HYDROSTATIC PRESSURE DEPENDENCE OF THE SUPERCONDUCTING AND STRUCTURAL PROPERTIES OF MgB_2

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1 INTRODUCTION

The past fifteen years have witnessed some of the more memorable discoveries in the ninety-year-old field of superconductivity, including the high-T_c oxides in 1986 [1], the alkali-doped fullerenes in 1991 [2], the charge-injected fullerenes in 2000 [3], and the binary compound MgB_2 in January 2001 [4]. The discovery of superconductivity at such high temperatures (40 K) in the simple s,p-metal compound MgB_2 was quite unexpected. The absence [5] of the problematic weak-link behavior of the high-T_c oxides and the relative ease of synthesis in various forms [6] has raised hopes that MgB_2 may be suitable for numerous technological applications.

To aid in the search for related compounds with even better superconducting properties and to help identify the pairing mechanism, a great deal of current research is dedicated to fully characterizing MgB_2 in both its normal and superconducting states. A wide range of experiments, including isotope effect [7, 8], heat capacity [9, 10], inelastic neutron scattering [11, 12], NMR [13], and photoemission spectroscopy [14], support the picture that MgB_2 is a phonon-mediated BCS superconductor in the moderate coupling regime. The fact that the B isotope effect is fifteen times that for Mg [8] is clear evidence that the superconducting pairing originates within the graphite-like B_2-layers, consistent with electronic structure calculations [12, 15–18] whereby MgB_2 is a quasi-2D material with strong covalent bonding within the boron layers. The anisotropy in the superconducting properties is appreciable, the upper critical field ratio H_{c2}^{ab}/H_{c2}^{c} reportedly being 1.7 [19] or 2.7 [20], but far less than that observed in the high-T_c oxides [21]. A full characterization of all anisotropic properties

awaits the synthesis of sufficiently large single crystals.

High pressure studies traditionally play an important role in superconductivity. Even without a detailed understanding of *why* T_c changes with pressure, a large magnitude of the pressure derivative dT_c/dP is a good indication that higher values of T_c are possible at ambient pressure 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. In fact, in simple s, p-metal BCS superconductors like Al, In, Sn, or Pb, T_c is found to invariably *decrease* with increasing hydrostatic pressure [22] or isotopic mass; in both cases the reduction in T_c arises from changes in the lattice vibration spectrum, electronic properties having minimal effect. In transition-metal systems the isotope coefficient may deviate considerably from the BCS value $\alpha = 0.5$ and the pressure dependence $T_c(P)$ is determined by changes in both lattice vibration and electronic properties.

Soon after the discovery of superconductivity in MgB_2, three groups reported independently that T_c decreased under the application of high pressure, but the rate of decrease varied considerably. Lorenz *et al.* [23] carried out ac susceptibility measurements in a piston-cylinder cell to 1.8 GPa using the fluid pressure medium Fluorinert FC77 and obtained $dT_c/dP \simeq$ -1.6 K/GPa. Saito *et al.* [24] measured the electrical resistivity ρ to 1.4 GPa using a similar pressure technique with Fluorinert FC70 and reported the pressure derivative -1.9 K/GPa. Monteverde *et al.* [25] extended the pressure range to 25 GPa in resistivity measurements in an opposed anvil cell with solid steatite pressure medium; three of the four samples studied exhibited widely differing pressure dependences with initial values of dT_c/dP ranging from -0.35 to -0.8 K/GPa. When pressure is applied to a solid pressure medium like steatite, the sample is subjected to sizeable shear stresses which may plastically deform a dense sample or compact a loosely sintered sample, as in the experiments of Monteverde *et al.* [25]. Shear stresses are known to influence the pressure dependence of T_c, particularly in elastically anisotropic materials such as the high-T_c oxides [26] or organic superconductors [27]. Fluid pressure media such as Fluorinert, methanol-ethanol or silicon oil remain fluid at RT to a certain pressure, but soon freeze upon cooling at temperatures well above the superconducting transition temperature $T_c \approx 40$ K of MgB_2, thus subjecting the sample to shear stresses, albeit relatively small ones. Only helium remains fluid at 40 K for pressures to 0.5 GPa.

Since in electronic structure calculations T_c is determined by the unit cell dimensions and atom positions, for a quantitative comparison with theory it is essential to complement the determination of $T_c(P)$ with accurate measurements of the pressure dependence of the structure parameters. Effects of pressure on the structure can affect the superconducting transition temperature through changes in the electronic structure, phonon frequencies, or electron-phonon coupling. For structures where the pressure effects are isotropic, changes in the electronic structure are usually subtle because the Fermi energy and features of the Fermi surface tend to simply scale together with the cell volume. However, when the compression is anisotropic, as a result of significantly different bonding strengths in different crystallographic directions, large pressure-induced changes in the electronic structure can occur. For example, in the layered copper oxide superconductor $HgBa_2CuO_{4+x}$, where the compression is 37% larger along the c axis than in the basal plane [28], the pressure-induced increase in T_c for optimally doped material is thought to occur because pressure moves a band associated with the HgO_x layer across the Fermi energy, creating new carriers and "metallizing" the blocking layer [29, 30]. Even when such dramatic effects do not occur, the anisotropic compression in layered materials, such as the copper oxides, can move critical

features of the density of states (such as the van Hove singularity) with respect to the Fermi energy resulting in changes in the carrier density[31].

MgB_2 presents a situation where similar phenomena could occur. The superconductivity is thought to result from strong electron-phonon coupling to a particular feature of the electronic structure associated with boron σ bonds which lies close to the Fermi energy [16]. The layered structure of MgB_2, characterized by Mg-B bonds along the c axis and B-B bonds in the basal plane, is expected to compress anisotropically. Thus, accurate structural data versus pressure are needed to evaluate the pressure-induced changes in the electronic structure, as well as the changes in phonon frequencies and electron-phonon coupling, and how these might contribute to the pressure dependence of T_c.

Within months after the discovery of superconductivity in MgB_2, several groups reported structural measurements versus pressure [32–35]. The compression is clearly anisotropic, but quantitative agreement among the experimental results for the bulk modulus and compression anisotropy was poor. Measurements made in helium gas appear to exhibit the largest compression anistropy $\{[(dc/dP)/c_0]/(da/dP)/a_0]\}$ = 1.64(4) [34] and 1.9(3) [35], while measurements made in other fluids yield lower values $\sim$ 1.5 in a methanol:ethanol:water mixture [32] and $\sim$ 1.4 in silicone oil [33]. Some of these differences may be due to the degree to which the pressure fluid is truely hydrostatic. Errors in the accurate *in situ* measurement of lattice parameters and the extrapolation of the results to zero pressure could also contribute to the differences. Some authors [25, 36] have concluded that different samples of MgB_2 can exhibit different pressure-dependent behavior. It has been speculated that samples may differ in the amount of Mg or B vacancies, but there is no clear evidence that such deviations in stoichiometry are possible in MgB_2. An alternative is that impurity phases such as MgB_4, or elemental Mg or B, distributed at grain boundaries or at the center of grains, modify the pressure, and amount of shear, seen by individual crystallites of MgB_2 in sintered grains when pressure is applied.

In this paper, we report parallel *in situ* neutron powder diffraction and $T_c(P)$ measurements versus pressure on the same MgB_2 sample in a He-gas apparatus to 0.6 GPa, thus avoiding any problems with non-hydrostatic pressure fluids or sample dependent differences. In addition, we present measurements in a helium-loaded diamond-anvil-cell to 20 GPa on the same sample. The high precision achieved in these measurements allows a quantitative interpretation of the change in T_c versus the changes in structure.

2 EXPERIMENTAL METHODS

2.1 Sample Preparation

The powder sample of MgB_2 for these studies was made using isotopically-enriched ^{11}B (Eagle Picher, 98.46 atomic % enrichment). A mixture of ^{11}B powder (less than 200 mesh particle size) and chunks of Mg metal was reacted for 1.5 hours in a capped BN crucible at 800°C under an argon atmosphere of 50 bar. As discussed below, the resulting sample displays sharp superconducting transitions in the ac susceptibility with full shielding. At ambient pressure the temperatures of the superconducting onset and midpoint lie at 39.25 K and 39.10 K, respectively. Since this sample contains isotopically pure ^{11}B, a temperature shift of $\Delta T_c \simeq 0.2$ K should be added to our T_c values before comparing them with those from other groups using samples not isotopically enriched ($^{10.81}$B).

2.2 Neutron Powder Diffraction Measurements

Neutron powder diffraction measurements were made on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratory [37] in a He-gas pressure cell [38] at room temperature. Typical data collection times were one hour at each pressure. Pressures were measured continuously at the pumping station, connected to the pressure cell by a capillary line, and are accurate and stable within 0.02 GPa. The data were analyzed by the Rietveld technique using the GSAS code [39]. In initial refinements, the Mg/^{11}B ratio was refined. There was no indication of non stoichiometry within a refinement precision of about 0.5%. Fig. 1 shows the raw data and refined diffraction pattern at 0.63(2) GPa. The sample is single phase and the diffraction pattern is nicely fit with peak widths near the instrumental resolution. This is true at all pressures. There is no evidence for any structural transitions.

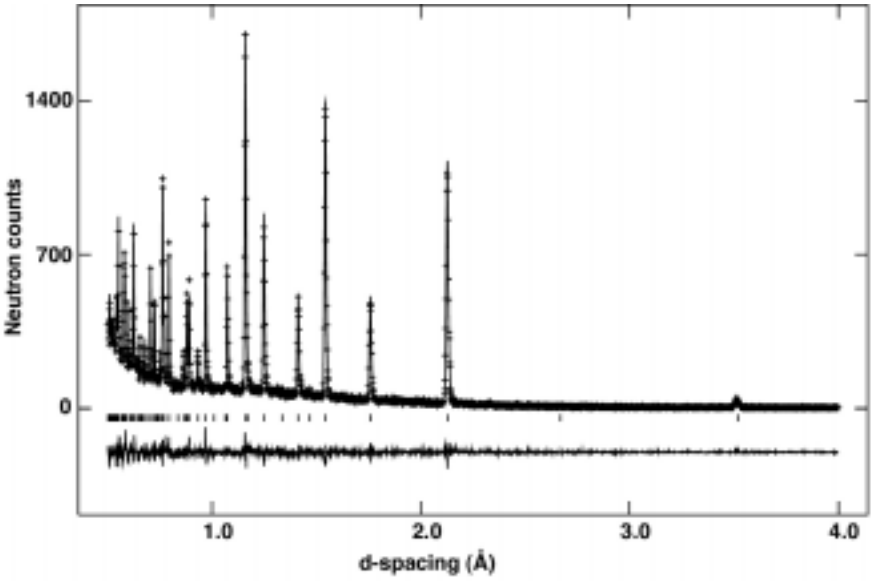

Fig. 1. Observed time-of-flight neutron powder diffraction data and best-fit Rietveld refinement profile for MgB_2 at 0.63(2) GPa. Data collection time was one hour. Crosses (+) are the raw data. The solid line is the calculated profile. Tick marks indicate the positions of all allowed reflections. A difference curve (observed minus calculated) is plotted at the bottom.

2.3 $T_c(P)$ Measurements in He-Gas Apparatus

The measurements of $T_c(P)$ to 0.7 GPa were carried out using a He-gas high-pressure system (Harwood). The pressure is determined by a calibrated manganin gauge at room temperature (RT) located in the compressor system. The CuBe pressure cell (Unipress) is inserted into a closed-cycle cryocooler (Leybold) with a base temperature of 2 K and connected to the compressor system by a 3 mm O.D. $\times$ 0.3 mm I.D. CuBe capillary tube approximately 3 m long. To minimize shear stresses on the sample when the helium pressure medium freezes, a technique developed by Schirber [40] is applied, whereby the top of the 15 cm long pressure cell and the capillary tube are kept at a slightly higher temperature than the bottom so that helium freezes from the bottom up around the sample as the pressure cell is slowly cooled (30 min) through the melting curve of helium. The pressure in the cell can be changed at any temperature above the melting curve $T_m(P)$ 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 [41]). For pressures $P > 0.5$ GPa, T_m lies above the superconducting transition temperature of MgB_2 and the sample is in frozen helium during the T_c measurement; the slight pressure drop (few 0.01 GPa's) on cooling in the solid helium pressure medium from T_m to T_c is estimated using the known isochores of He [41]. All pressures are determined at T_c.

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. An EG&G 5210 lock-in amplifier with a transformer preamplifier is used at 0.113 Oe (rms) field and 1,023 Hz. A small Pb sphere with 1.76 mm dia (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 is used as an internal manometer [42] to check the pressure indicated by the external manganin gauge.

2.4 $T_c(P)$ Measurements in Diamond-Anvil-Cell

$T_c(P)$ can be determined to much higher pressures using a helium-loaded diamond-anvil-cell made of hardened Cu-Be alloy fitted with 1/6-carat diamond anvils and 0.5 mm culet diameter. The MgB_2 sample ($80 \times 80 \times 25$ μm^3) together with several small ruby spheres (5-10 μm dia.) [43] are placed in a 240 μm dia. hole drilled through the center of the TaW gasket. The pressure in the gasket hole can be changed at any temperature from 1.6 K to RT. Temperature is measured by calibrated Pt and Ge thermometers thermally anchored to the top diamond. The pressure in the cell can be determined at any temperature below room temperature (RT) to within 0.2 GPa by measuring the pressure-induced shift in the ruby R1 fluorescence line. The pressure is normally measured at temperatures close to the T_c of MgB_2.

The superconducting transition itself is determined inductively to $\pm$ 0.1 K using two balanced primary/secondary coil systems connected to a Stanford Research SR830 digital lock-in amplifier. The ac susceptibility studies were carried out using a 3 G (r.m.s.) magnetic field at 1000 Hz. Over the transition the signal changed by $\sim$ 3 nV with a background noise level of $\sim$ 0.2 nV. Further details of the He-gas and diamond-anvil-cell high-pressure techniques are given elsewhere [44, 45].

3 RESULTS OF EXPERIMENT

3.1 Pressure-Dependent Structural Properties

The simple hexagonal structure of MgB_2 (space group P6/mmm, No. 191) is shown in Fig. 2. The structure contains graphite-like boron layers which are separated by hexagonal close-packed layers of metals. The center of a hexagonal boron ring lies both directly above and below each metal.

The variation of the a and c lattice parameters vs. pressure is shown in Fig. 3. Over the pressure range of this study, the changes are linear and can be expressed as

$$a = a_0[1 - 0.00187(4)P] \text{ and } c = c_0[1 - 0.00307(4)P], \quad (1)$$

where $a_0 = 3.08489(3)$ and $c_0 = 3.52107(5)$ are the zero-pressure lattice parameters and P is the pressure in GPa. Numbers in parenthesis are standard deviations of the last significant digit. The bulk modulus $[V_0(dP/dV)]$ obtained from these measurements is 147.2(7) GPa.

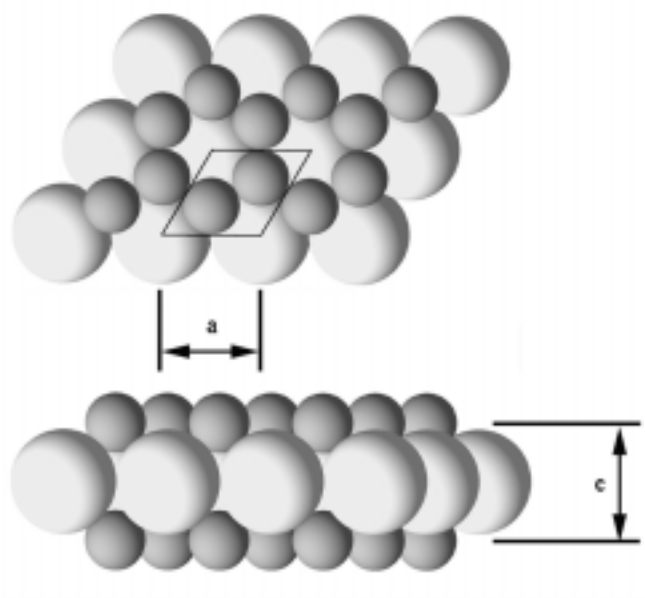

Fig. 2. Crystal structure of MgB_2 [AlB_2-type structure; hexagonal space group P6/mmm, No. 191, with Mg at (0, 0, 0) and B at (1/3, 2/3, 1/2)] viewed along the c axis (top) and perpendicular to an a axis (bottom). Small spheres are B atoms; larger spheres are Mg atoms.

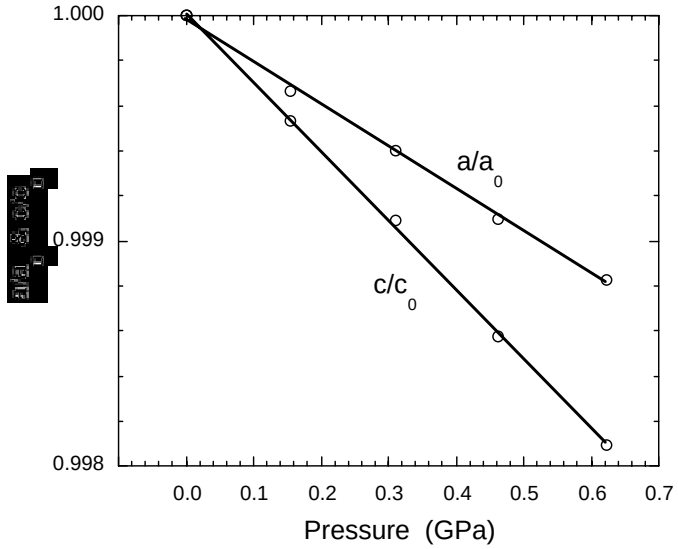

Fig. 3. Normalized a and c lattice parameters vs. pressure at room temperature for MgB_2 based on neutron diffraction measurements from Ref. [34] at five pressures using helium as the pressure transmitting medium. Standard deviations of the individual points are smaller than the symbols. The straight lines are linear least-sqaures fits to the data.

Loa and Syassen [46] used electronic structure calculations vs. cell volume to calculate a bulk modulus of 140.1(6), in good agreement with the experimental result. They also calculated the pressure dependence of the c/a ratio, getting a result in nice agreement with the observed compression anisotropy.

The compression anisotropy, defined as $[(dc/dP)/c_0]/(da/dP)/a_0]$, is 1.64(4). Compression along the c axis is 64% larger than along the a axis, consistent with the comparatively weaker (Mg-B) bonds that determine the c axis length. A similar anisotropy, but not as large, has been reported in the refractory diboride TiB_2 [47], which is of considerable technological interest because of its high elastic moduli, high hardness, and high electric conductivity. By comparison, the compression anisotropy in the layered cuprate $YBa_2Cu_3O_7$ is about a factor of two [38]. Not surprisingly, the intrinsic compression anisotropy is not observed when pressure measurements are made in non-hydrostatic media. Recent room-temperature x-ray diffraction measurements in diamond anvil cells using methanol:ethanol:water [32] and silicone oil [33] as the pressure fluids gave anisotropies of 1.5 and 1.4, respectively. An x-ray diffraction study to much higher pressures using helium as the pressure fluid in a diamond anvil cell [35] gives a compression anisotropy of 1.9(3), in agreement with our result within the error bars.

3.2 Pressure-Dependent Superconducting Properties

3.2.1 $T_c(P)$ Measurements in the He-Gas System

In Fig. 4 we show representative examples of the superconducting transition for MgB_2 in the ac susceptibility at both ambient and high pressure in the He-gas system [48]. 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 $\pm$ 10 mK. Remarkably, close inspection of the data for 0.50 GPa reveals a slight jog 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.

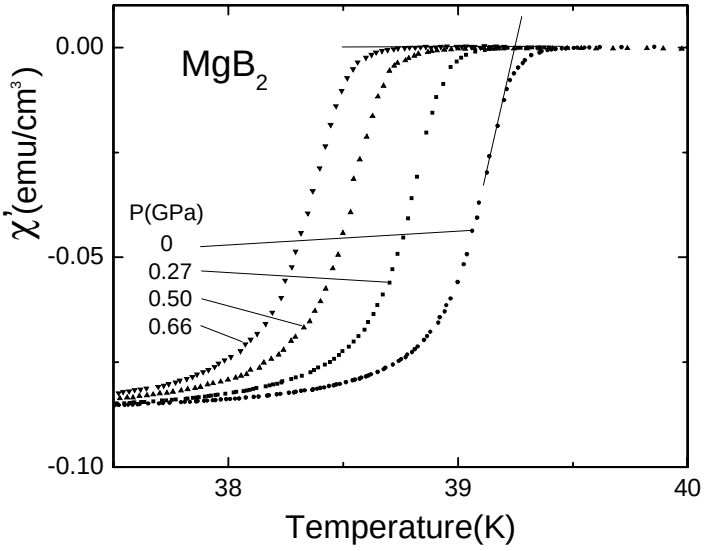

Fig. 4. Real part of the ac susceptibility of MgB_2 versus temperature at ambient and high pressures from Ref. [48]. The applied magnetic field is 0.113 Oe (rms) at 1,023 Hz. Intercept of straight tangent lines defines superconducting onset at ambient pressure $T_c^{onset}(0) \simeq 39.25$ K, with the superconducting midpoint $T_c^{mid}(0) \simeq 39.10$ K. No correction is made for demagnetization effects.

In Fig. 5, the dependence of T_c on pressure is seen to be highly linear $dT_c/dP \simeq -1.11(2)$ K/GPa. Data were obtained following pressure changes at both RT (unprimed data) and low temperature (primed data). The dependence of T_c on pressure thus does not depend on the pressure/temperature history of the sample. Such history effects are rare in superconductors without pressure-induced phase transitions, but do occur in certain high-T_c oxides containing defects with appreciable mobility at RT [49].

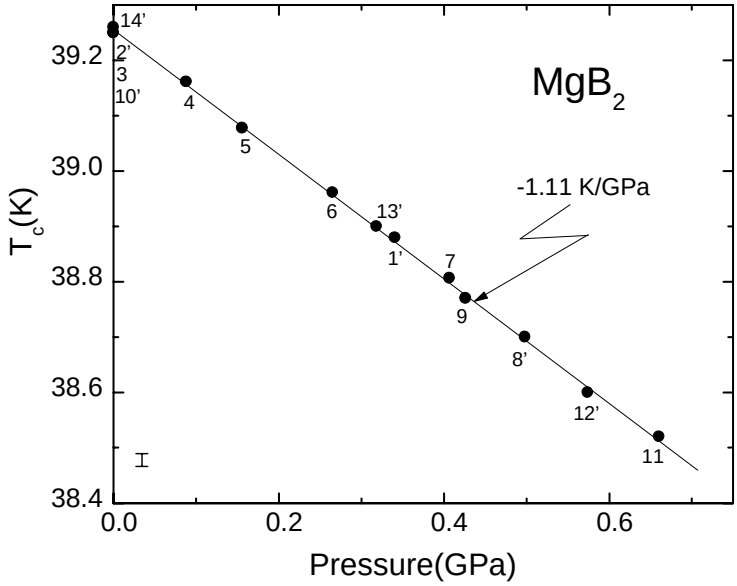

Fig. 5. Superconducting transition temperature onset versus applied pressure from Ref. [48]. Numbers give order of measurement. Data for pts. 2′, 6, 8′, and 11 are shown in Fig. 4. A typical error bar for T_c (± 0.01 K) is given in lower left corner; the error in pressure is less than the symbol size. Pressure was either changed at RT (unprimed numbers) or at low temperatures $\sim$ 60 K (primed numbers).

In selected loosely bound solids with large molecular units, like C_{60}, helium atoms are able to intercalate inside when pressure is applied, diminishing the pressure-induced changes in the sample properties [50]. An analysis of the MgB_2 structure readily reveals that its hexagonal unit cell is tightly packed with insufficient space for helium atoms to readily travel through. To verify that helium does not intercalate inside MgB_2 under pressure, we carried out a parallel experiment to 0.077 GPa with neon gas instead of helium. In analogy with the results on C_{60} [50], the intercalation of the larger neon atoms into MgB_2 would be more difficult than for helium. The fact that the pressure derivative dT_c/dP is the *same* for both helium and neon confirms the absence of intercalation effects in the present experiments.

Since for pressures less than 0.5 GPa the sample is surrounded by fluid helium during the T_c measurement, the measured slope $dT_c/dP \simeq$ -1.11 K/GPa to this pressure gives the true hydrostatic pressure dependence for MgB_2. For $P > 0.5$ GPa the sample is in frozen helium at temperatures near T_c, but, as seen in Fig. 5, no change in the pressure dependence $T_c(P)$ is observed. This is not surprising since solid helium is the softest solid known; in addition, the shear stresses are held to a minimum by the carefully controlled manner [40] in which solid helium is allowed to freeze around the sample.

A similar pressure derivative $dT_c/dP \simeq -1.07$ K/GPa to ours has very recently been obtained by Lorenz *et al.* [36] in He-gas studies to 0.8 GPa on a MgB_2 sample synthesized to stoichiometry with superconducting midpoint at $T_c^{mid}(0) \simeq 39.2$ K. These authors also reexamined in a He-gas system the same sample studied earlier [23] with $T_c^{mid}(0) \simeq 37.5$ K and find $dT_c/dP \simeq -1.45$ K/GPa which they report agrees within experimental error with their previous result $dT_c/dP \simeq -1.6$ K/GPa to 1.8 GPa in a piston-cylinder device with Fluorinert FC77 pressure medium. This appears to imply that the shear stresses from frozen Fluorinert have little effect on the pressure dependence of T_c in the pressure range to 1.8 GPa.

Choi *et al*. [51] have recently carried out resistivity studies to 1.5 GPa pressure in daphne-kerosene pressure medium, obtaining $dT_c/dP \simeq -1.36$ K/GPa. The results of all known $T_c(P)$ measurements on MgB_2 are summarized in the Table.

3.2.2 $T_c(P)$ Measurements in the Diamond-Anvil System

In Fig. 6 we show the dependence of T_c on pressure to 20 GPa for MgB_2 using a diamond-anvil-cell with dense helium pressure medium [45], thus extending the pressure range of the above He-gas studies nearly thirtyfold. T_c is seen to decrease nearly linearly with pressure to 10 GPa, consistent with the rate -1.11 K/GPa (dashed line), but begins to display a positive (upward) curvature at higher pressures. As will be discussed below, this deviation originates from the increasing lattice stiffness of MgB_2 at higher pressure. In these experiments the pressure was always changed at RT, but measured at temperatures near T_c.

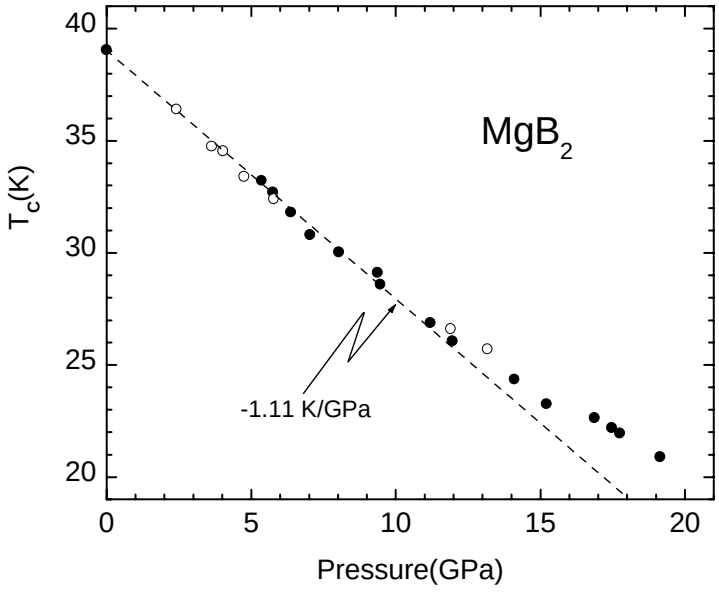

Fig. 6. Superconducting transition temperature midpoint T_c^{mid} versus pressure to 20 GPa from diamond-anvil-cell measurements in Ref. [45]. Data with filled circles (●) taken for monotonically increasing pressure, with open circles (○) for monotonically decreasing pressure. The straight dashed line has slope -1.11 K/GPa.

In Fig. 6 it is seen that the width of the superconducting transition gradually increases from $\sim$ 0.3 K for P ≤ 10 GPa to 0.9 K at 19.2 GPa, increasing somewhat further for the data

with decreasing pressure. This increase in width ΔT_c is seen to be usually accompanied by a slight broadening of the ruby R1 fluorescence line; both broadening effects point to a pressure gradient of approximately $\pm$ 0.3 GPa ($\pm$ 1.5%) at the highest pressures. The magnitude of the shear stresses on the sample would be expected to be larger in the diamond-anvil-cell than in the He-gas experiment since the pressure range is much greater; above 12 GPa helium freezes at RT so the diamonds must push on solid helium to increase the pressure further. In addition, in the diamond-anvil-cell it is not possible to cool slowly through the melting curve of helium with a well-defined temperature gradient. However, the data in Fig. 6 give no clear indication for shear stress effects on T_c at any pressure.

Very recently Tissen *et al.* [52] have carried out ac susceptibility measurements in a diamond-anvil-cell to 28 GPa on a MgB_2 sample with $T_c^{mid}(0) \simeq 37.3$ K at ambient pressure. They find an initial slope $dT_c/dP \simeq -2$ K/GPa, T_c decreasing to 11 K at 20 GPa and 6 K at 28 GPa, a 50% greater decrease than observed by either us (see Fig. 6) or Monteverde *et al.* [25]. They also report that the pressure dependence $T_c(P)$ shows a bump near 9 GPa which they speculate may arise from an electronic Lifshitz transition. We suggest that shear stress effects may also play a role in their measurements. At 20 GPa the width in their superconducting transition has increased by $\sim$ 3 K which would correspond to a pressure gradient of $\sim$ 3.5 GPa, an order of magnitude higher than in our helium-loaded diamond-anvil-cell measurements.

The degree to which shear stresses affect the data of Monteverde *et al.* [25] is unknown. However, since shear stresses are potentially much larger in solid pressure media such as steatite than in frozen fluids such as helium or Fluorinert, it would seem likely that they are responsible for at least part of the widely differing $T_c(P)$ dependences to 25 GPa observed in three of their four experiments.

Table. Summary of available high-pressure $T_c(P)$ data on MgB_2. T_c values are at ambient pressure from superconducting midpoint in ac susceptibility χ_{ac} and electrical resistivity ρ measurements. dT_c/dP is initial pressure derivative. $P^{\max}$(GPa) is the maximum pressure reached in experiment .

T_c(K)	$\frac{dT_c}{dP}$(K/GPa)	$P^{\max}$(GPa)	**measurement**	**pressure medium**	**reference**
39.1	-1.1	19.2	χ_{ac}, ^{11}B isotope	helium	Fig. 6 [45]
39.1	-1.11(2)	0.66	χ_{ac}, ^{11}B isotope	helium	Fig. 5 [48]
39.1	-1.09(4)	0.63	χ_{ac}, ^{11}B isotope	helium	[53]
39.2	-1.11(3)	0.61	χ_{ac}, ^{11}B isotope	helium	[53]
40.5	-1.12(3)	0.64	χ_{ac}, ^{10}B isotope	helium	[53]
39.2	-1.07	0.84	χ_{ac}	helium	[36]
37.4	-1.45	0.84	χ_{ac}	helium	[36]
37.4	-1.6	1.84	χ_{ac}	Fluorinert FC77	[23]
37.3	-2	27.8	χ_{ac}	4:1 meth.-ethanol	[52]
38.2	-1.36	1.46	ρ	daphne-kerosene	[51]
37.5	-1.9	1.35	ρ	Fluorinert FC70	[24]
$\sim$ 35	-0.35 to -0.8	25	ρ	steatite, RT solid	[25]

As discussed in the Introduction, the initial pressure derivative dT_c/dP in the present experiment (-1.11 K/GPa) differs significantly from those (-0.3 to -2.0 K/GPa) obtained by other groups using pressure media which are either solid at RT or readily freeze upon cooling [23–25,51,52]. It is not yet clear whether these widely varying results reflect differences in the make-up of the samples or differing degrees of shear stress exerted on the samples by the various frozen or solid pressure media. An inspection of the data in the Table suggests a possible correlation voiced by Tissen *et al.* [52] that larger values of $|dT_c/dP|$ are associated with lower ambient-pressure values of T_c. However, it is difficult to accurately compare T_c values determined in ac susceptibility and electrical resistivity measurements, the latter usually lying higher; in addition, in the ac susceptibility the value of T_c may depend somewhat on the ac field strength. Further experimentation under carefully controlled conditions is clearly necessary to investigate this possible correlation.

4 DISCUSSION

The present studies of both the superconducting and structural properties of MgB_2 under hydrostatic pressure were carried out on the same high quality MgB_2 sample used in the He-gas measurements to 0.7 GPa. These combined studies thus allow an accurate determination of the change in T_c with unit cell volume V for comparison with theory. The change in T_c with V is given by

$$\frac{d\ln T_c}{d\ln V} = \frac{B}{T_c}\left(\frac{dT_c}{dP}\right) = +4.16(8), \tag{2}$$

using the above values $dT_c/dP \simeq -1.11(2)$ K/GPa, $B = 147.2(7)$ GPa, and $T_c = 39.25$ K. This value of $d\ln T_c/d\ln V$ is somewhat smaller than that (+6.6) obtained by Neaton and Perali [54] in an estimate based on density functional theory.

We will now discuss the implications of this result for the nature of the superconducting state in MgB_2. First consider the McMillan equation [55]

$$T_c \simeq \frac{\langle\omega\rangle}{1.20}\exp\left\{\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right\}, \tag{3}$$

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 [56]. The coupling parameter is defined by $\lambda = N(E_f)\langle I^2\rangle/[M\langle\omega^2\rangle]$, where $N(E_f)$ is the electronic density of states at the Fermi energy, $\langle I^2\rangle$ the average squared electronic matrix element, M the molecular mass, and $\langle\omega^2\rangle$ the average squared phonon frequency. Taking the logarithmic volume derivative of T_c in Eq. (3), we obtain the simple relation

$$\frac{d\ln T_c}{d\ln V} = -\gamma + \Delta\left\{\frac{d\ln\eta}{d\ln V} + 2\gamma\right\}, \tag{4}$$

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 [57], and

$$\Delta \equiv \frac{1.04\lambda[1+0.38\mu^*]}{[\lambda-\mu^*(1+0.62\lambda)]^2}. \tag{5}$$

Eq. (4) has a simple interpretation. The first term on the right, which comes from the prefactor to the exponent in the above McMillan expression for T_c, is usually small relative to the second term, as will be shown 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 second "electronic" term in Eq. (4) involves the logarithmic volume derivative of the Hopfield parameter $\eta \equiv N(E_f)\,\langle I^2 \rangle$, an "atomic" property which can be calculated directly in band-structure theory [55]. In his landmark paper [55], McMillan demonstrated that whereas $N(E_f)$ and $\langle I^2 \rangle$ individually may fluctuate appreciably as one element is substituted for another across a transition-metal alloy series and the d-electron count varies, their product $\eta \equiv N(E_f)\,\langle I^2 \rangle$ changes only gradually, i.e. η is a well behaved "atomic" property. One would thus anticipate that η changes in a relatively well defined manner under pressure, reflecting the character of the electrons near the Fermi energy. An examination of the body of high-pressure data on simple s,p-metal superconductors, in fact, reveals that η normally increases under pressure at a rate given by $d\ln\eta/d\ln V \approx -1$ [58]. For transition-metal (d-electron) superconductors, on the other hand, Hopfield has pointed out that $d\ln\eta/d\ln V \approx -3$ to -4 [57].

The second "lattice" term in the curly brackets in Eq. (4) is positive, typically $2\gamma \approx 3-5$. Since in simple metal superconductors, like Al, In, Sn, and Pb, this positive "lattice" term dominates over the electronic term $d\ln\eta/d\ln V \approx -1$, 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 $d\ln T_c/d\ln V$ is negative and T_c would be expected to *increase* with pressure, as observed, for example, in experiments on V [59] and La [60].

Let us now apply Eq. (4) 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 $d\ln T_c/d\ln V \simeq +7.2$ [42]. We note that this value of $d\ln T_c/d\ln V$ is almost twice as large as that for MgB_2 (see Eq. (2)); this is exactly what is expected from Eq. (4) since Δ increases for *decreasing* values of T_c. Inserting for Sn $T_c(0) \simeq 3.73$ K, $\langle\omega\rangle \simeq 110$ K [61], and $\mu^* = 0.1$ into the above McMillan equation, we obtain $\lambda \simeq 0.69$ from which follows that $\Delta \simeq 2.47$. Inserting the above values into Eq. (4) and setting $d\ln\eta/d\ln V \approx -1$ for simple metals, we can solve Eq. (4) for the Grüneisen parameter to obtain $\gamma \simeq +2.46$, in reasonable agreement with experiment for Sn ($\gamma \approx +2.1$) [42]. Similar results are obtained for other conventional simple metal BCS superconductors.

We now repeat the same calculation with the McMillan equation for MgB_2 using the logarithmically averaged phonon energy from inelastic neutron studies [11] $\langle\omega\rangle = 670$ K, $T_c(0) \simeq 39.25$ K, and $\mu^* = 0.1$, yielding $\lambda \simeq 0.90$ and $\Delta \simeq 1.75$ from Eqs. (3) and (5), respectively. Our estimate of $\lambda \simeq 0.90$ agrees well with those of other authors [16, 18]. Since the pairing electrons in MgB_2 are believed to be s,p in character [15, 17, 18, 54], we set $d\ln\eta/d\ln V \approx -1$, a value close to $d\ln\eta/d\ln V = Bd\ln\eta/dP \approx -0.81$, where $B = 147.2$ GPa from Ref. [34] and $d\ln\eta/dP \approx +0.55$ %/GPa from first-principles electronic structure calculations by Medvedera *et al.* [62]. Inserting the values of $d\ln T_c/d\ln V = +4.16$, $\Delta = 1.75$, and $d\ln\eta/d\ln V = -1$ into Eq. (4), we find $\gamma \simeq 2.36$, in reasonable agreement with the value $\gamma \approx 2.9$ from Raman spectroscopy studies [35] or $\gamma \approx 2.3$ from *ab initio* electronic structure calculations on MgB_2 [63].

In spite of the significant compression anisotropy, electronic structure calculations based on the high-pressure structural data show that the electronic structure does not change much at high pressure [62]; the calculations show that the electric field gradient in MgB_2 is essentially independent of pressure up to 10 GPa. As the electric field gradient is a very sensitive characteristic of the electronic charge distribution, one may conclude that no large changes in

the partial charges of the B $2p$ states and boron electronic structure take place under pressure. Further results from theory support this conclusion. Medvedera *et al.* [62] find the Hopfield parameter for MgB_2 to only depend weakly on pressure $d\ln\eta/dP \approx +0.55$ %/GPa. The change in the electronic density of states $d\ln N(E_f)/dP$ is also estimated to be very small: Loa and Syassen [46] (-0.31 %/GPa), Medvedera *et al.* [62] (-0.51 %/GPa), and Vogt et al. [32] (-0.38 %/GPa). Assuming $B = 147.2$ GPa, one thus obtains $d\ln N(E_f)/d\ln V \simeq$ +0.46, +0.75, and +0.56, respectively. These values are near that (+0.67) expected for a 3D free electron gas. Since $d\ln\eta/dP = d\ln N(E_f)/dP + d\ln\langle I^2\rangle/dP$, these results imply that the average squared electronic matrix element $\langle I^2\rangle$ in MgB_2 increases under pressure at the approximate rate of only +1 %/GPa. The sign and magnitude of the changes in $N(E_f)$ and $\langle I^2\rangle$ under hydrostatic pressure for MgB_2 are comparable to those found for simple s,p-metal superconductors. Larger changes are anticipated if uniaxial pressure is applied [64]. The main reason for the observed decrease of T_c with pressure is not an electronic effect, but a strong pressure enhancement of the phonon frequencies, an effect which has been directly observed in Raman measurements [35].

Taken as a whole, the above results thus give considerable evidence that the superconducting state of MgB_2 is strongly related to that in simple s,p-metal superconductors like Al, Sn, In, and Pb which exhibit BCS phonon-mediated superconductivity. This is not to say that superconductivity in MgB_2 is identical to that in the simple metals. Extensive specific heat [10] and high-resolution photoemission studies [65] on MgB_2 give evidence for a multicomponent superconducting gap.

The above analysis is based on the results of the present high-pressure studies using the He-gas technique to 0.7 GPa . We now consider the diamond-anvil-cell data to 20 GPa in Fig. 6. For comparison to theory it is advantageous to use the Murnaghan equation-of-state to convert pressure to relative volume V/V_0

$$\frac{V(P)}{V_0} = \left[1 + \frac{B'P}{B}\right]^{-1/B'}, \tag{6}$$

where we use the value $B = 147.2$ GPa from Ref. [34] and the canonical value $B' \equiv dB/dP = 4$ supported by a recent calculation [46]. In Fig. 7 we replot the data from Fig. 6 as T_c versus relative volume V/V_0. The maximum pressure applied in the present experiment (19.2 GPa) results in a volume decrease of $\sim 10\%$. Much of the nonlinearity in the T_c versus pressure plot in Fig. 6 appears to disappear when T_c is plotted versus V/V_0.

We now compare the T_c versus V/V_0 dependence in Fig. 7 to the result from the He-gas data which yields the initial volume dependence $d\ln T_c/d\ln V \simeq$ +4.16 given in Eq. (2). If we assume this relation holds at all pressures, then we can integrate it to obtain

$$\frac{T_c}{(39.25\ \mathrm{K})} = \left(\frac{V}{V_0}\right)^{+4.16}, \tag{7}$$

which is plotted as the upper solid line in Fig. 7. This volume dependence must be accurate for small pressures where $V/V_0 \simeq 1$, corresponding to the pressure dependence $dT_c/dP = -1.11$ K/GPa from the He-gas data, but rises well above the experimental data at higher pressures.

Another way to extrapolate the He-gas data to higher pressures is to assume that T_c varies linearly with volume change ΔV, yielding from Eq. (7)

$$\frac{T_c}{39.25\ \mathrm{K}} = \left(\frac{V_0 + \Delta V}{V_0}\right)^{+4.16} \simeq \left(1 + 4.16\frac{\Delta V}{V_0}\right) = \left(-3.16 + 4.16\frac{V}{V_0}\right), \tag{8}$$

which is plotted as the straight dashed line in Fig. 7. As they must, the upper solid and dashed lines agree exactly near $V/V_0 = 1$. The dashed line is seen to lie above the experimental data points at higher pressures and to extrapolate to $T_c = 0$ K for $V/V_0 = 0.76$ which corresponds to an applied pressure of ~ 75 GPa. A least-squares straight line fit through all data in Fig. 7 leads to the estimate that $T_c = 0$ K for $P \approx 60$ GPa.

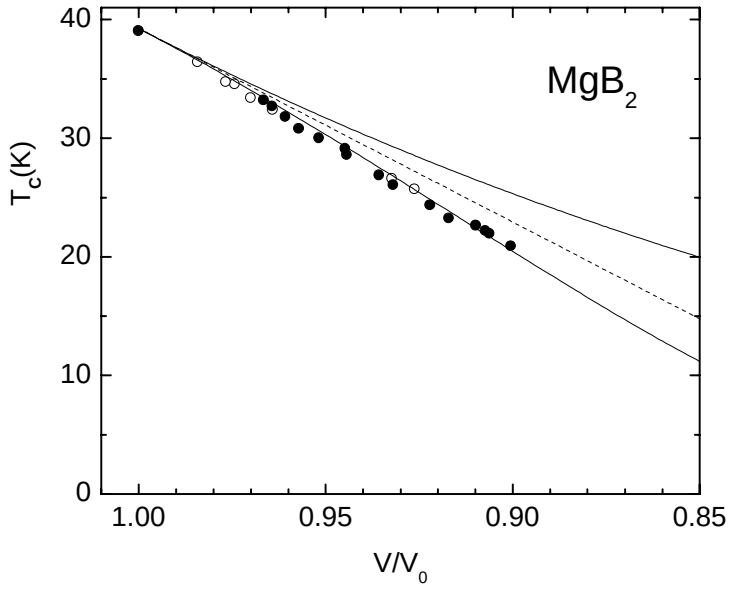

Fig. 7. T_c data from figure 6 plotted versus relative volume V/V_0 (from Ref. [45]). See text for explanation of solid and dashed lines.

It is not surprising that T_c is not a linear function of V/V_0 to very high pressures. In the McMillan formula in Eq. (3) T_c depends exponentially on the solid state parameters and it is the relatively small changes in these parameters which lead to the large change in T_c under pressure see in Figs. 6 and 7. As pointed out by Chen *et al.* [56], a more appropriate method to estimate the dependence of T_c on relative volume V/V_0 would thus be to integrate the volume derivatives of these parameters $\gamma \equiv -d\ln\langle\omega\rangle / d\ln V = +2.36$, $d\ln\lambda/d\ln V = d\ln\eta/d\ln V - d\ln\langle\omega^2\rangle/d\ln V = -1 - 2(-2.36) = +3.72$ to obtain $\langle\omega\rangle = (670\text{ K})(V/V_0)^{-2.36}$ and $\lambda = 0.90(V/V_0)^{3.72}$. Inserting these two volume dependences in the McMillan equation, and assuming $\mu^* = 0.1$ is independent of pressure [56], we obtain the dependence of T_c on relative volume shown as the lower solid line in Fig. 7. The agreement with the experimental data is quite impressive. Note that according to this estimate approximately 50 GPa pressure would be required to drive T_c to below 4 K. A similar calculation was very recently carried out by Chen *et al.* [56] over a much wider pressure range; this paper also contains a detailed discussion of the pressures dependences of η, λ, and μ^*. The good agreement between the experimental data to 20 GPa and the predictions of the McMillan formula using the volume dependences determined from the He-gas high-pressure data to 0.7 GPa lends additional evidence that superconductivity in MgB_2 originates from standard BCS phonon-mediated electron pairing.

In conventional metals, electron-phonon scattering makes the dominant contribution to the temperature-dependent electrical resistivity $\rho(T)$. At sufficiently high temperatures,

Bloch-Grüneisen [66] theory gives a linear dependence on temperature $\rho_{RT} = bT$, where $b \propto r_s^{-2}\Theta_D^{-2}$, r_s is the radius of the Wigner-Seitz sphere, and Θ_D is the Debye temperature. Near RT Choi *et al.* [51] find the electrical resistivity of MgB_2 to increase linearly with temperature. Under pressure these authors find that the RT electrical resistivity decreases under pressure at the rate $d\ln\rho_{RT}/dP \simeq -3$ %/GPa. Using the bulk modulus $B = 147.2$ GPa, this yields $d\ln\rho_{RT}/d\ln V \simeq$ +4.42. Taking the logarithmic volume derivative of the above Bloch-Grüneisen expression and using the free-electron expression for r_s and setting $\gamma = 2.36$ from above, we obtain $d\ln\rho_{RT}/d\ln V = 2\gamma - 2/3 = +4.05$, in surprisingly good agreement with the measured value. It is significant that the same value of the Grüneisen parameter yields the pressure dependence of the electron-phonon interaction which accounts for both $T_c(P)$ and $\rho_{RT}(P)$.

At first glance the present results appear to be inconsistent with the hole superconductivity model of Hirsch and Marsiglio [67, 68] which predicts that T_c should increase with pressure if there is no change in the doping level of holes. Indeed, the pressure-induced change in the concentration of hole-carriers in the boron σ-band is estimated to be extemely small [46,62]. Further experiments, such as high-pressure Hall effect measurements, are necessary to determine what, if any, change in the carrier concentration occurs. The success of the above analysis of the dependence of T_c on pressure gives further evidence that MgB_2 is an extraordinary superconductor which makes the most out of its conventional BCS electron-phonon pairing interaction.

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