First-Principles Calculation of the Superconducting Transition in MgB$_2$ within the Anisotropic Eliashberg Formalism

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We present a study of the superconducting transition in MgB$_2$ using the ab-initio pseudopotential density functional method and the fully anisotropic Eliashberg equation. Our study shows that the anisotropic Eliashberg equation, constructed with ab-initio calculated momentum-dependent electron-phonon interaction and anharmonic phonon frequencies, yields an average electron-phonon coupling constant $\lambda = 0.61$, a transition temperature $T_c = 39K$, and a boron isotope-effect exponent $\alpha_B = 0.31$ with a reasonable assumption of $\mu^* = 0.12$. The calculated values for $T_c$, $\lambda$, and $\alpha_B$ are in excellent agreement with transport, specific heat, and isotope effect measurements respectively. The individual values of the electron-phonon coupling $\lambda(\vec{k}, \vec{k}')$ on the various pieces of the Fermi surface however vary from 0.1 to 2.5. The observed $T_c$ 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.

Although MgB$_2$ is a readily available sp-bonded material, superconductivity in this material with a transition temperature of $T_c = 39$ K was found only very recently. This relatively high $T_c$ has motivated many studies, as has the observation that the detailed superconducting properties of MgB$_2$ show significant deviations from those calculated using the standard BCS model. The isotope effect exponent for boron $\alpha_B$ is reduced substantially from the conventional value for sp metals, and the average electron-phonon coupling strength $\lambda$ obtained from specific heat measurement seems too small to justify the high $T_c$. In addition, specific heat measurements, tunneling and photoemission spectra, and point-contact spectroscopy show low energy excitations suggesting a secondary gap. Theoretical calculations show that the Fermi surface has several pieces and is very anisotropic, and that the electron-phonon coupling is dominated by the in-plane B–B stretching modes ($E_{2g}$) which have a large anharmonicity. The electron-phonon interaction varies strongly on the Fermi surface, and a two-band model suggests a multigap scenario. However, there has not yet been a quantitative, first-principles calculation of $T_c$ including the full variation of the electron-phonon interaction on the Fermi surface and the anharmonicity of the phonons to help confirm the phonon-mediating pairing mechanism for superconductivity in MgB$_2$.

In this letter, we present $T_c$ and isotope-effect exponents for MgB$_2$ obtained by solving the $\vec{k}$ and $\omega$ dependent Eliashberg equation. It is shown that the anisotropy (i.e., the electronic-state dependence) of the electron-phonon interaction on the Fermi surface is strong enough to raise $T_c$ to 39K even though the interaction is weakened by the anharmonicity of the phonons as compared to the harmonic case. In addition, it is shown that the anharmonicity of the phonons reduces $\alpha_B$ to 0.31. These results show that conventional phonon-mediated electron pairing theory can explain superconductivity in MgB$_2$ when both the anisotropy of the electron-phonon interaction and the anharmonicity of the phonons are properly taken into account. The solution of the full Eliashberg equation at low $T$ further yields different gap values for the different parts of the Fermi surface. The gap value distribution clusters into two groups – a small value of $\sim$ 2 meV and a large value of $\sim$ 7 meV. This feature and its physical consequences will be described in more details in a future publication.

The phonon frequencies and electron-phonon matrix elements are calculated using ab-initio pseudopotentials and the local density approximation. We used a 18 $\times$ 18 $\times$ 12 k-point grid in the Brillouin zone (BZ), and included planewaves up to 60 Ry as a basis to expand the electronic wavefunctions. The calculated equilibrium lattice constants are $a = 3.071A$ and $c = 3.578A$, in good agreement with measured values. We performed total energy calculations with frozen phonons for all phonon modes at all the high symmetry points of the BZ. The variation of the total energy with a frozen phonon amplitude is fitted with a fourth order polynomial to account for the phonon anharmonicity. To obtain the harmonic phonon frequency, we use the quadratic term of the fitted curve and calculate the frequency classically; whereas for the anharmonic phonon frequency, we calculate quantum-mechanical vibrational states including the anharmonic terms, and take the energy difference of the two lowest states. In the case of the degenerate, in-plane B–B stretching modes ($E_{2g}$) at $\Gamma$ and $A$, we calculate quantum-mechanical vibrational states in two dimensions after the total energy is fitted in a plane with $E(r, \theta) = E_0 + c_2 r^2 + c_4 r^4 + (c_3 \cos \theta + c_3 \cos \theta^3)$. We use natural atomic weights for B and Mg, that is, 10.81 for B and 24.31 for Mg, but $^{10}$B or $^{26}$Mg are used when we recalculate the phonon frequency for the isotope effect. The linear electron-phonon matrix elements are evaluated directly from the total self-consistent change in the

\[ V_{\text{el-ph}}(\vec{k}, \vec{k}') = \sum_{\gamma} \frac{\mathcal{G}_\gamma^c \mathcal{G}_\gamma^s}{\omega_{\gamma}} \delta(\vec{k} - \vec{k}') \]
crystal potential caused by a frozen phonon.

Table I shows the frequency of the in-plane B–B stretching mode ($E_{2g}$) at Γ. This mode is doubly degenerate along the line from Γ to A, and has a large anharmonicity and a large electron-phonon coupling. Anharmonicity increases the frequency by 20% and weakens the corresponding electron-phonon couplings by 30%. The calculated anharmonic frequency, 75.9 meV, for the $E_{2g}$ mode at Γ agrees very well with the results from Raman measurements (75.9 meV [7] and 76.9 meV [8]) as well as other theoretical calculations [13,14]. The $E_{2g}$ modes at $M$, $L$, $K$, and $H$ however have very little anharmonicity and small electron-phonon coupling. The strong anharmonicity and the large electron-phonon coupling are thus confined to phonons in a small volume in $k$-space near the Γ to A line.

The calculated phonon frequencies and electron-phonon matrix elements $g_{j,k,k'}^a = \langle \vec{k}|\delta V^a |\vec{k}'\rangle$ for the $j$th phonon mode are interpolated onto a $18 \times 18 \times 12$ grid in the BZ through the following three-step process. First, we interpolate the dynamical matrices using a weighted average of those at the symmetry points and obtain the phonon frequencies and eigenvectors on the grid by diagonalizing the dynamical matrices. Second, we interpolate the induced crystal potential change by a phonon on the grid from the calculated crystal potential changes at the symmetry points using weighting factors determined from the phonon frequencies and polarization vectors calculated on the fine grid. Finally, we calculate the electron-phonon matrix elements on the grid using the interpolated crystal potential change. All calculations are done twice for comparison: one with harmonic phonon frequencies and another with anharmonic phonon frequencies. To study the isotope effect, we repeat the entire procedure with an isotopic atomic mass.

![FIG. 1. Phonon density of states $F(\omega)$ and the isotropic Eliashberg function $\alpha^2 F(\omega)$ for MgB$_2$.](image)

Figure 1 shows the phonon density of states $F(\omega)$ and the standard Eliashberg function $\alpha^2 F(\omega)$. The phonon density of states shows a large peak at 37 meV arising from the van Hove singularities in the acoustic phonons, but these phonons make no significant contribution to $\alpha^2 F(\omega)$. There is a large dominant peak in $\alpha^2 F(\omega)$ at 63 meV for the case of harmonic phonons, but at 77 meV for anharmonic phonons. The dominant peak in $\alpha^2 F(\omega)$ is caused by the in-plane B–B stretching modes ($E_{2g}$). Because the $E_{2g}$ modes are highly anharmonic and have very large electronic-phonon coupling only for phonons within a small volume along the Γ to A line in $k$-space, anharmonicity has little effect on $F(\omega)$, but it causes a big shift in $\alpha^2 F(\omega)$. In the case of harmonic phonons, as is shown in Table I, the isotropic average electron-phonon coupling constant, $\lambda = 2 \int d\omega \alpha^2 F(\omega)/\omega$, is 0.73 and the logarithmic average frequency, $\omega_n = \exp[(2/\lambda) \int d\omega \alpha^2 F(\omega) \ln \omega / \omega]$, is 59.4 meV. These values and the overall shape of $\alpha^2 F(\omega)$ without anharmonicity in the present calculation are in good agreement with previous calculations [12,14]. With anharmonicity, $\lambda$ is reduced to 0.61 and $\omega_n$ is increased to 63.5 meV. Since $\lambda$ corresponds to the mass enhancement factor for the density of states at the Fermi level regardless of anisotropy in the electron-phonon interaction [19], we can compare the calculated $\lambda$ with results of specific heat measurements. The reduced value of $\lambda = 0.61$ due to anharmonicity agrees very well with result of specific heat measurements which give a $\lambda$ of 0.58 [1] and 0.62 [3]. This agreement is evidence that phonon anharmonicity weakens the electron-phonon interaction in MgB$_2$. However if this value of $\lambda = 0.61$ is used in the McMillan [20] or the Allen-Dynes [21] formula for $T_c$, the predicted $T_c$ would be far lower than experiment.

Unlike previous studies, we solve the fully anisotropic Eliashberg equation for superconductivity in MgB$_2$. The anisotropic Eliashberg equation at $T_c$ [19] is

$$Z(\vec{k}, i\omega_n) = 1 + f_n s_n \sum_{\vec{k}', \vec{k}''} W_{\vec{k}'\vec{k}} \lambda(\vec{k}, \vec{k}'', n) n',$$

$$Z(\vec{k}, i\omega_n) \Delta(\vec{k}, i\omega_n) = \sum_{\vec{k}', \vec{k}''} W_{\vec{k}'\vec{k}} f_n \left[ \lambda(\vec{k}, \vec{k}'', n - n') - \mu^* \right] \times \Delta(\vec{k}'', i\omega_n),$$

(1)

where $\omega_n = (2n + 1)\pi T_c$, $f_n = 1/(2n + 1)$, and $W_{\vec{k}}$ is the fraction of the density of states at $\vec{k}$ on the Fermi surface. For the definition of $Z$, $\Delta$, $\lambda(\vec{k}, \vec{k}'', n)$, and $s_n$, see Ref. [19]. With the exception of $\mu^*$, our calculation of the phonon frequencies and electron-phonon interaction provides all the material parameters for solving Eq. (1) and hence for obtaining $T_c$ from first principles. The dimensionless Coulomb pseudopotential, $\mu^*$ [22], is the only free parameter in our calculation; but it is known to be of order 0.1 in most metals [20,22,23] and we show below that the superconducting properties of MgB$_2$ are insensitive to $\mu^*$. For comparison, we also calculate $T_c$ using the isotropic Eliashberg equation,

$$Z(i\omega_n) = 1 + f_n s_n \sum_{n'} \lambda(n - n') n',$$

$$Z(i\omega_n) \Delta(i\omega_n) = \sum_{n'} f_n \left[ \lambda(n - n') - \mu^* \right] \Delta(i\omega_n),$$

(2)

where $\lambda(n) \equiv \sum_{\vec{k}'\vec{k}} W_{\vec{k}'\vec{k}} \lambda(\vec{k}, \vec{k}'', n)$. Hence $\lambda(n)$ is the electron-phonon coupling averaged over all pairs of $(\vec{k}, \vec{k}')$.
on the Fermi surface. \((\lambda(n = 0)\) is equal to the specific heat \(\lambda\) discussed above.) The isotropic Eliashberg equation is thus a special limited case of the more general anisotropic equation. If the electron-phonon interaction \(\lambda(\vec{k}, \vec{k}', n)\) did not depend strongly on the electronic states on the Fermi surface, the isotropic equation would be an appropriate approximation.

\[ \lambda(\vec{k}, \vec{k}', n) = \sum_{\vec{k}} W_{\vec{k}} \lambda(\vec{k}, \vec{k}', n) \]

The left plot shows the mass enhancement factor given by \(\lambda(\vec{k}, n = 0)\). The right plot shows \(\lambda(\vec{k} = \vec{k}_0, \vec{k}', n = 0)\) as a function of \(\vec{k}'\) for a fixed \(\vec{k}_0\) on the Fermi surface near \(\Gamma\).

The anisotropic Eliashberg equation including anharmonicity in the phonon frequencies yields \(42K \leq T_c \leq 37K\) for \(0.10 \leq \mu^* \leq 0.14\). In particular, \(T_c\) is 39K when \(\mu^* = 0.12\). To investigate the role of anisotropy in the electron-phonon interaction and of anharmonicity of the phonons, we calculate \(T_c\) disregarding one or the other, as shown in Table I. If we neglect the anisotropy and calculate \(T_c\) with the isotropic Eliashberg equation, \(T_c\) drops to 19K for \(\mu^* = 0.12\). This shows that the strong variation in the electron-phonon coupling of scattering on the Fermi surface is crucial to the observed high \(T_c\) in MgB\(_2\). As another comparison, if we calculate \(T_c\) using the anisotropic Eliashberg equation but neglecting the anharmonic effect in the phonon frequencies, \(T_c\) goes up to 55K for \(\mu^* = 0.12\). Hence anharmonicity lowers \(T_c\) in MgB\(_2\). Thus we conclude that anisotropy in MgB\(_2\) is essential to produce the anomalously high \(T_c\), especially in view of the fact that the electron-phonon interaction is weakened by anharmonicity. We note that in MgB\(_2\), an average electron-phonon coupling \(\lambda\) cannot be correctly determined from \(T_c\) using the McMillan [20,24] or Allen-Dynes equations [21], however a determination of \(\lambda\) from the specific heat measurement is still valid. The \(T_c\) of MgB\(_2\) is not a function of the usual isotropically averaged electron-phonon interaction \(\lambda\) given above; it depends on the details of electron-phonon interactions on the full Fermi surface. This explains the apparent discrepancy between the values of \(\lambda\) estimated from specific heat measurements and \(\lambda\) estimated from \(T_c\) using simplified isotropic models.

To calculate the isotope-effect exponent \(\alpha\) \((T_c \propto M^{-\alpha})\), we recalculate \(T_c\) using the mass of either \(^{10}\text{B}\) or \(^{26}\text{Mg}\) in place of the natural atomic weight. Since the relevant phonons are related to motion of the B atoms, the Coulomb pseudopotential \(\mu^*\) also depends on the atomic mass of boron \(M_B\). The change of \(\mu^*\) is simply

\[ \delta \mu^* = -\langle \mu^* \rangle^2 \delta M_B \frac{2 M_B}{2 M_B} \]

using \(\mu^* = \mu/[1 + \mu \ln(\epsilon_f/\omega_0)]\) and \(\omega_0 \propto M_B^{-0.5}\).

Table I shows calculated isotope-effect exponents with \(\mu^* = 0.12\) both with and without phonon anharmonicity. Without anharmonicity, the slight deviation of the sum of the two exponents, \(\alpha_B\) and \(\alpha_M\), from the value of 1/2 is due to the change of \(\mu^*\) given by Eq. (3). If we neglect \(\delta \mu^*\), the total isotope-effect exponent would be
0.5. In contrast, when we include anharmonicity in the phonon frequency, the isotope-effect exponent for boron is substantially suppressed. We obtain $\alpha_B = 0.31$ and $\alpha_{\mu_g} = 0.05$ from the anisotropic Eliashberg equation with anharmonic phonon frequencies. In this case, the contribution of $\delta \mu^*$ to the decrease of $\alpha_B$ is only 0.02, so the anomalously low isotope-effect exponent is primarily due to phonon anharmonicity.

In conclusion, we have shown from first-principles calculations that MgB$_2$ is a conventional phonon-mediated superconductor whose properties require, for a correct description, a solution of the fully anisotropic Eliashberg equation including phonon anharmonicity. The isotropic Eliashberg equation seriously underestimates $T_c$ due to phonon anharmonicity. The isotropic Eliashberg equation seriously underestimates $T_c$ because it fails to account for the $(\vec{k}, \vec{k}')$-dependency of the electron-phonon interaction on the Fermi surface [2]. We show that the electron-phonon coupling is exceedingly strong for certain pairs of $(\vec{k}, \vec{k}')$ on the disconnected Fermi surface of this material. The anisotropy of the electron-phonon interaction in MgB$_2$ is strong enough to produce the observed $T_c$ of 39 K in spite of a moderate average electron-phonon interaction as also seen in specific heat measurements. In addition, we have shown that the anharmonicity of the phonons in MgB$_2$ weakens the electron-phonon interaction and reduces the boron isotope-effect exponent.

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[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature 410, 63 (2001)
[2] S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. 86, 1877 (2001).
[3] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature 411, 457 (2001).
[4] Y. Wang, T. Plackowski, and A. Junod, Physica C, 355, 179 (2001).
[5] F. Bouquet, R. A. Fisher, N. E. Phillips, D. G. Hinks, and J. D. Jorgensen, Phys. Rev. Lett. 87, 47001 (2001).
[6] F. Giubileo, D. Roditchev, W. Sacks, R. Lamy, D. X. Thanh, J. Klein, S. Miraglia, D. Fruchart, J. Marcus, and Ph. Monod, Phys. Rev. Lett. 87, 177008 (2001).
[7] S. Tsuda, T. Yokoya, T. Kiss, Y. Takano, K. Togano, H. Kito, H. Ihara, and S. Shin, Phys. Rev. Lett. 87, 177006 (2001).
[8] P. Szabó, P. Samuely, J. Kačmarčík, T. Klein, J. Marcus, D. Fruchart, S. Miraglia, C. Marcenat, and A. G. M. Jansen, Phys. Rev. Lett. 87, 137005 (2001).
[9] F. Laube, G. Goll, J. Hagel, H. v. Lohneysen, D. Ernst, and T. Wolf, cond-mat/0106407 (2001).
[10] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. 86, 4656 (2001).
[11] J. M. An and W. E. Pickett, Phys. Rev. Lett. 86, 4366 (2001).
[12] K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. 86, 5771 (2001).
[13] T. Yildirim, O. Gülseren, J. W. Lynn, C. Brown, T. J. Udovic, Q. Huang, N. Rogado, K. A. Regan, M. A. Hayward, J. S. Shusky, T. He, M. K. Haas, P. Khalifah, K. Inumaru, and R. J. Cava, Phys. Rev. Lett. 87, 37001 (2001).
[14] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. 87, 87005 (2001).
[15] Y. Kong, O. V. Dolgov, O. Jepsen, and O. K. Andersen, Phys. Rev. B 64 20501 (2001).
[16] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, to be published.
[17] J. Hlinka, I. Gregora, J. Pokorný, A. Plecenik, P. Kúš, L. Satrapinsky, and Š. Beňačka, Phys. Rev. B 64, 140503 (2001).
[18] A. F. Goncharov, V. V. Struzhkin, E. Gregoryanz, J. Hu, R. J. Hemley, H.-k. Mao, G. Lapertot, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 64, 100509 (2001).
[19] P. B. Allen and B. Mitrović, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, D. Turnbull (Academic, New York 1982), Vol. 37, p. 1. and references therein.
[20] W. L. McMillan, Phys. Rev. 167, 331 (1968) and references therein.
[21] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
[22] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).
[23] J. P. Carbotte, Rev. Mod. Phys. 62, 1027 (1990).
[24] We have also tested the widely used McMillan formula for $T_c$ [20]. In MgB$_2$, the McMillan formula underestimates $T_c$ by typically 30% even when compared with results from the isotropic Eliashberg equation.

| Table I. Transition temperature $T_c$ and isotope-effect exponents $\alpha$ with $\mu^*$ = 0.12. Numbers in parentheses are the values of $\alpha_B$ when $\delta \mu^*$ of Eq.(3) is ignored. The averaged electron-phonon coupling $\lambda$ and the frequency $\omega_{ph}$ of the in-plane B–B stretching modes $(E_{2g})$ at $\Gamma$ are also included. |
| --- |
| $T_c$ | 28 K | 55 K | 19 K | 39 K | 39 K |
| $\alpha_B$ | 0.41 | 0.48 | 0.21 | 0.31 | 0.26 | 0.30 |
| $\alpha_{\mu_g}$ | 0.04 | 0.02 | 0.06 | 0.05 | 0.02 |
| $\lambda$ | 0.73 | 0.61 | 0.58 | 0.62 | 0.62 |
| $\omega_{ph}$ | 62.7 meV | 75.9 meV | 75.9 meV | 76.9 meV | 76.9 meV |