Structural and Superconducting Transitions in Mg$_{1-x}$Al$_x$B$_2$

Sergey V. Barabash and David Stroud

Department of Physics, The Ohio State University, Columbus, Ohio 43210

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From systematic ab initio calculations for the alloy system Mg$_{1-x}$Al$_x$B$_2$, we find a strong tendency for the formation of a superstructure characterized by Al-rich layers. We also present a simple model, based on calculated energies and an estimate of the configurational entropy, which suggests that the alloy has two separate concentration regimes of phase separation, with critical points near $x = 0.25$ and $x = 0.75$. These results, together with calculations of electronic densities of states in several ionic arrangements, give a qualitative explanation for the observed structural instabilities, as well as the $x$-dependence of the superconducting $T_c$ for $x < 0.6$.

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The superconducting properties of MgB$_2$ \[1\] remain the subject of intense research. Although superconductivity in MgB$_2$ ($T_c = 39$ K) appears to result from a phonon-mediated BCS-like interaction \[2,3\] the details of this mechanism, including the possible relevance of anharmonic effects \[4\], multiple gaps \[5\] and Fermi nesting \[6\], are still being investigated. Studying the effects of doping is very important, as it may not only give additional evidence on the origins of superconductivity in pure MgB$_2$, but is also needed to explain the observed structural instabilities \[8–10\] and experimental difficulties in verifying the predicted increase in $T_c$ with Na or Ca substitutions \[11\].

Alloys of the form Mg$_{1-x}$Al$_x$B$_2$ are the most widely studied experimentally of all the doped MgB$_2$ materials \[12,13\]. These systems exhibit a variety of unusual behavior. For example, X-ray diffraction results suggest that Mg$_{1-x}$Al$_x$B$_2$ is unstable against phase separation in the concentration range $0.09 < x < 0.25$ and again near $x = 0.7$ \[14,15\]. Secondly, the superconducting transition shows unusual behavior as a function of $x$: the transition is broad around $x = 0.25$, consistent with phase separation, then the transition temperature $T_c$ drops sharply \textit{within} the single phase region ($0.25 < x < 0.4$) \[16\], but superconductivity persists (with $T_c \sim 10$ K) up to $x \sim 0.7$. Thirdly, a superstructure appears to form near $x = 0.5$ \[17\], corresponding to Al ordering in the $c$ direction, and possibly also at other Al concentrations.

In this study we investigate the energetics of Al-doped MgB$_2$, and their possible relation to superconductivity. Our particular aim is, first, to determine which structures have the lowest energy at several concentrations, especially $x = 0.5$ and $x = 0.333$, and, secondly, to use this knowledge to shed light on the phase separation which may occur at small and at large $x$, and the relation of these structural phase transitions to the loss of superconductivity with doping. While the influence of Al doping on superconductivity in Mg$_{1-x}$Al$_x$B$_2$ has been discussed theoretically by several authors \[18\], none have considered the effects of these superstructural transitions.

We have carried out ab initio calculations of the total energy for several compositions of Mg$_{1-x}$Al$_x$B$_2$, using the Vienna Ab Initio Simulation Package (VASP) \[14,15\], which employs a plane wave implementation of density functional theory \[17\]. We used ultra-soft pseudopotentials \[17\] within the generalized gradient approximation \[18\]. For all compositions, we first arranged the ions into an ideal MgB$_2$-like structure, then relaxed the positions of individual ions within a computational supercell until the energy had converged to a chosen tolerance. At most $x$ considered, we did calculations for several possible ionic arrangements, in an effort to determine the energetically favored superstructure.

Our main numerical results are summarized in Table I. For $x = 0$ and 1, our calculated lattice parameters, band structure and density of states are in very good agreement with experiment or with those calculated by other authors. We now discuss our results at other $x$, starting with $x = 1/3$. In Fig. 3(a), we show the supercell used to model this composition assuming equal concentrations of Al ions in the different Mg layers (entry $d$ in Table I). After ionic relaxation, the B ions shift from their original positions towards the neighboring Al atoms, as indicated by arrows. This behavior is not surprising, since the fully ionized Al$^{+3}$ ions carry an additional +e charge compared to the Mg$^{+2}$ ions, thus attracting the B$^-$ ions. But this ionic relaxation, since it requires altering the length of the strong in-plane $\sigma$-bonds formed by the B sp$^2$ orbitals, is very small ($\sim 0.01$ Å) \textit{in-plane}, with a correspondingly small energy change ($\sim 0.02$ eV per Al).

By contrast, if the Al atoms are assumed to completely fill every third Al/Mg layer [see Fig. 3(b)], the entire B layers shift towards the Al layers by more than 0.1 Å. Table I shows that this relaxation reduces the energy by about 0.2 eV per Al atom. Hence, this layered superstructure is much more favorable energetically than that with Al ions uniformly distributed in the Mg layers.
Similar behavior is observed at other values of \(x\) [see Table I and Fig. 1(c)]. The energies of “fully layered” superstructures are always lower than those of structures in which Al is uniformly distributed in the Mg layers, because of this relaxation effect. The large effect of layering is made clear in Fig. 3 where we plot \(\Delta E(x) = E_{\text{ground}}(x) - E_{\text{lin}}(x)\). \(E_{\text{ground}}(x)\) is the energy per \(\text{Mg}_{1-x}\text{Al}_x\text{B}_2\) formula unit of the fully layered ground state superstructure at concentration \(x\), and \(E_{\text{lin}}(x) = (1-x)E_{\text{MgB}_2} + xE_{\text{MgAlB}_2}\) is the linear interpolation. Clearly, \(\Delta E(x)\) is just proportional to the number of B layers situated between neighboring Mg and Al layers. This behavior is reasonable, since only these B layers can undergo the preferential relaxation which favors the layered superstructure [1].

Although the fully layered superstructure is always the lowest in energy at any \(x\), one can attain nearly the same reduction in energy by segregating the Al into various partially layered superstructures. We illustrate this point by considering \(x = 1/3\). In the fully layered superstructure, the Al ions occupy all the Mg sites in every third Mg layer [Fig. 1(b)]. In an arrangement we denote the “2/3” structure, the Al’s fill 2/3 of the sites in every second layer [cf. Fig. 1(d) and Table I]. These two structures have nearly the same energy [20], which is significantly lower than that in which the Al’s are randomly distributed in the Mg layers. We now use this fact as the basis of a simple model for phase separation in these alloys, considering for simplicity only the regime \(x \leq 1/2\).

At a given value of \(x\), the quantity of interest is the Helmholtz free energy per three-atom primitive cell of the \(\text{MgB}_2\) structure, which we write \(F(x, T) = E(x) - TS(x)\). We consider a sample that has a total of \(N_z\) layers, each layer having \(N_t\) of Mg/Al sites. We assume that \(x_zN_z\) of these layers are Al-rich, each with Al concentration \(x_a\), and \((1-x_z)N_z\) layers are Al-poor, with concentration \(x_m\). In the regime \(x < 0.5\), we assume for simplicity that \(x_m \sim 0\), from which it follows that \(x_ax_z = x\). (When we include \(x_m\) as a variable, in a suitably generalized free energy, we find that \(F(x, T)\) is minimized by \(x_m \sim 0\) for

![FIG. 1. Some of the Mg\(_{1-x}\)Al\(_2\) superstructures studied: (a), (b), (c) and (d) correspond to entries \(d, g, k\) and \(f\) in Table I. Large circles denote Al (shaded) and Mg (open) ions; small open circles denote B ions. (a) Top view of \(x = 1/3\) structure with no Al layering, showing both B and Al/Mg layers (actually separated by c/2 in the c direction). The in-plane displacement of the B ions by \(\sim 0.01\) \(\text{Å}\) towards the Al ions is indicated by arrows. (b) The ground state superstructure at \(x = 1/3\): Al ions occupy every third Mg/Al layer; two layers of B’s are displaced towards Al’s by \(\sim 0.1\) \(\text{Å}\). (c) The ground state superstructure at \(x = 1/2\). (d) Example of an alternative, higher-energy “2/3 structure” \((x = 1/3)\): The Al ions fill 2/3 of the sites in every second Mg/Al layer.)

![FIG. 2. Energy \(E_{\text{ground}}(x)\) of the fully layered (ground state) structure per \(\text{Mg}_{1-x}\text{Al}_x\text{B}_2\) formula unit, as given in Table I, minus the linear interpolation \(E_{\text{lin}}(x)\) between the energies of \(\text{MgB}_2\) and \(\text{MgAlB}_2\), plotted versus \(x\). The full line simply connects the calculated points, and the dotted line connects the points at \(x = 0, 0.5\) and 1.)

| \(x\) | superstructure | \(a, \text{Å}\) | \(r\) | \(E_x, \text{eV}\) | \(E_{\text{lin}}, \text{eV}\) |
|---|---|---|---|---|---|
| 0 | pure \(\text{MgB}_2\) | 3.07 | 1.145 | -15.416 | 0 |
| 1/3 | fully layered | 3.05 | 1.135 | -15.8573 | -0.048 |
| 2/3 | fully layered | 3.05 | 1.13 | -15.9661 | -0.050 |
| \(1/3\) | no layering (eclipsed) | 3.05 | 1.105 | -16.117 | -0.006 |
| \(1/3\) | no layering (staggered) | 3.05 | 1.11 | -16.107 | -0.001 |
| \(2/3\) | partially layered | 3.05 | 1.115 | -16.148 | -0.042 |
| \(2/3\) | fully layered | 3.04 | 1.125 | -16.1512 | -0.067 |
| \(2\) | fully layered (2+3 layers) | 3.04 | 1.12 | -16.294 | -0.074 |
| \(3\) | no layering (eclipsed) | 3.04 | 1.095 | -16.459 | -0.007 |
| \(3\) | no layering (staggered) | 3.04 | 1.10 | -16.439 | -0.0004 |
| \(3\) | fully layered | 3.03 | 1.11 | -16.512 | -0.079 |
| \(4\) | fully layered | 3.02 | 1.105 | -16.772 | -0.068 |
| 1 | pure \(\text{AlB}_2\) | 3.056 | 1.09 | -17.245 | 0 |

**TABLE I.** Calculated equilibrium lattice parameters \(a\) and \(r = c/a\), total energy \(E\) per \(\text{Mg}_{1-x}\text{Al}_x\text{B}_2\) formula unit, and the change in energy per formula unit \(E_{\text{lin}}\) due to ionic relaxation for several possible superstructures of \(\text{Mg}_{1-x}\text{Al}_x\text{B}_2\) at different values of \(x\). For entries denoted “eclipsed” (as opposed to “staggered”) the Al ions are situated directly above another in successive Al/Mg layers in the c direction.
temperatures up to \(\sim 500 \text{ K}\).\(^{19}\)

We assume that the internal energy \(E\) does not depend on the arrangement of the Al ions within the Al-rich layer, but only on \(x_2\) and \(x_1\),\(^{21}\), and we consider only the region \(0 \leq x \leq 0.5\). We then make the approximation that

\[
E(x_a, x_z) = E_{\text{random}}(x) - n(x)(E_1x_a + E_2x_z^2),
\]

(1)

where \(E_{\text{random}}(x)\) is the energy of random Mg\(_{1-x}\)Al\(_x\)B\(_2\). We approximate \(E_{\text{random}}(x)\) as varying linearly between \(x = 0\) and \(x = 0.5\), as is approximately true from our numerical results. The second term in eq. (1) is the energy reduction due to superstructural ordering, \(E_{\text{ord}}\), discussed above. It is proportional to the fraction of B layers \(n(x) = 0.5 - |x_z - 0.5|\) which are situated between Al-rich and Al-depleted layers; this effectively bounds the range of possible values of \(x_z\) by \(x_z \leq 0.5\). From our numerical calculations, \(E_{\text{ord}}\) is also roughly proportional to \(x_a\). In addition, we allow for a term quadratic in \(x_a\), to insure that the “fully layered structure” has an energy lower than that of “partially layered” structures. This quadratic term is crucial for phase separation. We obtain estimates of \(E_1\) and \(E_2\) from the model described in the text for \(T > T_{\text{inst}}\); concave up for \(T > T_{\text{inst}}\); concave down for \(T < T_{\text{inst}}\). In the latter regime, the concentrations of the two coexisting phases are determined by the standard common tangent construction sketched in Figure 6. The critical temperature \(T_{\text{inst}}\) and critical concentration \(x_{\text{inst}}\) for phase separation are determined as the maximum \(T\), and corresponding \(x\), where \((\partial^2F/\partial x^2)_T = 0\). We find \(T_{\text{inst}} = E_2/2\) (independent of \(E_1\)), and \(x_{\text{inst}} = 1/4\). For our choice \(E_2 = 0.03 \text{ eV}\), this procedure gives \(T_{\text{inst}} \approx 175 \text{ K}\). The experimental value of \(T_{\text{inst}}\) is unknown but must exceed the temperature at which a phase separated mixture was reported\(^{3,4}\)(presumably room temperature). But our estimate is obtained using an extremely simple means of estimating \(E_2\), and would probably be improved by a more elaborate calculation (moreover, our data suggest slight deviation of \(E_{\text{random}}\) from linear behavior, favoring phase instability).

For concentrations \(x > 0.5\), a similar model could also be applied, probably with different parameters \(E_1\) and \(E_2\), leading once again to a region of phase separation with a critical concentration \(x_{\text{inst}} = 0.75\). On the other hand, the upward curvature in \(E(x)\) at \(x > 0.5\) (cf. Fig. 6) should oppose phase separation, decreasing the width of the two-phase region at a given temperature. This behavior once again appears to agree with experiment, as the observed two-phase region near \(x \sim 0.7\) is reported to have much smaller width at comparable \(T\).

Finally, we discuss the observed variation of superconducting transition temperature \(T_c(x)\) with \(x\), based on these results. Our calculations confirm the suggestion\(^{11,13}\) that the decrease of \(T_c\) with increasing \(x\) is due primarily to a reduction in the density of states (DOS) near the Fermi energy. By way of illustration, we show in Fig. 6 our calculated Kohn-Sham DOS \(N(\varepsilon)\) in pure MgB\(_2\) and the fully layered \(\text{Mg}_{0.5}\text{Al}_{0.5}\)B\(_2\). (We have attempted to minimize structure due to spurious Van Hove singularities produced by the computational algorithm\(^{22,24}\) by using \(k\)-meshes as fine as \(35 \times 35 \times 35\).) Indeed \(N(\varepsilon; x = 0.5) < N(\varepsilon, x = 0)\) as expected. The observed large width \(\Delta T(x)\) of the superconducting transition near \(x = 1/4\) occurs, we believe, because this concentration lies in the two-phase regime. To some extent, DOS behaves as predicted from the rigid-band model, simply shifting in energy, relative to \(\varepsilon_F\), without greatly changing its shape. However, the slightly broader DOS at \(x = 0.5\) is, we believe, a real departure from the rigid-band picture, and due to the increased physical unit cell size.

For further insight into the occurrence of superconductivity, we have examined the calculated band structures at different values of \(x\) and \(z\). We paid special attention to the \(\sigma\)-bonding \(p_{x\sigma}\) bands believed to be primarily responsible for the superconductivity. Using a rigid-band model for small variations in \(x\) at fixed \(x_z\), we found that
for any value of $x_2$, these $\sigma$-bands fill at $x \approx 0.6$. (For example, they are filled for structure $l$). If these were the only occupied bands, the superconducting $T_c$ would seem to vanish above $x \approx 0.6$. Since the electron-phonon coupling constant $\lambda_{c,p}$ for those bands that remain partially filled at $x > 0.6$ is very small ($\lambda_{c,p} \sim 0.28$ [4]), it could not produce superconductivity for $T > T_{c,p} \sim 0.01$ K, according to the Allen-Dynes formula [23,24]. Thus, the persistence of a finite $T_c$ ($\sim 10$ K) may result from some kind of coupling between electrons in the $p_z$ and $\sigma$ bands. For example, a strong pairing interaction between $\sigma$ electrons could make it energetically favorable for some electrons to transfer into the $p_z$ band.

To summarize, the present $ab$ initio study of Mg$_{81-x}$Al$_x$B$_2$ has led to three principal findings. First, we find that at low temperatures a layered superstructure is energetically preferred, not only at $x = 0.5$ as was found experimentally [20,21], but also at other values of $x$. Secondly, we have described a very simple model for phase separation in these alloy systems. The model is based on a balance between the calculated $ab$ initio energies and configurational entropy, and leads to critical points at $x = 0.25$ and $x = 0.75$, also consistent with experiment. Finally, we find that at $x < 0.5$ the experimental trends in both $T_c(x)$ and the width $\Delta T(x)$ of the superconducting transition can be qualitatively interpreted in terms of the calculated $x$-dependent density of states $N(\varepsilon_F,x)$, but that the interband coupling must be crucial in maintaining finite $T_c$ at $x > 0.6$.

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