## PRESSURE DEPENDENCE OF THE ENERGY GAP OF SUPERCONDUCTING Pb  $\dagger$

J. P. Franck and W. J. Keeler Department of Physics, University of Alberta, Edmonton, Canada (Received 8 January 1968)

The electron-phonon coupling strength in Pb, as measured by the "gap ratio"  $2\Delta_0/kT_c$ decreases with increasing pressure.

We report here the results of a study of the gap (at the gap edge)  $\Delta$ , the transition temperature  $T_c$ , and the "gap ratio"  $2\Delta_0/kT_c$  of Pb as a function of pressure and temperature. These results were obtained from electrontunneling measurements on Pb-insulator -Al junctions subjected to approximately hydrostatic pressures in solid helium. A study of Gruneisen gammas of Pb by this method has been reported previously' and showed the feasibility of the method.

The Pb-insulator-Al junctions were prepared by conventional methods on microscope slides. The junctions were mounted in a pressure cell and could be pressurized by freezing helium at constant pressure. The pressure at the working temperatures  $(\leq 7^\circ K)$  was determined by the ~method described in Ref. 1 and was known to  $\pm 6\%$ . Pressures up to 3400 bar were used. The pressure cell could be thermally isolated from the bath, its temperature could be lowered to 1.4'K by pumping on a small helium reservoir or raised above the bath temperature by electrical heating. The cell temperature was determined with a germanium thermome-



FIG. 1. Energy gap (at the gap edge) of Pb as a function of temperature. Order of runs: black dots  $(P=0)$ ; open circles  $(P = 2730 \text{ bar})$ ; black squares  $(P = 0)$ .

ter to  $\pm 0.1\%$ .

Direct measurements of  $di/dv$  were made by an ac bridge technique. We obtained the gap  $\Delta(T)$  from these measurements by fitting the normalized conductance  $\left(\frac{di}{dv}\right)_{\mathbf{s}}/\left(\frac{di}{dv}\right)_{\mathbf{n}}$  at zero bias to Bermon's' calculations for the BCS superconductor. We believe that this choice gives very nearly the gap at the gap edge. This method, however, becomes increasingly inaccurate at low reduced temperatures and was therefore only used for  $t > 0.55$ . The measurements were supplemented by a direct determination of the gap at 2.0'K, giving very nearly the zero-temperature energy gap  $\Delta_{0}$ .

The transition temperature  $T_c$  of the films was obtained by noting the disappearance of the gap in  $di/dv$ ; its uncertainty is estimated at  $\pm 0.15\%$ .

The results for one particular junction are shown in Fig. 1; similar, although not as extensive, data were obtained for eight other junctions. The zero-pressure curve was measured before and after the pressure run and found to be reproducible. Figure 2 shows the same results in reduced form as  $[\Delta(T)/kT_c]^2$  vs  $t = T/T_c$ .



FIG. 2. Squared reduced energy gap (at the gap edge) of Pb as a function of reduced temperature. Black dots and squares,  $P=0$ ; open circles,  $P = 2730$  bar.

It is clear that the relation between reduced gap and temperature varies with pressure; increasing pressure moves this relation closer to the universal BCS curve for a weak-coupling superconductor. From Fig. 2 one can determine the relative shift of  $\Delta(T)/kT_c$  with pressure at constant reduced temperature. It is found that this shift is independent of reduced temperature, within the accuracy of the experiment, and given by  $d \ln[\Delta(T)/kT_c]/dP$  $= -(5.6 \pm 0.6) \times 10^{-6}$ /bar,  $t > 0.55$ . As mentioned, we also determined the gap at  $T = 2.0\text{°K, i.e., } t$  $\approx$  0.28. The relative shift of  $\Delta(T)/kT_c$  with pressure at this temperature was obtained from the shift in the extremum of  $d^2i/dv^2$ ; we found a slightly smaller value,  $d \ln(\Delta(T)/kT_c)/dP$  $= -(4.8 \pm 0.5) \times 10^{-6}$ /bar. At present, we do not believe that the difference between the values in the two temperature ranges is significant and therefore base the following discussion on an average value given by

$$
\{d \ln[\Delta(T)/kT_c]/dP\}_{t=\text{const}}
$$
  
= -(5.2 \pm 0.6) \times 10^{-6}/\text{bar.} (1)

The pressure dependence of  $T_c$  observed in this experiment was

$$
d \ln T / dP = -(4.9 \pm 0.2) \times 10^{-6} / \text{bar}, \qquad (2)
$$

in good agreement with determinations on bulk material. $3,4$  From this it follows that

$$
[d \ln \Delta(T)/dP]_{t = \text{const}}
$$
  
= -(10.1 ± 0.8) × 10<sup>-6</sup>/bar, (3)

$$
[d \ln \Delta(T)/d \ln T_c]_t = \text{const} = 2.06 \pm 0.3. \tag{4}
$$

It was further found that the reduced gap-temperature relation for Pb, Fig. 2, can be obtained from the BCS relation by scaling with a constant factor; remaining deviations are of the order 3%. One can therefore, in good approximation, describe the temperature-dependent energy gap of Pb by a BCS relation, but assuming an empirical gap ratio  $2\Delta_0/kT_c$  deviating from 3.53. In the present experiment, we find for this parameter  $2\Delta_0/kT_c$  = 4.47 (*P* = 0) and 4.41

 $(P = 2730 \text{ bar}).$ 

Hodder and Briscoe<sup>5</sup> recently reported a study of Pb-insulator-Pb junctions that were mechanically strained at liquid-helium temperatures. They observed a reduction of the energy gap with strain. Unfortunately, the volume reduction achieved in these experiments does not seem to be very well known, so that a comparison with our results is not possible. No information on the strain dependence of  $T_c$  is given, in fact this is calculated assuming a constant gap ratio.

The main result of these experiments is that the coupling strength in Pb, as measured approximately by the gap ratio, decreases with increasing pressure (i.e., decreasing volume). This effect was also observed as a reduction in the phonon-induced anomalies in the tunneling characteristics. We believe that the coupling strength is reduced due to the combined effect of a reduction with pressure of  $N(0)$ , the single-particle density of states at the Fermi surface (Ref. 3), and to the increase in phonon frequencies with pressure. The effect can probably be understood in terms of the present strongcoupling theory<sup>6,7</sup> along the lines indicated, e.g., by Wu.<sup>8</sup> Similar effects have been reported for Pb-based alloys by Adler, Jackson, and Will<sup>9</sup> and by Claeson.<sup>10</sup> In these experiments the coupling strength was reduced by changing the density of states through alloying.

From Eq. (4) it follows that in Pb the energy gap is proportional to the square of the transition temperature. We do not know of any reason for this particular exponent, but expect that this dependence goes over into the familiar linear dependence at sufficiently high pressures.

The present results can be combined with published data on the pressure dependence of the condensation energy at  $0^{\circ}K$ . Wada<sup>11</sup> has shown that, in general,

$$
H_0^2/8\pi = N(0)I
$$
,

where  $H_0$  is the critical field at  $0^\circ$ K and *I* is a function of the renormalization factor and of the complex gap function. In the weak-coupling limit the function  $I$  goes properly over into  $I = \frac{1}{2}\Delta_0^2$  to yield the BCS result. One can then introduce the ratio  $I/\frac{1}{2}\Delta_0^2$  and use this as an approximate measure of the coupling strength, similar to the use of the gap ratio  $2\Delta_0/kT_c$ . For Pb,  $I/\frac{1}{2}\Delta_0^2 = 0.83$ ,<sup>6</sup> i.e., the condensation energy is smaller then given by the BCS expression. The pressure dependence of this ratio is given by

$$
d \ln(I/\frac{1}{2}\Delta_0^2)/dP = 2(d \ln H_0/dP - d \ln \Delta_0/dP)
$$
  
-d \ln N(0)/dP. (6)

We use  $d \ln H_0 / dP = -9.4 \times 10^{-6} / \text{bar}$ , representing an average between the more recent measurements of Garfinkel and Mapother<sup>3</sup> and of surements of Garfinkel and Mapother<sup>3</sup> and of<br>White,<sup>12</sup> and  $d \ln N(0)/dP = -8.2 \times 10^{-6}/\text{bar}$ , Ref. 3. Combining this with our result, Eq. (3), we get

$$
d \ln(I/\tfrac{1}{2}\Delta_0^2)/dP = +(9.6 \pm 3.4) \times 10^{-6}/\text{bar.}
$$
 (7)

The indicated error includes the errors for  $d \ln H_0/dP$  and  $d \ln N(0)/dP$  quoted in Ref. 3. We find therefore again that increasing pressure changes the properties of Pb towards those of a BCS superconductor.

)This work has been supported in part by Major

Equipment Grant No. E-358 of the National Research Council of Canada.

 $1$ J. P. Franck and W. J. Keeler, Phys. Letters 25A, 624 (1967).

<sup>2</sup>S. Bermon, University of Illinois Technical Report No. 1, Grant No. NSF-GP 1100, 1964 (unpublished).  ${}^{3}$ M. Garfinkel and D. E. Mapother, Phys. Rev. 122,

459 (1961).

 ${}^{4}$ T. F. Smith and C. W. Chu, Phys. Rev. 159, 353 (1967).

 ${}^{5}R$ . E. Hodder and C. V. Briscoe, in International Conference on Tunneling, Risø, Denmark, 1967 (to be published).

6J. C. Swihart, D. J. Scalapino, and Y. Wada, Phys. Rev. Letters 14, 106 (1965).

 ${}^{7}D.$  J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev, 148, 263 (1966).

 ${}^{8}$ T. M. Wu, Phys. Rev. Letters 19, 508 (1967).

 $^{9}$ J. G. Adler, J. E. Jackson, and T. A. Will, Phys. Letters 24A, 407 (1967).

 $10$ T. Claeson, Solid State Commun. 5, 119 (1967).

 $^{11}Y.$  Wada, Phys. Rev.  $135,$  A1481 (1964).

 ${}^{12}$ G. K. White, Phil. Mag. 7, 271 (1962).

## QUANTUM PHASE FLUCTUATIONS IN SUPERCONDUCTING TIN

B. T. Ulrich Ford Scientific Laboratory, Newport Beach, California (Received 18 December 1967)

We have directly observed quantum phase fluctuations at the onset of long-range quantum phase coherence in single-crystal bulk tin as it becomes superconducting.

Upon becoming superconducting a normal metal develops long-range quantum mechanical phase coherence.<sup>1</sup> Observable secondary effects at the onset of this macroscopic quantum state include the Meissner effect, vanishing electrical resistance, and a discontinuity in the specific heat. This Letter reports the first direct observation of the behavior of the quantum phase during the superconducting transition. We find that the superconductor passes through a regime of temperature-dependent quantum phase fluctuation at the superconducting transition.

A technique has been developed to establish a superconducting junction between a normal metal and a superconductor in which quantum phase coherence already exists. The resistance of a point contact junction between normal tin and superconducting niobium has been found to vanish at temperatures as high as 4.0'K, significantly above the 3.72'K superconducting transition of bulk tin.<sup>2</sup> Above the transition

of bulk tin this junction exhibits superconducting characteristics typical of a weak link between two superconductors: (1) Current-voltage (I-V) characteristics possess a zero-voltage critical supercurrent, above which the junction is resistive. (2) Microwave radiation induces structure in the  $I-V$  characteristics similar to that observed in thin-film bridges or point contacts between two superconductors.<sup>3</sup> When used in a quantum interferometer<sup>4</sup> these junctions serve as probes to investigate the onset of quantum phase coherence in tin during the superconducting transition. Such an interferometer is shown schematically in Fig.  $1(a)$ . Interference is observed only when quantum phase coherence exists along a path within the bulk tin as well as in the niobium. In this experiment the temperature is lowered through the tin transition temperature and quantum phase fluctuations at the onset of quantum phase coherence are directly observed. In the usual quantum interferometer the temperature depen-