Superconducting Properties of MgB_2 from First Principles

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Solid MgB_2 has rather interesting and technologically important properties, such as a very high superconducting transition temperature. Focusing on this compound, we report the first nontrivial application of a novel density-functional-type theory for superconductors, recently proposed by the authors. Without invoking any adjustable parameters, we obtain the transition temperature, the gaps, and the specific heat of MgB_2 in very good agreement with experiment. Moreover, our calculations show how the Coulomb interaction acts differently on σ and π states, thereby stabilizing the observed superconducting phase.

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Understanding and predicting superconducting properties of real materials is of both fundamental and technological importance. While there are interesting classes of materials, such as the high T_c Cu oxides, where the superconducting mechanism is still under debate, the recent discovery of phonon-mediated superconductivity at 39.5 K in MgB_2 [1]—but also in other materials—keeps the interest in the phonon-driven mechanism alive. MgB_2 has rather peculiar properties, such as the presence of two superconducting gaps at the Fermi level. While two-band or, more generally, multiband superconductivity has long been known [2] to favor a high critical temperature, there remains the challenging question: Could anyone have predicted quantitatively the peculiar superconducting phase in MgB_2, including its high $T_c$value, by means of ''physically unbiased'', first-principles calculations?

As a matter of fact, despite the theoretical and technological interest involved, the capability to predict from first-principles material-specific properties, such as the critical temperature and the gap, has been out of reach so far. This is because (conventional) superconductivity appears as the result of a subtle competition between two opposite effects, the phonon-mediated attraction (denoted ''e-ph'' in the following) and the direct Coulomb repulsion (denoted ''e-e'') between the electrons. Historically, after the microscopic identification of the superconducting order parameter by Bardeen, Cooper, and Schrieffer (BCS) [3], the first theoretical framework aiming at the description of real materials was put forth by Eliashberg [4]. In this theory the e-ph interaction is perfectly accounted for, however the effects of the e-e Coulomb repulsion are condensed in a single parameter, μ^*, which is difficult to calculate from first principles and which, in most practical applications, is treated as an adjustable parameter, usually chosen as to reproduce the experimental T_c. In this sense, the Eliashberg theory, in spite of its tremendous success, has to be considered a semiphenomenological theory.

Looking at normal-state properties, density-functional theory (DFT) [5] has enjoyed increasing popularity as a reliable and relatively inexpensive tool to describe real materials. In 1988 the basic concepts of DFT were generalized to the superconducting phase by Oliveira, Gross, and Kohn (OGK) [6] via including the superconducting order parameter as an additional ''density'' in the formalism. The theory of OGK, however, was restricted to weak e-ph coupling. Along the lines of a recently presented multicomponent DFT [7] of electrons and ions, the theory of OGK was successfully generalized to the strong-coupling case [8]. In this Letter we apply the strong-coupling DFT to the challenging case of MgB_2.

The central equation of the DFT for superconductors is a generalized gap equation of the form

$$\Delta_{n\mathbf{k}} = -Z_{n\mathbf{k}}\Delta_{n\mathbf{k}} - \frac{1}{2}\sum_{n'\mathbf{k}'} \mathcal{K}_{n\mathbf{k},n'\mathbf{k}'} \frac{\tanh(\frac{\beta}{2}E_{n'\mathbf{k}'})}{E_{n'\mathbf{k}'}}\Delta_{n'\mathbf{k}'}, \tag{1}$$

where n and $\mathbf{k}$ are, respectively, the electronic band index and the wave vector inside the Brillouin zone. β is the inverse temperature and $E_{n\mathbf{k}} = \sqrt{(\varepsilon_{n\mathbf{k}} - \mu)^2 + |\Delta_{n\mathbf{k}}|^2}$ are the excitation energies of the superconductor, defined in terms of the gap function $\Delta_{n\mathbf{k}}$, the Kohn-Sham eigenenergies of the normal-state $\varepsilon_{n\mathbf{k}}$, and the chemical potential μ. The kernel, $\mathcal{K}$, appearing in the gap equation consists of two contributions $\mathcal{K} = \mathcal{K}^{e\text{-ph}} + \mathcal{K}^{e\text{-}e}$, representing the effects of the e-ph and of the e-e interactions, respectively. The first of these terms involves the e-ph coupling matrix, while the second contains the matrix elements of the

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screened Coulomb interaction. Equation (1) has the same structure as the BCS gap equation, with the kernel $\mathcal{K}$ replacing the model interaction of BCS theory. This similarity allows us to interpret the kernel as an effective interaction responsible for the binding of the Cooper pairs. On the other hand, $\mathcal{Z}$ plays a similar role as the renormalization term in the Eliashberg equations. We emphasize that Eq. (1) is not a mean-field equation (like in BCS theory), since it contains correlation effects. Furthermore, it has the form of a static equation—i.e., it does not depend explicitly on the frequency—and therefore has a simpler structure than the Eliashberg equations. However, this certainly does not imply that retardation effects are absent from the theory: as a matter of fact, an Eliashberg-type spectral function $\alpha^2F(\Omega)$ enters the calculation of $\mathcal{Z}$ and $\mathcal{K}^{e\text{-ph}}$.

Coming back to MgB_2, its Fermi surface (FS) has several sheets with different orbital character (see, e.g., Ref. [9]). In particular, the tubular structures with σ character are very strongly coupled to the E_{2g} phonon mode, corresponding to a B-B bond-stretching in the boron planes [9,10]. MgB_2 also has three-dimensional π bands, that give rise to a complicated Fermi surface. Without holes in the σ bands, the compound would not be superconducting, like AlB_2. The π bands are coupled much less efficiently to phonons, but are nevertheless crucial to superconductivity. A remarkable feature of this compound is the presence of two gaps on the σ and π bands, as clearly demonstrated by several different experiments [11–18]. On the theoretical side, this system has been treated within the **k**-resolved Eliashberg theory [19,20], using a two-band scheme [21], with four e-ph spectral functions to represent the distinct couplings. Correspondingly, the anisotropy of the Coulomb interaction has also been investigated [22,23], with μ^* treated as a matrix.

In our density-functional calculations we used the four, band resolved, Eliashberg functions, $[\alpha^2F_{n,n'}(\Omega); n, n' = \sigma, \pi]$, previously employed within a two-band Eliashberg scheme by Golubov *et al.* [24]. Our procedure keeps the fundamental distinction between σ and π gaps, analogously to the Eliashberg calculations reported to date. We recall here that a fully consistent calculation should not use the $\alpha^2F_{n,n'}(\Omega)$ functions, but rather the $n\mathbf{k}$, $n'\mathbf{k}'$-resolved couplings: By using the $\alpha^2F_{n,n'}(\Omega)$, the e-ph interaction is averaged over $\mathbf{k}$ and $\mathbf{k}'$ at the FS, which may have a small, but non-negligible effect. We define the bands crossing the FS to be of σ character if they are contained in a cylinder of basis radius $1/4$ of a reciprocal lattice vector, and of π character otherwise. Away from the Fermi surface this distinction is meaningless but harmless, as the phonon terms die off quickly and the Coulomb term is independent of this distinction. As we described our computational strategy elsewhere [8], we shall not report the details here. We just mention that extreme care needs to be taken with the sampling of the region in **k** space around the FS. We accomplish this task by using around 65 000 independent **k** points, chosen according to a Metropolis algorithm. This places $\approx$8000 points within $\approx \hbar\omega_{E_{2g}}$ of the FS. We estimate the overall numerical stability of our results to be roughly 5%.

As for the e-e interaction, we calculated the matrix elements of the screened Coulomb potential with respect to the Bloch functions of MgB_2, for the whole energy range of relevant valence and conduction states, using the full-potential linearized augmented plane wave method. In our previous work [8], the Coulomb interaction was screened using a simple Thomas-Fermi model. However, the different nature of σ and π bands in MgB_2, and, in particular, the highly localized character of the former, strongly calls for the use of a nondiagonal screening, including local field effects. To avoid the cumbersome calculation of the dielectric matrix of MgB_2, we used a dielectric matrix obtained with the method of Hybertsen and Louie [25]. In particular, we substituted the model dielectric function in Eq. (7) of Ref. [25] by a Thomas-Fermi model, computed at the local (valence) density of MgB_2. The diagonal part of our model compares rather well with the calculations of Zhukov *et al.* [26].

In Fig. 1 we plot the energy gap as a function of (positive) energy distance from the Fermi energy (the gap function exhibits particle-hole symmetry to a good extent). We can see that the two gaps of the material, Δ_σ and Δ_π, appear naturally from our calculations. The σ gap is defined only up to the energy of the top of the σ band. Both Δ_σ and Δ_π are anisotropic. This results from the anisotropy of the Coulomb potential matrix elements— roughly 0.4 meV, $\approx$ 6% of Δ_σ at the FS and gets much larger at high energy, where there are many bands with different characters. The averages of Δ_σ and Δ_π at the Fermi level (6.8 meV and 2.45 meV, respectively) are in excellent agreement with experiment. Both gaps change sign, which is a necessary condition to find superconductivity in the presence of the repulsive Coulomb interaction. In fact, our gap equation does not converge to a superconducting

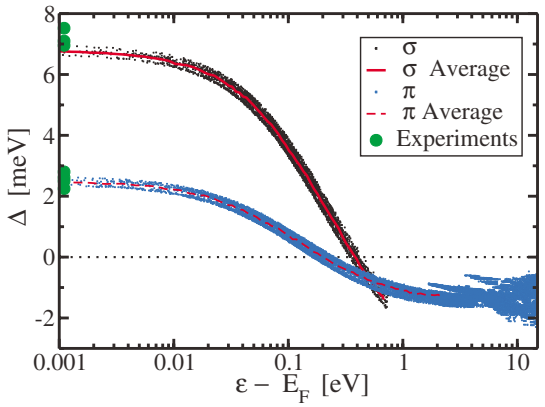

FIG. 1 (color). Calculated superconducting gap of MgB_2 as a function of energy ($T = 0$ K).

solution, unless all electronic states in a large energy window are included.

In Fig. 2(a), the superconducting gaps are plotted versus temperature, together with a few recent experimental results. The agreement is striking: the values of T_c (34.1 K) and of Δ_σ and Δ_π at $T = 0$ K are very close to the experimental data. Moreover, the temperature behavior of both gaps, along with their strongly non-BCS behavior, are very well reproduced. We believe that such an agreement for a highly nontrivial superconductor such as MgB_2, without any adjustable parameter, is unprecedented in the field of superconductivity. Obviously, unlike calculations performed using Eliashberg theory, we do not reproduce exactly the experimental critical temperature, as our calculations are not fitted to match any experimental quantity.

We also calculated the Kohn-Sham entropy as a function of temperature and, from its temperature derivative, the specific heat. In order to compare our results with experiments [16–18], we plot in Fig. 2(b) the reduced specific heat versus temperature, normalized to T_c (using the corresponding experimental and calculated T_c values). Both the shape of the curve as well as the discontinuity at T_c are almost perfectly reproduced. We recall that the low temperature shoulder comes from the presence of the smaller π gap and that our Δ_σ/Δ_π is slightly different from the experimental ratio.

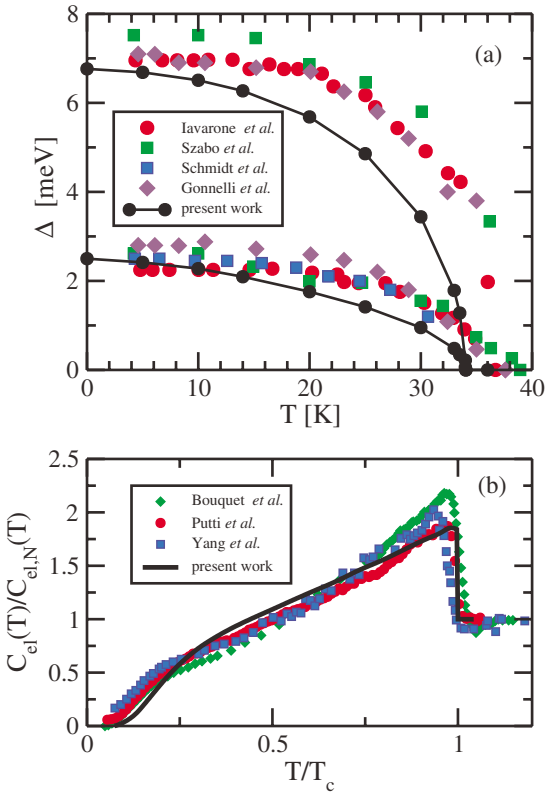

FIG. 2 (color). Superconducting gaps at the FS and specific heat of MgB_2 . Panel (a): Comparison between theoretical and experimental gap at the FS plotted as a function of temperature. The calculated gaps and T_c (34.1 K) are obtained without the use of any adjustable parameter. Panel (b): Experimental and calculated electronic specific heat, as a function of T/T_c.

While the good agreement with experiment underlines the predictive power of our method, it is only one part of our investigation. Another important aspect is to gain further insight into the peculiar superconductivity of MgB_2. To this end, we performed a calculation using an average functional form for the Coulomb interaction, not distinguishing between σ and π bands. This functional, described in detail in Ref. [8], corresponds to a semiclassical treatment valid in the limit of slowly varying densities, and actually leads to a good agreement with the full matrix element calculation for s, p metals, and works reasonably also in d metals as Nb. We obtain $T_c = 52$ K, with the σ and π gaps being 9.8 meV and 1.9 meV, respectively. This test shows that the repulsion among σ states, stronger than within π and between σ and π, is crucial in achieving good agreement with experiment. We also see clearly that the more delocalized π electrons are reasonably well described by an average formula derived from free-electron concepts, while the repulsion among σ electrons needs the real matrix element calculations. Reversely, if we average all the e-ph spectral functions, we obtain a single gap $\Delta = 3.7$ meV and the much lower $T_c \approx 20$ K, in agreement with the analysis of Ref. [21] and with a similar test carried out by Choi *et al.* [19].

Of course, in the search for novel superconductors with higher transition temperatures, it would be desirable to keep the extremely strong e-ph coupling for σ states, while reducing the corresponding Coulomb interaction to that of the more delocalized π states. Unfortunately, the two features are linked together, as both the strong e-ph coupling and the strong Coulomb repulsion derive from the covalent nature of the corresponding electronic states.

To push this analysis further, we plot, in the upper panel of Fig. 3, the energy dependence of the Coulomb contri-

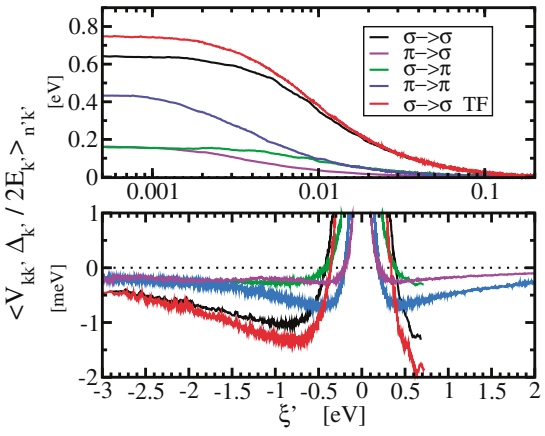

FIG. 3 (color). Electronic repulsion contributions to the gap equation [see Eq. (1)], at an arbitrary $\mathbf{k}$, averaged over $\mathbf{k}'$ and bands on isoenergy surfaces, but keeping the σ, π distinction.

bution to Eq. (1) at $T \approx 0$ K, namely $\mathcal{K}^{el}_{n\mathbf{k},\mathbf{n}'\mathbf{k}'}\Delta_{n'\mathbf{k}'}/(2E_{n'\mathbf{k}'}) \equiv \mathcal{K}^{el}_{n\mathbf{k},\mathbf{n}'\mathbf{k}'}\chi_{n'\mathbf{k}'}$ against $\xi_{n'\mathbf{k}'} = \varepsilon_{n'\mathbf{k}'} - E_F$, for a few $\mathbf{k}$ points arbitrarily chosen on the Fermi surface. As $\chi_{n'\mathbf{k}'}$ goes to 0.5 on the Fermi surface, Fig. 3 shows the larger magnitude of the intraband σ-σ and π-π, relative to the interband σ-π matrix elements (see also Ref. [23]). The different behavior of the $\sigma \rightarrow \pi$ and $\pi \rightarrow \sigma$ terms results from the χ factor, as the matrix elements themselves are symmetric. Obviously, the σ-σ repulsive matrix elements are the strongest. The scattering of data for a given energy comes from the different orbital character of wave functions at $n'\mathbf{k}'$. The energy dependence of the quantities plotted in Fig. 3 comes almost entirely from $\chi_{n'\mathbf{k}'}$, as the matrix elements themselves have a marginal energy dependence. In order to show how the reduction of Coulomb repulsion takes place, we emphasize in the lower panel of Fig. 3 the region corresponding to low matrix elements (on a linear scale). We see how, when Δ becomes negative, the Coulomb interaction actually gives a constructive contribution due to the minus sign in Eq. (1). Although the negative values are much smaller (by almost 3 orders of magnitude) than the positive ones, the corresponding energy range is much larger, resulting into the well-known, substantial reduction of the effective Coulomb contribution. The most important energy region is located in between 0.50 to 3 eV below E_F, in particular, due to the strong intraband σ-σ matrix elements. The interband contribution from π bands (violet in Fig. 3), on the other hand, is considerably smaller, which is obviously the case also for the σ contribution to Δ_π (green in Fig. 3). Summing up over $n'\mathbf{k}'$, the negative contribution to Δ_σ coming from the (positive gap) region of the σ Fermi surface overcomes by a factor of ≈ 7 the contribution coming from the corresponding π region.

Finally, it is also interesting to investigate the importance of local field (LF) effects on the superconducting properties of MgB_2. It turns out that by using a diagonal Thomas-Fermi screening (TF) (which completely neglects LF's) the σ-σ matrix elements increase by roughly 15% (red in Fig. 3), while the σ-π and π-π terms remain basically unchanged. As a consequence, neglecting LF effects leads to a marginal ($\approx 4\%$) decrease of Δ_π, but decreases significantly Δ_σ (by about 14%). The different behavior of Δ_σ and Δ_π can be understood quite naturally: LF corrections imply a better screened interaction among electrons when they are located in a high density region inside the unit cell. This is precisely the case of the σ bands. On the other hand, the π bands are more delocalized—the electrons reside in the interstitial region—and are therefore reasonably described by diagonal screening.

In this Letter we presented the first nontrivial application of a recently developed *ab initio* theory of superconductivity. In particular, we obtained for MgB_2 the value of T_c, the two gaps, as well as the specific heat as a function of temperature in very good agreement with experiment. We stress the predictive power of the approach presented: being, by its very nature, a fully *ab initio* approach, it does not require semiphenomenological parameters, such as μ^*. Nevertheless, it is able to reproduce with good accuracy superconducting properties, up to now out of reach of first-principles calculations. Furthermore, our calculations allow for a detailed analysis of the contribution of the Coulomb repulsion to the superconducting gap, opening the way to tailoring the electronic properties of real materials in order to optimize superconducting features.

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[1] J. Nagamatsu *et al.*, Nature (London) **410**, 63 (2001).
[2] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. **3**, 552 (1959).
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[4] G. M. Eliashberg, Sov. Phys. JETP **11**, 696 (1960).
[5] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer Verlag, Berlin, 1990).
[6] L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. Lett. **60**, 2430 (1988).
[7] T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. **86**, 2984 (2001).
[8] M. Lüders *et al.*, cond-mat/0408685; M. A. L. Marques *et al.*, cond-mat/0408686.
[9] J. Kortus *et al.*, Phys. Rev. Lett. **86**, 4656 (2001).
[10] J. M. An and W. E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001); Y. Kong *et al.*, Phys. Rev. B **64**, 020501(R) (2001); K. P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. **86**, 5771 (2001).
[11] M. Iavarone *et al.*, Phys. Rev. Lett. **89**, 187002 (2002).
[12] P. Szabo *et al.*, Phys. Rev. Lett. **87**, 137005 (2002).
[13] H. Schmidt *et al.*, Phys. Rev. Lett. **88**, 127002 (2002).
[14] R. S. Gonnelli *et al.*, Phys. Rev. Lett. **89**, 247004 (2002).
[15] F. Giubileo *et al.*, Phys. Rev. Lett. **87**, 177008 (2001).
[16] M. Putti *et al.* Phys. Rev. B **68**, 094514 (2003).
[17] F. Bouquet *et al.* Phys. Rev. Lett. **87**, 47001 (2001).
[18] H. D. Yang *et al.*, Phys. Rev. Lett. **87**, 167003 (2001).
[19] H. J. Choi *et al.*, Phys. Rev. B **66**, 020513(R) (2002).
[20] H. J. Choi *et al.*, Nature (London) **418**, 758 (2002).
[21] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[22] I. I. Mazin *et al.*, Phys. Rev. B **69**, 056501 (2004).
[23] C.-Y. Moon *et al.*, Phys. Rev. B **70**, 104522 (2004).
[24] A. A. Golubov *et al.*, J. Phys. Condens. Matter **14**, 1353 (2002).
[25] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **37**, 2733 (1988).
[26] V. P. Zhukov *et al.*, Phys. Rev. B **64**, 180507(R) (2001).