Compressibility of the MgB_2 superconductor

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Considerable excitement has been caused recently by the discovery that the binary-boride system with stoichiometry MgB_2 is superconducting at the remarkably high temperature of 39 K [J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature **410**, 63 (2001)]. This potentially opens the way to even higher-T_c values in a new family of superconductors with unexpectedly simple composition and structure. The simplicity in the electronic and crystal structures could allow the understanding of the physics of high-T_c superconductivity without the presence of the multitude of complicated features, associated with the cuprates. Synchrotron x-ray diffraction was used to measure the isothermal compressibility of MgB_2, revealing a stiff tightly packed incompressible solid with only moderate bonding anisotropy between intralayer and interlayer directions. These results, combined with the pressure evolution of the superconducting transition temperature, T_c, establish its relation to the B and Mg bonding distances over a broad range of values.

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MgB_2 adopts a hexagonal crystal structure (AlB_2-type, space group $P6/mmm$)[2] that is analogous to intercalated graphite with all hexagonal prismatic sites of the primitive graphitic structure (found in hexagonal BN) completely filled and resulting in two interleaved B and Mg layers. In addition, allowing for full charge transfer from Mg to the boron two-dimensional (2D) sheets, the latter are themselves isoelectronic with graphite.

Detailed information on the properties of MgB_2 is being, currently, rapidly accumulated. Band structure calculations clearly reveal that, while strong B-B covalent bonding is retained, Mg is ionized, and its two electrons are fully donated to the B-derived conduction band.[3–6] Superconductivity in MgB_2 is then essentially due to the metallic nature of the boron 2D sheets and the presence of strong electron-phonon interactions together with the high-vibrational frequencies of the light B atoms ensure a high-transition temperature.[3] Support for such a phonon-mediated BCS-type mechanism has been provided by measurements of the boron isotope effect ($\Delta T_c = 1.0$ K, isotope exponent $\alpha_B \sim 0.26$).[7] In addition, T_c has been found to decrease with applied pressure at the rate of $-dT_c/dP \sim 1.6$ K/GPa up to 1.84 GPa,[8] again consistent with mediation of the pairing interaction by phonons. An alternative scenario derives from the fact that MgB_2 is hole doped and superconductivity may be understood within a formalism developed for high-T_c cuprate superconductivity.[9] Such a theory predicts a positive-pressure coefficient on T_c as a result of the decreasing intraplane B-B distance with increasing pressure and appears to disagree with the experimental observations. However, the response of the system may be more complex if pressure also affects the charge transfer between the B planes and Mg, and will vary depending on whether the system is in the overdoped or underdoped regime.

Here, we address the problem of the evolution of the structural properties of the MgB_2 superconductor with applied pressure using synchrotron x-ray powder diffraction techniques. We find that MgB_2 remains strictly hexagonal to the highest pressure used. The isothermal interlayer compressibility, $d\ln c/dP$ at zero pressure is only 1.4 times the value of the in-plane compressibility, $d\ln a/dP$, manifesting the anisotropic nature of the crystal structure. Nonetheless, the bonding anisotropy in this material is not as large as other quasi-2D systems like alkali-metal intercalated graphite, and the elastic properties appear only moderately anisotropic. This information is valuable in testing the predictions of competing models for the mechanism of superconductivity. The diffraction experiments in combination with the data on the pressure dependence of T_c permit us to determine its variation over a wide range of unit-cell volume with an initial pressure coefficient, $d\ln T_c/dV = 0.18$ Å^{-3}.

The MgB_2 sample used in this work was prepared, as reported in Ref. 1, by heating a pressed pellet of stoichiometric amounts of Mg and amorphous B for 10 h at 700 °C under an argon pressure of 196 MPa and was superconducting with $T_c = 39$ K. Phase purity was confirmed by powder x-ray diffraction. The high-pressure synchrotron x-ray diffraction experiments at ambient temperature were performed on beamline BL10XU at Spring-8, Japan. MgB_2 was loaded in a diamond anvil cell (DAC), which was used for the high-pressure generation and was equipped with an inconel gasket. The diameter of the top face of the diamond culet was 1 mm, and the sample was introduced in a hole made in the

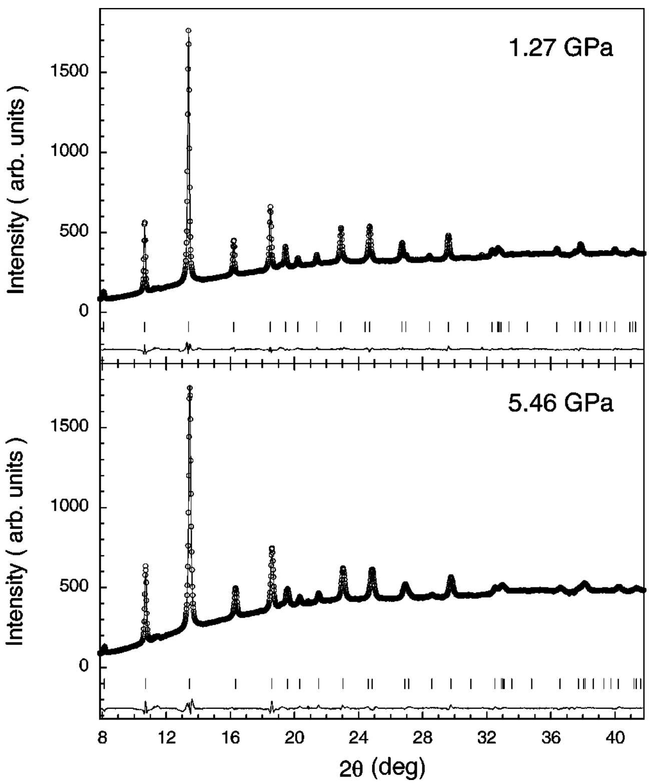

FIG. 1. Final observed (open circles) and calculated (solid line) ambient temperature synchrotron x-ray powder diffraction profiles of MgB_2 at 1.27 and 5.46 GPa in the range of 7°–43° ($\lambda = 0.49556$ Å). The lower lines show the difference profiles and the vertical marks indicate the observed reflections.

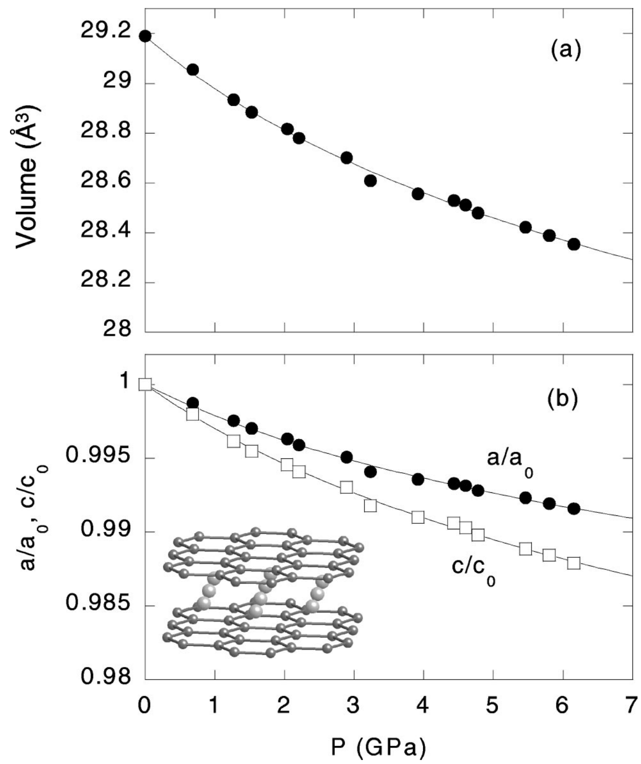

FIG. 2. Pressure dependence of (a) the unit-cell volume, V and (b) the normalized hexagonal lattice constants (a/a_0) and (c/c_0) of MgB_2 at ambient temperature. The lines through the data points are least-squares fits to the Murnaghan equation-of-state [Eq. (1)] in (a) and its variants in (b) (see text). Inset. Schematic diagram of the MgB_2 structure.

gasket 0.2 mm deep and 0.4 mm diameter. Silicone oil loaded in the DAC was used as a pressure medium. Pressure was increased at room temperature and was measured with the ruby-fluorescence method. The diffraction patterns were collected using an image-plate detector ($\lambda = 0.49556$ Å) with 5 min exposure times. Integration of the two-dimensional diffraction images was performed with the local PIP software and data analysis with the Fullprof suite of Rietveld analysis programs.[10]

Synchrotron x-ray powder diffraction profiles of MgB_2 were collected at pressures between ambient and 6.15 GPa. Inspection of the diffraction data indicated that the pattern could be indexed as hexagonal at all pressures. Thus the same structural model (space group $P6/mmm$) was employed in the refinements of all datasets.[11] The Rietveld refinements (2θ range=7–43° proceeded smoothly (Fig. 1), leading to values for the hexagonal lattice constants, $a = 3.0906(2)$ Å and $c = 3.5287(3)$ Å at ambient pressure (agreement factors: $R_{wp} = 3.9\%$, $R_B = 5.9\%$), and $a = 3.0646(1)$ Å and $c = 3.4860(2)$ Å at 6.15 GPa ($R_{wp} = 1.0\%$, $R_B = 7.0\%$)]. Figure 2(a) shows the pressure evolution of the volume of the unit cell of MgB_2 together with a least-squares fit of its ambient-temperature equation-of-state (EOS) to the semiempirical second-order Murnagham EOS:[12]

$$P = (K_0/K_0')[(V_0/V)^{K_0'} - 1], \qquad (1)$$

where K_0 is the atmospheric-pressure isothermal bulk modulus, K_0' is its pressure derivative ($= dK_0/dP$), and V_0 is the unit-cell volume at zero pressure. The fit results in values of $K_0 = 120(5)$ GPa and $K_0' = 36(3)$. The extracted value of the volume compressibility, $d \ln V/dP = 8.3(3) \times 10^{-3}$ GPa^{-1} implies a stiff tightly packed incompressible solid.

The anisotropy in bonding of the MgB_2 structure (Fig. 2 inset) is clearly evident in Fig. 2(b) that displays the variation of the hexagonal lattice constants a and c with pressure. As the applied pressure increases, the (c/a) ratio smoothly decreases (by $\sim 0.4\%$ to 6.15 GPa). We described the pressure dependence of each lattice constant with a variant of Eq. (1), in which K_0 and its pressure derivative, K_0' were substituted by the individual K_x and K_x' $(x = a, c)$ values. The results of these fits are also included in Fig. 2(b) and give $K_a = 410(20)$ GPa, $K_a' = 13(1)$; $K_c = 292(12)$ GPa, $K_c' = 85(7)$. These values clearly reveal the diversity in bonding interactions present, with the solid being least compressible in the basal plane ab, in which the covalent B-B bonds lie [$d \ln a/dP = 0.0024(1)$ GPa^{-1}]. However, the interlayer linear compressibility, $d \ln c/dP = 0.0034(1)$ GPa^{-1} is only 1.4 times larger, implying very stiff Mg-B bonding; significantly, it is considerably smaller than those of the structurally related strongly anisotropic alkali-metal intercalated

TABLE I. Bond distances (Å) for MgB_2 at selected pressures.

Pressure (GPa)	B-B	Mg-B	Mg-Mg
ambient	1.7844(1)	2.5094(1)	3.0906(2)
3.23	1.7738(1)	2.4917(1)	3.0724(1)
6.15	1.7694(1)	2.4837(1)	3.0646(1)

graphite (cf. KC_8, $d \ln c/dP = 0.0206$ GPa^{-1}.[13] Table I summarizes bond-distance information at selected pressures.

The pressure coefficient of T_c in MgB_2 is strongly negative, $-d \ln T_c/dP \sim 0.042$ GPa^{-1}.[8] It straddles the values of conventional noncuprate sp and d superconductors (>0.08 and <0.02 GPa^{-1}, respectively), while it is more than an order of magnitude smaller than those in fulleride superconductors [0.5 GPa^{-1} for K_3C_{60} (Ref. 14) and 1.0 GPa^{-1} for Na_2CsC_{60} (Ref. 15)]. Of course, the relevant comparison must be between the volume coefficients of T_c. Using the measured volume compressibility of MgB_2, we obtain $d(\ln T_c)/dV = 0.18$ $\mathrm{Å}^{-3}$. This is even larger than the ''universal'' value of alkali fullerides [0.07 $\mathrm{Å}^{-3}$ (Ref. 16)] and implies a very sensitive dependence of the superconducting properties to the interatomic distances. The results of converting the $V(P)$ data in Fig. 2(b) to $T_c(V)$ are shown in Fig. 3. Within the BCS formalism for superconductivity, $T_c \propto (\hbar\omega_{ph})\exp[-1/JN(\epsilon_F)]$, where $\hbar\omega_{ph}$ is a phonon energy, $N(\epsilon_F)$ is the density-of-states at the Fermi level, and J is the electron-phonon coupling constant. Given the highly incompressible nature of the MgB_2 solid, it is conceivable that the pressure coefficients of both $\hbar\omega_{ph}$ and J are negligible. Then, to first order, Fig. 3 reflects the modulation of T_c with decreasing $N(\epsilon_F)$, which results from the broadening of the conduction band as the B-B (and the Mg-B) orbital overlap increases with increasing external pressure. Such a situation is reminiscent of the C_{60}-based superconductors and suggests that higher T_c's may be also achieved, for the same band filling, by increasing the size of the unit-cell volume by chemical substitution at the interstitial sites (negative-pressure effect).

In conclusion, synchrotron x-ray powder diffraction at elevated pressures has been used to derive the evolution of the structural properties of the high-T_c MgB_2 superconductor with pressure. In combination with the pressure dependence of T_c, these results provide the detailed dependence of the superconducting properties as both B-B and Mg-B bonding distances decrease and should form a stringent test of competing models for the interpretation of the superconducting pairing mechanism in this material. Detailed band structure calculations should be able to also shed light on the evolution of the charge transfer between Mg and B and decipher the relative importance between the boron layers and the interstitial metal ions to superconductivity.

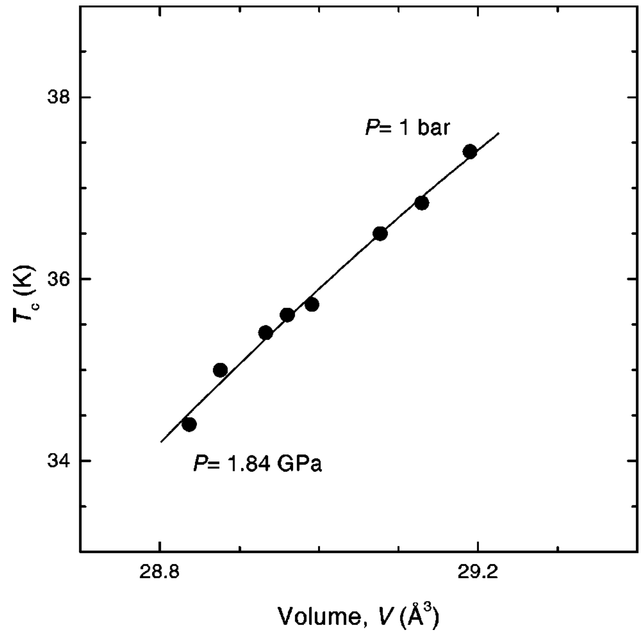

FIG. 3. Superconducting transition temperature, T_c vs unit-cell volume, V for MgB_2. The $V(P)$ data from Fig. 2(a) were converted to $T_c(V)$ by using the $T_c(P)$ data (solid circles) of Ref. 8 to 1.84 GPa. The line through the points is a guide to the eye.

Note added in proof. Recently, we have extended the high-pressure study of MgB_2 to 30 GPa using helium and methanol/ethanol as pressure media. No phase transition was identified to this pressure and the bulk moduli have been extracted from Eq. (1) as $K_0 = 154(8)$ GPa and $K_0' = 4.4(8)$.[17]

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