PRESSURE DEPENDENCE OF THE ENERGY GAP OF SUPERCONDUCTING Pb†

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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) Δ, 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 electron-tunneling measurements on Pb-insulator-Al junctions subjected to approximately hydrostatic pressures in solid helium. A study of Grüneisen gammas of Pb by this method has been reported previously[1] 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 ($\lesssim$7°K) was determined by the method described in Ref. 1 and was known to ±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 thermometer to ±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 $(di/dv)_s/(di/dv)_n$ at zero bias to Bermon's[2] 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 $t \geq 0.55$. The measurements were supplemented by a direct determination of the gap at 2.0°K, giving very nearly the zero-temperature energy gap Δ_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 ±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 $t = T/T_c$.

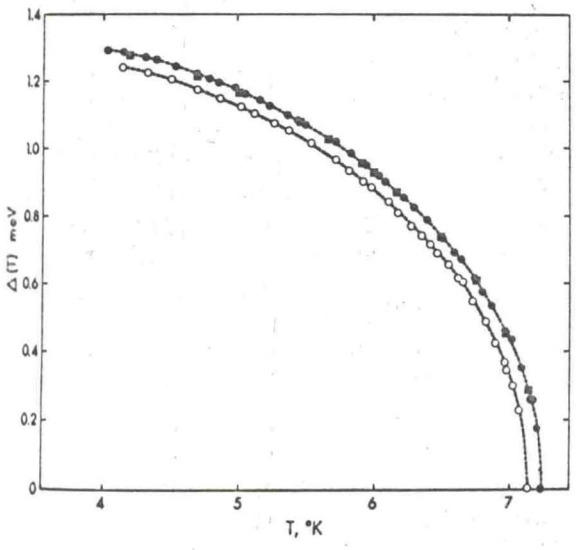

FIG. 1. Energy gap (at the gap edge) of Pb as a function of temperature. Order of runs: black dots ($P = 0$); open circles ($P = 2730$ bar); black squares ($P = 0$).

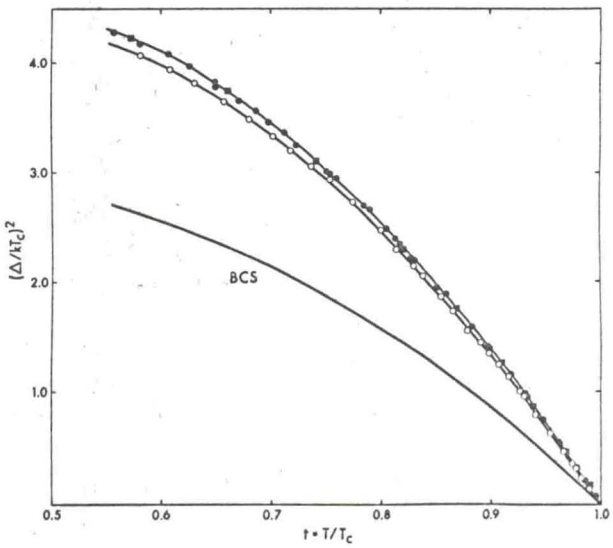

FIG. 2. Squared reduced energy gap (at the gap edge) of Pb as a function of reduced temperature. Black dots and squares, $P = 0$; open circles, $P = 2730$ bar.

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 $d\ln[\Delta(T)/kT_c]/dP = -(5.6\pm0.6)\times10^{-6}$/bar, $t>0.55$. As mentioned, we also determined the gap at $T=2.0$°K, i.e., $t\simeq0.28$. 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, $d\ln(\Delta(T)/kT_c)/dP = -(4.8\pm0.5)\times10^{-6}$/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

$$\{d\ln[\Delta(T)/kT_c]/dP\}_{t=\text{const}} = -(5.2\pm0.6)\times10^{-6}/\text{bar}. \quad (1)$$

The pressure dependence of T_c observed in this experiment was

$$d\ln T_c/dP = -(4.9\pm0.2)\times10^{-6}/\text{bar}, \quad (2)$$

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

$$[d\ln\Delta(T)/dP]_{t=\text{const}} = -(10.1\pm0.8)\times10^{-6}/\text{bar}, \quad (3)$$

$$[d\ln\Delta(T)/d\ln T_c]_{t=\text{const}} = 2.06\pm0.3. \quad (4)$$

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 ($P=2730$ bar).

Hodder and Briscoe[5] 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 strong-coupling theory[6,7] along the lines indicated, e.g., by Wu.[8] Similar effects have been reported for Pb-based alloys by Adler, Jackson, and Will[9] and by Claeson.[10] 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°K. Wada[11] has shown that, in general,

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

where H_0 is the critical field at 0°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, $I/\frac{1}{2}\Delta_0^2=0.83$,[6] i.e., the condensation energy is smaller then given by the BCS expres-

sion. The pressure dependence of this ratio is given by

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

We use $d\ln H_0/dP = -9.4\times10^{-6}$/bar, representing an average between the more recent measurements of Garfinkel and Mapother[3] and of White,[12] and $d\ln N(0)/dP = -8.2\times10^{-6}$/bar, Ref. 3. Combining this with our result, Eq. (3), we get

$$d\ln(I/\tfrac{1}{2}\Delta_0^2)/dP = +(9.6\pm3.4)\times10^{-6}/\text{bar}. \quad (7)$$

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.

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QUANTUM PHASE FLUCTUATIONS IN SUPERCONDUCTING TIN

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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.[1] 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.[2] 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.[3] When used in a quantum interferometer[4] 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-

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PRESSURE-DEPENDENCE OF THE PHONON SPECTRUM OF Pb FROM TUNNELING MEASUREMENTS*

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The phonon spectrum of Pb has been obtained as a function of pressure from electron-tunneling data. The pressure-dependence of the electron–phonon coupling constant λ, and other parameters, shows that Pb tends towards weaker coupling with increasing pressure.

ELECTRON-tunneling measurements on Pb under approximately hydrostatic pressure make it possible to investigate the pressure-dependence of several microscopic parameters for this strong-coupling superconductor. We have previously published[1,2] information on the Grüneisen gamma and the gap ratio $2\Delta_0/kT_c$. Similar data have also been obtained by Zavaritskii *et al.*[3]

We present here results on $\alpha^2(\omega)F(\omega)$ – where $\alpha^2(\omega)$ is the energy-dependent electron–phonon interaction and $F(\omega)$ is the phonon density of states – and results on U_c, the Coulomb pseudo-potential, both at zero pressure and at a pressure of 3445 bar. These results were obtained by inverting the gap equation, using the experimental tunneling density of states, $N_s(\omega)$, and the energy gap at the gap edge, Δ_0, as input-data.[4] From a knowledge of $\alpha^2(\omega)F(\omega)$ we can obtain several parameters, and their pressure-dependence, that are of interest in the theory of strong-coupling superconductors.

The experimental data used in this inversion were obtained from Pb-insulator-Al tunnel junctions at $T \simeq 2°K$, the Al being normal. Repetition of the measurement at 1.4°K showed no change in the tunneling data. The pressure data were taken at $P = 3445$ bar, generated in solid helium. The uncertainty in the applied pressure is approximately ± 6 per cent and this constitutes the major error in these measurements. Several other pressure runs were taken at pressures between 2300 and 3400 bar to establish reproducibility. The results at 3445 bar were taken for the inversion process, since they give a maximum effect. For more details of the pressure method see references 1 and 2.

In Fig. 1 the phonon spectrum $\alpha^2(\omega)F(\omega)$ is shown. The zero-pressure result is in good agreement with the data of McMillan and Rowell,[5] and Adler *et al.*[6] Under pressure the spectrum shifts to higher energies as expected. Grüneisen constants corresponding to the shift of the transverse and longitudinal phonon peaks were given in reference 1, the present method cannot improve on these estimates. For energies away from these peaks we cannot obtain Grüneisen constants, since the pressure-dependence of $\alpha^2(\omega)$ is not known. For this one has to await accurate determinations of $F(\omega)$ under pressure by inelastic neutron scattering.

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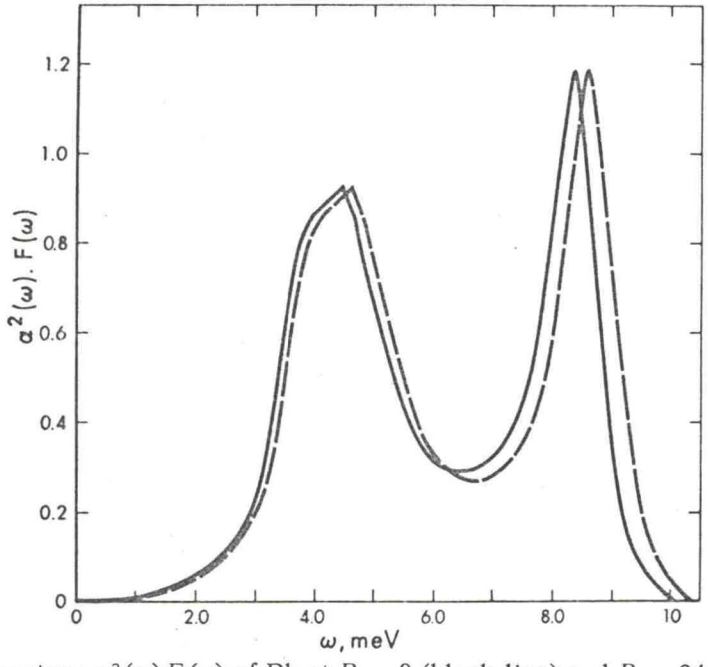

FIG. 1. The phonon spectrum $\alpha^2(\omega)F(\omega)$ of Pb at $P = 0$ (black line) and $P = 3445$ bar (dashed line).

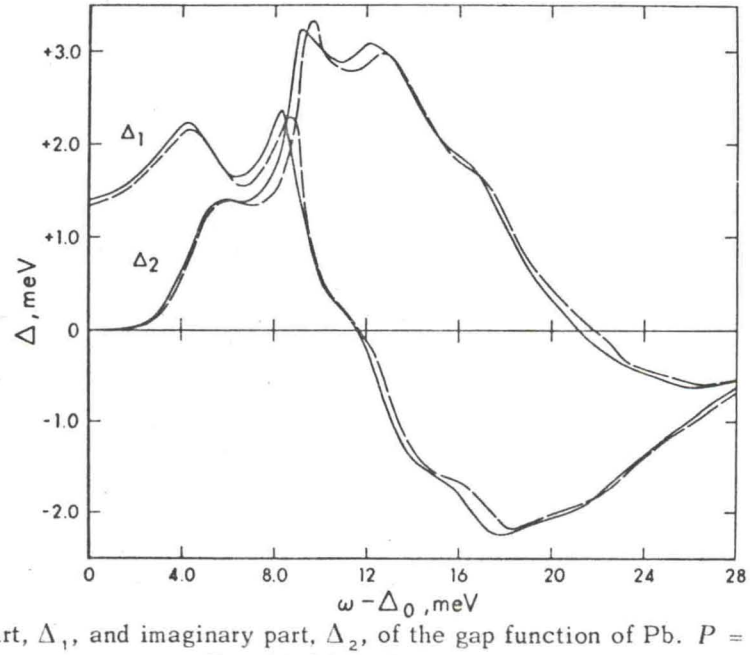

FIG. 2. Real part, Δ_1, and imaginary part, Δ_2, of the gap function of Pb. $P = 0$, black lines, $P = 3445$ bar, dashed lines.

In Fig. 2 we give the complex gap function $\Delta(\omega) = \Delta_1(\omega) + i\Delta_2(\omega)$ as function of energy and pressure. The phonon emission resonances are shifted to higher energies and somewhat reduced under pressure, indicating a move towards weaker coupling.

The Coulomb pseudo-potential, U_c, obtained from the inversion program is 0.12 at $P = 0$ and 0.14 at $P = 3445$ bar. This result is in good agreement with McMillan and Rowells'[5] result, and also with the theoretical estimate[7] of $U_c \simeq 0.11$. It should be stated, however, that

U_c is obtained from the inversion program only with moderate accuracy; the apparent pressure-dependence of U_c can therefore not be taken seriously.

The following parameters were calculated from $\alpha^2(\omega)F(\omega)$:

(i) the average electron–phonon interaction:

$$\langle\alpha^2\rangle = \int \alpha^2(\omega)F(\omega)\,d\omega \Big/ \int F(\omega)\,d\omega; \quad (1)$$

(ii) the electron–phonon coupling constant λ, defined by:

$$\lambda = 2\int \frac{\alpha^2(\omega)F(\omega)}{\omega}\,d\omega; \quad (2)$$

(iii) the renormalization constant $Z = 1 + \lambda$;

(iv) an average squared phonon frequency $\langle\omega^2\rangle$, introduced by McMillan:[8]

$$\langle\omega^2\rangle = \int \omega\alpha^2(\omega)F(\omega)\,d\omega \Big/ \int \alpha^2(\omega)\,\frac{F(\omega)}{\omega}\,d\omega. \quad (3)$$

The results are given in Table 1.

Table 1

P (bar)	$\langle\alpha^2\rangle$ (meV)	λ	Z	$\langle\omega^2\rangle$ (meV)^2
0	1.30	1.53	2.53	30.5
3445	1.32	1.43	2.43	33.7

The pressure-dependence of the various quantities is then given by:

$$d\ln\langle\alpha^2\rangle/dP = + 4.4 \times 10^{-6}/\text{bar}, \quad (4)$$

$$d\ln\lambda/dP = - 18.8 \times 10^{-6}/\text{bar}, \quad (5)$$

$$d\ln Z/dP = - 11.2 \times 10^{-6}/\text{bar}, \quad (6)$$

$$d\ln\langle\omega^2\rangle/dP = + 28.9 \times 10^{-6}/\text{bar}. \quad (7)$$

We estimate the error in these derivatives at ± 10 per cent.

The small, positive pressure derivative of $\langle\alpha^2\rangle$ is not too surprising. In calculating the average, the region near the phonon peaks is heavily weighted and in this region one has $d\alpha^2/d\omega > 0$, according to the estimates given by Scalapino *et al.*[7] The shift of the phonon peaks to higher energies under pressure can therefore explain a positive pressure derivative of $\langle\alpha^2\rangle$. In spite of this, it is obvious from the pressure derivative of λ and Z, that the coupling strength is reduced under pressure. The reason for this is that all phonon frequencies are shifted to higher energies, where they enter the integral for the energy gap with reduced weight.

Electron–phonon renormalization changes most parameters of the metal. We want to comment here on the density of states, N_0 which is given by:

$$N_0 = N_{bs} Z, \quad (8)$$

where N_{bs} is the band-structure density of states. The densities of states are here referred to unit volume. The measured pressure-dependence of Z allows us therefore to estimate the pressure-dependence of N_0:

$$d\ln N_0/dP = d\ln N_{bs}/dP + d\ln Z/dP. \quad (9)$$

From the work of Anderson, O'Sullivan and Schirber[9] it is known that the Fermi-surface of Pb scales under pressure approximately twice as fast as the Brillouin zone. We can therefore estimate, that the change of the band-structure density of states is about twice the free electron value. Numerically this gives $d\ln N_{bs}/dP \simeq 2/3\,\kappa = 1.4 \times 10^{-6}$/bar, where κ is the low temperature compressibility of Pb.[10] Using our result (6) we get then:

$$d\ln N_0/dP = - 9.8 \times 10^{-6}/\text{bar}. \quad (10)$$

The pressure-dependence of N_0 is therefore negative and almost totally due to the change in electron–phonon renormalization with pressure. An experimental determination of this derivative has been published by Garfinkel and Mapother,[11] who measured the pressure-dependence of γ, the coefficient of the normal electronic specific heat. These authors quote $d\ln N_0/dP = (-8.2 \pm 1.5) \times 10^{-6}$/bar, in good agreement with our result.

In a recent paper, McMillan[8] has derived approximate relations for T_c and λ of strong-coupling superconductors. One of his central results is that

$$\lambda = C/\langle\omega^2\rangle, \quad (11)$$

where $\langle\omega^2\rangle$ is the average defined by (3). C is found by McMillan to be approximately constant within a given class of materials, and *a fortiori* could be expected to be a constant for a metal

at different pressures. The relation (11) predicts correctly the decrease of λ with pressure; numerically, however, it does not hold too well as a comparison between our results (5) and (7) shows. This may not be too surprising in view of the approximations used in McMillan's work. It appears that for the very strong-coupling superconductors like Pb (and Hg) only the full strong-coupling theory will give satisfactory results.

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Das Phononspektrum von Blei, und seine Abhängigkeit vom Druck, wurden durch die Auswertung von Tunneleffektmessungen an supraleitendem Blei erhalten. Die Druckabhängigkeit der Elektron-Phonon Kopplungskonstante λ, und von anderen Parametern, zeigt, dass Blei mit steigendem Druck zu schwächerer Kopplung neigt.