Calculated elastic and electronic properties of MgB$_2$ at high pressures

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Received February 26, 2001; accepted March 2, 2001 by M. Cardona

Solid State Commun., in press

Abstract

The effect of high pressure on structural and electronic properties of the novel superconductor MgB$_2$ has been calculated using the full-potential linearized augmented-plane-wave method. Despite the layered crystal structure of MgB$_2$ nearly isotropic compression (bulk modulus $B_0 = 140.1(6)$ GPa) is found with only a 1.2% decrease of the $c/a$ ratio at 10 GPa. The effect of pressure on the critical temperature has been estimated on the basis of BCS theory and good agreement with experimental data is found. Our results suggest that it is a combination of increasing phonon frequency and decreasing electronic density of states at the Fermi level which leads to the observed decrease of the critical temperature under pressure.

Key words: A. Superconductors; D. Crystal binding and equation of state; D. Electronic band structure; A. Metals

PACS: 74.62.Fj; 74.25.Ld; 74.25.Jb; 74.62.-c

A recent report of Nagamatsu et al. [1] on superconductivity in MgB$_2$ with a relatively high critical temperature of $T_c = 39$ K has raised great interest in this compound. At ambient conditions MgB$_2$ has a layered hexagonal crystal structure of the AlB$_2$ type (space group $P6/mmm$, $Z = 1$) [2] and shows metallic conductivity [3,4]. Ab initio calculations of the electronic properties [5–7] indicate the coexistence of strong covalent bonding within the honeycomb B layers and metallic bonding between the Mg and B layers. On the basis of BCS theory, the high critical temperature was attributed to a fortunate combination of strong bonding, ‘reasonable’ electronic density of states at the Fermi level, and high phonon frequencies [6]. This view of phonon-mediated superconductivity is supported by the observation of a sizable boron isotope effect with $\Delta T_c = +1.0$ K for substitution of $^{11}$B by $^{10}$B [8]. The effect of high pressure on $T_c$ was studied by Lorenz et al. [9] and Monteverde et al. [10].
Both groups observed a decrease of $T_c$ with increasing pressure. Hirsch, on the other hand, predicted on the basis of his theory of ‘hole superconductivity’ an increase of $T_c$ provided that the intralayer B–B distances decrease and that no charge transfer between the Mg and B layers occurs [11].

Motivated by the experimental high-pressure study of MgB$_2$ and failure of the theoretical prediction we have calculated the effect of high pressure on structural and electronic properties of MgB$_2$ using the full-potential linearized augmented-plane-wave method (FPLAPW). Total-energy calculations as a function of unit cell volume with optimized $c/a$ lattice parameter ratios yield the equation of state. Despite the layered crystal structure we find nearly isotropic compression. We furthermore estimated the pressure dependence of the transition temperature $T_c$. Based on BCS theory with some simplifying assumptions we find good agreement with the experiment. Our results suggest that it is a combination of increasing phonon frequency and decreasing electronic density of states at the Fermi level which leads to the observed decrease of the critical temperature under pressure.

We have used the first-principles FPLAPW method as implemented in the WIEN97 code [12]. For the exchange-correlation potential we employed the generalized gradient approximation of Ref. [13]. Scalar-relativistic corrections were included. Atomic spheres were kept constant in size for the total energy calculations [14] whereas they were scaled with the unit cell volume for the DOS calculations [15]. For $k$-point sampling 296 points were used in the irreducible wedge of the Brillouin zone (4536 in total). The Mg 2$s$ and 2$p$ states were treated as band states using the local orbital extension of the LAPW method [12,16].

The total energy of MgB$_2$ was calculated for reduced volumes $V/V_0$ in the range 0.85–1.00 [Fig. 1(a)] (the subscript ‘0’ marks zero-pressure parameters throughout this paper). At each volume, the $c/a$ lattice parameter ratio was optimized [Fig. 1(b)]. An energy-vs-volume relation, obtained from integrating the Birch $P(V)$ function [17], was fitted to the total-energy data to obtain the bulk modulus $B_0 = 140.1(6)$ GPa, its pressure derivative at zero pressure $B' = 3.93(14)$, and the unit cell volume $V_0 = 28.888(11)$ Å$^3$ (the errors denote the standard error of the least-squares fit). The corresponding pressure-vs-volume relation is shown in Fig. 1(b). We did not consider possible structural phase transitions.

The calculated zero-pressure, zero-temperature $V_0 = 28.888(11)$ Å$^3$ and $c/a = 1.1468(3)$ are in good agreement with the experimental room-temperature data $V_0 = 29.00$ Å$^3$ and $c/a = 1.142$ [2,9]. A rather isotropic compressibility is indicated by the small changes of the $c/a$ ratio. This shows that the intra- and the interlayer bonding are of similar strength and that MgB$_2$, in this respect, is distinct from layered compounds such as (intercalated) graphite...
where the sheets are only weekly bonded. This view is in agreement with the finding of Belashchenko et al. that the structure of MgB$_2$ is characterized by the coexistence of strong covalent bonding within the B layers and delocalized, ‘metallic-type’ bonding between the Mg and B sheets [5].

In the context of bonding properties it is also of interest to examine the changes of the charge distribution at high pressures. Figure 2(a) shows the charge density distribution in the (110) plane of MgB$_2$. Mg nuclei are located at the corners of the map and B nuclei at the (1/3, 1/2) and (2/3, 1/2) positions, all of them in the plane of the figure. One can clearly see the directional, covalent B–B bonds. In addition there is a significant amount of charge in the interstitial region giving rise to metallic-type bonding between the Mg and B sheets. The charge distribution and bonding properties of MgB$_2$ at ambient pressure are discussed in detail in Refs. [5–7]. Figure 2(b) shows the difference between the charge densities at 20 and 0 GPa. The 20-GPa charge density has been scaled by $V/V_0$ in order to take into account the change of volume. There occurs a transfer of charge from the region between the B ions into the nearby interstitial region. This can be regarded as a transfer from $\sigma$ to $\pi$ type bonds which has been termed ‘hole doping’ [18]. This trend is also found in the decomposition of the charge in the boron atomic sphere. These changes are, however, rather moderate so that the main characteristics of the bonding in MgB$_2$ remain unchanged at pressures up to 20 GPa.

In the framework of BCS theory, the transition temperature of a monoatomic superconductor can be expressed according to the McMillan formula [19,6] as

$$T_c = \frac{\langle \omega_{\log} \rangle}{1.20} \exp \left[ -1.02 \frac{1 + \lambda}{\lambda - \mu^* - \mu^* \lambda} \right].$$

Here, $\lambda = N(0) \langle I^2 \rangle / M \langle \omega^2 \rangle$ denotes the electron–phonon coupling constant, $\mu^*$ the Coulomb pseudopotential, $N(0)$ the electronic density of states at the Fermi level, $\langle I^2 \rangle$ the averaged electron–ion matrix element, $M$ the atomic mass, $\langle \omega^2 \rangle$ the averaged square of a characteristic phonon frequency, and $\langle \omega_{\log} \rangle$ the logarithmically averaged phonon frequency.

In order to estimate the pressure dependence of $T_c$, we have calculated the electronic density of states for pressures up to 20 GPa. Figure 3(a) shows the total DOS and the decomposition into partial densities near the Fermi energy $E_F$. Qualitatively, the main effect of pressure is to spread the DOS over an increasing range of energies. The total density of states $N(0)$ at the Fermi level decreases continuously under pressure [Fig. 3(b)]. This reduction is linear in pressure at a rate of $d \ln N(0)/dP = -0.31\%/\text{GPa}$. The decomposition into partial densities crucially depends on the choice of atomic spheres. The apparent redistribution of B and Mg partial densities into the interstitial DOS probably results from the slight decrease of the $c/a$ ratio and the characteristics
of the charge distribution of MgB$_2$ [5–7].

The pressure dependence of the frequency $\omega$ of a quasi-harmonic phonon can be expressed via the mode Grüneisen parameter $\gamma$ as

$$\frac{d \ln \omega}{dP} = \frac{\gamma}{B_0} . \quad (2)$$

For solids with isotropic compression, the mode Grüneisen parameters of zone-center phonons are typically close to 1. Kong et al. as well as An and Picket concluded that in MgB$_2$ only the branch of the in-plane $E_{2g}$ phonon of B ions exhibits a large electron-phonon coupling [20,18]. The mode Grüneisen parameter of the corresponding phonon of graphite was experimentally determined as $\bar{\gamma} = 1.06$ where the anisotropic compressibility of graphite was taken into account [21]. We therefore assume that in MgB$_2$ phonons with a frequency $\omega$ close to that of the $E_{2g}$ mode ($\langle \omega_{\log} \rangle \approx 500 \text{ cm}^{-1}$[6,20]) are responsible for the superconductivity and have $\gamma = 1$. Using the calculated $B_0$ of MgB$_2$ we obtain the estimate $d \ln \omega / dP \approx 1/B_0 = +0.71\%$/GPa.

We now assume the Coulomb pseudopotential $\mu^*$ and the electron-ion matrix element $I$ to be constant in first approximation. With the calculated pressure dependences of the density of states at the Fermi level and the phonon frequency we estimate the pressure dependence of the electron-phonon coupling constant $d \ln \lambda / dP \approx -1.7\%$/GPa. Expressing the pressure dependence of $T_c$ as

$$\frac{d \ln T_c}{dP} = \frac{\partial \ln T_c}{\partial \lambda} \frac{d \lambda}{dP} + \frac{\partial \ln T_c}{\partial \langle \omega_{\log} \rangle} \frac{d \langle \omega_{\log} \rangle}{dP} \quad (3)$$

and using Eqs. (1) and (2) gives

$$\frac{d \ln T_c}{dP} \bigg|_{P=0} = \frac{1.02 \lambda}{(\lambda - \mu^* - \mu^* \lambda)^2} \frac{d \ln \lambda}{dP} \bigg|_{P=0} + \frac{d \ln \langle \omega_{\log} \rangle}{dP} \bigg|_{P=0} \quad (4)$$

$$= \alpha \left[ \frac{d \ln N(0)}{dP} - \frac{d \ln \omega^2}{dP} \right] + \frac{d \ln \langle \omega_{\log} \rangle}{dP} \bigg|_{P=0} \quad (5)$$

$$\approx \alpha \left[ \frac{d \ln N(0)}{dP} - 2 \frac{d \ln \omega}{dP} \right] + \frac{d \ln \omega}{dP} \bigg|_{P=0} \quad (6)$$

$$\approx \alpha \frac{d \ln N(0)}{dP} + (1 - 2\alpha) \frac{\gamma}{B_0} \bigg|_{P=0} . \quad (7)$$

The first term of the r.h.s. of Eq. (7) expresses the effect of a change of $N(0)$ on $T_c$, the second one that of the change of the phonon frequency. For any combination of the parameters $\lambda$ and $\mu^*$ in the relevant ranges $\lambda = 0.1–2.0$ and $\mu^* = 0–0.2$ an increasing phonon frequency alone would result in a decrease of $T_c$ ($\alpha > 1/2$). The electron-phonon coupling constant of MgB$_2$ at ambient
pressure was calculated in Ref. [20] as $\lambda = 0.65$ and estimated in Ref. [6] as $\lambda \approx 0.7$. With $\lambda = 0.7$ and a typical value of $\mu^* = 0.1$ we obtain $\frac{d \ln T_c}{d P} \approx -3.6\%$/GPa. However, this set of parameters and $\langle \omega_{\log} \rangle \approx 500$ cm$^{-1}$ [6,20] underestimates $T_c = 23$ K. If we choose an exceptionally small $\mu^* = 0.04$ in order to reproduce the measured $T_c$ we obtain a smaller $\frac{d \ln T_c}{d P} \approx -2.3\%$/GPa. Both of these values fall in the range marked by the experimental results of $-4.1\%$/GPa [9] and $-1.8\%$/GPa [10]. Under the assumptions made, i.e., that the pressure dependences of $I$ and $\mu^*$ are negligible, it is not sufficient to consider only the change of density of states $N(0)$. It would reduce the estimated pressure dependences of $T_c$ by a factor of $\sim 4$ making them at least a factor of 2 smaller than the smallest experimental value. Thus, the increase of the characteristic phonon frequency appears to be the dominant contribution to the decrease of $T_c$ under pressure.

The implications of our calculations are threefold. Firstly, the results regarding the elastic properties show that the combination of covalent bonding within the B layers and metallic bonding between the Mg and B sheets is quite well-balanced in terms of compressibility. Consequently, the hydrostatic compression is rather isotropic despite the layered crystal structure of MgB$_2$. Secondly, Kortus et al. concluded that the high critical temperature of MgB$_2$ can be explained in the framework of BCS theory [6]. The agreement of our estimate of the pressure dependence of $T_c$ with experimental results supports this view. Thirdly, our results suggest that it is the combination of increasing phonon frequency and decreasing electronic density of states at the Fermi level which leads to the observed decrease of the critical temperature under pressure. Here, the phonon contribution appears to be the dominant one.
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Fig. 1. (a) Total energy of MgB$_2$ as a function of reduced volume (symbols). The solid line represents a fit of a Birch-type $E(V)$ relation to the data. (b) Calculated pressure (solid line) and optimized $c/a$ ratio (symbols) as a function of reduced volume. The dashed line represents a quadratic fit to the $c/a$ data [22]. The upper axes show the unit cell volume.
Fig. 2. (a) Charge density distribution of MgB$_2$ in the (110) plane with contour lines at intervals of 0.05 $e/\text{Å}^3$. (b) Change of the charge density distribution $\rho$ at 20 GPa compared to 0 GPa ($\rho_{20}V_{20}/V_0 - \rho_0$; the 20-GPa charge density has been scaled by $V_{20}/V_0$ to take into account the change of volume). Contour lines are at intervals of 0.005 $e/\text{Å}^3$. 
Fig. 3. (a) Total and partial electronic densities of states near the Fermi level of MgB$_2$ at pressures of 0 GPa, 10 GPa ($V/V_0 = 0.939$), and 20 GPa ($V/V_0 = 0.892$) (dotted, dashed and solid lines, respectively). The inset shows the total DOS over a wider energy range. (b) Total and partial densities of state at the Fermi level as a function of pressure, normalized to their respective zero-pressure values.