Two-gap superconductivity in MgB_2: clean or dirty?

I. I. Mazin,^1 O. K. Andersen,^2 O. Jepsen,^2 O. V. Dolgov,^2 J. Kortus,^2 A. A. Golubov,^3 A. B. Kuz'menko,^4 and D. van der Marel^4

^1Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375-5000, USA
^2Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany
^3University of Twente, Department of Applied Physics, NL-7500 AE Enschede, The Netherlands
^4University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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A large number of experimental facts and theoretical arguments favor a two-gap model for superconductivity in MgB_2. However, this model predicts strong suppression of the critical temperature by interband impurity scattering and, presumably, a strong correlation between the critical temperature and the residual resistivity. No such correlation has been observed. We argue that this fact can be understood if the band disparity of the electronic structure is taken into account, not only in the superconducting state, but also in normal transport.

Most researchers ascribe the superconductivity in MgB_2 [1] to the electron-phonon mechanism, enhanced by interband anisotropy of the order parameter [2, 3]. Interband anisotropy, as expressed by the two-gap model [2, 4], offers a simple explanation of many anomalous experimental findings, most importantly of tunneling and thermodynamic measurements [5]. But there is a strong argument against it: As illustrated in Fig. 1, existing bulk samples of MgB_2 have essentially the same critical temperature although their residual resistivities, \( \rho_0 \), vary greatly, between 0.4 and 40 \( \mu \)Ω cm. Such a behavior is expected for s-wave pairing (Anderson’s theorem), but not when two gaps are present. In that case one expects \( T_c \) to fall with increasing \( \rho_0 \). Indeed, impurity interband scattering (magnetic and nonmagnetic) with rate \( \gamma_{\text{inter}} \) suppresses two-band superconductivity as: \( \Delta T_c \propto \gamma_{\text{inter}}/(\pi T_c) \) [1], and it is tempting to assume that \( \gamma_{\text{intra}} \approx \gamma_{\text{inter}} \approx \rho_0 \). For a sample with \( \rho_0 \approx 40 \) \( \mu \)Ω cm it seems unlikely that \( \gamma_{\text{inter}} \) can be smaller than \( \pi T_c \). In fact, the body of experimental evidence (Fig. 1) can be reconciled with the two-gap model only if \( \gamma_{\text{intra}} \ll \gamma_{\text{inter}} \). Until this paradox is resolved, the two-gap model for superconductivity in MgB_2 cannot be accepted, despite much compelling evidence. Two further problems are: (a) The high-temperature slope of the resistivity is clearly correlated with the residual resistivity (violation of Matthiessen’s rule) [6], and (b) the plasma frequency estimated from the measured infrared reflectivity is 5 times smaller than the calculated one [7, 8, 9].

In this letter we shall show that the paradox can be resolved by support the two-gap model. It turns out that due to the particular electronic structure of MgB_2, the impurity scattering between the \( \sigma \)- and \( \pi \)-bands is exceptionally small. Thus, the large variation of the residual resistivities reflects primarily a large variation of the scattering rate inside the \( \sigma \)- and the \( \pi \)-bands, while the interband \( \sigma\pi \)-scattering plays no role in normal transport. In the superconducting state, the two different gaps in the \( \sigma \)- and the \( \pi \)-bands are preserved even in dirty samples due to the extreme weakness of the \( \sigma\pi \)-interband impurity scattering.

MgB_2 has two \( \pi \) and three \( \sigma \)-bands (Fig. 2) formed by, respectively, the two \( p_z \) and the three bond-orbitals per cell, or, more correctly, by the corresponding Wannier-like functions. A bond orbital is the bonding linear combination of the two \( sp^2 \)-hybrids which are directed along a B-B bond. The attractive potential from the Mg\(^{2+}\) ions in the hollows between the hexagonal boron layers is felt much stronger by a \( p_z \)-electron than by a bond-electron and, as a result, the \( \pi \)-band is pulled so far down in energy that \( \sim 0.17 \) holes are left at the top of the \( \sigma \)-band. The strong coupling of these holes to the optical bond-stretching modes [14] is what drives the superconductivity. Since the top of the \( \sigma \)-band is at \( k_z \equiv (k_x, k_y) = 0 \) and is doubly degenerate, the holes are distributed in an upper heavy and a lower light band.

The basic reason why \( \sigma\pi \)-impurity scattering is small...
is that the \(\sigma\) and \(\pi\)-bands are formed from different local orbitals, and therefore are orthogonal on the atomic scale, rather than merely on an intermediate scale because of Bloch factors. Moreover, the layered structure and the compactness of the B \(2s\) and \(2p\) orbitals makes the \(\sigma\pi\)-disparity in MgB\(_2\) much stronger than, say, the \(sd\)-disparity in a transition metal, where the \(sd\)-hybridization gap is almost as large as the \(d\)-bandwidth.

Specifically, since a \(\pi\)-orbital has odd-parity, and a bond-orbital has even parity with respect to the B-layer, the only route for \(\pi\sigma\)-hybridization is via interlayer hopping, from a \(\pi\)-orbital in one layer to a bond orbital in another layer. The corresponding hopping integral, \(t_{\|z}\), is, essentially, the geometrical average of the integrals \(t_{\perp z}^0 \sim 0.1\) eV and \(t_{\perp z}^1 \sim 1\) eV, responsible for the \(k_z\)-dispersions of the \(\sigma\) and \(\pi\)-bands \(^{14}\), and therefore small. Two further factors limit \(\sigma\pi\)-coupling:

1. The second is that, in its interaction with the nearest boron, the \(\sigma\)-band when \(k_\|\) is along a bond, nor with the light \(\pi\)-band when \(k_\parallel\) is perpendicular to a bond. As may be realized from the pictures of the \(\sigma\)-orbitals (Fig. 3), the crossing with the heavy band occurs because the B \(s\)-character of that band vanishes exactly along this \(k\)-line, and the crossing with the light band occurs because, along that \(k\)-line, the B \(s\)-character is purely antibonding between two borons, whereas the \(\pi\)-band is purely bonding (\(\varphi = 0\)). The two \(\sigma\pi\)-gaps seen in the figure are 0.2–0.3 eV, i.e., the \(\sigma\pi\)-hybridization matrix elements, \(|\langle \sigma|\pi\rangle|\), are merely a per cent of the \(\sigma\) and \(\pi\) bandwidths!

We now discuss impurity scattering and use \(^{15}\):

\[
\Gamma_{nn'} = \frac{2}{\hbar N} \sum_{kk'} \delta(\varepsilon_{nk}) |\langle n|V|n'k'\rangle|^2 \delta(\varepsilon_{n'k'}),
\]

for the rate of scattering to band \(n'\) of an electron in band \(n\), by a weak localized impurity potential, \(V(r)\). Here, \(\delta(\varepsilon_{nk})\) denotes the average over the Brillouin zone, \(\varepsilon_{nk}\) is the band energy with respect to the Fermi level, and \(N(0) = \sum_n N_n(0) = \sum_n \delta(\varepsilon_{nk})\) is the density of states per spin and cell. Typical defects for MgB\(_2\) are Mg-vacancies and Mg-substitutional impurities, which form easily, and B-site substitutions like N and C, which have a higher energy cost. The potential \(V(r)\) for a localized Mg-defect has the full point-symmetry of the site and, like the Mg\(^{2+}\)impurity potential in the crystal, is felt more by a \(\pi\)-orbital than by a bond orbital. Hence, the largest matrix elements are those involving \(\pi\)-orbitals near the impurity, i.e., the largest perturbation is of the energies of the \(\pi\)-orbitals on the B hexagons immediately above and below the impurity, and of the corresponding \(t_{\|z}\).

This means that \(\Gamma_{\pi\pi}\) should be large. Screening perturbs the energies of the bond orbitals surrounding the impurity, and also perturbs \(t_{\|z}\) but to a lesser extent. Hence, we expect that \(\Gamma_{\pi\pi} > \Gamma_{\sigma\sigma}\) for Mg-defects, albeit not for B-site substitutions. What contributes to \(\Gamma_{\sigma\pi}\), are matrix elements involving a \(\pi\) and a bond-orbital, and most importantly, those on either side of a Mg-defect. Since this matrix element is the perturbation of \(t_{\|z}\), it is expected to be intermediate between those of \(t_{\|z}\) and \(t_{\perp z}\), like for the \(\sigma\pi\)-hybridization. Moreover, since the impurity potential is fairly constant around a neighboring
boron, a \( p_z \)-orbital still picks up merely the B \( s \)-character which vanishes as \( k_F^2 \) for the heavy and as \( k_F \) for the light holes. This makes \( |\langle \sigma \mathbf{k} | V | \pi \mathbf{k}' \rangle| \) minute because \( k_F^2 \) and \( k_F \) are very small. Also the mismatch of phases between the \( \sigma \) and \( \pi \)-functions will tend to reduce \( |\langle \sigma \mathbf{k} | V | \pi \mathbf{k}' \rangle| \). Finally, squaring this small matrix element and inserting it in \( \Gamma \), leads to an exceedingly small \( \Gamma_{\sigma \pi} \).

To gain quantitative understanding of the disparity between the scattering rates we have performed LMTO supercell calculations for various impurities. Since the induced \( \sigma \pi \)-gaps, \( 2|\langle \sigma \mathbf{k} | V | \pi \mathbf{k}' \rangle| \), are sensitive to their position within the \( \sigma \)-band (the B \( s \)-factor), we must choose a supercell which provides band-foldings near \( \varepsilon_F \). The results shown in Fig. 2 were obtained with a \( 6 \times 6 \) supercell which provides band-foldings near \( \varepsilon_F \). While the heavy-light and light-light crossings are a bit further down, the \( \pi \)-band (fat) slightly above the top of the \( \sigma \)-band was originally at ML/2 and has been folded 3 times into \( \Gamma \). The Mg\(_{31}\)B\(_{24}\) bands illustrate the effects of a Mg-vacancy: While the three \( \pi \)-bands get split by 0.35 eV, and the heavy and light \( \sigma \)-bands by 0.27 eV (but by 0.04 eV at \( \Gamma \)), the \( \sigma \pi \)-splitting of the heavy band is merely 0.015 eV and that of the light band is merely 0.030 eV! The squares of these splittings give estimates for the corresponding \( \Gamma \)'s. For Mg-vacancies therefore,

\[
\Gamma_{\pi \pi} > \Gamma_{\sigma \sigma} \gg \Gamma_{\sigma \pi}.
\] (2)

We found very similar results for systems in which the Mg-vacancy was compensated by substitution of B by \( 3\) C or one N: For Mg\(_{31}\)B\(_{31}\)N, the \( \pi \pi \)-splitting of the heavy band was originally at ML/2 and has been folded 3 times into \( \Gamma \). The Mg\(_{31}\)B\(_{24}\) bands illustrate the effects of a Mg-vacancy: While the three \( \pi \)-bands get split by 0.35 eV, and the heavy and light \( \sigma \)-bands by 0.27 eV (but by 0.04 eV at \( \Gamma \)), the \( \sigma \pi \)-splitting of the heavy band is merely 0.015 eV and that of the light band is merely 0.030 eV! The squares of these splittings give estimates for the corresponding \( \Gamma \)'s. For Mg-vacancies therefore,

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\Gamma_{\pi \pi} > \Gamma_{\sigma \sigma} \gg \Gamma_{\sigma \pi}.
\] (2)

We found very similar results for systems in which the Mg-vacancy was compensated by substitution of B by two C or one N: For Mg\(_{12}\)B\(_{24}\), the \( \pi \pi \)-splitting was 0.4 eV, the \( \sigma \sigma \)-splitting 0.3 eV, and the \( \sigma \pi \)-splittings less than 0.03 eV.

Let us now investigate how the relation (2) influences the transport properties. These depend both on the impurity scattering and on the electron-phonon interaction (EPI). The interband anisotropy should be taken into account both in the impurity scattering (as outlined above), and in the EPI. The latter can be characterized by two sets of four spectral functions each: the standard Eliashberg functions \( \alpha_\sigma^2 \mathcal{F}_{\mathbf{nn}'}(\omega) \), which define the superconducting properties and thermodynamical properties like the electronic specific heat and the de Haas-van Alphen mass renormalizations, and the transport Eliashberg functions \( \alpha_t^2 \mathcal{F}_{\mathbf{nn}'}(\omega) \). Of the calculated \( \alpha_\sigma^2 \mathcal{F}_{\mathbf{nn}'}(\omega) \) functions \( \alpha_t^2 \mathcal{F}_{\mathbf{nn}'}(\omega) \) (the details are as the calculations are in Ref. [13]), \( \alpha_\sigma^2 \mathcal{F}_{\sigma \sigma}(\omega) \) exhibits a large peak at \( \omega \approx 70 \) meV. Defining \( \lambda_{\mathbf{nn}'} = 2 \int \omega^{-1} \alpha_\sigma^2 \mathcal{F}_{\mathbf{nn}'}(\omega) d\omega \), we obtain the partial EPI constants, shown in Table 4 which are similar to those obtained in [3]. In the following we assume that \( \Gamma_{\text{inter}} = 0 \), so the clean limit is appropriate \( (T_c \) is independent of the intraband \( \Gamma \)'s). The superconducting properties in the clean two-band model have been investigated in detail [3, 16]. Therefore we shall now concentrate on the normal transport.

The explicit expression for the conductivity in the two-band model is [17] (omitting Cartesian indices)

\[
1/\rho_{\text{DC}}(T) = \frac{1}{4\pi} \sum_{n=\sigma, \pi} \frac{\omega_{\mathbf{nn}}^2}{W_n(0, T)},
\] (3)

\[
W_n(0, T) = \gamma_{\sigma} + \frac{\pi}{T} \int_{0}^{\infty} d\omega \frac{\omega}{\sinh^2(\omega/2T)} \times \left[ \alpha_t^2(\omega) \mathcal{F}_{\sigma \sigma}(\omega) + \alpha_t^2(\omega) \mathcal{F}_{\pi \pi}(\omega) \right],
\]

where \( \gamma_{\sigma} = \gamma_{\sigma \sigma} + \gamma_{\sigma \pi}, \gamma_{\pi} = \gamma_{\pi \sigma} + \gamma_{\pi \pi}, \) and \( \gamma_{\mathbf{nn}'} \approx 2\Gamma_{\mathbf{nn}'} \).

In Fig. 3 we show the temperature dependence of the DC resistivity for (a) a clean case with \( \gamma_{\sigma} = \gamma_{\pi} = 2 \) meV, and (b) a dirty case with \( \gamma_{\sigma} = 54 \) meV and \( \gamma_{\pi} = 1.2 \) eV. In the two cases, all plasma frequencies are the same. The model is seen to describe both cases well. Note that \( \gamma_{\sigma} \) and \( \gamma_{\pi} \) determine not only the residual resistivity, but also the temperature dependence of the resistivity. In a one-band model, it would be impossible to reconcile the data of Refs. [3, 7] with those of Ref. [10] if they differ only by impurity concentrations, and the corresponding violation of Matthiessen’s rule would be totally inexplicable.

Why is the temperature dependence of the resistiv-
TABLE I: Superconducting and transport coupling constants \( \lambda \) for the effective two-band model. The partial densities of states at the Fermi level for the two bands have values of \( N_{\pi}(0) = 0.15 \) and \( N_{\sigma}(0) = 0.21 \) (states/cell·eV).

|          | \( \lambda_{\pi\pi} \) | \( \lambda_{\pi\sigma} \) | \( \lambda_{\sigma\pi} \) | \( \lambda_{\sigma\sigma} \) |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|
| transport| 0.80                    | 0.41                    | 0.30                    | 0.15                    |
| superconducting| 1.02 | 0.45 | 0.21 | 0.16 |

ity so different in these two cases? Let us compare the clean limit, \( \gamma_\sigma = \gamma_\pi = 0 \), with the dirty-Mg-layer's limit, \( \gamma_\pi = \infty \), \( \gamma_\sigma = 0 \). Of the two parallel conducting channels, in the former case the \( \pi \)-bands are responsible for conductivity at high temperatures, as was mentioned above, and even at \( T \approx 0 \) the conductivity is mostly due to the \( \pi \)-bands, their plasma frequency being higher than that one of the \( \sigma \)-bands. Since the EPI constant for the \( \pi \)-bands is small, the temperature dependence of the resistivity is weak. On the contrary, in the dirty case, the \( \pi \)-bands do not conduct, due to an overwhelming impurity scattering, and the electric current is carried only by the \( \sigma \)-bands. It is the strong EPI for this band which causes the temperature dependence of the resistivity in dirty samples.

To conclude, we suggest a new model for electric transport in MgB\(_2\). The main ingredients of the model are (i) \textit{interband} impurity scattering in MgB\(_2\) is small, even in low-quality samples; (ii) \textit{intraband} impurity scattering in the \( \sigma \)-band is small relative to the \textit{intraband} \( \pi \)-band scattering; (iii) high-resistivity samples differ from good samples mostly by the \textit{intraband} \( \pi \)-band scattering rate. Of course, (iv) the phonon scattering is stronger in the \( \sigma \)-band. This model explains well such seemingly inexplicable experimental facts as (1) absence of direct correlation between the residual resistivity and the slope \( d\rho/dT \) in the normal state. Finally, we would like to point out that the existence of two qualitatively different samples mostly by the impurity scattering; (ii) high-resistivity samples differ from good samples mostly by the impurity scattering; (iii) high-resistivity samples differ from good samples mostly by the \( \pi \)-bands, their plasma frequency being higher than that one of the \( \sigma \)-bands. Since the EPI constant for the \( \pi \)-bands is small, the temperature dependence of the resistivity is weak. On the contrary, in the dirty case, the \( \pi \)-bands do not conduct, due to an overwhelming impurity scattering, and the electric current is carried only by the \( \sigma \)-bands. It is the strong EPI for this band which causes the temperature dependence of the resistivity in dirty samples.

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