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Dependence of T_c on hydrostatic pressure in superconducting MgB_2

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The dependence of T_c on hydrostatic (He-gas) pressure for superconducting MgB_2 has been determined to 0.7 GPa. We find that T_c decreases linearly and reversibly under pressure at the rate $dT_c/dP \simeq -1.11 \pm 0.02$ K/GPa. These studies were carried out on the same sample used in earlier structural studies under He-gas pressure which yielded the bulk modulus $B = 147.2 \pm 0.7$ GPa. The value of the logarithmic volume derivative of T_c is thus accurately determined, $d \ln T_c / d \ln V = +4.16 \pm 0.08$, allowing quantitative comparison with theory. The present results support the emerging picture that MgB_2 is a BCS superconductor with electron-phonon pairing interaction.

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The recent discovery[1] of superconductivity in MgB_2 at $T_c \simeq 39$ K has sparked worldwide a torrent of experimental and theoretical activity, reminiscent of the frenzy following the observation[2] of superconductivity in La-Ba-Cu-O at a comparable temperature almost 15 years ago. Replacing ^{10}B with ^{11}B results in a sizable isotope shift[3] to lower temperatures which points to BCS superconductivity. Other experiments, such as heat capacity,[4,5] photoemission spectroscopy,[6] and inelastic neutron scattering,[7,8] also support the picture that MgB_2 is a phonon-mediated superconductor in the weak-to-moderate coupling regime.

High-pressure studies traditionally play an important role in superconductivity. A large magnitude of the pressure derivative dT_c/dP is a good indication that higher values of T_c may be obtained through chemical means. It is not widely appreciated, however, that the pressure dependence $T_c(P)$, like the isotope effect, contains valuable information on the superconducting mechanism itself. For example, in simple-metal BCS superconductors, like Al, In, Sn, and Pb, T_c invariably decreases under pressure due to the reduced electron-phonon coupling from lattice stiffening.[9] More generally, an accurate determination of the dependence of both T_c and the lattice parameters on pressure yields the functional dependence $T_c = T_c[a(P), b(P), c(P)]$ which provides a critical test of theoretical models. Hirsch[10] and Hirsch and Marsiglio[11] have applied a theory of hole superconductivity to MgB_2 and predicted that for an optimally doped sample T_c should increase with pressure, in contrast to the expected decrease in T_c from lattice stiffening.

Precise structural data on MgB_2 at room temperature (RT) have recently been obtained by Jorgensen *et al.*[12] for hydrostatic pressures to 0.6 GPa in a He-gas neutron diffraction facility which yield the anisotropic compressibilities $d \ln a/dP = -1.87 \times 10^{-3}$ GPa^{-1}, $d \ln b/dP = -3.07 \times 10^{-3}$ GPa^{-1}, and the bulk modulus $B = 147.2 \pm 0.7$ GPa; the compressibility along the c axis is thus significantly (64%) larger than that along the a axis. The binding within the boron layers is evidently much stronger than between the layers. These results are in reasonable agreement with electronic structure calculations by Loa and Syassen.[13]

Recent synchrotron x-ray diffraction studies at RT in a diamond-anvil cell (DAC) to much higher pressures (8–12 GPa) using dense He (Ref. 14) or methanol-ethanol[15] as hydrostatic pressure media yield the bulk moduli $B = 155 \pm 10$ GPa and 151 ± 5 GPa, respectively, in agreement, within experimental error, with the He-gas study.[12] A further DAC study[16] to 7 GPa with silicon oil as pressure medium gives the significantly smaller value $B = 120 \pm 5$ GPa, even though the reported 2.9% decrease in unit cell volume upon applying 6.5 GPa pressure is *less* than the 4% decrease found in the other two DAC studies.[14,15] The strong deviation of the ‘‘silicon oil’’ data[16] may arise from difficulties in extrapolating the data to zero pressure to obtain the bulk modulus and/or from shear stresses arising from the solidification of the silicon oil under pressure. The relatively large compressibility anisotropy in MgB_2 mandates the use of hydrostatic pressure in quantitative studies, since shear stresses applied by nonhydrostatic pressure media to an elastically anisotropic sample can lead to erroneous results.

Several studies of the dependence of T_c on pressure have appeared for MgB_2. In an experiment utilizing a fluid pressure medium (Fluorinert), Lorenz *et al.*[17] report that T_c decreases linearly with pressure to 1.8 GPa at the rate $dT_c/dP \simeq -1.6$ K/GPa. On the other hand, using the same pressure medium, Saito *et al.*[18] find the more rapid decrease $dT_c/dP \simeq -2.0$ K/GPa. Both groups cite their results to argue that MgB_2 is a BCS phonon-mediated superconductor,[17,18] as is also argued by Loa and Syassen.[13] In further experiments to 25 GPa utilizing the solid pressure medium steatite, Monteverde *et al.*[19] find that T_c decreases under pressure at differing initial rates (-0.35 K/GPa to -0.8 K/GPa), $T_c(P)$ showing a quadratic behavior for two of the four samples studied; each of the four samples was prepared using a different synthesis procedure.

In the present experiment, $T_c(P)$ is determined to 0.7 GPa in an ac susceptibility measurement using a He-gas pressure system; the helium pressure medium remains fluid at $T_c \simeq 39$ K up to 0.5 GPa and thus applies true hydrostatic pressure (no shear stresses) to the sample. We find that T_c decreases linearly and reversibly with pressure at the rate

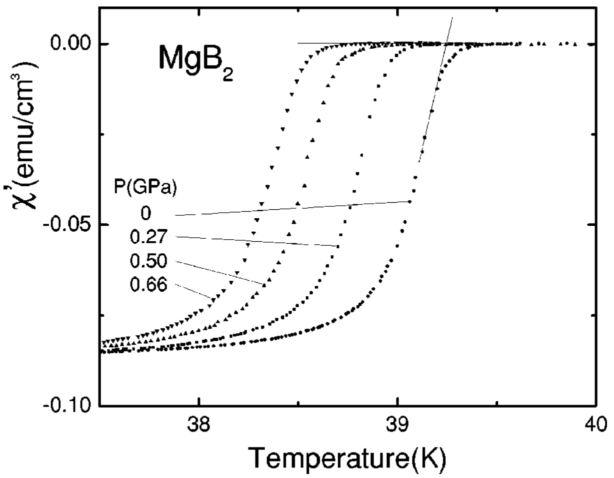

FIG. 1. Real part of the ac susceptibility of MgB$_2$ vs temperature at ambient and high pressures. The applied magnetic field is 0.113 Oe (rms) at 1023 Hz. The intercept of straight tangent lines defines the superconducting onset at ambient pressure $T_c(0) \simeq 39.25$ K. No correction is made for demagnetization effects.

$dT_c/dP \simeq -1.11 \pm 0.02$ K/GPa. Implications for the nature of the superconducting state are discussed.

The powder sample for this study was taken from the same mother sample used in parallel neutron diffraction studies.[12] It is made using isotopically enriched ^{11}B (Eagle Picher, 98.46 at. % enrichment). A mixture of ^{11}B powder (less than 200-mesh-particle size) and chunks of Mg metal were reacted for 1.5 h in a capped BN crucible at 800 °C under an argon atmosphere of 50 bars. As seen in Fig. 1, the resulting sample displays sharp superconducting transitions in the ac susceptibility with full shielding and an onset temperature at ambient pressure $T_c(0) \simeq 39.25$ K. Both x-ray and neutron diffraction data show the sample to be single phase with AlB$_2$-type structure.

The present high-pressure studies were carried out using a He-gas high-pressure system (Harwood) to 1.4 GPa; the pressure is determined by a calibrated manganin gauge in the compressor system at ambient temperature. The superconducting transition of the 8.12-mg MgB$_2$ powder sample is measured by the ac susceptibility technique using a miniature primary-secondary coil system located inside the 7-mm-i.d. bore of the pressure cell. A small Pb sphere with 1.76 mm diameter (38.58 mg) is also inserted in the coil system for susceptibility calibration purposes; for selected data the superconducting transition temperature of this Pb sphere serves as an internal manometer[20] to check the pressure indicated by the manganin gauge. The CuBe pressure cell (Unipress), which is connected to the compressor system by a 3 mm o.d. $\times 0.3$ mm i.d. CuBe capillary tube, is inserted into a two-stage closed-cycle refrigerator (Leybold) operating in the temperature range 2–320 K. The pressure can be changed at any temperature above the melting curve T_m of the helium pressure medium [for example, $T_m \simeq 13.6$ K at 0.1 GPa and $T_m \simeq 38.6$ K at 0.50 GPa (Ref. 21)]. For pressures above 0.5 GPa, T_m lies above T_c; the slight pressure drop (few 0.01 GPa) on cooling from T_m to T_c is estimated using the isochores of He.[21] All pressures are determined at the temperature $T_c \simeq 39$ K. Further details of the experimental techniques are given elsewhere.[22]

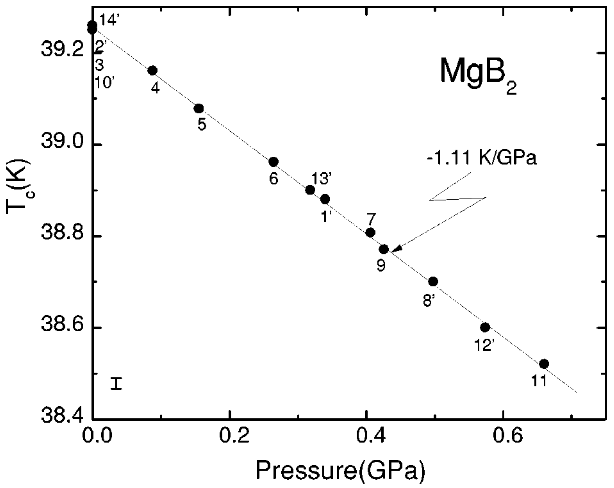

FIG. 2. Superconducting transition temperature vs applied pressure. Numbers give the order of measurement. Data for points 2′, 6, 8′, and 11 are shown in Fig. 1. A typical error bar for T_c (± 0.01 K) is given in the lower left corner; the error in pressure is less than the symbol size. Pressure was either changed at RT (unprimed numbers) or at low temperatures ~60 K (primed numbers).

In Fig. 1 are shown representative examples of the superconducting transition in the ac susceptibility at both ambient and high pressure. With increasing pressure the narrow transition is seen to shift bodily to lower temperatures, allowing a determination of the pressure-induced shift in T_c to within ± 10 mK. Remarkably, close inspection of the data for 0.50 GPa reveals a slight shift in the transition curve near its midpoint, accurately marking the position of the melting curve of helium ($T_m \simeq 38.6$ K) at this pressure.

In Fig. 2, T_c is plotted versus applied pressure to 0.7 GPa and is seen to follow a highly linear dependence $dT_c/dP \simeq -1.11 \pm 0.02$ K/GPa. The first data point 1′ was obtained after first applying a pressure of ~0.7 GPa at RT before cooling down to low temperatures (~60 K) and reducing the pressure, yielding $T_c \simeq 38.88$ K at 0.341 GPa. Point 2′ was measured after releasing the pressure at low temperature, giving $T_c \simeq 39.25$ K at ambient pressure (0 GPa); no change in T_c occurred after intermittently warming the sample to RT (point 3). Further data were obtained following pressure changes at both RT (unprimed data) and low temperature (primed data). As is observed for the vast majority of superconducting materials without phase change, the dependence of T_c on pressure for MgB$_2$ is single-valued and does not depend on the pressure-temperature history of the sample; such history effects do occur in certain high-T_c oxides containing mobile species at RT.[23] We thus find that for He-gas pressure changes at both ambient and low temperature, $T_c(P)$ for MgB$_2$ is a linear, reversible function of pressure to 0.7 GPa.[24]

In the present experiments the sample is surrounded by fluid helium near $T_c \simeq 39$ K for all data taken at pressures $P \leqslant 0.50$ GPa so that the slope $dT_c/dP \simeq$-1.11 K/GPa gives the true hydrostatic pressure dependence of T_c. The fact that the sample is in solid helium for $P > 0.5$ GPa is seen in Fig. 2 to have no effect on the pressure dependence $T_c(P)$; indeed, solid helium is the softest solid known. Our value of dT_c/dP differs significantly from those of other groups[17–19] (see discussion above) using pressure media which are either solid at RT or freeze upon cooling down at temperatures well above T_c.

In view of the strong compressibility anisotropy[12] and the sizable anharmonicity and nonlinear electron-phonon coupling[8] anticipated for MgB_2, it is likely that shear stresses of sufficient magnitude will cause appreciable changes in the pressure dependence of T_c, as observed for other anisotropic substances such as the superconducting oxides[25] and organic superconductors.[26] The largest shear stresses are generated by changing the pressure on a solid pressure medium, such as steatite, or using no pressure medium at all. The shear stresses generated in cooling Fluorinert or other comparable liquids through the melting curve are admittedly much smaller and depend on details of the individual experimental procedures used, such as the cooling rate, change in applied force upon cooling, etc. Only experiment can determine whether or not the $T_c(P)$ dependences measured in the Fluorinert pressure medium[17,18] are influenced by shear stresses. To exclude the possibility of sample-dependent effects, such experiments should be carried out on a single sample. Lorenz *et al.*[27] have very recently carried out He-gas high-pressure studies on the same sample studied by them previously in Fluorinert[17] and find a value of dT_c/dP equal to their previous value (-1.6 K/GPa), within experimental error; further measurements in the same He-gas system on a second, high-quality sample yielded the dependence $dT_c/dP \simeq -1.07$ K/GPa, a value very close to our present result. This finding lends support to the observation by Monteverde *et al.*[19] that dT_c/dP in MgB_2 may be sample dependent.

The present $T_c(P)$ studies and parallel high-pressure structural studies by Jorgensen *et al.*[12] were both carried out on the same MgB_2 sample over the same He-gas pressure range, thus allowing an accurate determination of the change in T_c with lattice parameter. The change in T_c with unit cell volume, for example, is given by

$$\frac{d\ln T_c}{d\ln V} = \frac{B}{T_c}\left(\frac{dT_c}{dP}\right) = +4.16 \pm 0.08, \tag{1}$$

using the above values $dT_c/dP \simeq -1.11 \pm 0.02$ K/GPa, $B = 147.2 \pm 0.7$ GPa, and $T_c = 39.25$ K.

We will now discuss the implications of this result for the nature of the superconducting state in MgB_2. First consider the McMillan equation[28]

$$T_c \simeq (\langle\omega\rangle/1.20)\exp\{[-1.04(1+\lambda)]/[\lambda - \mu^*(1+0.62\lambda)]\}$$

valid for strong coupling ($\lambda \lesssim 1.5$), which connects the value of T_c with the electron-phonon coupling parameter λ, an average phonon frequency $\langle\omega\rangle$, and the Coulomb repulsion μ^*, which we assume to be pressure independent. Taking the logarithmic volume derivative of T_c, we obtain the simple relation

$$\frac{d\ln T_c}{d\ln V} = -\gamma + \Delta\left\{\frac{d\ln\eta}{d\ln V} + 2\gamma\right\}, \tag{2}$$

where $\gamma \equiv -d\ln\langle\omega\rangle/d\ln V$ is the Grüneisen parameter, $\eta \equiv N(E_f)\langle I^2\rangle$ is the Hopfield parameter[29] given by the product of the electronic density of states and the average-squared electronic matrix element, and $\Delta = 1.04\lambda[1 + 0.38\mu^*]/[\lambda - \mu^*(1+0.62\lambda)]^2$.

Equation (2) has a simple interpretation. The first term on the right, which comes from the prefactor to the exponent in the McMillan expression for T_c, is usually small relative to the second term, as will be demonstrated below. The sign of the logarithmic derivative $d\ln T_c/d\ln V$, therefore, is determined by the relative magnitude of the two terms in the curly brackets. The first ‘‘electronic’’ derivative is negative [$d\ln\eta/d\ln V \approx -1$ for simple metals (s,p electrons),[30] but equals -3 to -4 for transition metals (d electrons) (Ref. 29)], whereas the second ‘‘lattice’’ term is positive (typically $2\gamma \approx 3$–5). Since in simple-metal superconductors, like Al, In, Sn, and Pb, the lattice term dominates over the electronic term and Δ is always positive, the sign of $d\ln T_c/d\ln V$ is the same as that in the curly brackets, namely, positive; this accounts for the universal decrease of T_c with pressure due to lattice stiffening in simple metals. In selected transition metals the electronic term may become larger than the lattice term, in which case T_c would be expected to increase with pressure, as observed in experiment.[29]

Let us now apply Eq. (2) in more detail to a canonical BCS simple-metal superconductor. In Sn, for example, T_c decreases under pressure at the rate $dT_c/dP \simeq -0.482$ K/GPa which leads to $d\ln T_c/d\ln V \simeq +7.2$.[20] Inserting $T_c(0) \simeq 3.73$ K, $\langle\omega\rangle \simeq 110$ K,[31] and $\mu^* = 0.1$ into the above McMillan equation, we obtain $\lambda \simeq 0.69$ from which follows that $\Delta \simeq 2.47$. Inserting these values into Eq. (2) and setting $d\ln\eta/d\ln V \approx -1$ from above for simple metals, we can solve Eq. (2) for the Grüneisen parameter to obtain $\gamma \simeq +2.46$, in reasonable agreement with experiment for Sn ($\gamma \approx +2.1$).[20] Similar results are obtained for other simple-metal superconductors.

We now repeat the same calculation with the McMillan equation for MgB_2 using the logarithmically averaged phonon energy from inelastic neutron studies[7] $\langle\omega\rangle = 670$ K, $T_c(0) \simeq 39.25$ K, and $\mu^* = 0.1$, yielding $\lambda \simeq 0.90$ and $\Delta \simeq 1.75$. From Eq. (1) we have $d\ln T_c/d\ln V = +4.16$. Since the pairing electrons in MgB_2 are believed to be s,p in character,[32] we set $d\ln\eta/d\ln V \approx -1$.[33] Inserting these values into Eq. (2), we find $\gamma \simeq 2.36$, in reasonable agreement with the value $\gamma \approx 2.9$ from Raman spectroscopy studies[14] or $\gamma \approx 2.3$ from *ab initio* electronic structure calculations on MgB_2.[34] If, on the other hand, one were to use the same bulk modulus but the pressure derivative $dT_c/dP \simeq -2.0$ K/GPa from Saito *et al.*,[18] one obtains from Eq. (2) the unusually high value $\gamma \simeq 3.7$.

In extensive specific heat[5] and high-resolution photoemission studies[35] on MgB_2, evidence is found for a multicomponent superconducting gap; the latter study also reports an inconsistency in the values of the electron-phonon coupling constant from McMillan's equation and the renormalization of the electronic density of states. These results call into question the suitability of the isotropic McMillan equation for describing this system.

Under the above assumptions, we thus conclude that the rate of decrease of T_c with pressure found in the present experiments on MgB_2 is consistent with BCS phonon-mediated superconductivity. From this rate and measurements of the bulk modulus on the same sample, we calculate the dependence of T_c on volume to be $d\ln T_c/d\ln V = +4.16 \pm 0.08$. At first glance the present results appear to be inconsistent with the model of Hirsch and Marsiglio[10,11] which predicts that T_c should increase with pressure for optimally doped samples. However, within their model, T_c for a nonoptimally doped sample may decrease if sufficient change in the carrier concentration occurs when pressure is applied. Further studies, such as high-pressure Hall effect measurements, are necessary to clarify this possibility.

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