Electron-phonon interaction in the normal and superconducting states of MgB$_2$

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For the 40K-superconductor MgB$_2$ we have calculated the electronic and phononic structures and the electron-phonon interaction throughout the Brillouin zone 	extit{ab initio}. In contrast to the isoelectronic graphite, MgB$_2$ has holes in the bonding $\sigma$-bands, which contribute 42 per cent to the density of states: $N(0)=0.355$ states/(MgB$_2$eV-spin). The total interaction strength, $\lambda=0.87$ and $\lambda_{tr}=0.60$, is dominated by the coupling of the $\sigma$-holes to the bond-stretching optical phonons with wavenumbers in a narrow range around 600 cm$^{-1}$. Like the holes, these phonons are quasi two-dimensional and have wave-vectors close to $\Gamma A$, where their symmetry is E. The $\pi$-electrons contribute merely 0.25 to $\lambda$ and to $\lambda_{tr}$. With Eliashberg theory we evaluate the normal-state resistivity, the density of states in the superconductor, and the B-isotope effect on $T_c$ and $\Delta_0$, and find excellent agreement with experiments, when available. $T_c=40$ K is reproduced with $\mu^*=0.10$ and $2\Delta_0/k_BT_c=3.9$. MgB$_2$ thus seems to be an intermediate-coupling e-ph pairing $s$-wave superconductor.

The recent discovery of superconductivity with $T_c = 39$ K in the graphite-like compound MgB$_2$ has caused hectic activity. Density-functional (LDA) calculations show that, in contrast to intercalated graphite ($T_c \leq 5$ K) and alkali-doped fullerides, A$_3$C$_{60}$ ($T_c < 40$ K), in MgB$_2$ there are holes at the top of the B-B bond $\sigma$-bands, and that these couple rather strongly to optically allowed B-B bond-stretching modes with wavenumbers around 600 cm$^{-1}$. These are the same type of modes as those believed to couple most strongly to the $\pi$-electrons in graphite and C$_{60}$, where their wavenumbers are 2.5 times larger, however. Rough estimates of the electron-phonon coupling-strength for $s$-wave pairing in MgB$_2$ yield: $\lambda \sim 1$. Measurements of the B-isotope effect on $T_c$, tunneling transport, thermodynamic properties, and the phonon density of states confirm that MgB$_2$ is most likely an electron-phonon mediated $s$-wave superconductor with intermediate or strong coupling.

In order to advance, detailed comparisons between accurate results of Eliashberg theory and experiments are needed. Consider again the example of A$_3$C$_{60}$, also believed to be conventional $s$-wave superconductors, with $T_c$'s described by the McMillan expression:

$$T_c^{\text{McM}} = \frac{\omega_{\text{ph}}}{1.2} \exp \left[ \frac{-1.04(1+\lambda)}{\lambda - (1+0.62\lambda)\mu^*} \right].$$  \hspace{1cm} (1)

The LDA values for $\lambda$ are 0.4–0.6 and the value of the Coulomb pseudopotential $\mu^*$ to be used in (1) is presumably considerably larger than the usual value, 0.1–0.2, for $sp$-materials due to the small width ($\sim$0.5 eV) of the $t_{1u}$-$\pi$-band compared with the on-ball Coulomb repulsion. For MgB$_2$, where the $\pi$-band is 15 eV broad, one expects $\mu^*$ to be 0.1–0.2 and the LDA plus generalized-gradient correction to give $\lambda$ with an accuracy better than 0.1. The result of such a $\lambda$-calculation will be presented here and should allow us to reach conclusions about the superconductivity in MgB$_2$.

MgB$_2$ consists of graphite-like B$_2$-layers stacked on-top with Mg in-between. The primitive translations are: $a=(\sqrt{3}/2, 1/2, 0)$, $b=(0, a, 0)$, $c=(0, 0, c)$, with $a=3.083\AA=5.826a_0$ and $c/a=1.142$. In reciprocal space, and in units of $2\pi/a$, the primitive translations are: $\Gamma=(0, 0, 0)$, $A=(2/\sqrt{3}, 0, 0)$, $B=(-1/\sqrt{3}, 1, 0)$, $C=(0, 0, a/c)$, and the points of high symmetry are: $\Gamma=(0, 0, 0)$, $\Lambda=(0, 0, 2c)$, $M=(1/\sqrt{3}, 0, 0)$, $L=(1/\sqrt{3}, 0, a/2c)$, $K=(1/\sqrt{3}, 1, 0)$, $H=(1/\sqrt{3}, 1/3, a/2c)$. To reach a numerical accuracy exceeding 0.1 for $\lambda$ requires careful sampling throughout the Brillouin-zone for electrons as well as for phonons, due to the small size of the cylindrical $\sigma$-hole sheets. We therefore used Savrasov’s linear-responce full-potential LMTO density-functional method, proven to describe the superconducting and transport properties of $e.g.$ Al and Pb with high accuracy. The Brillouin-zone integrations were performed with the full-cell tetrahedron method with the $k$-points placed on the ($A, B, C$)/24 sublattice. For the valence bands, a triple-kappa $sp$ LMTO basis set was employed and the Mg $2p$-semicore states were treated as valence states in a separate energy window. The charge densities and potentials were represented by spherical harmonics with $l \leq 8$ inside the non-overlapping MT spheres, and by plane waves with energies $\leq 201$ Ry in the interstitial region.

The resulting electronic structure is practically identical with that of previous calculations. Near and below the Fermi level there are two B $p_z$ $\pi$-bands and three quasi-2D B-B bonding $\sigma$-bands. The $\sigma$ and $\pi$ bands do not hybridize when $k_z=0$ and $\pi/c$. The $\pi$-bands lie lower with respect to the $\sigma$-bands than in graphite and have more $k_z$-dispersion due to the influence of Mg, the
on-top stacking, and the smaller c/a-ratio. This causes the presence of $p_{st}=0.056$ light and $p_{sh}=0.117$ heavy holes near the doubly-degenerate top along $\Gamma A$ of the $\sigma$-bands. For the density of states at $\varepsilon_F=0$, we find:

$$N(0) = N_{st}(0) + N_{sh}(0) + N_c(0) = 0.048 + 0.102 + 0.205 = 0.355\text{ states/(MgB}_2\text{eV-spin)}.$$ 

The $\sigma$ and $\pi$-bands may be understood and described with reasonable accuracy near $\varepsilon_F$ using the orthogonal tight-binding approximation with respective the B $p_z$ orbitals and the B-B two-center bond-orbitals formed from the B $sp^2$ hybrids: With two $p_z$ orbitals per cell and hopping between nearest neighbors only ($\varepsilon_z = 0.41\text{ eV}$, $t_z=0.92\text{ eV}$, and $t_z=1.60\text{ eV}$), the $\pi$-bands are respectively

$$\varepsilon_n(k) = \varepsilon_z + 2t_z^2 \cos k_z^2 + t_z \sqrt{1 + 4 \cos (ak_y/2) \cos (ak_z\sqrt{3}/2)}.$$

The bonding $\sigma$-band Hamiltonian is:

$$H_{\sigma}(k) = t_{sp^2} - 2t_b^2 \cos k_z,$$

in the representation of the three bond-orbitals per cell, with $t_{sp^2}$ being the energy of the two-center bond, and the integrals for hopping between nearest and 2nd-nearest bond orbitals in the same layer being respectively $t_b=5.69\text{ eV}$ and $t_b'=0.91\text{ eV}$, and with $t_z=0.094\text{ eV}$ being an order of magnitude smaller than $t_z$. Moreover, $\alpha = \frac{1}{2}k \cdot a$, $\beta = \frac{1}{2}k \cdot b$, and $\gamma = \frac{1}{2}k \cdot (b-a)$. Along $\Gamma A$, $\alpha=\beta=\gamma=0$ so that there is a singly-degenerate band of symmetry $A$ with dispersion $t_{sp^2} - 2t_b^2 \cos k_z - 4(t_b + t_b')$ and a doubly-degenerate band of symmetry $E$ with dispersion $t_{sp^2} - 2t_b^2 \cos k_z + 2(t_b + t_b')$. The E-band is slightly above the Fermi level and its eigenvectors are given in the two inserts at the bottom of Fig. 1. The Fermi-surface sheets are warped cylinders, which may be described by expanding the two upper bands of $H_{\sigma}(k)$ to lowest order in $k^2 + k^2 \equiv k^2_F$. This yields:

$$\varepsilon_{\sigma n}(k) = \varepsilon_0 - 2t_b^2 \cos k_z - k^2/2m_{\sigma n},$$

where $\varepsilon_0 \equiv t_{sp^2} + 2(t_b + t_b') = 0.58\text{ eV}$ is the average energy along $\Gamma A$ and the units of $k^2_F/m_{\sigma n}$ and $k^2_F$ are respectively $\text{Ry}$ and $a_0^{-1}$. The light and heavy-hole masses are respectively $m_{\sigma l} = 4/(t_b a^2) = 0.28$ and $m_{\sigma h} = 4/(3t_b a^2) = 0.59$ relatively to that of a free electron. For energies so closely below $\varepsilon_F$ that $\varepsilon(\varepsilon) \equiv \sum_{n,k} \delta[\varepsilon_n(k)] \delta(\varepsilon - \varepsilon_n(k)) |g_{nk,k+q,m}^n|^2 \equiv \pi N(0)\omega_m(q) \lambda_m(q),$ the factor 2 is from spin degeneracy and $\sum_k$ is the average over the Brillouin zone, so that $N(0) = \sum_{n,k} \delta[\varepsilon_n(k)]$. We have (safely) assumed that $\omega_m(q) \ll q \cdot v_n(k)$, where $v_n(k) \equiv \nabla_k \varepsilon_n(k)$ is the electron velocity. The e-ph matrix element is: $g_{nk,k+q,m} = \langle nk|\delta|v_n(k+q)|\delta Q\omega_m\rangle$, where the displacement in the $i$-direction of the $j$th atom is related to the phonon eigenvector $\epsilon_{ij,mq}$ and displacement $\delta Q\omega_m$ by: $\delta R_{ij} = \epsilon_{ij,mq} Q\omega_m/\sqrt{2M_j\omega_m}$. The Eliashberg spectral function is:

$$\alpha^2(\omega)F(\omega) \equiv \frac{1}{2\pi N(0)} \sum_{mq} \frac{\gamma_m(q)}{\omega_m(q)} \delta(\omega - \omega_m(q)),$$

and the strength of the e-ph interaction is finally: $\lambda \equiv 2 \int_0^\infty \omega^{-1} \alpha^2(\omega) F(\omega) \, d\omega = \sum_{mq} \lambda_m(q).$
The dominance of the σ-σ coupling via the optical bond-stretching mode is clearly seen in Fig. 1 where the area of a black circle is proportional to $\lambda_m(\mathbf{q})$. Along ΓA, except when $\mathbf{q} \cdot \mathbf{v} < \omega$, only the small $k_z$-dispersion ($t_1^b$) makes $\lambda_m(\mathbf{q})$ not diverge so that the numerical values are inaccurate due to the relative coarseness our k-mesh. The nearly cylindrical σ-sheets, whose diameters are of about the same size as the smallest, non-zero $q_2$ on the affordable (A,B,C)/6-mesh, require even more care in the numerical q-integration: In case of a single cylindrical sheet with μ holes, $\lambda(q_1)$ has the well-known $\text{Im} \chi(q_1,\omega \rightarrow 0)$-form: $\lambda(q_1) = (2\pi \rho x \sqrt{1-x^2})^{-1} \theta(1-x)$ with $x=q_{12}/2k_F$. This function vanishes when $q_{12}>2k_F$, has a flat minimum of value $(\pi p)^{-1}$ near $q_{12}=-\sqrt{2k_F}$, and has integrable divergencies at $q_{12}=2k_F$ and 0. The proper average of $\lambda(q_1)$ is $\lambda$. This means, that $\lambda(\mathbf{q})$ calculated on a coarse mesh scatter violently for small $|\mathbf{q}|$, but that weighting with $\lambda/\lambda(q_1)$ gives the same, correct result for all these points, provided that warping, as well as $\mathbf{k}, \mathbf{k}'$-dependence of $g$ and $\omega$, are neglected. In case of two cylindrical sheets, and no coupling between them, $\lambda_\alpha(q_1)/\lambda_\alpha$ should be weighted by $m_\alpha^2/(m_1^2 + m_2^2)$. In our numerical evaluation of the e-ph interaction with the linear-response code, we discarded the values of $\lambda_m(\mathbf{q})$ with $\mathbf{q}$ along ΓA, and added those on the (A/12, B/12, C/6)-mesh for which $\sqrt{2k_F} \lesssim q_{12} \lesssim \sqrt{2k_F}$, where the result was: $\lambda > 0.62+0.25$, where 0.62 was the contribution from $\mathbf{q}$'s so small that the σ-σ coupling occurs, and 0.25 was the contribution from the remaining part of $|\mathbf{q}|$-space, which must involve a π-sheet. Had we included the inaccurate $\lambda_m(\mathbf{q})$-values along the ΓA-line, the σ-σ result would have been 0.72 instead of 0.62. The result was finally checked by using the approximate $\lambda(q_1)/\lambda$ correction for the point $\mathbf{q}=A/12$. This yielded 0.58 instead of 0.62. In conclusion: $\lambda = 0.87 \pm 0.05 = (0.62 \pm 0.05) + 0.25 \equiv \lambda_\sigma + \lambda_\pi$.

The Eliashberg function shown on the right-hand side of Fig. 1 is dominated by the large σ-σ peak around $\omega_{\text{obs}}=590 \text{ cm}^{-1}$. The facts that the σ-sheets are narrow, warped cylinders whose coupling is dominated by intra-sheet coupling via the optical bond-stretching mode, and that the coupling between σ- and π-sheets is negligible, lead to the following approximation:

$$\alpha^2(\omega) F(\omega) \approx \alpha_\sigma^2(\omega) F(\omega) \frac{[N_{\sigma}(0)/N(0)]}{\left[2\pi \right] \left[ \omega - \omega_{\text{obs}} \right] + \left[ g_{\sigma,\text{obs}} \right]^2 \left[ \omega - \omega_{\text{obs}} \right] \left[ N_{\sigma}^2(0) + N_{\sigma}^2(0) \right] / N(0),$$

where $\alpha_\sigma^2(\omega) F(\omega)$ is the usual expression, but with π-electrons only. In An’s and Picket’s estimate $\lambda_\pi=0.95$, a factor $[N_{\sigma}^2(0) + N_{\sigma}^2(0)] / N(0) = 0.24$ appears to be missing. The rigid-atomic-sphere estimate $\lambda=0.7$ by Kortus et al. is closer to our value 0.87.

Knowing $\alpha^2(\omega) F(\omega)$ and a value of the Coulomb pseudopotential $\mu^*(\omega_c)$, we solve the Eliashberg equation on the real frequency axis, and obtain $T_c=40$K if $\mu^*(\omega_c)=0.14$. Taking retardation effects into account, we find $\mu^* \equiv \mu^*(\omega_c) / [1 + \mu^*(\omega_c) \ln(\omega_c/\omega_{\text{in}})] = 0.10$, where $\omega_{\text{in}}=504 \text{ cm}^{-1}$ is obtained from: $0=\int_{\omega_{\text{in}}}^{\omega_{\text{c}}} \ln(\omega/\omega_{\text{in}}) \omega^{-1} \alpha^2(\omega) F(\omega) \, d\omega$, and the cut-off frequency is taken as $\omega_{\text{c}}=10 \text{ max} \omega=8000 \text{ cm}^{-1}$. This value
of $\mu^*$ is the lower end of what is found for simple $sp$-metals. The relation back to a screened Coulomb interaction $U$ is: $\mu^* = \mu/[1 + \mu \ln(\omega_p/\omega_m)]$, where $\mu=UN(0)$ and $\omega_m \sim 7$ eV is the plasma frequency given below. We thus find: $\mu=0.19$ and $U=1.1$ eV, which are normal values. Had we used the approximate McMillan expression, the slightly higher value $\mu^*=0.14$ would be needed to reproduce the experimental $T_c$.

In Fig.2, we show our Eliashberg calculation with $\mu^*=0.10$ of the density of states, $N_s(\varepsilon)/N(0) = \text{Re} \left[ \varepsilon/\sqrt{\varepsilon^2 - \Delta_{3K}^2(\varepsilon)} \right]$, in the superconductor. The BCS singularity is at $\varepsilon=\Delta_{3K}(0)=6.8$ meV, which is in accord with the 4.9-6.9 meV found in tunneling experiments. This yields: $2\Delta_0/k_BT_c=3.9$ which is slightly higher than the BCS value of 3.52. The distinct feature near 80 meV corresponds to the peak in $\alpha^2(\omega)F(\omega)$ at 73 meV, shifted by the 6.8 meV gap. The latter function is also shown in the figure together with the measurable quantity $-d^2I/dV^2 \sim -dN_s(\varepsilon)/d\varepsilon$.

We have calculated the change in $T_c$ upon isotope substitution of $^{11}B$ for $^{10}B$ and get: $\delta T_c=-1.7$ K, which corresponds to the exponent $-\delta \ln T_c/\delta \ln M_B=0.46$. This agrees well with the measured value: $\delta T_c=-1$ K. For the change of the gap, which may be measured in tunneling and optical experiments, we calculate: $\delta\Delta_0=1.9$ cm$^{-1}$, which corresponds to the exponent $-\delta \ln \Delta_0/\delta \ln M_B=0.38$.

Finally, we have considered transport properties in the normal state. Here, solution of the kinetic equation leads to the transport e-ph spectral function $\alpha^2_F(\omega)F(\omega)$, and similarly for $y$ and $z$. These components are given by the previous expressions, but with the additional factor $\left[ \langle v_{nx}^2(\mathbf{k}) - v_{nz}(\mathbf{k}) \rangle v_{nx}(\mathbf{k} + \mathbf{q}) \right]_F/\langle v_z^2 \rangle$ inserted. $\langle v_z^2 \rangle = N(0)^{-1} \sum_{\mathbf{k}} v_{nx}(\mathbf{k}) \delta [\varepsilon_0(\mathbf{k})]$. In Fig. 2, the directional average, $\alpha^2_F(\omega)F(\omega)$, is seen to have the same shape as $\alpha^2(\omega)F(\omega)$, except for the $\sigma-\sigma$ interaction via the optical bond-stretching modes, whose $\alpha^2_F(\omega)F(\omega)$ is smaller, presumably due to the near two-dimensionality of the $\sigma$-bands. As a result, $\lambda_{tr} = 0.60$. For the plasma frequencies, $\omega_{p,x}^2 = 4\pi e^2 N(0) \langle v_z^2 \rangle / |abc|$, we find: $\omega_{p,x}^2=7.02$ eV and $\omega_{p,z}^2=6.68$ eV. Also the temperature dependence of the specific dc resistivity calculated with the standard Bloch-Grüneisen expression, $\rho_{dc,x}(T) = \langle \pi/\omega_{p,x}(T) \rangle \int_0^\infty \omega \sinh^{-1}(\omega/2T) \alpha^2_F(\omega)F(\omega)d\omega$, is nearly isotropic and, as shown in Fig. 2, in accord with recent measurements on dense wires over the entire temperature range. The crossover from power-law to linear temperature dependence is seen to occur near $\max\omega/5=160$ cm$^{-1}=230$ K, as expected.

![FIG. 2. Normalized density of states (full) and the negative of its energy-derivative (dotted) as obtained from the Eliashberg equation with $\mu^*=0.10$ and $T=3K$.](image)

![FIG. 3. Calculated dc-resistivities in different directions compared with the experiment in Ref. [2].](image)

In conclusion, we have presented an accurate $ab initio$ calculation of the e-ph interaction in MgB$_2$ and find $\lambda = 0.87 \pm 0.05$. Eliashberg theory with $\mu^*=0.10$ gives good agreement with available experiments and several predictions. The unexpected high $T_c$ is due to the large $\lambda$-value caused by the presence of holes in the B-B binding $\sigma$-band and the relative softness of the optical bond-stretching modes. MgB$_2$ thus seems to be a simple and clear case of an intermediate-coupling e-ph pairing $s$-wave superconductor.

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