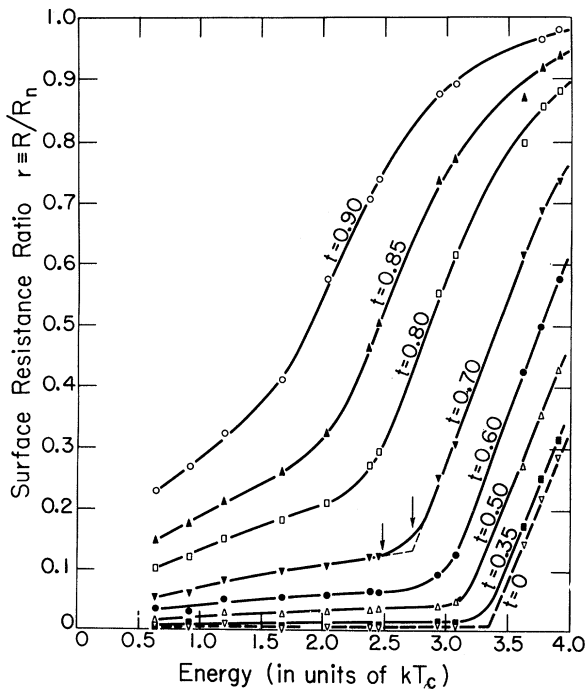


FIG. 2. Isotherms of surface resistance ratio versus photon energy. The experimental points are taken from the absorption curves at each of the measured frequencies. The arrows on the curve, $t=0.70$, indicate limits of uncertainty in determining the values of the energy gap.

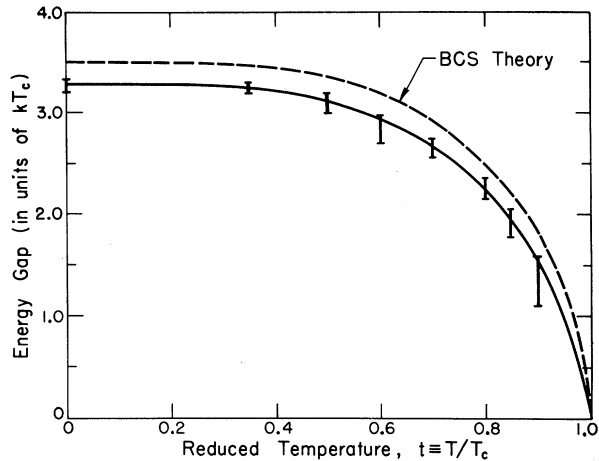


FIG. 3. Inferred energy gap variation with temperature. The solid line indicates the experimentally determined curve, the dashed line the theory of Bardeen, Cooper, and Schrieffer. The value of the gap at absolute zero is $\mathcal{E}_g(0) = (3.25 \pm 0.1)kT_c$.

temperature are shown in Fig. 3. The error limits shown result from uncertainty in the choice of the onset, as indicated by the arrows on the $t=0.70$ curve of Fig. 2. At small values of the reduced temperature ($t < 0.5$), where penetration effects are less important, uncertainty in the choice of gap values results from the rather long interpolation between our available photon energies. The values of the energy gap derived by this direct method are in essential agreement with the earlier results³ which were obtained by calculations based on a two-fluid model.

A comparison of the results with the theory of Bardeen, Cooper, and Schrieffer⁷ (the dashed curve of Fig. 3) shows that although there is good agreement concerning the shapes of the energy gap versus temperature curves, there is only fair agreement between the experimental value of the gap at absolute zero, $\mathcal{E}_g(0) = (3.25 \pm 0.10)kT_c$, and the theoretical value of $3.52kT_c$.

Richards and Tinkham⁸ have obtained the values $\mathcal{E}_g(0) = (4.1 \pm 0.2)kT_c$ for lead and $(3.4 \pm 0.3)kT_c$ for tin. Our result on aluminum continues the pattern of a slow, monotonic variation of $\mathcal{E}_g(0)/kT_c$ with T_c/Θ suggested by Goodman⁹; Θ is the Debye temperature of the metal. However, these three metals equally well fit a slow, monotonic variation of $\mathcal{E}_g(0)/kT_c$ with either T_c or Θ alone, and therefore studies of other metals are needed.

The authors wish to thank Mark Heald for his

assistance and suggestions concerning the microwave components of the apparatus.

¹A general review of both direct and indirect evidence for an energy gap is given in Biondi, Forrester, Garfunkel, and Satterthwaite, *Revs. Modern Phys.* **30**, 1109 (1958).

²R. E. Glover and M. Tinkham, *Phys. Rev.* **108**, 243 (1957).

³Biondi, Garfunkel, and McCoubrey, *Phys. Rev.* **108**, 495 (1957).

⁴Biondi, Forrester, and Garfunkel, *Phys. Rev.* **108**, 497 (1957).

⁵P. L. Richards and M. Tinkham, *Phys. Rev. Lett.* **1**, 318 (1958).

⁶See reference 1, p. 1127.

⁷Bardeen, Cooper, and Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

⁸B. B. Goodman, *Compt. rend.* **246**, 3031 (1958).

QUENCHED-IN LATTICE VACANCIES IN COPPER

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(Received January 22, 1959)

Preliminary experiments on quenching and annealing of pure copper are reported. Thin copper wires, of 0.04- and 0.07-mm diameter,¹ were electrically heated in purified argon; the wires were 30 cm long in order to minimize the effects of nonuniform temperature at their ends. Quenchings were performed by natural cooling after disconnecting the power supply: the total cooling times were oscillographically measured and were about 0.45 sec for 0.04-mm wires and 1.2 sec for 0.07-mm wires. The initial cooling rate was estimated to be about 5×10^3 °C/sec for the thinner wires.

Up to twenty quenchings and annealings could be done with reproducible results using the same specimen: later on smaller changes of resistivity due to quenching were found, the results depending somewhat upon the history of the specimen.

The changes in resistivity $\Delta\rho$, measured at room temperature, are exponentially dependent on $1/T$ for both diameters of wires, provided the quenching temperature T is less than 1150°K.

They tend to saturate at higher temperature and this fact indicates that cooling is not fast enough for retaining all defects within the quenched specimens at high temperature. Results which have been obtained at low quenching temperatures for both diameters of wires are given in Fig. 1. Extrapolation to the melting point of copper gives $\Delta\rho \approx 2 \times 10^{-7}$ ohm cm, which, according to calculations by Jongenburger² and Abelès,³ corresponds to a concentration of vacancies of about 1.5×10^{-3} . The formation energy of vacancies is equal to 1.0 ± 0.1 ev.

Isothermal annealing curves were obtained for temperatures ranging between 350°C and 470°C and with initial concentration of vacancies near to 10^{-5} ; the recovery of quenched-in resistivity was almost complete in any case.

Results given in Fig. 2 refer to 0.04-mm wires and show an activation energy equal to about 1.3 ev. The number of jumps a defect makes before disappearing at sinks is 10^6 - 10^7 .

On the other hand, annealing curves obtained with 0.07-mm wires suggest an activation energy for recovery near to 1.6 ev. This difference may be related to the slower cooling rate obtainable with these wires, the formation of complex defects due to clustering of vacancies being responsible for the higher activation energy. The effect is probably present to some extent even with the 0.04-mm wires, though it is presumable that 1.3 ev is nearer to the true value of the

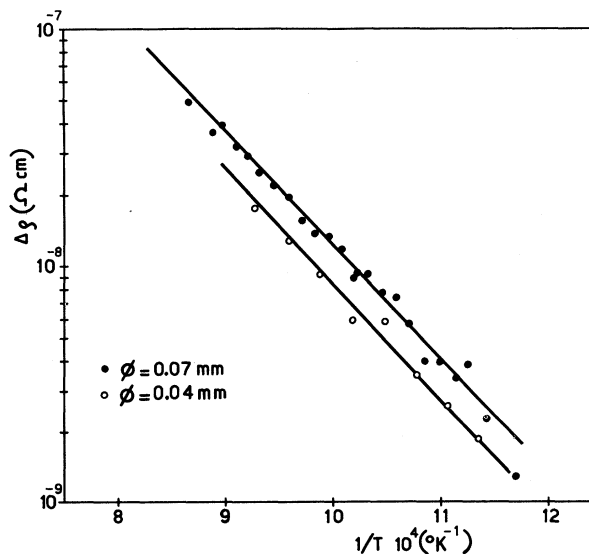


FIG. 1. Changes in resistivity due to quenching for 0.07- and 0.04-mm diameter copper wires.