Superconductivity of MgB_2 under ultrahigh pressure: A first-principles study

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(Received 6 February 2009; published 18 September 2009)

We report a first-principles investigation of the band structures, lattice dynamics and electron-phonon coupling of MgB_2 under ultrahigh pressure within the framework of density-functional theory. Reliable lattice parameters at ultrahigh-pressure regime are derived from full *ab inito* structural optimization. Our electron-phonon coupling results show that the superconducting T_c decreases monotonically to zero with increasing pressure up to 200 GPa. The reduced density of states of B $p_{x,y}$ at Fermi level and the enhanced frequency of E_{2g} phonon mode are suggested to be the main causes for the monotonically decreased T_c.

DOI: 10.1103/PhysRevB.80.092505 PACS number(s): 74.70.Ad, 62.50.−p, 74.25.Kc

The discovery of superconductivity in MgB_2 (Ref. 1) has stimulated worldwide excitement since the superconducting transition temperature (T_c=39 K) exceeds by almost two times of the record values for conventional simple compounds. It is well known that pressure could effectively shorten the interatomic distance of materials, and thus significantly alter their electronic bonding states to modify the physical properties. Several high-pressure experiments on MgB_2 (Refs. 2–9) are thus carried out to understand the pressure effects on T_c and revealed a continuous T_c reduction at a rate from −0.8 to −2.0 K/GPa up to 35 GPa.[7] Yet beyond 35 GPa no experimental T_c data are available, and only a few theoretical explorations have been attempted as reported in the literature.[9–13] Among them, Shao *et al.*[10] and Singh[13] studied the electron-phonon coupling (EPC) of MgB_2 under ultrahigh pressure. They both predicted that T_c vanishes at 100 GPa. Intriguingly, Singh[13] further reported that T_c reappears at 100 GPa and increases up to 12 K at 150 GPa. However, instead of using the state-of-art *ab initio* structural optimization technique, Singh[13] adopted the pressure-dependent lattice parameters derived from a shell-model (SM) method by Shao *et al.*[10] Within this model, the short-range interaction forces are presented by a Buckingham potential which is obtained by the empirical method (the "relaxed" fitting approach). In MgB_2, since the experimental lattice data is only available up to 40 GPa, an extensive extrapolation in the shell-model calculation to ultrahigh pressure (e.g., 150 GPa) is necessary to obtain the theoretical lattice parameters. Therefore, a fitting model potential[10] might not be suitable for the description of lattice behavior under ultrahigh pressure by seeing that the applied theoretical pressures are well beyond the experimental data. Indeed, as we will show later, the resulting lattice parameters through the full *ab initio* structural optimizations adopted by this work are more reliable and have significant deviation with the shell-model data.[10] Since the structural data is the basis for the correct description of physical properties of any materials, it is necessary to re-exam the superconducting behavior of MgB_2 at ultrahigh pressure based on the *ab initio* lattice parameters. Moreover, in our previous work,[14] we have predicted that a pressure-induced phase transition from ambient pressure AlB_2-type hexagonal structure to high-pressure orthorhombic KHg_2-type polymorph in MgB_2 occurs at 190 GPa. Thus, the extensive EPC calculation of MgB_2 within AlB_2-type structure is only performed up to 200 GPa based on the linear-response theory. We have then solved the isotropic Eliashberg gap equation to obtain T_c of MgB_2 as a function of pressure. Our results show that T_c decreases monotonically to zero with pressure up to the highest pressure (200 GPa). The decreased T_c is attributed to the reduced density of states of B $p_{x,y}$ at Fermi level and the enhanced frequency of E_{2g} phonon mode.

Before describing our results in details, we provide the computational details of our calculations. The geometrical optimization, phonon dispersion, electronic structure and superconducting properties were calculated using the density-functional theory (DFT) (Ref. 15) by the Quantum ESPRESSO package.[16] The Perdew-Wang generalized gradient approximation (GGA-PW91) (Ref. 17) for the exchange-correlation functional is employed. Vanderbilt ultrasoft pseudopotentials (PPs) (Ref. 18) are generated for Mg and B with the valence configuration of $2p^6 3s^2$ and $2s^2 2p^1$, respectively. Convergence tests gave the choice of kinetic-energy cutoffs as 50 Ry (680 eV) and $8\times8\times6$ Monkhorst-Pack (MP) (Ref. 19) grids of k-point sampling for the electronic Brillouin zone (BZ) integration. The electronic densities of states (DOS) was calculated on a much denser $20\times20\times18$ grid in the reciprocal space. Phonon frequencies were calculated based on the density function linear-response method.[20,21] A $5\times5\times4$ q mesh in the first BZ was used for the phonon-dispersion curve calculations. A MP grid of $15\times15\times12$ was used to ensure k-point sampling convergence with Gaussians of width 0.03 Ry, which approximates the zero-width limits in the calculations of EPC parameter λ. In addition, in order to double check the optimized lattice constants under pressure, the structure relaxations were performed using the all-electron projected augmented-wave (PAW) (Refs. 22 and 23) method, which was adopted with the choices of $1s^2$ cores both for Mg and B atoms, as implemented in the Vienna *ab initio* simulation package code.[24] The plane-wave kinetic-energy cutoff of 400 eV and a $12\times12\times10$ MP grid shown to give excellent convergence of the total energies and structural parameters.

We have fully optimized the structural parameters of AlB_2-type MgB_2 with increasing pressure by simultaneously varying the cell volume and the cell parameters. The theoretical equilibrium volume and equation of states of the MgB_2 studied here were determined by fitting the total energies as a function of volume to the Murnahan equation of states. The calculated equilibrium volume (V_0), equilibrium

TABLE I. Calculated equilibrium volume (V_0), equilibrium lattice parameters (a_0 and c_0), bulk modulus (B_0), and the pressure derivative (B_0') for MgB_2 at zero pressure. The experimental result (Ref. 7) through the fitting of equation of states is also shown for comparison.

	V_0 (Å^3)	a_0 (Å)	c_0 (Å)	B_0 (GPa)	B_0'
Our work	28.99	3.08	3.53	152	4.03
Expt.	29.00[a]	3.09[a]	3.53[a]	150(5)[a]	4.0(3)[a]

[a]Reference 7.

lattice parameters, bulk modulus (B_0), and the pressure derivative (B_0') within PP methods together with the experimental data[7] are listed in Table I. It is clear that the theoretical V_0, B_0, and B_0' are in excellent agreement with the experimental data. This lends a strong support on the validity of our theoretical model. The resulting lattice parameters a and c are shown in Fig. 1. It is found that the lattice parameters below 40 GPa are in excellent agreement with experimental data[7] and the shell-model results.[10] However, remarkable discrepancies between *ab initio* and shell-model results are revealed above 40 GPa. This discrepancy is ascribed to the failure of the "fitting" shell model at higher pressure as supported by the further enthalpy calculations plotted in the inset of Fig. 1(a). It is found that the lattice enthalpies with the choices of our structural parameters are significantly lower than those using the lattice data in Ref. 10 beyond 40 GPa (e.g., at 50 GPa it is ~15 meV/f.u. lower, here f.u. is a short abbreviation of formula unit). To double check our *ab initio* lattice data, we have also adopted PAW method to repeat the structural optimization. It appears that the two different *ab initio* calculations (Fig. 1) gave nearly identical lattice data to support the validity of our results.

Now with the *ab initio* structural data, we turn to discuss the electronic, phononic and superconducting properties of

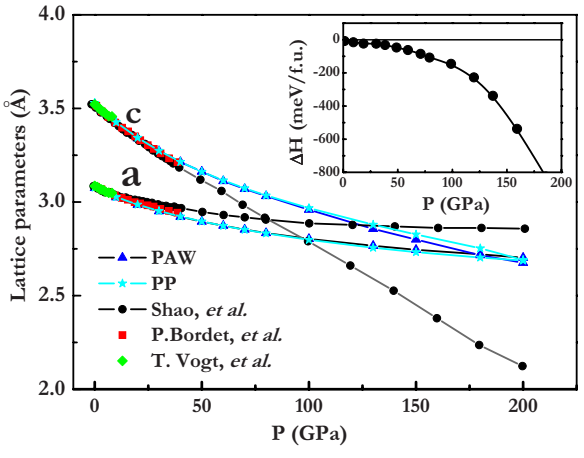

FIG. 1. (Color online) (a) Main figure: Calculated lattice parameters with pressure for MgB_2 using *ab initio* PAW and PP methods to compare with SM (Ref. 10, Shao *et al.*) and experimental data (Ref. 7, P. Bordet *et al.* and Ref. 9, T. Vogt *et al.*). Inset: enthalpies (relative to those with the lattice data in Ref. 10) calculated with our lattice data by using PP method.

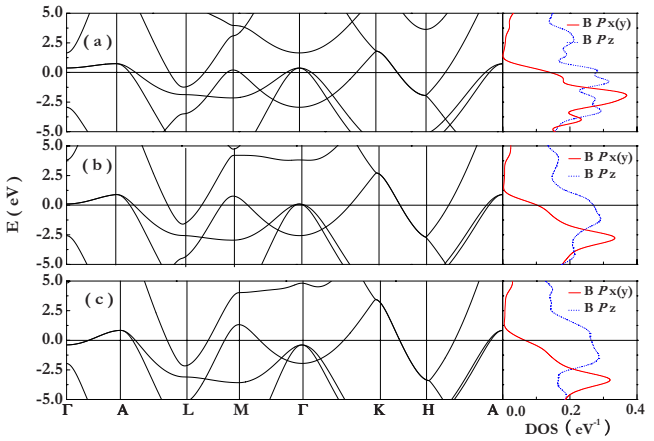

FIG. 2. (Color online) The band structure of MgB_2 at different pressures of (a) 0, (b) 100, and (c) 200 GPa, respectively. The right panels are the corresponding DOS of B $p_{x,y}$ and p_z.

MgB_2 under ultrahigh pressure. In Fig. 2, we present the calculated band structures along high-symmetry directions in the Brillouin zone and B $p_{x,y}$ and p_z DOSs for MgB_2 at 0, 100, and 200 GPa, respectively. It can be clearly seen that the B $p_{x,y}$ bands move toward Fermi level along Γ-A direction and it is completely down below Fermi level at Γ at 200 GPa. This results in a significant reduction of the B $p_{x,y}$ holes, which are the driving carriers for superconductivity.[7,25,26] The bands movement under pressure can also be reflected from the DOS results (right panel in Fig. 2) of B $p_{x,y}$ at the Fermi level, which decrease from 0.14 (states/eV/f.u.) to 0.06 (states/eV/f.u.) as pressure increases from 0 GPa to 200 GPa. It has been reported that the B $p_{x,y}$ DOS plays a crucial role in determining the superconducting properties of MgB_2.[13,26] The McMillan-Hopfield expression[27] takes the form of $\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle}$, where $N(E_F)$ is the DOS at Fermi level, $\langle I^2\rangle$ is the averaged square of the electron-phonon matrix element, $\langle\omega^2\rangle$ is the averaged square of the phonon frequency, and M is the mass of the ion involved. It is clear that the reduced B $p_{x,y}$ DOS at the Fermi level contributed to the decrease of $N(E_F)$ has a negative contribution to λ.

The structural stability of MgB_2 under high pressure has been examined through lattice dynamics calculations. The phonon dispersions at 0 and 200 GPa are shown in Fig. 3. The stability is confirmed by the absence of any imaginary frequency modes in the whole BZ in the pressure range of 0–200 GPa. It is clear from Fig. 3 that all the phonon modes shift to higher frequencies as pressure increases. In particular, the frequency of E_{2g} mode at Γ point, dominating the electron-phonon coupling in MgB_2,[13] is greatly enhanced as from 546.38 cm^{-1} at 0 GPa to 1290.23 cm^{-1} at 200 GPa. The enhanced frequency of E_{2g} mode contributes to the increase of $\langle\omega^2\rangle$ in the McMillan-Hopfield equation and thus results in the reduced EPC parameter λ. It should be pointed out that we did not support the earlier proposed unstable B_{1g} phonon mode at A point at 137 GPa (Ref. 13), which is suggested to be attributable to the increased EPC parameter λ under high pressure. Instead, our results show that B_{1g} mode frequency at A point maintains the stability with pres-

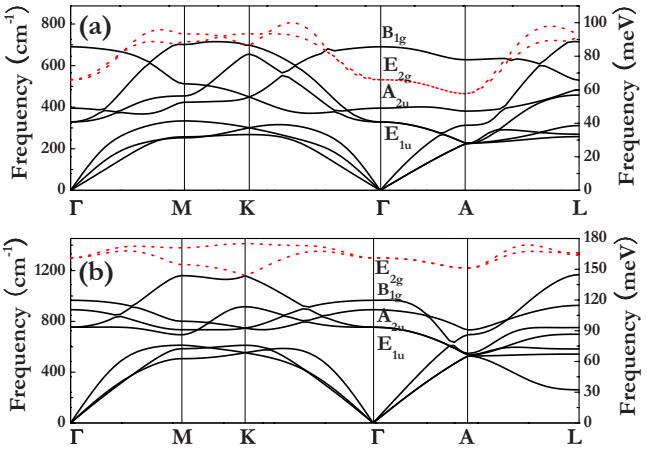

FIG. 3. (Color online) Calculated phonon-dispersion curves at (a) 0 and (b) 200 GPa, respectively. E_{2g} phonon mode is highlighted by the red dotted lines.

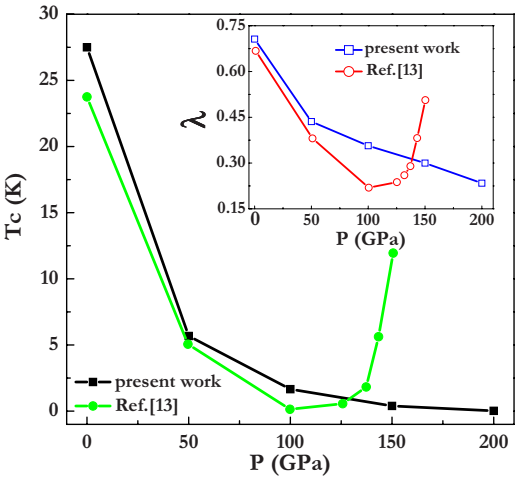

FIG. 4. (Color online) Main figure: T_c as a function of pressure with $\mu^*=0.1$. Inset: λ as a function of pressure. Our results are presented as squares and circles are from Ref. 13.

sure and is well above zero (e.g., at 200 GPa it is ~533.70 cm^{-1}).

Finally, we show the pressure dependence of λ and T_c for MgB_2 in Fig. 4. We find that λ below 50 GPa is in a good agreement with the previous data,[13] but the significant discrepancy is evidenced beyond 50 GPa originated from the different uses of pressure-dependent lattice parameters. Instead of the U shape pressure dependence of λ, We predicted a monotonically decreased λ from 0.71 at zero pressure to 0.23 at 200 GPa. For the strongly coupled superconductors, the McMillan formula[28] takes the form $T_c = \frac{\langle\omega\rangle}{1.2}\exp[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}]$, which connects the value of T_c with the EPC parameter λ, the logarithmically averaged phonon frequency $\langle\omega\rangle$, and Coulomb repulsion μ^*. By adopting the conventional value of μ^* as 0.1, we solve the McMillan equation[28] to derive T_c at different pressures in Fig. 4. The T_c was found to monotonically decrease from 0 to 200 GPa and reaches ~0 K at 200 GPa.

In conclusion, we have presented a first-principles investigation of the lattice dynamics and EPC of MgB_2 under ultrahigh pressure up to 200 GPa within the framework of density-functional theory. We predicted a monotonically decreased λ from 0.71 at zero pressure to 0.23 at 200 GPa. With the choice of $\mu^*=0.1$, the resulting T_c has a continuously reduced trend and vanishes at 200 GPa. Moreover, we did not find any imaginary phonon frequencies in the BZ up to 200 GPa. We believe that the reduced density of states of B $p_{x,y}$ at Fermi level and the enhanced frequency of E_{2g} phonon mode are the main causes for the monotonically decreased λ and then T_c.

The authors gratefully acknowledge the financial support of the NSAF of China (Grant No. 10676011), the National Natural Science Foundation of China under Grant No. 10874054, the China 973 Program (Grant No. 2005CB724400), the 2007 Cheung Kong Scholars Programme of China, and the National Found for Fostering Talents of Basic Science (Grant No. J0730311)

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