Searching for a higher superconducting transition temperature in strained MgB$_2$

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(Received 22 August 2005; revised manuscript received 7 November 2005; published 24 January 2006)

We present a detailed first-principles density-functional analysis of the effects of lattice strain on the superconducting transition temperature, $T_c$, of MgB$_2$, deriving a general rule that governs the enhancement (or suppression) of $T_c$ in strained MgB$_2$ in terms of electronic and phonon contributions. Based on the calculated structural, electronic, vibrational, and superconducting properties of a strained MgB$_2$ superconductor, we show how a higher $T_c$ might be achieved. Several candidate substrates are suggested for growing MgB$_2$ thin films to gain a higher $T_c$.

Tailoring the $T_c$ in MgB$_2$ requires a full atomic level understanding of the underlying mechanism of chemical and lattice effects. Immediately after the discovery of superconductivity in MgB$_2$, extensive research on chemical substitution was undertaken to understand and hence to improve its properties. In contrast, very few studies focused on lattice effects despite the fact that improving material properties by controlling lattice strain is a basic and practical approach in materials research. For example, various methods, such as applying pressures, including mechanical loads, or selecting different substrates with different lattice constants for film growth, are commonly employed to investigate the effects of lattice strain on material functionality. Lattice effects are believed to play an important role in the superconductivity of MgB$_2$. Although isotropic compression was applied to the crystal lattice of MgB$_2$ to investigate its properties, no research has systematically addressed the effects of strain on superconductivity. In fact, various strains exist in epitaxially grown MgB$_2$ films due to the use of different substrates. Very encouragingly, Pogrebnyakov et al., reported that the $T_c$ of MgB$_2$ can be increased by as much as about 5% using SiC as the substrate. Seemingly, a thorough exploration of the effects of both compressive and tensile strains on the superconducting properties of MgB$_2$ would be extremely useful for guiding the way toward a higher $T_c$. In this paper, we discuss the effects of lattice strain on the electronic (density of states and deformation potential), vibrational ($E_{2g}$ phonon), and superconducting ($T_c$) properties in MgB$_2$ using density functional theory (DFT).

We first describe the variation of $T_c$ as a function of strain in a way generalized for low-temperature superconductors and then specify them for strained MgB$_2$. The original McMillan formula for $T_c$ of superconductor is given as

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda(1-0.62\mu^*) - \mu^*}\right),$$

(1)

where $\Theta$ is Debye temperature, $\mu^*$ is the Coulomb pseudopotential, and $\lambda$ is electron-phonon coupling strength. The Allen-Dynes modified McMillan formula can be expressed as

$$T_c = \frac{\omega_{log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda(1-0.62\mu^*) - \mu^*}\right).$$

(2)

The Debye temperature $\Theta$ in Eq. (1) and $\omega_{log}$ in Eq. (2) are related to phonon frequencies. According to Morel and Anderson, $\mu^*$ can be expressed as

$$\mu^* = \frac{\mu}{1 + \mu \ln(E_F/\omega)},$$

(3)

where $\mu = 0.5 \ln[(1+g^2)/g^2]$ and $g^2 = \pi^2 N_F/k_F^2$. Here, $k_F = (3\pi^2 Z/V)^{1/3}$, where $Z$ is the valency and $V$ is the volume. The electron-phonon coupling strength $\lambda$ can be expressed as

$$\lambda = \frac{N_F\langle\tilde{F}\rangle}{M(\omega^*)^2} = \frac{\eta}{M(\omega^*)^2},$$

(4)

where $N_F$ is density of states (DOS) at Fermi energy level, $\langle\tilde{F}\rangle$ is the mean-square electron-ion matrix element, $M$ is the ionic mass, $\omega^*$ is the mean-square phonon frequency, and $\eta$ is McMillan-Hopfield parameter that includes the electronic components of electron-phonon coupling. In a strained superconductor, the relative change of $T_c$ as a function of strains can be expressed as

$$\frac{\Delta T_c}{T_{c0}} = -\frac{\Delta \omega_{log}}{\omega_{log}} + \alpha - \frac{\Delta \mu^*}{\mu_0} + \beta \frac{\Delta \lambda}{\lambda_0}.$$

(5)

All variables with subscript 0 are for a strain-free superconductor, and the strain-free parameters are

$$\alpha = \frac{1.04(1+\lambda_0)(1+0.62\mu_0^*)}{[\lambda_0(1-0.62\mu_0^*) - \mu_0]^2},$$

and

$$\beta = \frac{1.04\lambda_0(1+0.38\mu_0^*)}{[\lambda_0(1-0.62\mu_0^*) - \mu_0^*]^2}.$$

To achieve higher $T_c$ in terms of modulating the strain, the following condition should be fulfilled:

1098-0121/2006/73(2)/024509(6)/$23.00 024509-1 ©2006 The American Physical Society
The constants \(a_0\) and \(c_0\) results in the variation of \(\omega_0\), \(\omega_{E_{2g}}\), \(\mu^*\), and \(T_c\). The changes of \(T_c\) can be expressed as

\[
\frac{\Delta T_c}{T_c} = \frac{\Delta \omega_{E_{2g}}}{\omega_{E_{2g}}} - \frac{\Delta \mu^*}{\mu_0} + \beta \frac{\Delta \lambda}{\lambda_0},
\]

(7)

where

\[
\frac{\Delta \lambda}{\lambda_0} = \frac{\Delta N_F(\sigma)}{N_{F0}(\sigma)} + \frac{2 \Delta |D|}{|D|_{0}} - 2 \frac{\Delta \omega_{E_{2g}}}{\omega_{E_{2g}}}.
\]

(8)

The first-principles DFT calculations were made using the full potential augmented plane wave (FPAPW) method implemented in the WIEN2k package, and the plane-wave pseudopotential method in the ABINIT package, respectively. For both methods, we employed the local density approximation (LDA) suggested by Perdew and Wang, and the generalized gradient approximant (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE96) to obtain the exchange-correlation potential. The results from the LDA and GGA agree well with each other with difference within 2%. For full potential calculations (WIEN2k), a muffin-tin radius \(R_{MT}\) of 1.7 bohr was chosen for Mg, and 1.5 bohr for B, and \(R_{MT}K_{\text{max}}\) was taken to be 8.0. The calculations used the angular momentum expansion up to \(l_{\text{max}} = 10\) for the potential and charge density representations. At convergence, the integrated difference between input and output charge densities (atomic unit) was less than \(10^{-5}\). We also employed 3000 \(k\) points in the Brillouin zone in the calculations. (The convergence of total energy and properties of MgB\(_2\) was tested in terms of the number of \(k\) points.) In pseudopotential calculations (ABINIT), we employed a very large energy cut-off (40 Hartree) and \(10 \times 10 \times 10\) Monkhorst-Pack \(k\) points, and a very small tolerance on the potential \(V(r)\) residual \((10^{-10})\) for self-consistent field (SCF) stopping; this ensured good convergence of the results in ground-state and linear-response calculations. Well-tested Troullier-Martins pseudopotentials were adopted.

With the chosen typical value \(\mu^* = 0.15\), as well as our calculated phonon frequency \((\omega_{E_{2g}})_0\) \(= 579.9\) cm\(^{-1}\), we obtain \(T_c = 39.4\) K for bulk MgB\(_2\) with the lattice constant \(a = 3.083\) Å, \(c = 3.521\) Å, agreeing with experimental data. We note that the changes in superconducting properties (e.g., \(T_c\)) as a function of strains are mainly determined by the relative changes of \(\omega_0\), \(\lambda_0\), and \(\mu^*\) (which are, in turn, determined by the relative changes of \(\omega_0\), \(N_F\), and \(D\)), while the actual values of \(\mu^*\) and \(\lambda_0\) are less sensitive to the strain-induced variation of \(T_c\) in MgB\(_2\). This can be demonstrated by Eqs. (7) and (8), in which we express the variation of \(T_c\) relative to \(T_{c0}\) based on the relative changes of \(\omega_0\) and \(\lambda_0\). Other coefficients that are associated with \(\lambda_0\) and independent of \(\omega_0\) and \(D\), and are cancelled out in the ratio of \(\Delta \omega_0/\lambda_0\). We show numerical results later in this work, demonstrating that the trends in the superconducting properties of MgB\(_2\) as a function of strains are not affected significantly by the choice of \(\mu^*\) and \(\lambda_0\).

The change of \(\mu^*\) in strained MgB\(_2\) is rather small and is only about ten times less than the relative changes of \(\lambda_0\), which is consistent with Chen et al.’s findings for MgB\(_2\) under hydrostatic pressure. Using our calculated value of \(\sigma = 0.97\), the contribution of the \(-\alpha \Delta \mu^*/\mu_0\) term modifies \(\Delta T_c/T_{c0}\) by about 1%–2% in the range of strains described in this work. Hereafter, the term of \(\Delta \mu^*/\mu_0\) will not be included explicitly.

We note that the \(T_c\) of MgB\(_2\) is controlled collectively by three components: phonon frequency \((\Delta \omega_0/\omega_0)\), density of states \([\Delta N_F(\sigma)/N_{F0}(\sigma)]\), and the deformation potential \((2\Delta |D|/|D|_0)\). By sorting out the individual contributions and defining the electron contribution \(\delta_e = \Delta N_F(\sigma)/N_{F0}(\sigma) + 2\Delta |D|/|D|_0\), and the phonon contribution \(\delta_p = \Delta \omega_0/\omega_0\), we derive a simple expression,

\[
\delta_T = \frac{\Delta T_c}{T_{c0}} = \beta \delta_e + (1 - 2\beta) \delta_p,
\]

(9)

where the subscripts \(e\) and \(p\) indicate the contribution from the electron and phonon component, respectively. For the strain-free bulk, we obtain the parameter \(\beta = 2.09\); then, \(\delta_T = 2.09\delta_e - 3.18\delta_p\). This clearly demonstrates that the contributions from the electron and phonon parts can be considered as two separate competing entities, i.e., \(\delta_T\) increases with an increase in \(\delta_e\) but with a decrease in \(\delta_p\), and vice versa.

Thus, to improve the \(T_c\) in strained MgB\(_2\), the following condition should be fulfilled:

\[
\delta_T > 0 \quad \text{or} \quad \delta_e > \frac{(2\beta - 1)}{\beta} \delta_p \approx 1.52 \delta_p.
\]

(10)

This simple rule indicates the general direction to take for enhancing the \(T_c\) of MgB\(_2\): no matter whether the \(E_{2g}\) pho-
non is softened or strengthened, if the electron contribution, \( \delta_e \), is greater than 1.52\( \delta_p \), \( T_c \) can be raised.

So far, we have clarified the underlying mechanism of variation for \( T_c \) in terms of the contributions of electrons and phonons. However, in searching for a higher critical temperature in strained MgB\(_2\), it is worth looking at their de-

\[
\delta_{T_c} = a_1x + a_2x^2 + b_1y + b_2y^2 + c_1xy, \tag{11}
\]

where \( x = \Delta a/a \), and \( y = \Delta c/c \). The quality of the fit is excellent with the following fitting parameters: \( a_1 = 9.836 \, 028 \), \( a_2 = -0.865 \, 501 \), \( b_1 = 2.782 \, 717 \), \( b_2 = -0.642 \, 597 \), and \( c_1 = 1.786 \, 229 \) [Figs. 1(a) and 1(b)]. The importance of this fitting formula is that once the strain condition (\( \Delta a/a \) and \( \Delta c/c \)) in MgB\(_2\) is known, \( \delta_{T_c} \) can be predicted directly, and, thus, by using \( T_c = T_{c0}(1 + \delta_{T_c}) \), where \( T_{c0} = 39.4 \, K \) is the value of unstrained MgB\(_2\), \( T_c \) can be obtained without needing expensive DFT calculations.

We now compare the calculated \( \delta_{T_c} \) both from DFT calculations and the fitting formula Eq. (11) with that from experimental data for two typical cases in MgB\(_2\): (i) bulk material with uniaxial pressure (Figs. 1 and 2) and (ii) thin films grown on different substrates (Figs. 1 and 3). With hydrostatic pressure, both the lattice constants \( a \) and \( c \) are compressed (bold red line in Fig. 1), and \( \delta_{T_c} \) falls as the lattice...
constants decrease. Figure 2 compares the experimentally measured $T_c$ as a function of applied pressure with the results of DFT calculations and with Eq. (11); there is excellent agreement between the three. We conclude that applying hydrostatic pressure always leads to a drop in $T_c$.

A higher $T_c$ can be attained in MgB$_2$ thin film under biaxial strain in the $a$-$b$ basal plane in-plane, as depicted in Fig. 1 (bold blue line) and Fig. 3(a). Furthermore, the optimized variation in lattice constant, $\Delta c/c$, determined from minimizing total energy, declines slightly with an increase in $\Delta a/a$ with a negative slope close to $-1/3$. The calculated $T_c$ in strained MgB$_2$ from DFT agrees well with the experimental values using SiC as a substrate [Fig. 3(a)]. The $\delta T_c$ predicted from the fitting formula [Eq. (11)] is consistent with the measured $\delta T_c$ with an error of about $-2\%$ (the same order as the experimental error bar). Our results are striking because not only do they agree with the experiments, but they also reveal the possibility of further improving $T_c$ by using large tensile strains [1% to 3%, Fig. 3(a)]. The enhancement of $T_c$ originates from the decrease in the phonon ($\delta_p$) and electron ($\delta_e$) contributions due to the increase in biaxial strains [see Fig. 3(c)] that satisfy the condition of Eq. (10) in the 3% range of strains. Our finding that decreasing the $E_{2g}$ phonon frequency [Fig. 3(c)] will generate a high $T_c$ in MgB$_2$ agrees well with the experimental observations and

**FIG. 2.** (Color online) Comparison of critical temperature between experiments and the DFT calculation of MgB$_2$ as a function of hydrostatic pressure. The solid line is from the fitting formula [Eq. (11)]. The experimental data is taken from Ref. 7.

**FIG. 3.** (Color online) The critical temperature and other variables in MgB$_2$ as a function of in-plane biaxial strains. (a) Critical temperature $\Delta T_c/T_c$, (b) lattice variation $\Delta c/c$, (c) electron($\delta_e=\Delta N_F(\sigma)/N_F(\sigma)+2\Delta D/D$, red squares) and phonon ($\delta_p=\Delta \omega/\omega$, blue dots) contribution, and (d) boron $\sigma$ band density of state $\Delta N_F(\sigma)/N_F(\sigma)$ (red squares) and deformation potential $\Delta D/D$ (blue dots).
theoretical predictions; i.e., the softened Raman phonon peak in strained MgB$_2$ gives a higher $T_c$.

Our calculations further demonstrate that the $\delta_T$ in MgB$_2$ increases with rising biaxial strains until reaching its maximum of about 10% at ~3% tensile strains; thereafter, it decreases with any further rise in tensile strains and then falls to a negative value at very high strains (~6% or more). The reason this occurs is that Eq. (10) is not fulfilled: thus, although both $\delta_e$ and $\delta_T$ decline, $\delta_e$ decreases at a rate faster than $1.52 \delta_T$. The fall in $T_c$ at high tensile strains reflects the sharp decrease of density of states of the B $\sigma$ band, $N_F(\sigma)$ [Fig. 3(d)].

Taking into account both $\delta_T$ and strained energy in MgB$_2$, we found there is still plenty of room for raising $T_c$ to higher value: if biaxial strains of about 1%–3% can be achieved, the $T_c$ can be enhanced by about 7%–12% (corresponding to $T_c$=42–44 K). So, the question is how to increase biaxial strains. This problem can be resolved by selecting appropriate substrates for growing MgB$_2$ thin films that have a slightly larger lattice constant than that of bulk (or unstrained) MgB$_2$, or applying biaxial tensile stress with a mechanical load in a single crystal. There are several possible substrates: hexagonal SiC, Si$_{1-x}$C$_x$ alloys with a small tunable composition $x$, to vary lattice constant, AlN, GaN and their alloys Al$_{x}$Ga$_{1-x}$N, as well as MgB$_2$ doped with Ca (or Mg$_{1-x}$Ca$_x$B$_2$ alloys). All these materials have a slightly larger biaxial lattice constant than does bulk MgB$_2$ at low temperatures, and, as substrates for MgB$_2$, they will generate tensile strains in the films. In particular, if high-quality MgB$_2$ films can be grown on alloys of Si$_{1-x}$C$_x$, Al$_{x}$Ga$_{1-x}$N, or Mg$_{1-x}$Ca$_x$B$_2$, then, by controlling the composition $x$ of the alloy substrates, the tensile strains, and, thus, $T_c$ can be tuned. For materials that have lattice constants comparable with (or even smaller than) those of MgB$_2$ at room temperature, for example, 6H–SiC ($a=3.0806$ Å at 300 K, $^{27}$) it still is possible to induce tensile strains by cooling the sample to below the $T_c$ of MgB$_2$ because the thermal coefficient of MgB$_2$ ($5.4 \times 10^{-8}$ K$^{-1}$)$^{28}$ is about twice as large as that of SiC ($2.77 \times 10^{-6}$ K$^{-1}$)$^{27}$ resulting in a small tensile strain for MgB$_2$ at low temperatures on a SiC substrate. For AlN with its wurtzite structure, its lattice constant ($a=3.111$ Å)$^{27}$ is slightly larger than that of MgB$_2$, but its thermal expansion coefficient ($4.2 \times 10^{-6}$ K$^{-1}$)$^{29}$ is less. Therefore, by growing MgB$_2$ on an AlN substrate, the tensile strains in the films (~1%) will be larger than those (~0.5%) of films grown on a SiC substrate, and accordingly, the $T_c$ of MgB$_2$ will be enhanced by about 7%–8%.

Finally, we discuss the validation of our approach. Although we used some approximations (for example, the McMillan-Allen-Dynes formula for $T_c$, the variation of $\mu^*$ in strained MgB$_2$ is neglected) in calculating $T_c$ in the strain-induced modulation of MgB$_2$, the excellent agreement between the calculated and experimental $T_c$ for MgB$_2$ in two typical cases (applied hydrostatic pressure and tensile strain) justifies the validity of this approach and suggests that the superconducting properties of MgB$_2$ as a function of strains are mainly dominated by the strain-induced modulation of the $\sigma$ band (e.g., density of states, deformation potentials, $E_{2g}$ phonon frequency). In fact, the McMillan-Allen-Dynes formula has been used for calculating $T_c$ of MgB$_2$ in many cases, for example, for bulk MgB$_2$, $^{26,32}$ MgB$_2$ under pressure, $^{26,32}$ MgB$_2$ doped with carbon, $^{13,33}$ or aluminum$^{34}$ and strained MgB$_2$. $^8$ Another concern centers on the effects of the selected values of $\mu^*$ and $\lambda_0$ on the strain-induced modulation of $T_c$. It was found that the trends of superconducting properties of MgB$_2$ as a function of strains are not affected significantly by the choice of $\mu^*$ and $\lambda_0$. We proved this point by using a wide range of values of $\mu^*$ and $\lambda_0$ with $\mu^*$ being 0.1–0.2, and $\lambda_0$ being 0.6–1.0, for strain-free MgB$_2$, to reproduce $T_c=39.4$ K. As clearly demonstrated in Fig. 4, the $\Delta T_c/T_c$ of strained MgB$_2$ is insensitive to the values of $\mu^*$ and $\lambda_0$. It is worth mentioning that our method describes the relative changes of $T_c$ in terms of relative changes of related physical quantities and, therefore, it will have more precision than the straight calculation of the absolute value of $T_c$ by using the McMillan-Allen-Dynes formula on MgB$_2$, an anisotropic and anharmonic two-band material.

In summary, we used first-principles DFT calculations to determine the electronic, vibrational, and superconducting properties of MgB$_2$ under various conditions of strain. We derived a general rule governing the enhancement (or suppression) of $T_c$ in strained MgB$_2$ in terms of electron and phonon contributions. Based on this rule, we found that the direction of increasing $T_c$ should lie in efforts to increase tensile strains (from 0% up to 4%). The maximum $T_c$ in strained MgB$_2$ may be achieved at tensile strains of 2%–3%. Several candidate substrates for growing MgB$_2$ thin films were suggested. We emphasize that our rule is not limited to MgB$_2$, but it is applicable to other conventional BCS superconductors (with different values of $\beta$), especially those having similar lattice structures to MgB$_2$. Our approach to strain engineering, with the target of enhancing $T_c$ as demonstrated in this work, can be applied to various strain-engineering...
problems in other functional materials. In fact, we have demonstrated, by first-principles calculations, that half-metallic ferromagnetism (an important property for spintronics) can be enhanced in strained zinc-blende structures of MnSb and MnBi.\textsuperscript{15}


ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Materials, Office of Basic Energy Science, under Contract No. DE-AC02-98CH10886.