Thermodynamic properties of Pb determined from pressure-dependent critical-field measurements

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We have carried out extensive low-temperature (1.5–10 K) measurements of the critical field H_c for the element Pb up to a pressure of $P=1.2$ GPa. From these data, the electronic entropy, specific heat, thermal-expansion coefficient, and compressibility are calculated as a function of temperature, pressure, and magnetic field. The zero-field data are consistent with direct thermodynamic measurements, and the P dependence of T_c and specific-heat coefficient $\gamma(T,P)$ allows the determination of the P dependence of the pairing interaction.

The thermodynamic and superconducting properties of the metal Pb have been extensively studied, including specific heat,[1,2] isotope effect,[3,4] critical field,[5] and thermal expansion.[6] In addition, the effects of pressure on its superconducting properties have also been well studied.[7–9] Subsequently, the use of the pressure-dependent superconducting transition temperature $T_c(P)$ for Pb as a low-temperature manometer has also been proposed.[10–12] The above quoted references are only the early ones, and one would assume that the thermodynamic properties of this material have been comprehensively investigated.

In the course of investigations into the pressure dependence of the oxygen isotope effect on T_c for the high-T_c superconductor YBa$_2$Cu$_4$O$_8$, we used the metal Pb as an internal pressure calibrant. Using a clamp cell in a superconducting quantum interference device (SQUID) magnetometer, we tracked the pressure using the reported pressure dependence of T_c for Pb.[10] Despite the many above-noted early studies on Pb, we discovered that the pressure P and temperature dependences of the critical field H_c for Pb have not been reported except at very low pressures (≤ 0.03 GPa).[7] We therefore carried out a study of $H_c(T,P)$ from 1.5 to 10 K and up to 1.2 GPa from which we have derived a full set of thermodynamic parameters. This paper presents a summary of these measurements and the deduced values of the T and P dependences of the electronic entropy $S(T,P)$, electronic specific-heat coefficient $\gamma(T,P)$, thermal-expansion coefficient $\alpha(T,P)$, and electronic compressibility $\kappa(T,P)$.

The sample used was a bar of dimensions 1.1×0.93 mm^2 cross section and 5.58-mm-long, shaped from Puratronic 99.9985%, 2-mm-diameter Pb wire from Johnson Matthey. Using the formulas of Osborn, the demagnetization factor was calculated as 0.97, and this value was used throughout. The Pb sample was annealed in vacuum at 300 °C for 8 h to reduce magnetic hysteresis.[5] This was loaded in a 2.67-mm-diameter, 9-mm-long Teflon capsule along with Fluorinert FC70 and FC77 mixed in 1:1 ratio as a cryogenic hydrostatic pressure medium. The sample capsule was then placed in a miniature homebuilt nonmagnetic Be-Cu (Mico Metal, 97.75% Cu and 2% Be) piston clamp cell [8.8 mm diameter, 65 mm length, with cobalt-free tungsten carbide pistons (Boride)]. The pistons of this cell are lightly tapered using electric-discharge machining.[13] To ap-

ply pressure, the cell was preloaded before clamping at room temperature using a laboratory press with calibrated digital pressure gauge (Ashcroft model 2089, 0.05% accuracy). The magnetization measurements were carried out in a Quantum Design MPMS SQUID magnetometer. The pressure in the sample was measured from the reported shift in T_c of Pb at zero field.[10] For in-field measurements, the cell was always zero-field cooled to avoid hysteresis error.

Figure 1 shows the measured T dependence of the magnetic moment M up to a field of 700 G and at pressures of 0 GPa (1 bar) and 0.5, 0.9, and 1.15 GPa. T_c was determined by the extrapolation to zero of the steepest slope of $M(T)$. This gives $T_c(H)$ which is replotted in Fig. 2 as $H_c(T,P)$ versus T. The data show a progressive decline in both T_c and $H_c(T)$ with increasing pressure. We will see that the combination of these two pressure effects allows access to the pressure dependence of the density of states $N(E_F)$ at the Fermi level E_F and of the pairing interaction.

To fit these data, we expand $H_c(T)$ as a power series in T. The first-order term must be zero, otherwise $S_s \neq 0$ at $T=0$, and the third-order term must also be zero to avoid a negative γ at low T. It is usual, therefore, to adopt an even polynomial of the form[5]

$$H_c(T,P) = H_{c0}(P) + H_{c1}(P)T^2 + H_{c2}(P)T^4, \quad (1)$$

where, as indicated, each of the coefficients is an independent function of pressure. As we will see, H_c cannot be linear in T because of the third law requirement that the entropy $S \to 0$ as $T \to 0$. It turns out that the coefficients are not independent, and it is common to adopt the "similitude principle" which separates the P- and T-dependent terms as follows:[7]

$$H_c(T,P) = H_{c0}(P)f(t) = H_{c0}(P)[1 - \alpha t^2 + (1 - \alpha)t^4], \quad (2)$$

where $t=T/T_c$. A free fit of Eq. (1) to the data consistently yielded H_{c2}/H_{c0} very close in value to $1 - H_{c1}/H_{c0}$, consistent with Eq. (2). We therefore proceeded to fit the data with Eq. (2) for all subsequent analyses. The fits are shown by the solid curves through the data shown in Fig. 2. We obtain H_{c0} values of 804.08, 770.88, 739.99, and 729.01 G for $P=0$, 0.5, 0.9, and 1.15 GPa, respectively. A linear fit yields

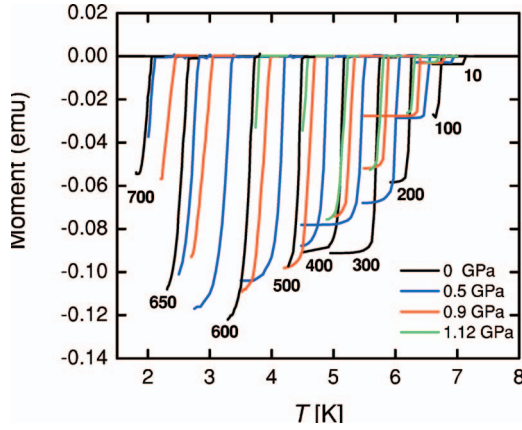$$H_{c0}(P) = (803.72 - 67.028P)\text{G}. \quad (3)$$

FIG. 1. (Color) Magnetization curves for the Pb sample plotted for various applied fields (annotated in gauss as 10, 100, 200, etc.) and four different pressures (0, 0.5, 0.9, and 1.15 GPa).

This now allows the scaling of all the data by plotting $H_c(T,P)/H_{c0}(P)$ versus t^2, as shown in Fig. 3. The small departure from linearity in Fig. 3 reflects the small quartic term ($\alpha=0.954\,75$, $1-\alpha=0.045\,25$), and the scaled data in Fig. 3 allow a global fit to determine α that provides an overall consistency in the data fits that is necessary when second derivatives of $H_c(T,P)$ are used to determine the electronic specific-heat coefficient, thermal-expansion coefficient, or compressibility.

These parameters may be determined as follows. We restrict our thermodynamic parameters to the electronic contribution, thus ignoring the lattice contribution to the specific heat or thermal expansion. The difference in free energy between the normal and superconducting states at the same T and P is given by

$$G_s(T,P) = G_n(T,P) - \frac{1}{2}\mu_o H_c(T,P)^2 V_M, \qquad (4)$$

where μ_o is the permeability of free space and V_M is the molar volume. As shown by Shoenberg,[14] the thermodynamic parameters are obtained by differentiation with respect to T and P, giving

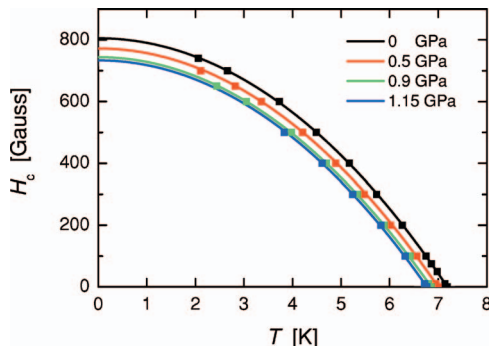$$S_s(T,P) = S_n(T,P) + \mu_o H_c V_M (\partial H_c/\partial T)_P,$$

FIG. 2. (Color) The T dependence of the critical field H_c for pressures of 0, 0.5, 0.9, and 1.15 GPa. Data points are measured data from Fig. 1, and curves are fits using Eq. (2).
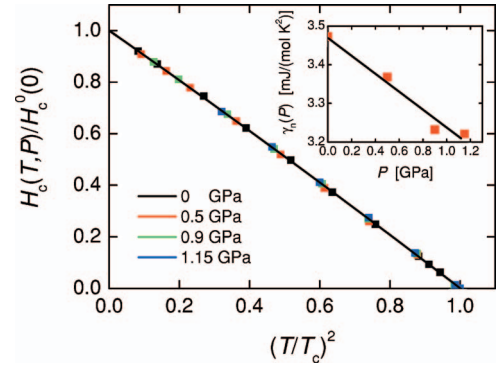

FIG. 3. (Color) Scaling of the T-dependent critical field, showing $H_c(T,P)/H_c(T=0,P)$ versus $t^2=(T/T_c)^2$ for pressures of 0, 0.5, 0.9, and 1.15 GPa. The solid curve is the function $f(T)=1-0.954\,75t^2-0.045\,25t^4$. Inset: γ_n calculated from Eq. (6).

$$\gamma_s = \gamma_n + \mu_o V_M (\partial H_c/\partial T)_P^2 - \mu_o H_c V_M (\partial^2 H_c/\partial T^2)_P,$$

$$V_s = V_n - \mu_o H_c V_M (\partial H_c/\partial P)_T$$

$$\alpha_s = \alpha_n - \mu_o (\partial H_c/\partial T)_P (\partial H_c/\partial P)_T - \mu_o H_c (\partial^2 H_c/\partial T \partial P),$$

$$\kappa_s = \kappa_n + \mu_o (\partial H_c/\partial P)_T^2 + \mu_o H_c (\partial^2 H_c/\partial P^2)_T. \qquad (5)$$

Here, terms such as $(1/2)\mu_o H_c^2 V_M \alpha_{tot}$ in the entropy or $\mu_o \kappa_{tot} H_c (\partial H_c/\partial P)_T$ in the compressibility obtained by differentiation of the molar volume are ignored as negligible, where α_{tot} is the total volume coefficient of thermal expansion including lattice and electronic terms, and similarly for κ_{tot}.

Taking the first of these expressions, that for the entropy $S_s(T,P)$, and dividing through by T, we note the requirement that $S_s/T \rightarrow 0$ as $T \rightarrow 0$ due to the opening of a full superconducting gap in the density of states (DOS). At the same time, if γ_n is constant, then S_n/T is just γ_n. This then imposes a relationship between γ_n and the quadratic term in $H_c(T)$. In particular,

$$\gamma_n = -\lim_{T\rightarrow 0} \mu_o T^{-1} H_c V_M (\partial H_c/\partial T)_P. \qquad (6)$$

In this way, γ_n is calculated from the fits in Fig. 3, and its value is plotted in the inset of Fig. 3. The value at ambient pressure, $\gamma_n=3.47$ mJ/(mol K^2), compares favorably with the value $\gamma_n=3.13$ mJ/(mol K^2) determined from direct specific-heat measurements.[1] The pressure dependence of γ_n shown in the inset reveals a dimensionless volume dependence given by $\partial \ln \gamma_n/\partial \ln V=3.26\pm0.27$ (where we assume a total compressibility of[15] $\kappa_0=0.0205$ GPa^{-1}). There have been various estimates of this dimensionless parameter ranging from 1.7 ± 0.5 from thermal-expansion measurements,[16] 1.8 ± 0.5 from volume expansion at T_c,[17] 6.0 based on pressure dependence of H_c,[7] and 3.1 ± 0.8, in good agreement with our present value based on more recent measurements of volume change at T_c by Ott.[18] Note that this is considerably stronger than the value for the free-electron gas, $\partial \ln \gamma_n/\partial \ln V=2/3$.

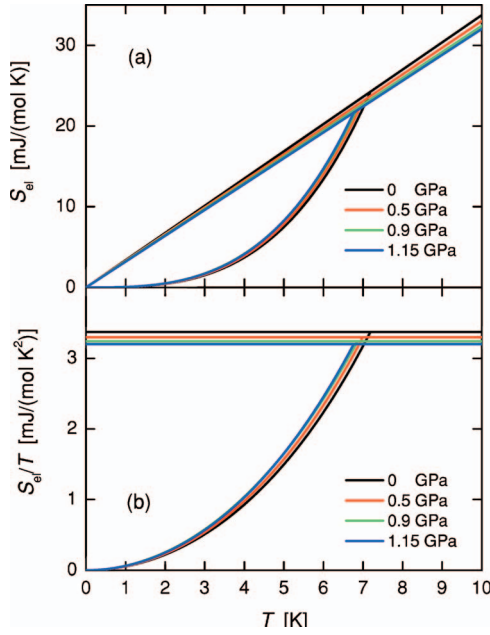With these relations in place, we proceed to calculate the

FIG. 4. (Color) The T dependence of (a) the electronic entropy in the normal state and superconducting state for pressures of 0, 0.5, 0.9, and 1.15 GPa and (b) of S/T.

entropy, as shown in Fig. 4(a). The linear slope in the normal state is just the above-determined $\gamma_n(P)$. The entropy in both states must vanish at $T=0$. A more rigorous test of the polynomial fits to the data is whether S_s/T also vanishes as $T \to 0$ and whether the data preserve monotonic systematics in this region. The T dependence of S/T is plotted in Fig. 4(b), and this indeed shows a quadratic behavior at low T, which is perfectly systematic with increasing pressure and extrapolates to zero as $T \to 0$. In a finite external field, the same entropy curves are retraced up to the reduced $T_c(H)$ value and then the entropy jumps discontinuously to the normal-state value, consistent with a first-order phase transition in magnetic field and second order when $H=0$.

The condensation energy U_o is determined from

$$U_o = \int_0^{T_c} [S_n(T,P) - S_s(T,P)]dT, \qquad (7)$$

from which we obtain the following values: U_o=47, 43.2, 39.8, and 38.6 mJ/mol for P=0, 0.5, 0.9, and 1.15 GPa, respectively. The condensation energy reduces with pressure due to the twin effects of reduced T_c and reduced γ_n.

Turning to the specific-heat coefficient, this is calculated using the second equation in Eqs. (5) and is shown in Fig. 5 for both the normal and superconducting states. The entropy balance is evident from the equal areas above and below the temperature, where $\gamma_s = \gamma_n$, and is confirmed by the fact shown in Fig. 4(b) that $S_s/T = \gamma_n$ at T_c. We find that the jump in $\gamma(T,P)$ at T_c is $\Delta\gamma_c$=7.85, 7.51, 7.05, and 7.17 mJ/(mol K^2) for P=0, 0.5, 0.9, and 1.15 GPa, respectively. Values of $\Delta\gamma_c/\gamma_n$ are, respectively, 2.33, 2.28, 2.18, and 2.24. There is a weak pressure dependence here in this ratio that is not expected with a simple BCS picture, where $\Delta\gamma_c/\gamma_n$=1.55. Direct specific-heat
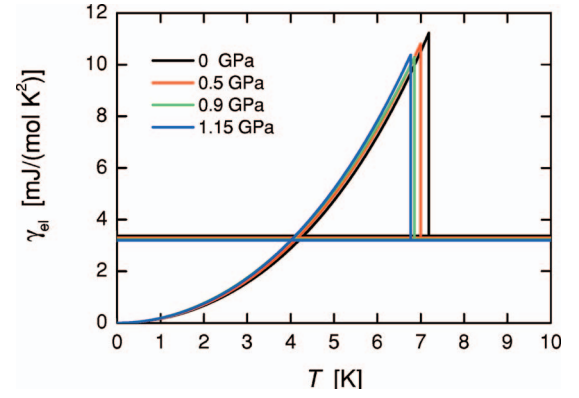
measurements at ambient pressure have obtained various values for $\Delta\gamma_c$ such as 7.33 ± 0.3 mJ/(mol K^2) (Clement and Quinnel[19]), 7.96 ± 0.08 mJ/(mol K^2) (Shiffman et al.[20]), and 8.13 ± 0.13 mJ/(mol K^2) (Neighbor et al.[21]), in good agreement with our ambient result. Combining with the measurement by Horowitz et al.[1] of γ_n=3.13 mJ/(mol K^2) gives $\Delta\gamma_c/\gamma_n$=2.34, 2.54, and 2.60, again in good agreement with our present ambient-pressure result. We note that for the purely parabolic form $H_c=H_c^o\{1-t^2\}$, then $\Delta\gamma_c/\gamma_n=2$ exactly, and so the experimentally observed excess of $\Delta\gamma_c/\gamma_n$ is a direct indication of the presence of a higher-order (quartic) term in the T-dependent critical field.

Finally, Fig. 6(a) shows the calculated difference in volume thermal-expansion coefficient between the superconducting and normal states at each pressure and Fig. 6(b)
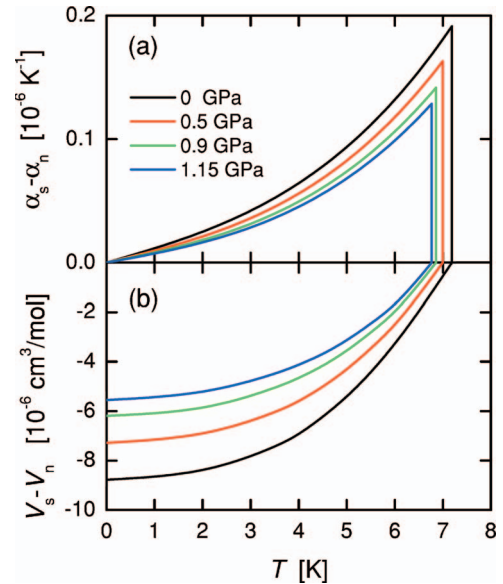

FIG. 5. (Color) The T dependence of the specific-heat coefficient $\gamma(T,P)$ in the normal and superconducting states for pressures of 0, 0.5, 0.9, and 1.15 GPa. The small departure from monotonic systematics in the specific-heat jump for 0.9 GPa reflects the accumulation of errors in the second derivatives.

FIG. 6. (Color) (a) The T dependence of the difference in volume thermal-expansion coefficient between the superconducting and normal states for pressures of 0, 0.5, 0.9, and 1.15 GPa. (b) The difference in molar volume for the same pressures.

shows the difference in molar volume. Given that the absolute molar volume at $T=0$ K is 18.26 cm^3/mol, these changes in volume seem extremely small but they are readily measurable. The jumps in thermal-expansion coefficient at T_c in zero field are $\Delta\alpha = 1.91 \times 10^{-7}$, 1.63×10^{-7}, 1.42×10^{-7}, and 1.29×10^{-7} K^{-1} for $P=0$, 0.5, 0.9, and 1.15 GPa, respectively. We omit the calculations of the electronic compressibility because these involve double derivatives with respect to pressure and here the errors begin to accumulate markedly. Nonetheless, the discontinuous jumps in isothermal compressibility may be calculated from the Ehrenfest equation for a second-order transition:

$$dT_c/dP = \Delta\kappa/\Delta\alpha \qquad (8)$$

Empirically we find that

$$T_c(P) = 7.1863 - 0.3847P + 0.017\,69P^2, \qquad (9)$$

so that the absolute jumps in isothermal compressibility at T_c in zero field are $\Delta\kappa = -7.3 \times 10^{-8}$, -6.0×10^{-8}, -5.0×10^{-8}, and -4.4×10^{-8} GPa^{-1} for $P=0$, 0.5, 0.9, and 1.15 GPa, respectively, while the relative jumps are $\Delta\kappa/\kappa_0 = -3.56$, -2.93, -2.44, and -2.15 ppm. Direct measurements[22] of the ambient-pressure elastic moduli for Pb in the superconducting state yield $\Delta\kappa/\kappa_0 = -4.0$ ppm, again in excellent agreement with our analysis for $P=0$ GPa.

We conclude by using the above results to estimate the pressure dependence of key parameters in the BCS model.[23] The condensation energy is

$$\frac{1}{2}\mu_0 H_{c0}(P) = \frac{1}{2}N(0)N_A\Delta_0^2 = (47.11 - 7.75P) \text{ mJ/mol}, \qquad (10)$$

where P is in gigapascals. The jump in specific heat is given by

$$\gamma_s - \gamma_n = 10.2k_B^2 N(0)N_A = (7.85 - 0.68P) \text{ mJ/(mol K}^2). \qquad (11)$$

Therefore, we obtain

$$N(0) = (1.07 - 0.093P) \text{ states/atom/eV}, \qquad (12)$$

$$\Delta_0 = (11.1 - 0.432P)\text{K}, \qquad (13)$$

$$2\Delta_0/k_B T_c = 3.09 + 0.037P. \qquad (14)$$

This should be compared with the BCS result $2\Delta_0/k_B T_c = 3.53$ and the value of $\Delta_0 = 15.76 \pm 0.05$ K observed from tunneling,[24] giving $2\Delta_0/k_B T_c = 4.37$.

If, on the other hand, we determine the DOS from the nearly-free-electron expression[23]

$$\gamma_n = (2/3)\pi^2 k_B^2 N(0)N_A = (3.47 - 0.232P) \text{ mJ/(mol/K}^2), \qquad (15)$$

then we obtain

$$N(0) = (0.736 - 0.0492P) \text{ states/atom/eV}, \qquad (16)$$

$$\Delta_0 = (13.7 - 0.653P)\text{K}, \qquad (17)$$

$$2\Delta_0/k_B T_c = 3.72 + 0.007P, \qquad (18)$$

and the ratio $2\Delta_0/k_B T_c$ is more or less pressure independent. Finally, using the BCS expression[23] for T_c

$$T_c = 0.85\Theta_D \exp\left(-\frac{1}{N(0)W}\right), \qquad (19)$$

where Θ_D is the Debye temperature [$=96$ K for Pb (Ref. [23])] and W is the pairing interaction, then, using Eq. (12),

$$W = (0.343 + 0.0167P)\text{eV} \qquad (20)$$

or, using Eq. (16),

$$W = (0.499 + 0.0143P)\text{eV}. \qquad (21)$$

Here, we have used the Gruneisen coefficient $\gamma_G = -2.6$ for Pb.[25]

In summary, we have measured the pressure dependence of the superconducting critical field in Pb to 1.15 GPa using a clamp cell in a SQUID magnetometer. By using thermodynamic identities, we have determined the electronic free energy, entropy, specific-heat coefficient, thermal-expansion coefficient, and compressibility, including the jumps in these properties at T_c. The calculated results match rather well the experimentally observed ambient-pressure data, where it is available. The present results allow calculation of the these parameters as pressure-dependent quantities and an estimation of the pressure dependence of the density of states, superconducting energy gap, and the pairing interaction.

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