Crystal Structure of the Mg$_{1-x}$Al$_x$B$_2$ superconductors near $x \approx 0.5$

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Precise structural information on the Mg$_{1-x}$Al$_x$B$_2$ superconductors in the vicinity of $x \approx 0.5$ is derived from high-resolution synchrotron X-ray powder diffraction measurements. We find that a hexagonal superstructure, accompanied by doubling of the $c$-axis, ordering of Mg and Al in alternating layers, and a shift of the B layers towards Al by $\sim0.12$ Å, is formed. The unusually large width of the (002) superlattice peak implies the presence of microstrain broadening, arising from anisotropic stacking of Al and Mg layers and/or structural modulations within the $ab$ plane. The ordered phase survives only over a limited range of compositions away from the optimum $x=0.5$ doping level.

The discovery of superconductivity in the binary boride, MgB$_2$ at the high temperature of 39 K has generated considerable interest because of the apparent simplicity of its chemical composition, crystal structure and electronic properties. MgB$_2$ possesses a simple hexagonal structure (AlB$_2$-type, space group P6/mmm) comprising graphitic-type B layers interleaved with Mg layers. Band structure calculations reveal that, while the electronic properties of the system can provide crucial tests for the mechanism of superconductivity and they have been investigated through chemical substitution between B and Al, or within the boron layers. In all cases, the critical temperature of MgB$_2$ decreases at various rates for different substitutions. Among the various ternary compositions, the properties of the Al-doped series Mg$_{1-x}$Al$_x$B$_2$ are of particular interest and have been extensively studied both experimentally and theoretically. Electron doping through Al substitution leads to a decrease in $T_c$ which can be rationalized by the filling of the electronic states by the additional electron donated by Al and the resulting decrease in the density of states at the Fermi level. However, very importantly the rate of decrease of $T_c$, $dT_c/dx$ sensitively depends on the doping level, $x$. For $T_c$ first decreases smoothly in the region $0 < x < 0.1$, then the transition becomes broader up to $x = 0.25$. For compositions with $0.25 < x < 0.4$, $T_c$ drops more sharply and then vanishes in the vicinity of $x = 0.4$. These results imply a more complicated crystal structural and/or electronic response for the Mg$_{1-x}$Al$_x$B$_2$ series than that expected for solid solution and rigid band behavior. Indeed early X-ray diffraction measurements have revealed the presence of structural anomalies associated with a miscibility gap and multiphase behavior in the regions $0.1 < x < 0.25$ and $0.7 < x < 0.8$. In addition, electron diffraction and transmission electron microscopy studies have provided direct evidence for the existence of a superstructure at $x \approx 0.5$ resulting from ordered arrangements of Al and Mg atoms both along the $c$-axis and in the $a-b$ plane.

In this paper, we report a structural determination of the Mg$_{1-x}$Al$_x$B$_2$ ($x = 0.45, 0.5, 0.55$) ternary superconductors by synchrotron X-ray powder diffraction at 16 and 298 K. A hexagonal superstructure, accompanied by the doubling of the $c$-axis of the MgB$_2$ structure is observed, arising from ordering of Al and Mg in subsequent layers. Formation of the superstructure is optimal for Mg$_{0.5}$Al$_{0.5}$B$_2$ but survives small deviations ($\approx10\%$) from the $x=0.5$ composition.

Powder samples with nominal composition Mg$_{1-x}$Al$_x$B$_2$ with $x = 0.4$, 0.45, 0.5, and 0.55 were prepared by liquid-vapor to solid reactions for 24 hours, as described in ref. 8. The reaction temperatures were between 800° and 870°C. SQUID measurements were performed on 50-mg samples in the temperature range 1.8-50 K with a Quantum Design SQUID magnetometer (MPMS5). High-resolution synchrotron X-ray diffraction experiments were carried out on the BM16 beamline at the European Synchrotron Radiation Facility (ESRF), France. The samples were sealed in 1.0-mm diameter glass capillaries and diffraction profiles ($\lambda = 0.85023\ \AA$) were collected at 16 K (and for $x = 0.5$ also at ambient temperature) in continuous scanning mode using nine Ge(111) analyzer crystals. The capillaries were continuously spun during data acquisition. The
data were rebinned in the 2θ range 1-80° to a step of 0.01° and refined using the GSAS suite of Rietveld analysis programs. The peakshape of the diffraction lines was modelled by a convolution of a pseudo-Voigt function and an asymmetry function, which is related to the instrumental axial divergence. In addition, in order to account for anisotropic peak broadening of different classes of (hkl) reflections evident in the high-resolution diffraction profiles, the Gaussian and Lorentzian portions of the peakshape function ascribed to microstrain broadening ($\sigma_x$ and $\gamma_x$) were described by the semi-empirical Stephens formalism. In this model, the width of each reflection can be expressed in terms of moments of a multi-dimensional distribution of lattice metric parameters and can be related to distributions of elastic strains caused by defects or dislocations.

Fig. 1 shows the results of the magnetic measurements at 10 Oe (ZFC conditions) for the Mg$_{1-x}$Al$_x$B$_2$ compositions with $x = 0.45, 0.5$, and 0.55. Diamagnetic shielding is evident at low temperature in all three samples. The one-step transitions are sharp and the transition temperatures $T_c$, defined by the intersection of line extrapolations below and above $T_c$, are 6, 3, and 4 K for $x = 0.45, 0.5$, and 0.55, respectively. Although the shielding fractions at 2 K are small, the sharpness of the transitions implies that superconductivity is of bulk nature and does not arise from sample inhomogeneities and composition fluctuations.

Inspection of the synchrotron X-ray diffraction profile of Mg$_{0.5}$Al$_{0.5}$B$_2$ at 16 K shows that all reflections can be assigned either to a hexagonal cell (space group $P6/mmm$ - AlB$_2$ type) with lattice constants $a \approx 3.045$ Å and $c \approx 3.506$ Å or to a small fraction (<1%) of MgO impurity. However, an additional weak peak not attributable to an impurity phase is clearly visible at $\theta \approx 4.1\%$ implying an anisotropic distribution along the $c$-axis of alternating ordered Al and Mg layers. This extra reflection whose intensity is $\sim 26\%$ of the weak (001) reflection indexes as (001) on the hexagonal unit cell and provides the unambiguous signature of the formation of a superstructure whose unit cell is exactly doubled along the $c$-axis. No other prominent peaks that could arise from the formation of the superstructure are observed under the present experimental conditions. The observed doubling of the $c$-axis allows ordering of Al and Mg in subsequent layers while maintaining the gross features of the original AlB$_2$-type structure. The simplest Al/Mg ordering motif consistent with the observed superreflection corresponds to an alternation of Al and Mg along the $c$-axis (space group $P6/mmm$), as suggested by TEM investigations in ref. [1]. Rietveld refinements using this model proceeded smoothly with Mg and Al placed in the 1a (0,0,$\frac{1}{2}$) and 1b (0,0,0) positions, respectively, and the B atoms located in the $4h$ ($\frac{1}{2}$, $\frac{1}{2}$, $z$; $z \approx \frac{1}{4}$) positions. The refined lattice parameters of Mg$_{0.5}$Al$_{0.5}$B$_2$ at 16 K are $a = 3.04436(2)$ Å and $c = 6.71248(10)$ Å. In addition to Al/Mg ordering, the present structural model allows for unequal separation between neighboring MgB$_2$ and AlB$_2$ slabs as the B atoms have the freedom to relax along the $c$-direction ($z \neq \frac{1}{4}$), while the strictly flat boron sheets of the original AlB$_2$-type structure are maintained (Fig. 3). In Mg$_{0.5}$Al$_{0.5}$B$_2$, the B position refines to ($\frac{1}{2}$, $\frac{1}{2}$, 0.2413(3)), corresponding to Mg-B and Al-B distances of 2.471(1) Å and 2.390(1) Å, respectively.

In the course of the Rietveld refinements, it was evident that the widths of the (00l) reflections were invariably larger than those of the (hkl) reflections, providing the signature of strong anisotropic strain broadening effects. These microstructural effects were modeled with the formalism developed by Stephens. For this model, the obtained microstrain broadening contribution to the width of the (001) reflection is $\sim 1.3\%$, almost twice as large as that to the (200) peak. This could be related to increased strains along the $c$-axis due to the presence of defects and stacking faults associated with the Al and Mg layers. Moreover, the microstrain contribution to the width of the (00$\frac{1}{2}$) superlattice peak is even higher ($\sim 4.1\%$) implying an anisotropic distribution along the $c$-axis of alternating ordered Al and Mg layers. Fig. 4 displays the final refinement of the synchrotron X-ray diffraction profile of Mg$_{0.5}$Al$_{0.5}$B$_2$ at 16 K, while the results of the analysis are summarized in Table I.

Despite the excellent quality of the Rietveld refinement of the synchrotron X-ray diffraction profile of Mg$_{0.5}$Al$_{0.5}$B$_2$ using the Al/Mg ordering model described above, alternative models of ordering were also considered. An attractive possibility consistent with the observed doubling of the hexagonal $c$-axis involves ordering of both Al and Mg on the same layer with each atom surrounded by as many atoms of the other kind as possible. However, the resulting crystal symmetry is $P6_3/mmc$ and the (00$\frac{1}{2}$) reflection will be extinct, clearly necessitating ordering of Al and Mg atoms in alternating layers. Finally, we considered the possibility that ordering of Mg and Al is accompanied by distortion of the B layers. The appropriate unit cell in this case is primitive orthorhombic with lattice constants $a \approx a_h$, $b \approx b_h \sqrt{3}$, and $c = 2c_h$. Rietveld refinements of the diffraction data using such models did proceed to convergence and improved quality of fit but the paucity of observed superreflections did not allow unambiguous conclusions concerning the existence of an orthorhombic distortion of the original hexagonal unit cell.

A synchrotron X-ray diffraction profile of Mg$_{0.5}$Al$_{0.5}$B$_2$ was also collected at 298 K. The (00$\frac{1}{2}$) superlattice peak is again present implying the absence of a phase change with increasing temperature. Rietveld refinement with the $P6/mmm$ superstructure model proceeded smoothly (Table I), leading to lattice constants of $a = 3.04705(2)$ Å and $c = 6.72409(12)$ Å and anisotropic expansion between 16 and 298 K of 0.088(1)% and 0.173(3)% along the $a$- and $c$-axis, respectively.

Synchrotron X-ray diffraction profiles were also collected at 16 K for the Mg$_{0.55}$Al$_{0.45}$B$_2$ and Mg$_{0.45}$Al$_{0.55}$B$_2$ compositions. In both cases, the peak at $2\theta \approx 7.26\degree$ which provides the signature of Mg/Al ordering and superstructure formation is present but with decreased in-
tially destroyed for Mg and 0.55, Table II). The ordered superstructure is essentially preserved (000q = 6.69127(12) Å, c = 6.09127(12) Å and a = 3.04988(2) Å, c = 6.73190(11) Å for Mg_{0.45}Al_{0.55}B_2 and Mg_{0.55}Al_{0.45}B_2, respectively (Table II).

A perspective view of the hexagonal superstructure of Mg_{0.55}Al_{0.45}B_2 is shown in Fig. 3. Compared to the unit cell of MgB_2, the present structure arises from ordering of the Mg^{2+} and Al^{3+} ions, leading to doubling of the unit cell along the c-axis. Both crystallographically distinct Mg^{2+} and Al^{3+} ions present in the unit cell have identical coordination environments, namely they lie directly above the centers of two B hexagons of A layers. Consistent with higher ionic charge and small ionic radius (0.675 Å) of Al^{3+} compared to Mg^{2+} (0.860 Å), the Al-B bond distances are smaller than the Mg-B ones, 2.390(1) Å and 2.471(1) Å, respectively, at 16 K. This leads to Al-B and Mg-B layer separations along the c-direction of 1.620(2) Å and 1.737(2) Å, respectively, and reflects a displacement of the B layers of ~0.12 Å towards each Al layer. As we deviate from the x = 0.5 ternary towards Mg or Al rich compositions, the difference between the Al-B and Mg-B layer separations rapidly decreases (only ~0.01 and 0.05 Å, respectively, for x = 0.45 and 0.55, Table II). The ordered superstructure is essentially destroyed for Mg_{0.6}Al_{0.4}B_2, as the (004 superlattice peak has now collapsed into the background (Fig. 2), while further it is unambiguously absent in compositions with even smaller Al doping levels. On the other hand, the in-plane B-B bond lengths decrease monotonically with increasing Al content across the stability boundary of the superstructure (from 1.76385(1) Å in Mg_{0.8}Al_{0.2}B_2 to 1.75692(1) Å in Mg_{0.45}Al_{0.55}B_2) in agreement with the strengthening of the in-plane α-bonds.

The superstructure derived in this work is identical to that proposed by earlier TEM measurements and is energetically preferred, according to recent theoretical calculations. In addition, a more complicated Mg/Al ordering scheme, involving both ordering along the c-axis and a sinusoidal modulation component, q in the hexagonal ab plane was observed in the HREM work of Zandbergen et al. The signature of the in-plane structural modulation came from the splitting of the observed superreflections which yielded diffraction rings. In the present powder X-ray diffraction experiments, no such clear splittings are observed. However, we first note that the observed (00\(\frac{1}{2}\)) superreflection is unusually broad (Fig. 2) and the large microstrain broadening (wide supra) required to account for its width may be precisely associated with such ordered distributions of the Mg and Al atoms within the hexagonal planes. In addition, there is a shoulder on the high angle side of the (00\(\frac{1}{2}\)) peak at 2θ ≈ 7.5° (marked * in Fig. 2) which indexes as (q_1,q_2,\(\frac{1}{2}\)) with (q_1^2 + q_2^2)^\frac{1}{2} ≈ 0.12, tantalizingly close to the incommensurate in-plane modulation vector, q ≈ 0.1 in real space.

The origin of the observed superstructure is of particular importance and may have consequences for the understanding of superconductivity in these systems. One possibility is that it is associated with an electronic instability near the 50% doping level. This is consistent with the extremely narrow stability range of the superstructure and its sensitivity to small compositional changes. On the other hand, the high quality of the present Mg_{0.5}Al_{0.5}B_2 sample precludes the presence of large compositional fluctuations that could be responsible for the observation of diamagnetic shielding and provides evidence that the superstructure does not suppress superconductivity, as it might be expected from the opening of a gap at the Fermi surface. Another possibility is that it is associated with a structural instability arising from the size mismatch between Al and Mg. The Al-B and Mg-B bond distances are 2.375 and 2.501 Å, respectively, near the Mg_{0.45}Al_{0.55}B_2 end members, while evidence exists for anisotropic distributions of Mg and Al in the metal layers. In the vicinity of x ≈ 0.5, the size mismatch effect is maximal and complete ordering of Mg and Al becomes energetically favourable. The observed Al-B and Mg-B bond distances of 2.390(1) Å and 2.471(1) Å in the Mg_{0.5}Al_{0.5}B_2 superstructure are comparable to those encountered for the x = 0.8 and 0.2 compositions, respectively, near the Al- and Mg-rich critical concentrations for the two-phase separation onsets in the Mg_{1−x}Al_{x}B_2 series.

In conclusion, a hexagonal superstructure is obtained in Mg_{1−x}Al_{x}B_2 for a small range of Al and Mg concentrations near x ≈ 0.5. The principal component of the structural modulation of the parent MgB_2 structure is along the c-axis, while evidence exists for anisotropic distributions of alternating Mg/Al planes in the c-direction or ordered Mg/Al distributions within the hexagonal planes. Size mismatch and electronic effects were considered as possible origins of the observed behavior.
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TABLE I: Refined parameters for Mg$_{0.5}$Al$_{0.5}$B$_2$ obtained from Rietveld refinement of synchrotron X-ray powder diffraction data at 16 K (space group $P6/mmm$; hexagonal cell constants: $a = 3.04436(2)$ Å, $c = 6.71248(10)$ Å; reliability factors: $R_{wp} = 5.4\%$, $R_{exp} = 4.0\%$). The lattice constants at 298 K are $a = 3.04705(2)$ Å, $c = 6.72409(12)$ Å and the reliability factors $R_{wp} = 6.1\%$, $R_{exp} = 5.1\%$.

| Atom | Site | $x$/$a$ | $y$/$a$ | $z/c$ | $B$ (Å$^2$) | Occupancy |
|------|------|--------|--------|------|-------------|-----------|
| Mg   | 1a   | 0      | 0      | 0    | 0.17(1)     | 1.0(1)    |
| Al   | 1b   | 0      | 0      | 0    | 0.17(1)     | 1.0(1)    |
| B    | 4h   | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.2413(3) | 0.93(3)     | 1.1(2)    |

TABLE II: Selected bond distances (Å) in Mg$_{1-x}$Al$_x$B$_2$ ($x = 0.4, 0.45, 0.5, 0.55$) at 16 K.

| $x$ | Mg-B | Al-B | (Mg/Al)-B | B-B |
|-----|------|------|-----------|-----|
| 0.4 | -    | -    | 2.44157(2) | 1.76365(1) |
| 0.45| 2.438(2) | 2.433(2) | -         | 1.76085(1) |
| 0.5 | 2.471(1) | 2.390(1) | -         | 1.75766(1) |
| 0.55| 2.442(2) | 2.410(2) | -         | 1.75692(1) |

Figure captions

Figure 1. Temperature dependence of the magnetic susceptibilities of Mg$_{1-x}$Al$_x$B$_2$ ($x = 0.45, 0.5, 0.55$) measured under ZFC conditions in a field of 10 Oe.

Figure 2. Synchrotron X-ray powder diffraction profiles of Mg$_{1-x}$Al$_x$B$_2$ ($x = 0.4, 0.45, 0.5, 0.55$) at 16 K in the vicinity of the (00$\frac{1}{2}$) superlattice reflection. The solid lines are guides to the eye.

Figure 3. Structural model of the Mg$_{0.5}$Al$_{0.5}$B$_2$ superstructure.

Figure 4. Final observed (points) and calculated (solid line) synchrotron X-ray powder diffraction profiles for Mg$_{0.5}$Al$_{0.5}$B$_2$ at 16 K in the range 6° to 80° ($\lambda = 0.85023$ Å). The lower panel shows the difference profiles and the ticks mark the positions of the Bragg reflections of Mg$_{0.5}$Al$_{0.5}$B$_2$ (upper) and MgO ($<$1%, lower). Inset. Rietveld fit in the range 6° to 15.6°.
Susceptibility, $\chi$ (emu/mol) vs Temperature (K) for Mg$_{1-x}$Al$_x$B$_2$ with different $x$ values:

- $x = 0.45$
- $x = 0.5$
- $x = 0.55$
