A magnetization and $^{11}$B NMR study of Mg$_{1-x}$Al$_x$B$_2$ superconductors

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We demonstrate for the first time the magnetic field distribution of the pure vortex state in lightly doped Mg$_{1-x}$Al$_x$B$_2$ ($x \leq 0.025$) powder samples, by using $^{11}$B NMR in magnetic fields of 23.5 and 47 kOe. The magnetic field distribution at $T = 5$ K is Al-doping dependent, revealing a considerable decrease of anisotropy in respect to pure MgB$_2$. This result correlates nicely with magnetization measurements and is consistent with $\sigma$-band hole driven superconductivity for MgB$_2$.

The synthesis of MgB$_2$ had been reported in 1954 but only recently Nagamatsu et al. discovered that this compound is a superconductor with a surprisingly high $T_c \approx 39$ K. At first it was suggested that a BCS-type mechanism with strong electron-phonon coupling and high phonon energy of the light boron atoms can be responsible for the observed high-$T_c$. This is based on the observation of the isotope effect on $T_c$ and a strong negative pressure coefficient of $T_c$. Alternatively, Hirsch proposed a "universal" mechanism where superconductivity in MgB$_2$ is driven by the pairing of dressed holes. Electronic band structure calculations indicate that in MgB$_2$ the charge carriers are situated in two bands derived from the $\sigma$-bonding $p_{x,y}$-orbitals of boron, which are essentially two-dimensional (2D), and in one electron and one hole bands derived from the $\pi$-bonding $p_z$-orbitals of boron. Both, $\sigma$ and $\pi$ bands have strong in-plane dispersion due to the large overlap between all $p$ orbitals of neighboring boron atoms. Despite some diversity in these models, there is a general agreement$^{3,7,8,9,10}$ that the key point for superconductivity in MgB$_2$ is the 2D $\sigma$ band of $p_{x,y}$ orbitals within the boron layers, and the delocalized metallic-type bonding between these layers. These calculations predict a strong anisotropy in the Fermi surface (and possibly in the electron phonon coupling) that is consistent with the observed$^{4,17}$ anisotropy in $H_{c2}$. Specifically, the anisotropic ratio: $\gamma = H_{c2}^b/H_{c2}^c$, was found$^{4,17}$ to be between 1.7 and 6, depending on the material and the experimental method.

In view of this description, measurements on electron- or hole-doped MgB$_2$ are of interest as they may help our understanding of how the electronic density-of-states and the Fermi surface depend on doping. Al substitution for Mg in Mg$_{1-x}$Al$_x$B$_2$ provides a way for electron doping. The similarity of the calculated electronic density of states between MgB$_2$ and AlB$_2$ indicates that doping results in simple filling of the available electronic states, with one electron donated per Al atom. A very first study of Al doped MgB$_2$ showed$^{10}$ that $T_c$ is slightly suppressed for $x \leq 0.1$. However, band structure calculations show that there is a sharp drop in the density of states of MgB$_2$ at only slightly higher electron concentrations. Suzuki et al. predict that in Mg$_{1-x}$Al$_x$B$_2$ the concentration of $\sigma$ holes varies with $x$ as $n_h = (0.8 - 1.4x) \times 10^{22}$ cm$^{-3}$, leading to $n_h = 0$ for $x \approx 0.6$. For $0.1 \leq x \leq 0.25$, a two phase mixture is formed, whereas for $x > 0.25$ a single non-superconducting phase is detected. The detrimental effect of doping on $T_c$ in Mg$_{1-x}$Al$_x$B$_2$ can be explained within the BCS model, as it increases the Fermi energy ($E_F$) and decreases the density of states $N(E_F)$. Besides, thermoelectric power and resistivity measurements show$^{1}$ that Mg$_{1-x}$Al$_x$B$_2$ alloys are hole-type normal metals. In order to analyze trends associated with the band filling and their relation to the loss of superconductivity, we have performed a detailed study of Mg$_{1-x}$Al$_x$B$_2$ ($0 \leq x \leq 0.1$) using structural, magnetic and $^{11}$B NMR line shape measurements. Powder samples with nominal composition Mg$_{1-x}$Al$_x$B$_2$ ($0 \leq x \leq 1$) were prepared by liquid-vapor to solid reaction as described elsewhere.$^{1}$ Synchrotron X-ray powder diffraction measurements were performed on Mg$_{1-x}$Al$_x$B$_2$ samples, sealed in thin-wall glass capillaries 0.5 mm in diam-
ter at 295 K. Inspection of Figure 1 which shows parts of the XRD patterns of the $x = 0.005$ and 0.025 samples shows that while Mg$_{1-\gamma}$Al$_{\gamma}\text{B}_2$ is single phase, a clear splitting of the (002) reflection is observed for Mg$_{1-\gamma}$Al$_{\gamma}\text{B}_2$. This implies the onset of macroscopic phase separation with increasing Al content. A similar observation has been reported for C-doped MgB$_2$ compositions in which the carbon miscibility is also very small, $x < 0.04$. For this reason we restrict our NMR study only to Mg$_{1-x}$Al$_x\text{B}_2$ samples with $x \leq 0.025$. The deduced lattice parameters are plotted in Fig. 2. For $x < 0.025$, the c-axis exhibits a negative slope $dc/dx \approx -0.2$ Å/at % Al), whereas the in-plane a-axis remains nearly constant. For $x \geq 0.025$, the coexisting phases differ mainly in their interlayer lattice constant.

Dc-magnetic measurements in a SQUID magnetometer under a magnetic field of $H = 10$ Oe show that all the examined samples are superconductors, with their $T_c$ decreasing quasilinearly with increasing Al content ($dT_c/dx \approx -0.1$ K/at % Al). A steeper decrease of $T_c$ is observed for $x > 0.1$ that becomes zero at $x \approx 0.55$. Figure 2 shows the reversible portion of the temperature dependence of the magnetization in various fields for $x = 0.01$. Contrary to high-temperature superconductors where fluctuation effects cause a substantial broadening of the transition with increasing temperature and field, the transition curves for Mg$_{0.99}\text{Al}_{0.01}\text{B}_2$ shift to lower temperatures in an almost parallel fashion. However, instead of the expected conventional linear dependence a pronounced curvature is present in $M(T)$ curves. This curvature has been attributed to the anisotropy of MgB$_2$. The dot-lines through the experimental points is a simulation of the reversible magnetic moment using the equation (1):

$$4\pi M = -\frac{\Phi_o}{8\pi\lambda(T)^2\beta_A\gamma^{1/3}} \sqrt{\gamma^2 - 1} \times \left(1 - \frac{4h^2}{3h^2\sqrt{1-h^2}} + \ln \left(1 + \sqrt{1-h^2} \right) \right)$$

where $h = H/H^c_{ab}$, $\lambda = (\lambda^2_0\lambda_o)^{1/3}$ is the average penetration depth, $\beta_A = 1.16$, $\Phi_o$ is the flux quantum, and $\gamma = H^c_{ab}/H^c_{c2}$ is the anisotropy constant. In order to simulate the $M(T)$ data we suppose a power law relation for $H^c_{ab}(T)$, $H^c_{ab} = H^c_{ab}(0)(1 - T/T_c)^\nu$ (with $H^c_{ab}(0) = 262 \pm 25$ kOe, $T_c = 37.9 \pm 0.1$ K and $\nu = 1.27 \pm 0.05$), a weak magnetic field dependence, $\lambda \sim 2$ nm, and an anisotropy constant $\gamma \sim 5.4$. Similarly, the $M(H)$ data have been simulated using the same $\gamma$ and a temperature dependent $\lambda(T)$. The value of the anisotropy constant, deduced from magnetic measurements, for $x = 0.01$ is smaller than that obtained from the $x = 0$ sample ($\gamma \sim 6$), in agreement with the NMR spectra (vide infra). The temperature variation of $H^c_{ab}$ has the same functional form with the $x = 0$ sample (i.e. the same exponent), while $T_c$ and $H^c_{ab}(0)$ are 0.7 K and 20 kOe smaller, respectively.

$^{11}$B NMR line shape measurements of the central transition ($-1/2 \rightarrow 1/2$) were performed on two spectrometers operating in external magnetic fields $H_o = 23.5$ and 47 kOe. The spectra were obtained from the Fourier transform of half of the echo, following a typical $\pi/2 - \tau - \pi$ spin-echo pulse sequence. NMR is a very sensitive local probe of the spatially inhomogeneous magnetic field associated with the vortex state, which is formed in external magnetic fields $H_o < H^c_{ab} < H^c_{c2}$. In a recent study we have observed that the $^{11}$B NMR line shapes in pure MgB$_2$ remain unchanged down to the temperature of the second critical field $T_{c2}$ whereas for $T < T_{c2}$, a second peak develops at lower frequencies. The intensity ratio of this second peak to the unshifted high-T peak was observed to increase in field $H_o = 23.5$ kOe when compared to that in field $H_o = 47$ kOe.

A direct comparison of the NMR line shapes with dc-magnetic measurements, that reveal the temperature dependence of $H^c_{ab}$ and $H^c_{c2}$, has shown that the intensity and shape of the low frequency peak follows the development of the vortex lattice as a function of temperature. Since in pure MgB$_2$, $H^c_{ab} \approx 150$ kOe, it was expected as showing that a part of the grains remains in the normal state (unshifted peak) for $H^c_{c2} < H_o < H^c_{ab}$ down to the lowest measured temperature $T = 5$ K. It is thus remarkable that by light Al doping, the normal state signal component disappears in the mixed superconducting state and only the pure vortex lattice signal is present. This is clearly seen in Figure 3 which shows the $^{11}$B NMR line shapes for $x = 0.01$ at various temperatures, in field 23.5 kOe. Alike to MgB$_2$ spectra, the line shapes in the normal state are temperature indepen-
FIG. 3: (a) (upper panel) Zero field and field cooling magnetic moment as a function of the temperature for $10 \leq H \leq 54$ kOe for the powder Mg$_{0.99}$Al$_{0.01}$B$_2$ sample used in the NMR measurements. The dot-lines through the experimental points are simulations of the reversible magnetic moment supposing an anisotropy $\gamma \approx 5.4$ (see main text). (b) (middle panel) Isothermal magnetization loops in the reversible regime at $26 \leq T \leq 36$ K for Mg$_{0.99}$Al$_{0.01}$B$_2$. (c) (lower panel) Variation of $H_{c2}^{ab}$ as a function of temperature for the $x = 0.01$ sample. The solid line is a fit through the experimental points with a power law relation $H_{c2}^{ab} = H_{c2}^{ab}(0)(1 - T/T_s)^\nu$ ($H_{c2}^{ab}(0) = 262 \pm 5$ kOe, $T_s = 37.9 \pm 0.1$ K and $\nu = 1.27 \pm 0.02$). Also included is the $H_{c2}^{ab}(T)$-curve (thick solid line) of the $x = 0$ sample, for direct comparison.

FIG. 4: $^{11}$B NMR line shapes as a function of temperature for Mg$_{0.99}$Al$_{0.01}$B$_2$ under a magnetic field $H = 23.5$ kOe.

FIG. 5: $^{11}$B NMR line shapes of Mg$_{1-x}$Al$_x$B$_2$ for $0.0 \leq x \leq 0.025$ at $T = 5$ K in field $H_o = 23.5$ kOe.

dent. For $T \leq 30$ K the vortex lattice is formed, inducing a gradual shift of the peak frequency (corresponding to $H_s$) that creates the characteristic asymmetric broadening of the NMR frequency distribution as expected from the vortex lattice only. This effect indicates an enhancement (relative to pure MgB$_2$) of $H'_{c2}$ above 23.5 kOe by Al doping, which leaves only the superconducting state at $T = 5$ K. At $T = 5$ K the shift of $H_s$ from the field $H_o$ in the normal state is about 50 Gauss. Since we measure an anisotropic polycrystalline sample, it is expected that the sharp singularities smear out. It is worth noting that at $T = 20$ K the line shape exhibits a shoulder (see arrow in Fig. 4). This shoulder indicates that $H_{c2}^{ab}$ is crossed at this temperature.

Figure 5 shows NMR spectra at $T = 5$ K in $H_o = 23.5$ kOe for Mg$_{1-x}$Al$_x$B$_2$ ($0 \leq x \leq 0.025$). At $T = 300$ K the NMR spectra are essentially identical for $0 \leq x \leq 0.2$. Since the cell constants change slightly in this concentration region, the observed similarity in the NMR spectra indicates that the induced line shape is resolution limited. At $T = 5$ K all the samples are in the mixed state and the line shape reflects the magnetic field distribution from the vortex lattice. Remarkably, the line shapes depend on $x$. As discussed above for the $x = 0$ system, the observed line shape is the result of the anisotropy. Hence, the disappearance of the normal state signal component and the variation of the vortex state signal with $x$ can be explained by supposing that the anisotropy decreases with Al doping. We stress that even at $x = 0.005$ the component from the normal state signal disappears. In figure 5 we have scaled for comparison the signal intensity of the $x = 0.005$ system under the low frequency tail of pure MgB$_2$. Apparently there is an excellent matching of the two signals, providing clear experimental evidence that this shoulder corresponds to the magnetic field distribution of the vortex state. We also notice that for $x \geq 0.025$ the line shape changes drastically. At this concentration either the anisotropy starts to increase abruptly, or the particular line shape is associated with the onset of
FIG. 6: $^{11}$B NMR line shapes of Mg$_{1-x}$Al$_x$B$_2$ for $0.0 \leq x \leq 0.025$ at $T = 5K$ in a magnetic field $H_0 = 47$ kOe.

phase separation at this composition. Figure 6 shows the dependence of the NMR spectra on Al doping for Mg$_{1-x}$Al$_x$B$_2$ ($0 \leq x \leq 0.025$), at $T = 5K$ and $H_0 = 47$ kOe. Contrary to Figure 6 in all samples the line shapes exhibit a low frequency tail and an unshifted peak, corresponding to coexisting vortex and normal-state components. This indicates that $3.2 \leq \gamma \leq 6.4$ (e.g for $x = 0.01$ sample) by considering $H_{\perp}^2 \approx 150$ kOe.

The observed decrease of anisotropy can be attributed to the progressive electron filling of the $\sigma$ bands with increasing $x$, which reduces the anisotropy of the boron $p$ states. In the microscopic theory the anisotropy parameter is given by

$$\gamma^2 = \langle \Delta(K_F) v_{\theta}^2 \rangle \langle \Delta(K_F) v_{\perp}^2 \rangle$$

where $v_i$ are the Fermi velocities and $\langle \cdots \rangle$ stands for Fermi surface averages. When the ratio $v_{\theta}^2/v_{\perp}^2$ is averaged over the entire Fermi surface for MgB$_2$ it is close to unity, which means a strong anisotropy of $\Delta(K_F)$. Following the arguments of Bud’ko et al. the electron-phonon interaction is particularly strong on the Fermi surface sheets which are shaped as slightly distorted cylinders along the $c$ crystal direction. If the gap $\Delta$ on the remaining Fermi surface sheets is negligible, the reduction of the anisotropy could originate from the reduction of the $\sigma$-holes, as we mentioned above.

In conclusion, we show for the first time the magnetic field distribution in the pure vortex state of lightly doped Mg$_{1-x}$Al$_x$B$_2$ by using $^{11}$B NMR line shape measurements. Our NMR and magnetization data reveal that substitution of Al for Mg reduces the anisotropy substantially, apparently due to reduction of the $\sigma$-holes. This shows up the important role of $p_{x,y}$ orbitals (which form the 2D $\sigma$-holes band) in the superconductivity of MgB$_2$. We argue that our results provide an experimental basis for further theoretical investigations concerning the role of the $\sigma$-bands in the superconducting mechanism of MgB$_2$.

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