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LETTER TO THE EDITOR

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Abstract
We present *ab initio* calculations of a set of physical properties for the newly discovered MgB$_2$ superconductor. The zero pressure bulk modulus, the pressure derivative of the bulk modulus and their in- and out-of-plane linear values are evaluated. An analysis of the calculated parameters reveals the diversity in bonding interactions. The diboride is characterized by a moderately sizable anisotropy of compressibilites, which is smaller than for cuprates, but larger than for other related diborides. The anisotropic compression is expected to induce different pressure effects on different phonon modes and also to influence the electronic structure at the Fermi energy.

The newly discovered magnesium diboride has generated considerable interest in the scientific community and instigated vigorous research activities in order to understand the structure, properties and to determine the underlying mechanism of superconductivity in this material (see [1–11]). As a result, various theoretical ideas and experimental data are being accumulated rapidly. The magnesium diboride possesses a hexagonal crystal structure. One thus expects anisotropy in the physical properties of this material. Within the Bardeen–Cooper–Schrieffer (BCS) picture, the reduction of the density of states (DOS) at the Fermi level, due to the contraction of the B–B and Mg–B interatomic distances dominates the hardening of the B phonon frequency that should enhance T_c as external pressure is applied [10]. An and Pickett [11] found that the remarkable superconducting properties require a very specific microscopic cause. The layers of Mg^{2+} ions donate their electrons to the B layer, thus lowering the non-bonding B $\pi(p_z)$ bands relative to the bonding $\sigma(sp_xp_y)$ bands compared to graphite. This causes charge transfer from σ to π bands, which creates holes at the top of the bonding σ bands and provides a high-T_c superconductivity of MgB$_2$. The σ bands, due to their two dimensionality, contribute strongly to the DOS at the Fermi level. The calculated deformation potentials of Γ point phonons identify the B band stretching modes as dominating the electron–phonon coupling [11]. This deformation potential is the largest ever observed in a metal superconductivity driven by the σ band. The idea of hole superconductivity by Hirsch [2] suggests that a decrease in the B–B separation should increase T_c. Although Hirsch has also focused on the hole character of the σ bands, his emphasis is otherwise quite different from that described by An and Pickett [11]. On the other hand, Baskaran [3], based on resonating

valence bands (RVB) theory, suggests that an increase in chemical pressure along the c-axis should decrease T_c and ultimately take MgB_2 to a normal metallic state. Thus it is important to have knowledge of the anisotropy in the mechanical behaviour of this material. Rabindran *et al* [4] noted that there are contradictory experimental results regarding the anisotropy in the elastic properties of MgB_2, ranging from isotropic, moderately isotropic to highly anisotropic. They carried out detailed electronic structure studies on superconducting MgB_2 and related compounds using a full potential linearized augmented plane wave (FPLAPW) method in a scalar-relativistic version without spin–orbit coupling. They found large anisotropy in the elastic properties and polarized dielectric tensor. Loa and Syassen [5], using the FPLAPW calculation, found that MgB_2 is isotropic both electronically and mechanically under pressure. Vogt *et al* [6], based on their experiment and *ab initio* calculations, indicated a nearly isotropic mechanical behaviour under pressure. On the other hand, Jorgensen *et al* [7] observed, from their neutron diffraction measurement, large anisotropy in thermal expansion and compressibility.

We report here the results of different *ab initio* calculations, hitherto not used, for the mechanical behaviour of MgB_2 under pressure. We use a self-consistent-field (SCF) Hartree–Fock linear combination of the atomic orbital computer programme CRYSTAL98 [12], which contains a density functional theory (DFT) option that permits one to solve the Kohn–Sham (KS) equation self-consistently. The basis sets used are 6-21G* and 8-61G for B and Mg, respectively. The exponents of the most diffuse sp and d shells for each atom have been optimized by searching for the minimum crystalline energy. The exchange correction potential proposed by Becke [13] is expanded in an auxiliary basis set of symmetrized atom-centred Gaussian-type functions. The quality of the calculation depends on the density of points with which the Brillouin zone (BZ) is sampled. The integrations over the BZ were performed using the Monkhorst–Pack scheme [14]. To ensure convergence for the BZ integration with accuracy, very tight tolerances were utilized in the evaluation of the infinite Coulomb and exchange series. A dense Gilat net [15] was defined with a total of 793 k-points in the reciprocal space, corresponding to a shrinkage factor of 24.

The total energy E of MgB_2 has been calculated at different primitive cell volumes (V). The results are shown in figure 1(a) as a function of the normalized volume V_n ($=V/V_0$, where V_0 is the equilibrium volume). The energy was minimized as a function of the c/a ratio for selected values of volume. The calculated c/a ratio is plotted as a function of normalized volume in figure 1(b). The zero pressure bulk modulus B_0 and its pressure dependence, B_0' ($=dB_0/dP$) were determined by fitting the Murnaghan equation of state [16]:

$$\Delta E(V) = E - E_0 = B_0 V_0 \left[\frac{V_n}{B_0'} + \frac{1}{1 - B_0'} - \frac{V_n^{1-B_0'}}{B_0'(B_0' - 1)} \right] \tag{1}$$

where E_0 is the equilibrium energy. The pressure (P) versus the primitive-cell volume is obtained through the thermodynamic relationship

$$P = -\frac{dE}{dV} = \frac{B_0}{B_0'}[V_n^{-B_0'} - 1]. \tag{2}$$

The resulting pressure dependence of the normalized primitive-cell volume of MgB_2 is shown in figure 1(c). We then utilize equation (2) and the optimized c/a ratio at each volume to get the pressure dependence of the MgB_2 lattice parameters which are as shown in figure 2. The linear bulk modulus at $P = 0$ along the crystallographic axes a and c (B_{a0} and B_{c0}) and their pressure derivatives are then obtained by fitting equation (2) to points in figure 1(c). The results obtained are shown in table 1.

The variation of the normalized lattice parameters with pressure is shown in figure 2 along with results from [17] for $P = 0$–12 GPa. This clearly shows the anisotropy in the
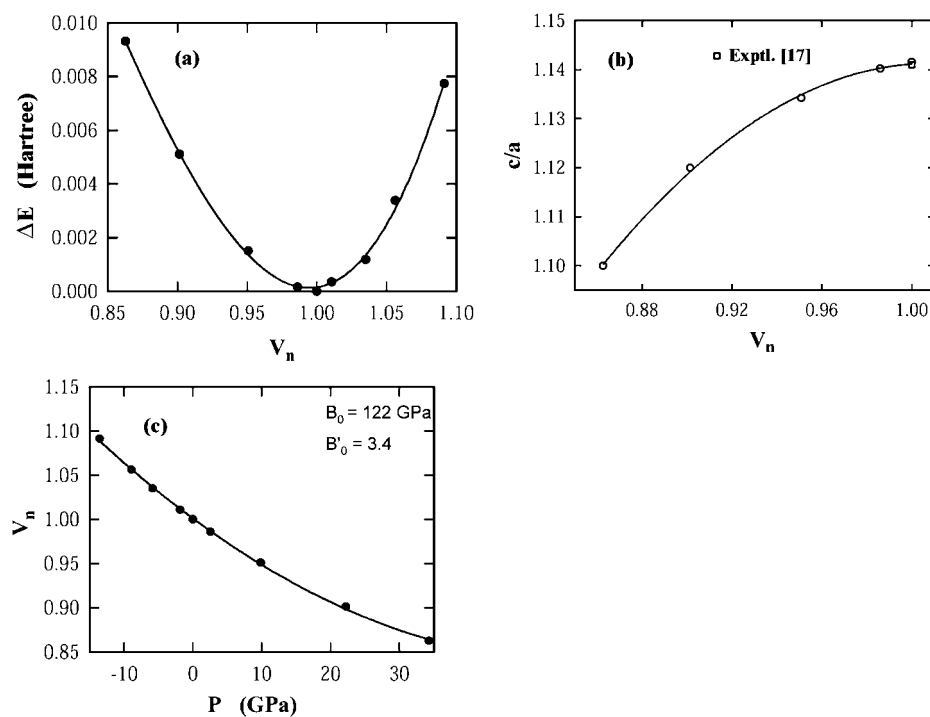
Figure 1. (a) MgB$_2$ energy (ΔE) as a function of the normalized primitive-cell volume V_n ($= V/V_0$). (b) Calculated c/a ratio as a function of normalized volume. The square represents experimental data [17]. (c) V_n as a function of pressure P. The curves through the data the points in (a) and (c) are the fits to the Murnaghan equation of state.

Table 1. The bulk modulus, the pressure derivative of the bulk modulus and their in- and out-of-plane linear values for MgB$_2$.

B_0 (GPa)	B_0'	B_{a0} (GPa)	B_{a0}'	B_{c0} (GPa)	B_{c0}'	Reference
122	3.4	653	15	397	5.5	This letter[a]
155	4.0	625	—	333	—	[17]
120	3.6	410	13	292	8.5	[18]
140	3.46	—	—	—	—	[19]
143	3.93	—	—	—	—	[5]
139; 151	—	—	—	—	—	[6]

[a] For the entire pressure range.

bonding of MgB$_2$. As the pressure increases from 0 to 10 GPa, the c/a ratio decreases by 0.51%. Compression along the c-axis is larger than along the a-axis, which is consistent with the comparatively weaker Mg–B bonds that determine the c-axis length. The result is in line with the measurements at room temperature [7], but has a larger magnitude. A similar but smaller anisotropy has been seen for TiB$_2$ [20]. The layered cuprates show much larger ($\sim$a factor of two) compression anisotropy [21]. The fitted values for B_{a0}, B_{a0}', B_{c0}, B_{c0}' clearly reveal the diversity in the bonding interactions which are present. MgB$_2$ is less compressible in the basal plane, in which the covalent B–B bonds lie. The interlayer linear compressibility, $\mathrm{d}\ln c/\mathrm{d}P = 0.002\,04$ GPa^{-1} is $\sim$1.4 times larger than the in-plane value ($\mathrm{d}\ln a/\mathrm{d}P = 0.0015$ GPa^{-1}). It is worth noting that the structurally related alkali-metal
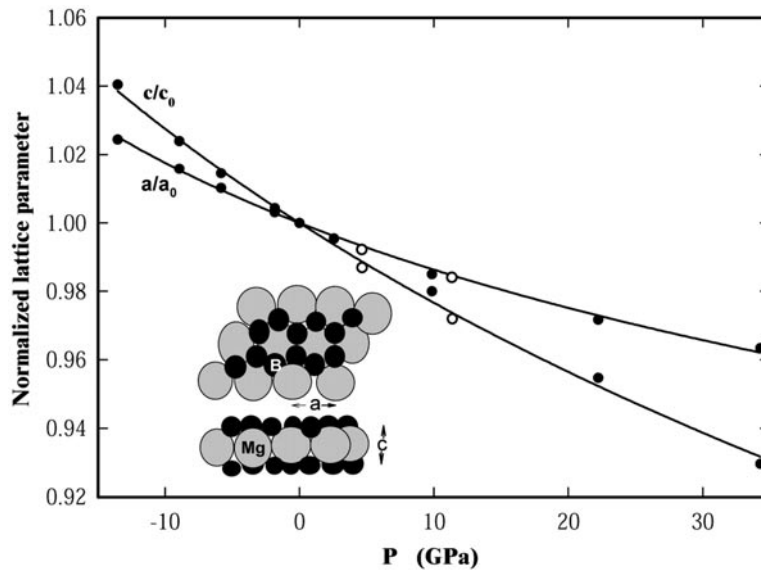
Figure 2. Pressure dependence of the normalized lattice parameters of MgB_2. The full curves through the data points are the fits to the Murnaghan equation of state. The open circles correspond to measured values [17] for $P = 0$–12 GPa. The inset shows a schematic diagram of the MgB_2 structure with lattice constants a and c.

intercalated graphite is strongly anisotropic (see [18]) with interlayer compressibility about ten times larger than the corresponding value in MgB_2.

For solids with isotropic compression, the mode Grüneisen parameter γ of zone-centre phonons is ~ 1. Loa and Syassen [5] assumed this to be 1 while estimating $d \ln T_c/dP$ using McMillan's formula for T_c. In doing so they had to choose an exceptionally small $\mu^* = 0.04$ in order to reproduce the measured T_c. In fact the expression for $d \ln T_c/dP$ contains λ (electron–phonon coupling), the pressure dependence of the DOS $d \ln N(0)/dP$ and $\gamma = B_0 \, d \ln \omega/dP$. Apart from other reasons, a smaller γ would require a smaller μ^*. Recently, Goncharov *et al* [17] determined γ to be 2.9 ± 0.3. Utilizing $\lambda = 0.9$ [9], $d \ln N(0)/dP = -0.004$ GPa^{-1} [6], $\mu^* = 0.1$, and the experimental value of $dT_c/dP = -1.9$ K GPa^{-1} [10], we estimate $\gamma \sim 1.88$–2.35 with $B_0 = 120$–150 GPa. If we ignore the pressure dependence of the DOS then these values become 2.21 and 2.77, respectively. Thus we find γ to be substantially larger than 1, which is as expected for a phonon in a compound with covalent bonding like graphite. For iron with partial metallic bonding $\gamma = 1.7$ [22]. Thus, for MgB_2 we should not expect γ to be ~ 1 as has been assumed in [5]. It is to be noted that a larger γ is usually associated with enhanced anharmonicity of the particular normal mode of vibration, and is broadly consistent with the theoretical prediction for the E_{2g} in-plane B stretching mode [17].

The volume coefficient of T_c, $d \ln T_c/dV$, is an important parameter which implies the sensitivity of superconducting properties to the interatomic distances. Using our volume compressibility ($d \ln V/dP$), we obtain $d \ln T_c/dV = 0.3$ Å^{-3} for MgB_2, a value comparable to that found by Saito *et al* [10], but significantly larger than those found in fulleride superconductors (~ 0.07 Å^{-3}).

Finally, the MgB_2 is characterized by a moderately large anisotropy of compressibility. This is smaller than those of the cuprates [21] but larger than other related diborides. A fortunate combination of strong bonding, dominant phonon frequency and reasonable DOS at

the Fermi level is now believed [6, 8] to lead to the observed T_c of MgB$_2$. It is in this respect that the pressure effect on phonon modes is relevant in this particular diboride. The markedly anisotropic compression behaviour of MgB$_2$ may induce different pressure effects on different phonon modes and is also more likely to influence the electronic structure at the Fermi energy than when compression is isotropic because B–B and Mg–B distances change at different rates. In other words, the pressure can influence the electronic band in different directions of the BZ in an unusually different manner [4] and hence the physical properties.

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