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# The pressure dependence of the structure and superconducting transition temperature of MgB<sub>2</sub>

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## Abstract

We have developed the potential parameters for the simulation of MgB<sub>2</sub> and calculated the variations of lattice parameters and volume with pressure up to 240 GPa. Our calculated results are in good agreement with experimental results below 40 GPa. By employing the McMillan expression, it is found that the lattice stiffening dominates the behaviour of the superconducting transition  $T_c$  under pressure in the scope of BCS theory. Using our calculated Grüneisen parameter  $\gamma_G$ , the simulated pressure effect on  $T_c$  accords well with experimental results. Our result shows that the  $T_c$  of MgB<sub>2</sub> can be destroyed by high pressure.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The recent discovery of superconductivity in MgB<sub>2</sub> [1], which has a high critical temperature  $T_c$  of about 40 K, has initiated a lot of interest. MgB<sub>2</sub> exhibits an AlB<sub>2</sub>-type hexagonal structure, with  $a = 3.084 \text{ \AA}$ ,  $c = 3.522 \text{ \AA}$  [2], space group  $P6/mmm$ . Soon after the discovery of MgB<sub>2</sub>, many experimental studies were reported on tunnelling [3], specific-heat measurement [4, 5], isotope effect [6, 7] and inelastic neutron scattering measurements of the phonon density of states [8]. All of these works have tried to understand the mechanism of superconductivity.

Pressure is an important variable as it can be used to test the validity of some theoretical models. A large value of  $dT_c/dP$  may indicate that a higher value of  $T_c$  can be obtained by chemical means. To our knowledge, all high-pressure studies on MgB<sub>2</sub> show that  $T_c$  decreases with pressure, but the values of the pressure derivative  $dT_c/dP$  are quite different. Monteverde *et al* [9] and Lorenz *et al* [10] found that MgB<sub>2</sub> has an initial  $dT_c/dP$  of  $-0.8$  and  $-1.6 \text{ K GPa}^{-1}$ , respectively. Saito *et al* [11] reported a somewhat larger  $dT_c/dP$  of  $-2.0 \text{ K GPa}^{-1}$  from high-pressure resistivity measurements. By using an He-gas apparatus, Tomita *et al* [12] obtained a  $dT_c/dP$  of  $-1.11 \text{ K GPa}^{-1}$  under pure hydrostatic pressure

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conditions. Deemyad *et al* [13] suggested that all these different values of  $dT_c/dP$  reported may result primarily from shear-stress effects in nonhydrostatic pressure media rather than from the differences in the samples, and  $dT_c/dP = -1.1 \text{ K GPa}^{-1}$  should be the true hydrostatic pressure dependence of  $T_c$  in  $\text{MgB}_2$ .

Two theoretical models were proposed to describe the systematics of the pressure effect on  $T_c$  in  $\text{MgB}_2$ . Based on the theory of hole superconductivity, Hirsch [14] predicted a positive pressure effect on  $T_c$ . However, this prediction has not been confirmed by experiments. On the contrary, analysing the experimental results [12, 15] in terms of the McMillan expression [16] derived from Eliashberg theory [17] supports the theory that  $\text{MgB}_2$  is an electron-phonon mediated superconductor.

Up to date, there has been no report about a pressure-induced structural transition of  $\text{MgB}_2$  up to 40 GPa [18], and the superconductivity is not destroyed up to 44 GPa where  $T_c$  is still as high as 12 K [19]. Much higher pressure may be necessary to test whether pressure can cause a structural transition or finally destroy the superconductivity.

In this paper, we developed the potentials for calculation of  $\text{MgB}_2$  through a GULP program [23], and with these potentials, we calculated the variations of lattice parameters and volume with pressure up to 240 GPa by using a PARAPOCS program [21]. Employing the McMillan expression and following the analysis of Chen *et al* [20], we investigated the pressure dependence of  $T_c$  of  $\text{MgB}_2$ .

## 2. Computational method

The crystal structure of a material at a given temperature and pressure can be predicted by minimizing its free energy. Our approach is to adjust the cell volume and atomic positions until the net pressure or stress is zero. The pressure  $P$  is simply the derivative of the free energy  $F$  with respect to volume  $V$ . Thus for a cubic material,

$$P = dF/dV. \quad (1)$$

Calculating the free energy at a given volume and then recalculating it after making a small adjustment to the cell volume  $dV$  determines the pressure. The problem becomes slightly more complicated for non-cubic material, as the volume will not expand isotropically. For these systems we have to consider six different strain components,  $\varepsilon_j$ . However, the same approach is used except that a small strain is applied in each of the six senses, and a pressure corresponding to the derivative of the free energy for each component is calculated assuming that the thermal contribution to the pressure is isotropic:

$$P_j = \frac{1}{V} \frac{dF}{d\varepsilon_j} \quad (2)$$

where  $V$  is the unit cell volume. During the iterative procedure a constant volume energy minimization is performed. Hence each time the cell volume is modified, all atomic positions are adjusted so that they remain at a potential energy minimum. Thus by minimizing to constant pressure and including the vibrational component of the free energy, the crystal structure at a given temperature and pressure can be predicted. This technique has been successfully used for simulation of many kinds of materials. Details of this technique are available in [21, 22].

Our simulation is based on the widely used and highly successful shell model generalization of the Born model of a solid. Short-range interaction forces are represented by a Buckingham potential:

$$V(r) = A \exp(-r/\rho) - Cr^{-6} \quad (3)$$

**Table 1.** Potential parameters for MgB<sub>2</sub>: short-range interaction and shell model parameters.

(a) Short-range interaction	$A$ (eV)	$\rho$ (Å)	$C$ (eV Å <sup>6</sup> )
Mg <sup>2+</sup> -B <sup>1-</sup>	86.9086	0.600 902	0.0000
B <sup>1-</sup> -B <sup>1-</sup>	79 557.5217	0.180 512	285.2026
Mg <sup>2+</sup> -Mg <sup>2+</sup>	500.0000	0.406 700	0.0000
(b) Shell model parameters	$Y$ (e)	$K$ (eV Å <sup>-2</sup> )	
Mg <sup>2+</sup> <sup>a</sup>	0.420	349.95	

<sup>a</sup> Reference [23].**Table 2.** Comparison of calculated and experimental structural data for MgB<sub>2</sub>.

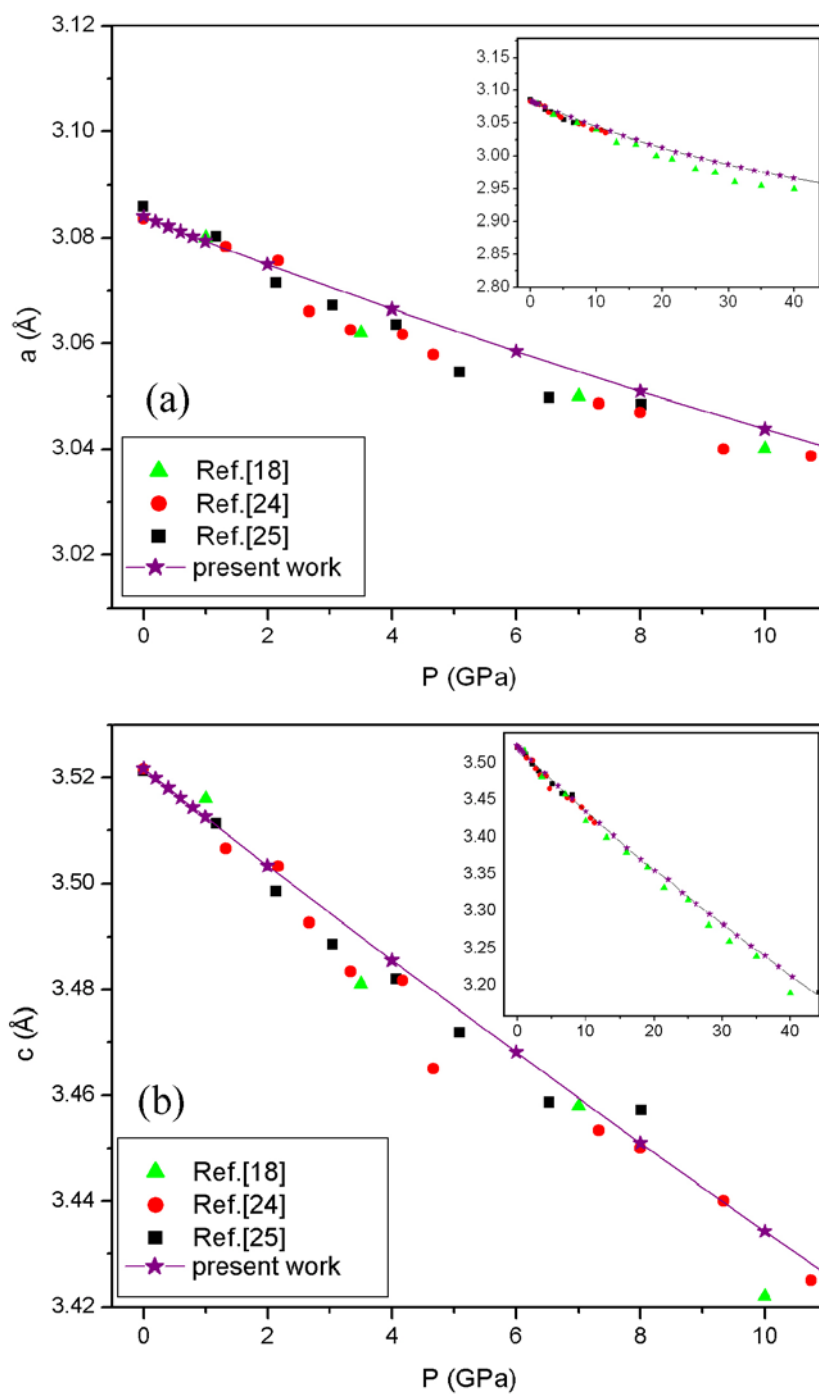
	Experimental <sup>a</sup>	Calculated	Difference
Lattice parameters (Å)			
$a$	3.084	3.0839	0.003 24%
$c$	3.522	3.5219	0.002 84%
Bond lengths (Å)			
Mg-Mg	3.084	3.0839	0.0001 Å
Mg-B	2.504	2.5043	0.0003 Å
B-B	1.781	1.7805	0.0005 Å

<sup>a</sup> Reference [2].

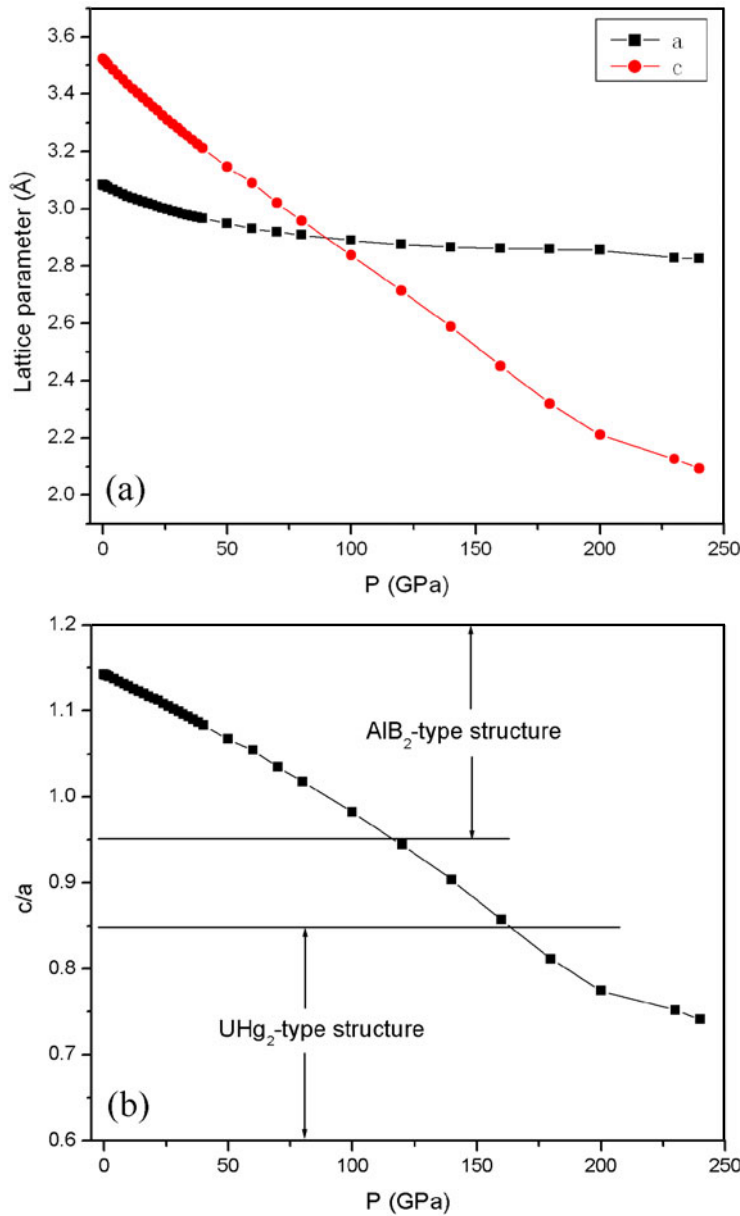
where  $A$ ,  $\rho$ , and  $C$  are constants. For MgB<sub>2</sub>, the charge states of 2+ and 1- are assigned to Mg and B, respectively. The potential parameters for MgB<sub>2</sub> are obtained by an empirical method (known as the ‘relaxed’ fitting approach), the structure is relaxed to zero strain for every evaluation of the sum of squares, and the difference between observed and calculated structural parameters is used in place of the derivatives. In each step in the fitting the minimization was started from the experimental structure to avoid the possibility that the fit becomes trapped in an undesirable local minimum in either potential of geometry space. It should be stressed that the reliability of the simulations depends on the validity of the potential model used in the calculation, and the latter is assessed primarily by its ability to reproduce experimental crystal properties. The potential parameters used in this work are given in table 1. The comparison of calculated and the experimental data is shown in table 2. The differences in lattice parameters and bond lengths between the calculated and experimental data are very small.

### 3. Results and discussion

Figure 1 shows the comparison of calculated lattice parameters  $a$  and  $c$  with the experimental data [18, 24, 25] up to 40 GPa. The calculated data agree well with the experimental data [18, 24, 25] below 10 GPa. The derivative of lattice parameter  $a$  ( $da/dP$ ) is  $-4.5 \times 10^{-3}$  Å GPa<sup>-1</sup> up to 10 GPa. At 40 GPa our calculated lattice parameter  $a$  is 2.97 Å, which is 0.68% larger than the experimental value [18]. The variation of calculated lattice parameter  $c$  with pressure below 10 GPa also agrees well with the experimental data [18, 24, 25]. The derivative of lattice parameter  $c$  ( $dc/dP$ ) is  $-9.2 \times 10^{-3}$  Å GPa<sup>-1</sup> up to 10 GPa, which is twice as large as  $da/dP$ . As the pressure increases to 40 GPa, our result also accords well with high-pressure experimental data. At 40 GPa our calculated value of  $c$  is 3.21 Å, which is 0.63% larger than the experimental value [18]. These results show that our calculated lattice parameters are in good agreement with experimental data up to 40 GPa. We find that there is



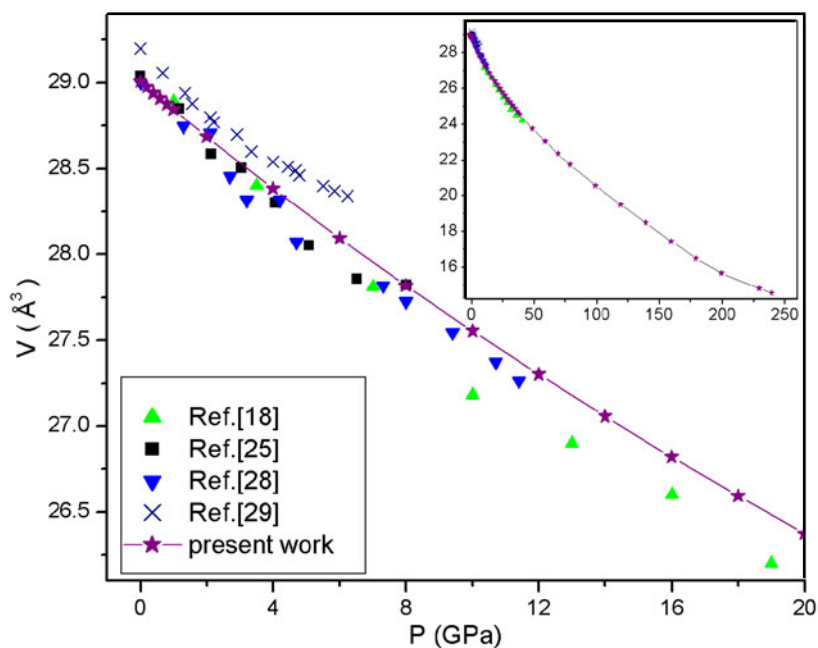
**Figure 1.** The calculated variation of lattice parameters of MgB<sub>2</sub> with pressure compared with experimental data up to 10 GPa. The inset shows the calculated lattice parameters up to 40 GPa. (a) The variation of lattice parameter  $a$  with pressure. (b) The variation of lattice parameter  $c$  with pressure.



**Figure 2.** (a) Calculated variations of lattice parameters  $a$  and  $c$  of MgB<sub>2</sub> with pressure up to 240 GPa. (b) The calculated variation of  $c/a$  with pressure up to 240 GPa.

no phase transition below 40 GPa, and this result is also in agreement with the experimental result [18].

Figure 2(a) shows the variations of the lattice parameters  $a$  and  $c$  with pressure up to 240 GPa. It is found that lattice parameter  $c$  decreases almost linearly with pressure up to 200 GPa while lattice parameter  $a$  decreases monotonically, following a quadratic dependence on applied pressure up to 40 GPa. It is interesting that the two curves intersect at about 90 GPa. After this point, lattice parameter  $c$  becomes much smaller than  $a$  as the pressure increases.



**Figure 3.** The calculated variation of volume of  $\text{MgB}_2$  with pressure up to 20 GPa compared with the experimental data. The inset shows the volume dependence on pressure up to 240 GPa.

We also find two cusps in each curve, which may correspond to two structural transition points: one is at 140 GPa and the other is at 200 GPa. Figure 2(b) shows that the ratio of  $c/a$  decreases with increasing pressure, following a quadratic dependence on pressure up to 180 GPa. The initial ratio of  $c/a$  is 1.142, which is similar to the value ( $c/a = 1.141$ ) obtained by Jorgensen *et al* [26]. It is known that when pressure is applied, the  $\text{AlB}_2$  structure tends to change to the  $\text{UHg}_2$  structure [27].  $\text{AlB}_2$  and  $\text{UHg}_2$  are isopointal structures, distinguished only by their  $c/a$  ratio, which are 0.95–1.20 and 0.60–0.85, respectively.  $\text{MgB}_2$  is of the  $\text{AlB}_2$  structure, so [27] predicts that  $\text{MgB}_2$  may also change to the  $\text{UHg}_2$  structure at high pressure, though the available applied pressures are not high enough to cause this structure transition. Our  $\text{MgB}_2$  high-pressure structure calculation show that the structure transition from  $\text{AlB}_2$  structure to  $\text{UHg}_2$  structure is possible (see figure 2(b)), and this result is in agreement with the result predicted by Loa *et al* [27].

Figure 3 shows the variation of the calculated volume of  $\text{MgB}_2$  with pressure up to 240 GPa. Our calculated result agrees well with the experimental data [18, 25, 28, 29] below 10 GPa. At 40 GPa our calculated result of  $24.48 \text{ \AA}^3$  is only 1.16% different from the experimental value [18]. The extracted value of the bulk modulus  $B_0 = -\partial P / \partial \ln V$  from figure 3 is 170.2 GPa, which is in good agreement with the experimental value of 172 GPa [30]. All our calculated results (lattice parameters and volume) are in excellent agreement with the experimental results. This shows that our potentials are good and the calculated results are reliable. For a superconductor, the change of structure may contain valuable information on the superconducting mechanism itself. Studying the structure dependence of pressure, especially under high-pressure, may find some unusual properties and benefit theoretical research. In this aspect our results are a useful supplement to predict structural variations of  $\text{MgB}_2$  under high pressure from 40 to 240 GPa, because no experimental data have been reported in this pressure range.

The superconducting transition temperature  $T_c$  is a result of both the raising effect of anisotropy in the electron–phonon couplings and the lowering effect of anharmonicity in the relevant phonon modes [31]. If we want to study the superconducting transition temperature of MgB<sub>2</sub>, a solution, which can be expressed by lattice parameters, of the fully anisotropic Eliashberg equations is needed. However, there is as yet no report on such a solution. So in this paper we employ the McMillan expression [18], which is a solution of the isotropic Eliashberg equations, to analyse the pressure effect on  $T_c$ . The McMillan expression is

$$T_c = \frac{\langle\omega\rangle}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - (1+0.62\lambda)\mu^*}\right], \quad (4)$$

which connects the value of  $T_c$  with the electron–phonon coupling parameter  $\lambda$ , the logarithmically averaged phonon frequency  $\langle\omega\rangle$ , and the Coulomb repulsion  $\mu^*$ .

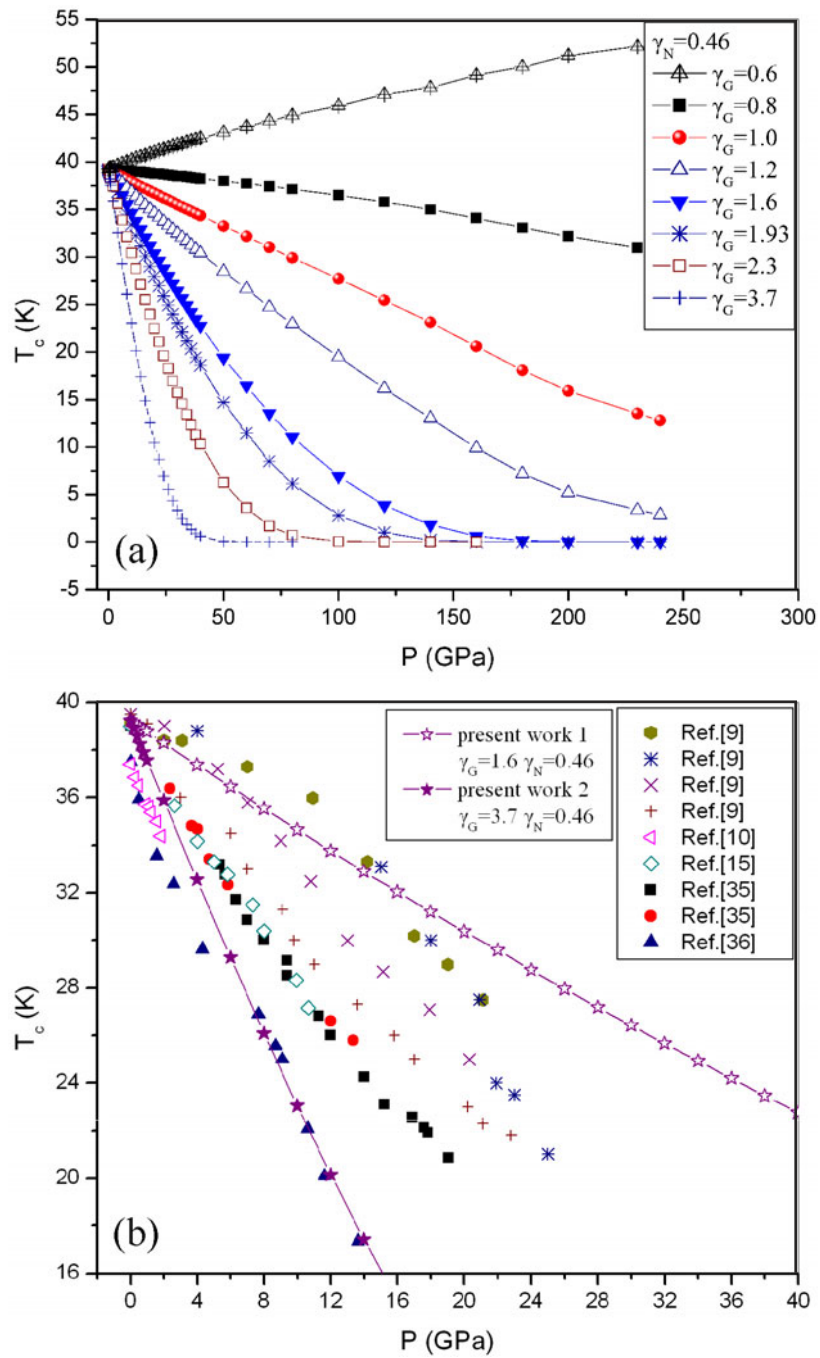
From inelastic neutron studies [8] we obtained the parameters at ambient pressure:  $\langle\omega_0\rangle = 670$  K,  $T_c = 39.2$  K and  $\lambda_0 = 0.9$  by using the most frequently cited value of  $\mu_0^* = 0.1$ . Following the analysis of Chen *et al* [20], we set  $\langle\omega\rangle = \langle\omega_0\rangle(V/V_0)^{-\gamma_G}$ ,  $\lambda = \lambda_0(V/V_0)^\phi$  and  $\mu^* = \mu_0^*(V/V_0)^\phi$ , where  $\phi = -0.1\gamma_G - 0.09\gamma_N + 6.7 \times 10^{-3}$  and  $\phi = -\gamma_N - 0.67 + 2\gamma_G$ . It is found that variations of the parameters  $\langle\omega\rangle$ ,  $\mu^*$  and  $\lambda$  with volume are only decided by two parameters:  $\gamma_N$  and the Grüneisen parameter  $\gamma_G$ . The former is defined as  $\gamma_N = \partial \ln N(E_f)/\partial \ln V$ , which represents an effect of the density of electronic states at the Fermi level, and the latter is defined as  $\gamma_G = -\partial \ln(\overline{\omega}^2)^{1/2}/\partial \ln V$ , which represents an effect of the lattice stiffening. The calculated values of  $\gamma_N$  in the literature are 0.46 [20] and 2/3 in the case of a free-electron gas, and the calculated Grüneisen parameter  $\gamma_G$  in the literature has values ranging from 1.0 to 3.7 [12, 13, 20, 32, 33] while the experimental value is 2.9 [24].

Using the calculated pressure dependence of volume for MgB<sub>2</sub>, we studied how the lattice stiffening and the density of electronic states at the Fermi level affect  $T_c$  under pressure by varying  $\gamma_G$  and  $\gamma_N$  using the McMillan expression. Figure 4(a) shows our calculated pressure dependence of  $T_c$  with different values of  $\gamma_G$  for a fixed  $\gamma_N = 0.46$ . It is found that  $\gamma_G$  determines the magnitude and sign of  $dT_c/dP$ . When  $\gamma_G$  is 0.6,  $T_c$  increases with increasing pressure. When  $\gamma_G$  is in the range of 0.8–1.2,  $T_c$  decreases slowly with increasing pressure. When  $\gamma_G$  is larger than 1.6,  $T_c$  can be destroyed by pressure below 160 GPa. The larger the  $\gamma_G$ , the lower the critical pressure. This suggests that the lattice stiffening has a significant effect on  $T_c$  under pressure. Figure 4(b) shows the comparison of our calculated pressure dependence of  $T_c$  using different values of  $\gamma_G$  with the experimental data. We find that most experimental data correspond to the  $\gamma_G$  range of 1.6–3.7. However, this range is wider than has been reported [20].

Figure 5 shows how the density of electronic states at the Fermi level affects  $T_c$  with fixed  $\gamma_G$  values of 1.6 and 3.7. For a fixed  $\gamma_G$ , a smaller  $\gamma_N$  causes faster decrease of  $T_c$  with increasing pressure. The smaller the  $\gamma_G$ , the larger the effects of  $\gamma_N$  on  $T_c$ . Compared with figure 4(a), we find that  $\gamma_G$  plays a more important role on  $T_c$  than  $\gamma_N$ . We conclude that the lattice stiffening under pressure plays a more crucial role on  $T_c$  than the density of electronic states at the Fermi level.

Employing the expression of  $\gamma_G = -2/3 - (V\partial^2 P/\partial V^2)/(2\partial P/\partial V)$  [34], we calculated the Grüneisen parameter  $\gamma_G = 2.55$  at 0 GPa from our calculated pressure dependence of volume, which is in reasonable agreement with the value of 2.9 from Raman spectroscopy studies [24]. Using  $\gamma_G = 2.55$  calculated by us and  $\gamma_N = 0.46$  obtained by Chen *et al* [20], we calculated the pressure dependence of  $T_c$  (figure 6). The calculated result agrees well with the experimental data [9, 10, 12, 15, 35, 36] below 30 GPa. We obtain the initial pressure derivative  $dT_c/dP = -1.05$  K GPa<sup>-1</sup> which accords with the hydrostatic pressure results [10, 12, 13]. This indicates that our calculated Grüneisen parameter  $\gamma_G$  is reasonable





**Figure 4.** (a) The calculated effect of  $\gamma_G$  on the pressure dependence of  $T_c$  of  $MgB_2$  with fixed  $\gamma_N = 0.46$  up to 240 GPa. (b) The calculated effect of  $\gamma_G$  on the pressure dependence of  $T_c$  of  $MgB_2$  with fixed  $\gamma_N = 0.46$  up to 40 GPa compared with the experimental data.

and the curves shown in figure 6 can roughly describe the behaviour of  $T_c$  under pressure. Lacking high-pressure experimental data, researchers can only predict whether high pressure

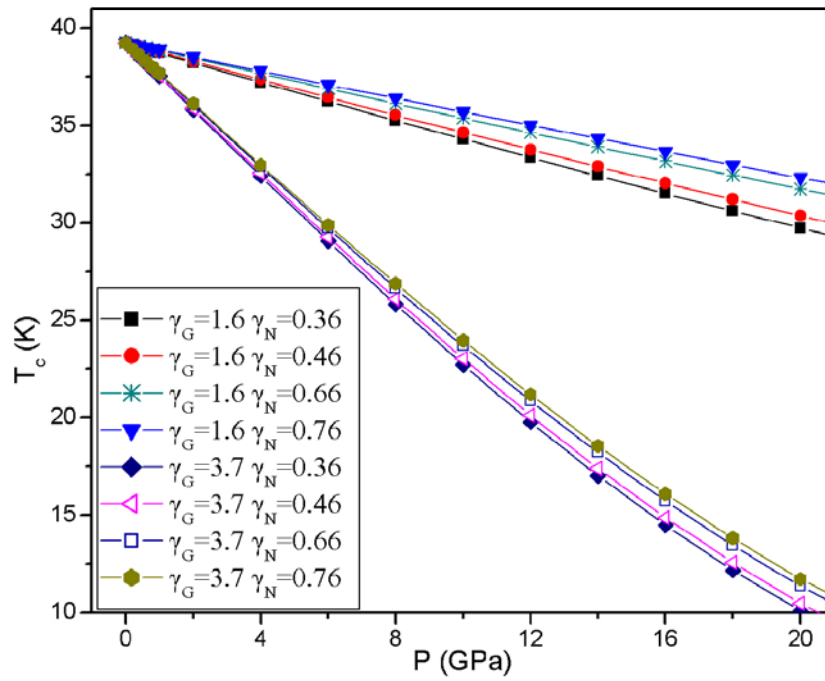


Figure 5. The calculated effect of  $\gamma_N$  on the pressure dependence of  $T_c$  of MgB<sub>2</sub> with  $\gamma_G = 1.6$  and 3.7.

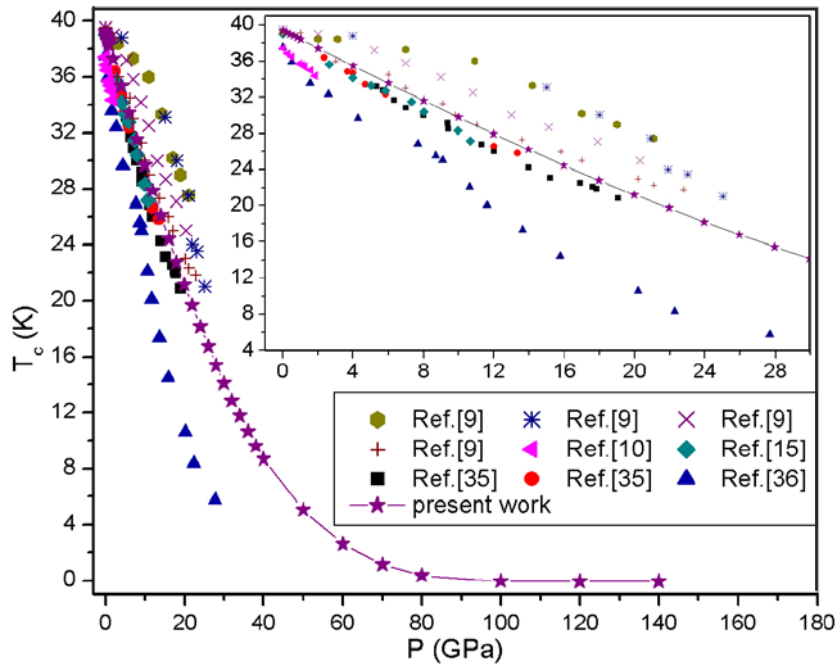


Figure 6. The calculated variation of  $T_c$  with pressure in MgB<sub>2</sub> compared with the experimental data.

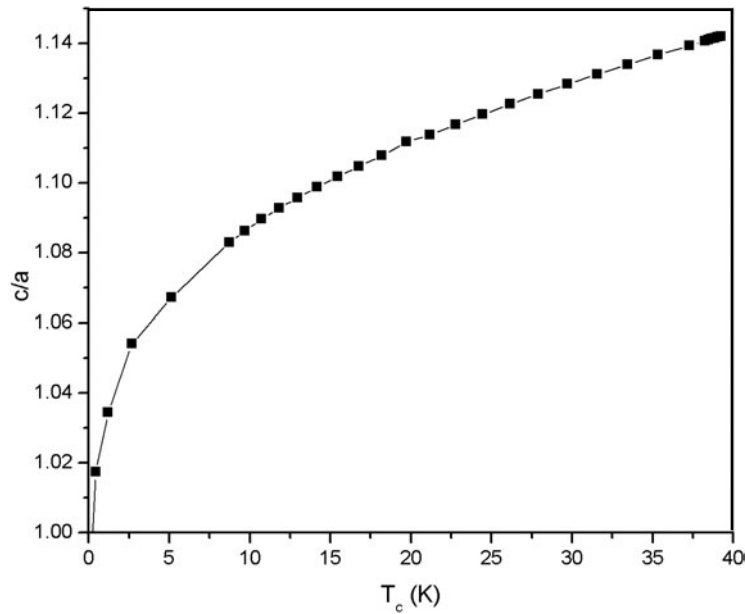


Figure 7. The calculated  $T_c$  of  $\text{MgB}_2$  versus structure parameter ( $c/a$ ).

will destroy the superconductivity by analysing the available low-pressure experimental data, in which  $T_c$  does still not reach zero. We can provide the pressure dependence of  $T_c$  in the high-pressure range. We find that  $T_c$  is destroyed at about 90 GPa (figure 6), which is larger than the predicted value of 75 GPa [35] and in agreement with 93 GPa predicted by Deemyad *et al* [13]. Our result supports the prediction that sufficiently high pressure may destroy the superconductivity [37, 38].

Among the four important phonon vibration modes ( $E_{1u}$ ,  $A_{2u}$ ,  $E_{2g}$  and  $B_{1g}$ ) in  $\text{MgB}_2$ , the  $E_{2g}$  mode seems to be a crucial contribution to  $T_c$  and to have a close correlation with the in-plane B–B bond length. When the pressure increases from 0 to 90 GPa where  $T_c$  is almost zero, from our calculations of the pressure dependence of lattice parameters, we find that the in-plane B–B bond length drops from 1.78 to 1.67 Å, which is close to its optimal value of 1.65 Å. This interesting result suggests that the stretched in-plane B–B bond length at ambient pressure may result in a higher  $T_c$ . Combining the calculated results of  $c/a$  and  $T_c$ , we plot  $T_c$  versus  $c/a$  (figure 7). It is found that  $T_c$  decreases with decreasing  $c/a$ , and  $T_c$  almost drops to zero when  $c/a = 1.0$ . These two results indicate a possible way to enhance  $T_c$  of  $\text{MgB}_2$  by changing the lattice parameters or in-plane B–B bond length of  $\text{MgB}_2$  through chemical means.

#### 4. Conclusion

The potentials for simulation of  $\text{MgB}_2$  were developed. With these potentials, we calculated the lattice parameters and volume dependence of pressure up to 240 GPa. The calculated results are in excellent agreement with the experimental results below 40 GPa and are reasonable predictions for the tendencies from 40 to 240 GPa. Our calculations show that the structure of  $\text{MgB}_2$  changed from the  $\text{AlB}_2$ -type structure to the  $\text{UHg}_2$ -type structure with increasing pressure, and three phase transition points were found at high pressure. We analyse the effect of pressure on  $T_c$  by employing the McMillan expression with our calculated structural parameters. It is found that  $dT_c/dP$  is governed by the lattice stiffening and does not heavily

depend on the density of electronic states at the Fermi level. Using our calculated Grüneisen parameter  $\gamma_G$ , our calculated  $T_c$  dependence of pressure agrees well with the experiments below 40 GPa. Our result predicts that the  $T_c$  of MgB<sub>2</sub> can be destroyed at about 90 GPa.

## References

- [1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63
- [2] Ralph W G and Wyckoff W G 1963–1964 *Crystal Structures* 2nd edn (New York: Interscience)
- [3] Karapetrov G, Iavarone M, Kwok W K, Crabtree G W and Hinks D G 2001 *Phys. Rev. Lett.* **86** 4374
- [4] Walti Ch, Felder E, Degen C, Wigger G, Monnier R, Delley B and Ott H R 2001 *Phys. Rev. B* **64** 172515
- [5] Bouquet F, Fisher R A, Phillips N E, Hinks D G and Jorgensen J D 2001 *Phys. Rev. Lett.* **87** 047001
- [6] Bud'ko S L, Lapertot G, Petrovic C, Cunningham C E, Anderson N and Canfield P C 2001 *Phys. Rev. Lett.* **86** 1877
- [7] Hinks D G, Claus H and Jorgensen J D 2001 *Nature* **411** 457
- [8] Osborn R, Goremychkin E A, Kolenikov A I and Hinks D G 2001 *Phys. Rev. Lett.* **87** 017005
- [9] Monteverde M, Nunez-Regueiro M, Rogado N, Regan K A, Hayward M A, He T, Loureiro S M and Cava R J 2001 *Science* **292** 75
- [10] Lorenz B, Meng R L and Chu C W 2001 *Phys. Rev. B* **64** 012507
- [11] Saito E, Takenobu T, Ito T, Iwasa Y, Prassides K and Arima T 2001 *J. Phys.: Condens. Matter* **13** L267
- [12] Tomita T, Hamlin J J, Schilling J S, Hinks D G and Jorgensen J D 2001 *Phys. Rev. B* **64** 092505
- [13] Deemyad S, Tomita T, Hamlin J J, Beckett B R, Schilling J S, Hinks D G, Jorgensen J D, Lee S and Tajima S 2003 *Physica C* **385** 105–16
- [14] Hirsch J E 2001 *Phys. Lett. A* **282** 392
- [15] Razavi F S, Bose S K and Ploczek H 2002 *Physica C* **366** 73–9
- [16] McMillan W L 1968 *Phys. Rev. B* **167** 331  
Allen P B and Dynes R C 1975 *Phys. Rev. B* **12** 905
- [17] Eliashberg G M 1960 *Zh. Eksp. Teor. Fiz.* **38** 966  
Eliashberg G M 1960 *Sov. Phys.—JETP* **11** 696 (Engl. Transl.)
- [18] Bordet P, Mezouar M, Nunez-Regueiro M, Monteverde M, Nunez-Regueiro M D, Rogado N, Regan K A, Hayward M A, He T, Loureiro S M and Cava R J 2001 *Phys. Rev. B* **64** 172502
- [19] Struzhkin V V, Goncharov A F, Hemley R J, Mao H K, Lapertot G, Bud'ko S L and Canfield P C 2002 unpublished  
(Struzhkin V V, Goncharov A F, Hemley R J, Mao H K, Lapertot G, Bud'ko S L and Canfield P C 2001 *Preprint cond-mat/0106576*)
- [20] Chen X J, Zhang H and Habermeier H U 2002 *Phys. Rev. B* **65** 144514
- [21] Parker S C and Price G D 1988 *Computer Modeling of Fluids, Polymers and Solid (NATO ASI Series vol 293)* ed C R A Catlow, S C Parker and M P Allen p 405
- [22] Parker S C and Price G D 1989 *Adv. Solid State Chem.* **1** 295
- [23] Bush T S, Gale J D, Catlow C R A and Battle P D 1994 *J. Mater. Chem.* **4** 831–7
- [24] Goncharov A F, Struzhkin V V, Gregoryanz E, Hu J Z, Hemley R J, Mao H K, Lapertot G, Bud'ko S L and Canfield P C 2001 *Phys. Rev. B* **64** 100509
- [25] Vogt T, Schneider G, Hriljac J A, Yang G and Abell J S 2001 *Phys. Rev. B* **63** 220505
- [26] Jorgensen J D, Hinks D G and Short S 2001 *Phys. Rev. B* **63** 224522
- [27] Loa I, Kunc K, Syassen K and Bouvier P 2002 *Phys. Rev. B* **66** 134101
- [28] Goncharov A F and Struzhkin V V 2003 *Physica C* **385** 117–30
- [29] Prassides K, Iwasa Y, Ito T, Chi D H, Uehara K, Nishibori E, Takata M, Sakata M, Ohishi Y, Shimomura O, Muranaka T and Akimitsu J 2001 *Phys. Rev. B* **64** 012509
- [30] Tang J, Qin L C, Matsushita A, Takano Y, Togano K, Kito H and Ihara H 2001 *Phys. Rev. B* **64** 132509
- [31] Choi H J, Roundy D, Sun H, Cohen M L and Louie S G 2002 *Phys. Rev. B* **66** 020513
- [32] Loa I and Syassen K 2001 *Solid State Commun.* **118** 279–82
- [33] Roundy D, Choi H J, Sun H, Louie S G and Cohen M L 2002 unpublished
- [34] Slater J C 1939 *Introduction to Chemical Physics* (New York: McGraw-Hill)
- [35] Deemyad S, Schilling J S, Jorgensen J D and Hinks D G 2001 *Physica C* **361** 227–33
- [36] Tissen V G, Nefedova M V, Kolesnikov N N and Kulakov M P 2001 *Physica C* **363** 194–7
- [37] Olsen J L and Rohrer H 1960 *Helv. Phys. Acta* **33** 872  
Levy M and Olsen J L 1964 *Solid State Commun.* **2** 137
- [38] Boughton R I, Brändli G, Olsen J L and Palmy C 1969 *Helv. Phys. Acta* **42** 587