

## Toward one-band superconductivity in MgB<sub>2</sub>

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The two-gap model for superconductivity in MgB<sub>2</sub> predicts that interband impurity scattering should be pair breaking, reducing the critical temperature. This is perhaps the only prediction of the model that has not been confirmed experimentally. It was previously shown theoretically that common substitutional impurities lead to negligible interband scattering—if the lattice is assumed not to distort. Here we report theoretical results showing that certain impurities can indeed produce lattice distortions sufficiently large to create measurable interband scattering. On this basis, we predict that isoelectronic codoping with Al and Na will provide a decisive test of the two-gap model.

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It is now widely accepted that MgB<sub>2</sub> is a two-gap superconductor: its Fermi surface consists of two distinct sheets characterized by strong and weak electron-phonon coupling, respectively (see Ref. 1 for a review). This view is supported by numerous experiments probing either the larger or smaller gap, or both simultaneously. Experimental observation of the merging of the two gaps would constitute even stronger evidence. Such a merging is expected, for example, from interband scattering by impurities. Within the theory of multiband superconductivity, interband scattering mixes the “weak” and “strong” Cooper pairs, averaging the order parameter and reducing  $T_c$ .<sup>2</sup> At small defect concentrations the suppression of  $T_c$  should be linear, with the larger gap decreasing and the smaller gap increasing. The effect should be pronounced in samples with high defect concentrations, but despite the relatively low quality of many samples such an effect has not been observed. Indeed, some samples with high resistivity have nearly the same critical temperatures as clean single crystals. On the other hand, samples doped with carbon show both gaps decreasing but not merging, despite a considerable reduction in  $T_c$ . Other types of intentional defects—whether from doping or irradiation—have also failed to produce a merged gap. Even efforts to introduce defects into MgB<sub>2</sub> for the explicit purpose of inducing interband scattering and merging the two gaps have failed to produce any observable effect.<sup>3–6</sup>

This apparent lack of evidence for a central prediction of the two-gap model is disturbing. In Ref. 7 it was shown that interband scattering from substitutional impurities is inherently weak, *if the lattice is assumed not to distort*. This partially explains the null results of current experimental efforts to induce pair breaking, but it does not address the possibility of pair breaking from impurities specifically chosen to maximize the interband scattering due to large lattice distortions. In this Brief Report we show that this strategy is likely to succeed and, by identifying a simple relationship between impurity atoms and the resulting lattice distortions in MgB<sub>2</sub>, suggest an impurity-doping protocol that will produce measurable pair breaking—and thereby provide the final “smoking gun” evidence for the two-band model.

Hampering such investigations is the currently limited insight into which defects are most effective in creating interband scattering. Since the states at the Fermi level of MgB<sub>2</sub>

are formed by the boron orbitals, one might expect impurities (such as carbon) in the B planes to produce large interband scattering. This is not borne out experimentally: substitutional C impurities have only a weak effect on the interband scattering.<sup>5</sup> This finding had been anticipated theoretically as a consequence of the special symmetry properties of the electronic states within the  $\sigma$  band near the  $\Gamma$  point.<sup>7</sup> The crucial point is that although impurities in the B plane do have a strong effect on the electronic structure, they do not change the local point symmetry and therefore do not lead to significant  $\sigma$ – $\pi$  scattering.

The situation can be quite different for substitutions in the Mg plane, which may create out-of-plane distortions of B atoms in neighboring planes. Such relaxations do change the local point symmetry of nearby B atoms, mixing the in-plane  $p_{x,y}$  and out-of-plane  $p_z$  orbitals, and for sufficiently large disturbances can lead to significant  $\sigma$ – $\pi$  scattering. Here we demonstrate by first-principles calculations that this is indeed the case for certain substitutional impurities but—surprisingly—not for Mg vacancies. We predict that the interband scattering effects will be most pronounced for isoelectronic co-doping with Na and Al, and that the effect on the superconducting properties should be detectable for impurity concentrations above 2%.

We used density-functional theory (DFT) to study the lattice distortion created by Mg-plane substitutional impurities from groups I, II, and III, by a Mg vacancy, and by B-plane C substitution. To model the distortion induced by single defects, we used  $2 \times 2 \times 2$  supercells of bulk MgB<sub>2</sub> (and  $3 \times 3 \times 3$  supercells for convergence checks). Total energies and forces were calculated using projector-augmented-wave potentials and the generalized-gradient approximation.<sup>9,10</sup> All atomic positions were relaxed within the constraint of fixed (theoretical) bulk lattice parameters. The resulting displacements of the nearest-neighbor B atoms are given in Table I. Given the strong intraplanar covalent bonding, it is not surprising that these displacements are dominated by the out-of-plane component  $\delta z$ , which ranges from  $-0.04 \text{ \AA}$  (for Be) to  $+0.09 \text{ \AA}$  (for K); for C it is zero by symmetry.

The out-of-plane displacements for seven different impurities on the Mg site are plotted in Fig. 1. In a previous related study, changes in interlayer spacing induced by the complete substitution of Al for Mg in a single plane were

TABLE I. First-principles displacements of nearest-neighbor B atoms, in angstrom, induced by various substitutional impurities. Positive values indicate displacements away from the impurity.

Impurity	Site	In plane, $\delta r$	Out of plane, $\delta z$
Be	Mg	-0.014	-0.039
Al	Mg	-0.012	-0.033
Sc	Mg	+0.012	-0.008
C	B	+0.044	0
Li	Mg	-0.006	+0.003
Vacancy	Mg	-0.005	+0.008
Ca	Mg	+0.015	+0.028
Na	Mg	+0.008	+0.040
K	Mg	+0.024	+0.092

ascribed to electrostatic effects.<sup>11</sup> We find no such correlation between  $\delta z$  and the formal valence of the impurity—for example, Be and Ca give displacements of opposite sign despite having identical valence—and thus infer that electrostatic effects are not important. On the other hand, Fig. 1 shows that there is an excellent correlation between  $\delta z$  and the ionic radius of the impurity atom. Hence we conclude that the out-of-plane displacement of B atoms by impurity atoms substituting for Mg is mostly a size effect.

In light of this, one might anticipate a Mg vacancy to produce a large inward displacement. Our DFT results reveal very different behavior: the vacancy creates a negligibly small displacement,  $\delta z < 0.01$  Å. This result is consistent with the experimental fact that pair breaking is not observed in low quality samples, which presumably contain many vacancies. However, it is very different from the trend shown in Fig. 1. Indeed, if one naively considers the vacancy as an impurity of zero size, the predicted displacement is almost twice that found for Be and Al, in sharp distinction to our DFT result.

A simple model explains the surprisingly small displacement created by the Mg vacancy. We consider a  $\text{MgB}_2$  crystal containing a single substitutional defect  $D$  (either an impurity atom or a vacancy) in the Mg plane. Such a defect has 12 nearest-neighbor B atoms, consisting of two hexagonal rings. We consider the out-of-plane displacement of the B

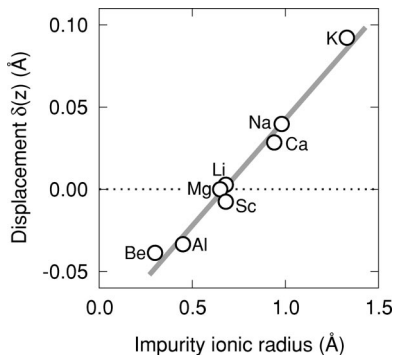


FIG. 1. First-principles theoretical displacements of nearest-neighbor B atoms around a substitutional impurity in the Mg plane. Ionic radii are from Ref. 8.

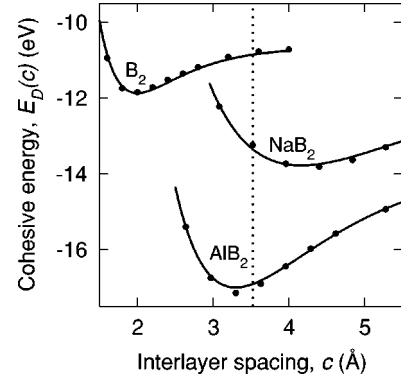


FIG. 2. First-principles cohesive energy of completely substituted  $\text{MgB}_2$ , versus interlayer spacing. Curves are fits to Morse potentials. The vertical dotted line marks the equilibrium interlayer spacing for  $\text{MgB}_2$ .

atoms in these rings to arise from two opposing effects. The first of these represents the change in covalent bonding *between* B planes. In the absence of any defects, the  $\text{MgB}_2$  interlayer spacing  $c_{\text{Mg}}$  is primarily determined by assisted hopping between B  $p_z$  orbitals through Mg orbitals; for each B atom there are three such hopping paths through nearest-neighbor Mg atoms. With the defect present, one of these three paths now passes through the defect site. This new hopping path results in an out-of-plane force on the B atom. We assume the magnitude of this effect to be one-third of that found for a fully substituted Mg plane, which we approximate using the energy vs layer spacing,  $E_D(c)$ , for fully substituted  $\text{DB}_2$ . Thus we consider the change in spacing between the two displaced hexagonal rings,  $2\delta z$ , to contribute an energy per B given by  $\frac{1}{3}E_D(c_{\text{Mg}} + 2\delta z)$ . We have calculated the binding-energy curves  $E_D(c)$  within DFT for  $\text{AlB}_2$ ,  $\text{NaB}_2$ , and “vacancy-substituted”  $\text{B}_2$ ; the results are shown in Fig. 2. All can be accurately represented by a Morse potential, which is the form we will use in the discussion below.

The second effect is the restoring force experienced by the displaced B atoms, due to the strong covalent bonding *within* the B planes. For the small displacements we are considering it is reasonable to take this effect to be harmonic in  $\delta z$ , again weighted by  $1/3$ . Thus we take the total-energy change per B to be

$$E(\delta z) = \frac{1}{3}K(\delta z)^2 + \frac{1}{3}kw^2[1 - e^{-(c_{\text{Mg}} + 2\delta z - c_D)/w}]^2, \quad (1)$$

where  $w$  is the width of the Morse potential,  $kw^2$  its depth, and  $c_D$  its equilibrium interlayer spacing. For small  $c_{\text{Mg}} - c_D$ , it is easy to show that this energy is minimized for  $2\delta z = (c_D - c_{\text{Mg}})/(1 + K/2k)$ . In other words, for impurities whose size is comparable to Mg, the displacement is linear in the size mismatch and reduced by the factor  $1 + K/2k$  (which is typically in the range 5–10); this is consistent with the DFT results shown in Fig. 1. Qualitatively, when  $c_D$  is close to  $c_{\text{Mg}}$ , as it is for  $\text{AlB}_2$  and  $\text{NaB}_2$ , the equilibrium displacement represents a balance between the harmonic restoring force  $\frac{2}{3}K|\delta z|$  and a nearly harmonic (attractive or repulsive) force  $\frac{2}{3}k(c_{\text{Mg}} - c_D + 2\delta z)$  from the interlayer bonding.

For the vacancy there is a very large size mismatch:  $c_{\text{vac}}$  is over 40% smaller than  $c_{\text{Mg}}$ . Thus for any reasonable displacement, the hexagons experience only a weak attractive force from the tail of the Morse potential. Hence the energy is minimized for a very small displacement,  $\delta z \approx -0.007 \text{ \AA}$ , in agreement with the negligible displacement given by DFT. Qualitatively, the result of a large size mismatch is to largely preempt the mechanism of interlayer binding, leading to very small displacements strongly suppressed by the penalty for perturbing the planarity of the B layer.

The origin of the large mismatch between  $c_{\text{Mg}}$  and  $c_{\text{vac}}$  can best be understood by comparing the band structures of the fully substituted  $DB_2$  compounds at their equilibrium interlayer spacings. For these pure compounds (as well as the parent material) interlayer bonding arises primarily from the interaction between B  $p_z$  orbitals in different layers. This interaction depends on the assisted hopping through  $s$  and  $p_z$  orbitals located on the  $D$  site. However, for the fully ‘‘vacancy substituted’’ compound the occupancy of the  $\pi$  bands is so much reduced that their contribution to bonding becomes quite small. At the same time, the  $\sigma$  bands acquire substantial  $z$  dispersion from  $pp\pi$  hopping, which contributes to bonding. Even for high vacancy concentrations (without complete removal of a Mg plane) it is impossible to engage the  $\sigma$  bands in interlayer bonding by any reasonable dimpling of the B planes, because the planes remain too far apart. As a result, hardly any distortion occurs at all: indeed, even for 50% vacancies within a single Mg plane, the interlayer spacing changes by less than  $0.05 \text{ \AA}$ .

We have established that the defects leading to the largest B displacements are Mg-plane substitutional impurities with a large size mismatch (but not Mg vacancies). We now estimate the magnitude of the interband scattering associated with displacements from such impurities. We assume that the only relevant scattering is that due to the out-of-plane distortion,  $\delta z$ , and use the analogy between the formulas<sup>12</sup> for the impurity-induced scattering rate,

$$\gamma_{\text{imp}} = \pi n_{\text{imp}} \frac{\sum_{\mathbf{k}, \mathbf{k}'} \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}'}) |\delta V_{\mathbf{k}, \mathbf{k}'}|^2}{\sum_{\mathbf{k}} \delta(\varepsilon_{\mathbf{k}})}, \quad (2)$$

and the electron-phonon coupling constant,

$$\lambda = \frac{\sum_{\nu, \mathbf{k}, \mathbf{k}'} \delta(\varepsilon_{\mathbf{k}}) \delta(\varepsilon_{\mathbf{k}'}) |M_{\nu, \mathbf{k}, \mathbf{k}'}|^2 / \hbar \omega_{\nu, \mathbf{k}-\mathbf{k}'}}{\sum_{\mathbf{k}} \delta(\varepsilon_{\mathbf{k}})}. \quad (3)$$

Here  $n_{\text{imp}}$  is the impurity concentration;  $\delta V_{\mathbf{k}, \mathbf{k}'}$  is the matrix element of the impurity perturbation potential (defined as the difference between the full crystal potentials with and without an impurity);  $\varepsilon_{\mathbf{k}}$  is the electron energy with respect to the Fermi level;  $\omega_{\nu, \mathbf{k}}$  is the phonon frequency;  $M_{\mathbf{k}, \mathbf{k}'}$  is the electron-ion matrix element  $\langle \mathbf{k} | dV/dQ_{\nu} | \mathbf{k}' \rangle$ , where  $dV/dQ_{\nu}$  is the derivative of the crystal potential with respect to the phonon normal coordinate  $Q = \sqrt{2m\omega/\hbar} x$ ; and the summations are over all electron states and all phonon branches.<sup>12</sup>

To proceed we make three approximations, all qualitatively reasonable if not quantitatively reliable. First, we as-

sume that in-plane phonons, including the well-known  $E_{2g}$  modes, contribute little to *interband* electron-phonon coupling; this follows from the same symmetry arguments given in Ref. 7. Second, we assume by the same reasoning that interband impurity scattering comes only from the out-of-plane relaxation of B atoms. Finally, we approximate Eq. (2) as

$$\gamma_{\text{imp}} \approx 12\pi n_{\text{imp}} \left( \sum_{\mathbf{k}} \delta(\varepsilon_{\mathbf{k}}) \right) \langle |dV/du_z|^2 \rangle (\delta z)^2, \quad (4)$$

and likewise Eq. (3) as

$$\lambda \approx 2 \left( \sum_{\mathbf{k}} \delta(\varepsilon_{\mathbf{k}}) \right) \langle |dV/du_z|^2 \rangle / 2m\omega^2. \quad (5)$$

Here we have assumed that the average of the crystal potential with respect to the vertical displacement of the B atom is the same in both cases. The numerical factors 12 and 2 are the coordination of Mg and the number of B atoms in the unit cell, respectively.

First-principles calculations give the interband part of the electron-phonon coupling as  $\sim 0.2$ .<sup>1</sup> The phonon frequencies for the out-of-plane modes are about  $400 \text{ cm}^{-1}$ . Using these values, the scattering rate is given by  $\gamma_{\text{imp}} \approx 50n_{\text{imp}}(\delta z)^2 \text{ eV}$ , where  $\delta z$  is in  $\text{\AA}$ . Hence for 2% Al doping we find  $\gamma_{\text{imp}} \approx 1.1 \text{ meV}$ . For 2% Na doping we estimate a similar scattering rate,  $\gamma_{\text{imp}} \approx 1.3 \text{ meV}$ . These scattering rates are small, but should still have a measurable effect on the superconducting gaps and temperature. The effect on the gaps is difficult to estimate without full Eliashberg calculations. The reduction of  $T_c$  can be easily estimated using Eq. (13) from Ref. 2, which gives 2.0–2.5 K (in addition to any suppression due to the electron doping of the  $\sigma$  band). While this is a small reduction compared to the changes observed in heavily electron-doped samples, the underlying mechanism is quite different. In particular, pair breaking from interband scattering is unique in that it reduces  $T_c$  and the gap ratio while simultaneously increasing the smaller gap.<sup>2</sup> This distinctive behavior should facilitate the separation of interband scattering from other sources of  $T_c$  reduction.

Finally, we suggest that an especially attractive test of these predictions would be simultaneous codoping by equal parts Al and Na. This would effectively be an isoelectronic substitution, and any effect on the superconducting properties could then be ascribed to impurity-induced interband scattering. Moreover, Na and Al induce distortions of the same magnitude but of the opposite sign, which should mitigate the effects of a reduction in scattering due to possible short-range ordering of the impurities.

In conclusion, we have performed first-principles calculations of the lattice distortion in  $\text{MgB}_2$  induced by several common substitutional (for Mg) impurities, and a Mg vacancy. We find out-of-plane displacements as large as  $0.04 \text{ \AA}$  for common impurities such as Al and Na. The magnitude and sign of the displacement are mainly determined by the ionic size of the impurity. On the other hand, for the Mg vacancy we find an essentially negligible displacement of

nearby B atoms. The different behavior of vacancies and impurities is explained by a simple physical model representing the competition between interlayer binding and intralayer planarity. We estimate the interband scattering rate due to the Na and Al impurities to be of order 1 meV, sufficiently large to give a detectable change in the superconducting transition

temperature. Finally, we propose that the codoped material  $\text{Mg}_{1-2x}\text{Na}_x\text{Al}_xB_2$ , which is isoelectronic with  $\text{MgB}_2$ , should provide an excellent test of these predictions.

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