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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, a fully anisotropic Eliashberg equation, and a conventional estimate for μ^*. 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 $T_c = 39$ K, and a boron isotope-effect exponent $\alpha_B = 0.32$. The calculated values for T_c, λ, and α_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.

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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.[1] 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 α_B is reduced substantially from the conventional value for sp metals,[2,3] and the average electron-phonon coupling strength λ obtained from specific-heat measurement[4–7] seems too small to justify the high T_c. In addition, specific-heat measurements,[4–7] tunneling[8] and photoemission[9] spectra, and point-contact spectroscopy[10,11] show low-energy excitations suggesting a secondary gap. Theoretical calculations show that the Fermi surface has several pieces and is very anisotropic,[12] and that the electron-phonon coupling is dominated by the in-plane B–B stretching modes (E_{2g}),[12–14] which have a large anharmonicity.[15,16] The electron-phonon interaction varies strongly on the Fermi surface,[16,17] and a two-band model suggests a multigap scenario.[16,18] 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 Communication, we present T_c and isotope-effect exponents for MgB_2 obtained by solving the $\vec{k}$- and ω-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 39 K 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 α_B to 0.32. 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 ~ 2 meV and a large value of ~ 7 meV. This feature and its physical consequences will be described in more detail in a future publication.[19]

The phonon frequencies and electron-phonon matrix elements are calculated using *ab initio* pseudopotentials and the local-density approximation. We used a $12\times12\times12$ k-point grid in the Brillouin zone (BZ) for self-consistent calculations and a $18\times18\times12$ grid for the Fermi surface properties, and included plane waves up to 60 Ry as a basis to expand the electronic wave functions. The calculated equilibrium lattice constants are $a = 3.071$ Å and $c = 3.578$ Å, in good agreement with measured values.[1] 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 Γ and A, we calculate quantum-mechanical vibrational states in two dimensions after the total energy is fitted in a plane with $E(r,\theta) = E_0 + c_2 r^2 + c_4 r^4 + (c_3 r^3 + c_5 r^5)\cos(3\theta)$. 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 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

TABLE I. Transition temperature T_c and isotope-effect exponents α with $\mu^*(\omega_c)=0.12$. Numbers in parentheses are the values of α_B when $\delta\mu^*(\omega_c)$ of Eq. (3) is ignored. The averaged electron-phonon coupling λ and the frequency ω_{ph} of the in-plane B–B stretching modes (E_{2g}) at Γ are also included.

	Harmonic		Anharmonic		Experiment
	Isotropic	Anisotropic	Isotropic	Anisotropic	
T_c	28 K	55 K	19 K	39 K	39 K [a]
α_B	0.42	0.46	0.25	0.32	0.26 [b],0.30 [c]
	(0.46)	(0.48)	(0.27)	(0.33)	
α_{Mg}	0.04	0.02	0.05	0.03	0.02 [c]
λ	0.73		0.61		0.58 [d],0.62 [e]
ω_{ph}	62.7 meV		75.9 meV		75.9 [f],76.9 [g]

[a]Reference 1.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.
[e]Reference 5.
[f]Reference 20.
[g]Reference 21.

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 (Ref. 20) and 76.9 meV (Ref. 21)] as well as other theoretical calculations.[15,16] 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 $g^j_{\vec{k},\vec{k}'}=\langle\vec{k}|\delta V^j_{\vec{q}}|\vec{k}'\rangle$ for the jth phonon mode are interpolated onto a $18\times18\times12$ 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.

Figure 1 shows the phonon density of states $F(\omega)$ and the standard Eliashberg function $\alpha^2F(\omega)$. 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 $\alpha^2F(\omega)$. There is a large dominant peak in $\alpha^2F(\omega)$ at 63 meV for the case of harmonic phonons but at 77 meV for anharmonic phonons. The dominant peak in $\alpha^2F(\omega)$ is caused by the in-plane B–B stretching modes (E_{2g}). Because the E_{2g} modes are highly anharmonic and have very large electron-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 $\alpha^2F(\omega)$. In the case of harmonic phonons, as is shown in Table I, the *isotropic* average electron-phonon coupling constant, $\lambda=2\int d\omega\alpha^2F(\omega)/\omega$, is 0.73 and the logarithmic average frequency, $\omega_{ln}=\exp[(2/\lambda)\int d\omega\alpha^2F(\omega)\ln\omega/\omega]$, is 59.4 meV. These values and the overall shape of $\alpha^2F(\omega)$ without anharmonicity in the present calculation are in good agreement with previous calculations.[14,16] With anharmonicity, λ is reduced to 0.61 and ω_{ln} is increased to 63.5 meV. Since λ corresponds to the mass enhancement factor for the density of states at the Fermi level regardless of anisotropy in the electron-phonon interaction,[22] we can compare the calculated λ 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 λ of 0.58 (Ref. 4) and 0.62.[5] 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[23] or the Allen-Dynes[24] formula for T_c, the predicted T_c would be far lower than experiment.

Unlike previous studies, we solve the fully anisotropic

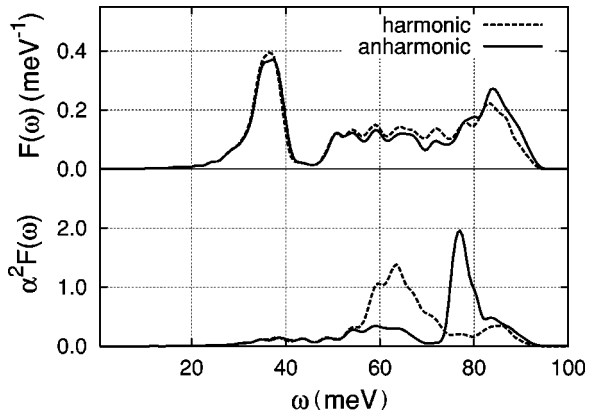

FIG. 1. Phonon density of states $F(\omega)$ and the isotropic Eliashberg function $\alpha^2F(\omega)$ for MgB_2.

Eliashberg equation for superconductivity in MgB_2. The anisotropic Eliashberg equation at T_c (Ref. 22) is

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

$$Z(\vec{k},i\omega_n)\Delta(\vec{k},i\omega_n)=\sum_{\vec{k}'n'} W_{\vec{k}'}f_{n'}[\lambda(\vec{k},\vec{k}',n-n')-\mu^*(\omega_c)] \times\Delta(\vec{k}',i\omega_{n'}), \quad (1)$$

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. The cutoff frequency ω_c is set to 0.5 eV which is about six times larger than the maximal phonon frequency. For the definition of Z, Δ, $\lambda(\vec{k},\vec{k}',n)$, and s_n, see Ref. 22. With the exception of $\mu^*(\omega_c)$, 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 $\mu^*(\omega)$, which is defined by $\mu^*(\omega)=\mu/[1+\mu\ln(\epsilon_F/\omega)]$, is known to be of order 0.1 in most metals when ω is a relevant phonon frequency,[23,25,26] and we show below that the superconducting properties of MgB_2 are not very sensitive to $\mu^*(\omega_c)$. For comparison, we also calculate T_c using the isotropic Eliashberg equation,

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

$$Z(i\omega_n)\Delta(i\omega_n)=\sum_{n'} f_{n'}[\lambda(n-n')-\mu^*(\omega_c)]\Delta(i\omega_{n'}), \quad (2)$$

where $\lambda(n)\equiv\Sigma_{\vec{k}\vec{k}'}W_{\vec{k}}W_{\vec{k}'}\lambda(\vec{k},\vec{k}',n)$. 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 λ 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.

Figure 2 shows the variation of the calculated electron-phonon interaction on the Fermi surface of MgB_2. The Fermi surface of MgB_2 consists of four sheets; two holelike coaxial cylinders consisting of σ-boron in-plane states along Γ to A, a holelike tubular network of π-boron states connecting regions near K and M, and an electronlike tubular network of π-boron states connecting regions near H and L. In Fig. 2, the mass enhancement factor for states at $\vec{k}$ given by $\lambda(\vec{k},n=0)=\Sigma_{\vec{k}'}W_{\vec{k}'}\lambda(\vec{k},\vec{k}',n=0)$ shows two well-separated sets of values on the Fermi surface. $\lambda(\vec{k},n=0)$ is about 0.8–1.0 on the two σ cylindrical sheets and is only about 0.3–0.5 on the two π sheets. For more detail, we depict the value of $\lambda(\vec{k}=\vec{k}_0,\vec{k}',n=0)$ as a function of $\vec{k}'$ for a fixed $\vec{k}=\vec{k}_0$ on the Fermi surface near Γ. It shows strong and varying

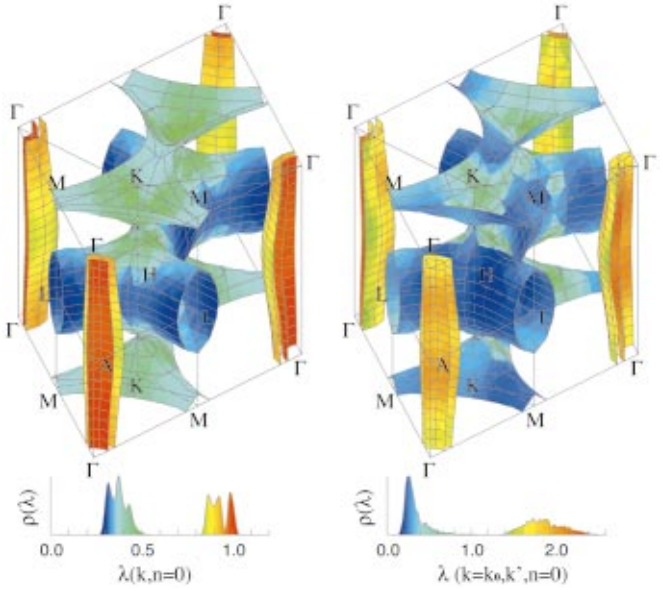

FIG. 2. (Color) Variation of the electron-phonon interaction λ on the Fermi surface of MgB_2. The left plot shows the mass enhancement factor given by $\lambda(\vec{k},n=0)$. The right plot shows $\lambda(\vec{k}=\vec{k}_0,\vec{k}',n=0)$ as a function of $\vec{k}'$ for a fixed $\vec{k}_0$ on the Fermi surface near Γ.

strength for scattering onto the σ cylindrical surfaces but rather weak strength for scattering to the π sheets. Figure 3 shows the number density of $(\vec{k},\vec{k}')$ pairs on the Fermi surface plotted as a function of the value of $\lambda(\vec{k},\vec{k}',n=0)$. The coupling strength $\lambda(\vec{k},\vec{k}',n=0)$ between states on the σ cylindrical sheets has values exceeding 2.0 which is much larger than those within the π tubular sheets or between a σ cylindrical sheet and a π tubular sheet. All this information and $\lambda(\vec{k},\vec{k}',n)$ with nonzero n are taken into account when solving the anisotropic Eliashberg equation.

The anisotropic Eliashberg equation including anharmonicity in the phonon frequencies yields 42 K$\geqslant T_c \geqslant$37 K

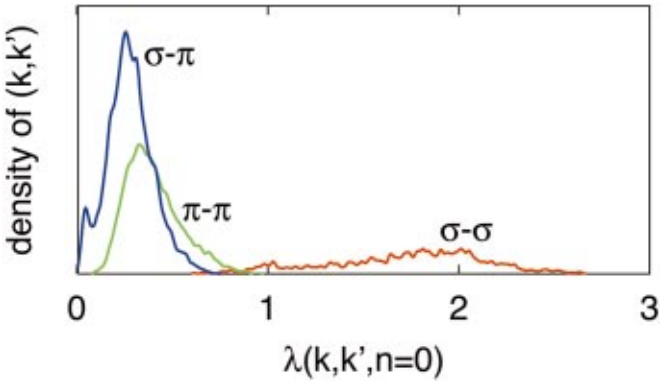

FIG. 3. (Color) Number density of (k,k') pairs on the Fermi surface versus the value of $\lambda(\vec{k},\vec{k}',n=0)$. The number density is split into three sets: both k and k' are on the two σ cylindrical sheets of the Fermi surface (red line), both on the two π tubular sheets (green line), and one on a σ cylindrical sheet and the other on a π tubular sheet (blue line).

for $0.10 \leqslant \mu^*(\omega_c) \leqslant 0.14$. In particular, T_c is 39 K when $\mu^*(\omega_c)=0.12$, which corresponds to $\mu^*(\omega_{\ln})=0.10$. 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 19 K for $\mu^*(\omega_c)=0.12$. 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 neglect the anharmonic effect in the phonon frequencies, T_c goes up to 55 K for $\mu^*(\omega_c)=0.12$. 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 λ cannot be correctly determined from T_c using the McMillan[23] or Allen-Dynes[24] equations. However, a determination of λ 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 λ given above; it depends on the details of electron-phonon interaction on the full Fermi surface. This explains the apparent discrepancy between the values of λ estimated from specific-heat measurements and λ estimated from T_c using simplied isotropic models.

To calculate the isotope-effect exponent α ($T_c \propto M^{-\alpha}$), we recalculate T_c using the mass of either ^{10}B or ^{26}Mg in place of the natural atomic weight. In these recalculations, we scale ω_c in proportion to T_c in order to avoid a *discrete* change of the number N of ω_n's in Eq. (1) [or Eq. (2)]. A change of N may introduce slight numerical errors in analyzing a small change in T_c. The scaling of ω_c causes a change in $\mu^*(\omega_c)$, which is simply

$$\delta\mu^*(\omega_c)=[\mu^*(\omega_c)]^2\frac{\delta T_c}{T_c}. \tag{3}$$

Table I shows calculated isotope-effect exponents with $\mu^*(\omega_c)=0.12$ both with and without phonon anharmonicity. Without anharmonicity, the slight deviation of the sum of the two exponents, α_B and α_{Mg}, from the value of 1/2 is due to the change of $\mu^*(\omega_c)$ given by Eq. (3). In contrast, when we include anharmonicity in the phonon frequency, the isotope-effect exponent for boron is substantially suppressed. We obtain $\alpha_B=0.32$ and $\alpha_{Mg}=0.03$ from the anisotropic Eliashberg equation with anharmonic phonon frequencies. In this case, the contribution of $\delta\mu^*(\omega_c)$ to the decrease of α_B is only 0.01, 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 because it fails to account for the $(\vec{k},\vec{k}')$ dependency of the electron-phonon interaction on the Fermi surface. 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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