**11**B and **27**Al NMR spin-lattice relaxation and Knight shift study of Mg$_{1-x}$Al$_x$B$_2$. Evidence for anisotropic Fermi surface.

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We report a detailed study of **11**B and **27**Al NMR spin-lattice relaxation rates ($1/T_1$), as well as of **27**Al Knight shift (K) of Mg$_{1-x}$Al$_x$B$_2$, $0 \leq x \leq 1$. The obtained ($1/T_1$T) and K vs. x plots are in excellent agreement with ab initio calculations. This asserts experimentally the prediction that the Fermi surface is highly anisotropic, consisting mainly of hole-type 2-D cylindrical sheets from bonding $2p_{x,y}$ boron orbitals. It is also shown that the density of states at the Fermi level decreases sharply on Al doping and the 2-D sheets collapse at $x \approx 0.55$, where the superconductive phase disappears.

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The discovery of superconductivity in MgB$_2$ attained recently a lot of interest, as this binary alloy reveals a remarkably high $T_c \approx 40$K. MgB$_2$ is isostructural and iso-electronic with intercalated graphite (ICG), with carbon replaced by boron, and therefore exhibits similar bonding and electronic properties as ICG. Thus the high $T_c$ value of MgB$_2$ in comparison to ICG ($\sim 5K$) was very surprising.

Band structure calculations have shown that Mg is substantially ionized in this compound, however the electrons donated to the system are not localized on the B anion, but rather are distributed over the whole crystal. The six B $p$ bands contribute mainly at the Fermi level. The unique feature of MgB$_2$ is the incomplete filling of the two $\sigma$ bands corresponding to prominently covalent $sp^2$-hybridized bonding within the graphite-like boron layer. Two isotropic $\pi$ bands are derived from B $p_z$ states and four two dimensional $\sigma$-bands from B $p_{x,y}$. Both $\pi$ bands cross the Fermi level, while only two bonding $p_{x,y}$ bands and only near the $\Gamma$ point $(0,0,0)$ do so, forming cylindrical Fermi surfaces around $\Gamma$-A line. Due to their 2D character, these bands contribute more than 30% to the total density of states (DOS). Such strong anisotropy in the Fermi surface (and possibly in the electron phonon coupling) conciles with the recently reported anisotropy in $H_{c2}$ and the existence of two superconducting gaps. The similarity of the calculated electronic density of states between MgB$_2$ and AlB$_2$ indicates that Al doping results in simple filling of the available electronic states. Suzuki et al. predicted 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 $x \approx 0.6$. A similar conclusion was deduced in Refs. Under these aspects, the detrimental effect of Al doping on $T_c$ can be explained by the fact that doping increases the Fermi energy ($E_F$), while decreasing the DOS $N(E_F)$.

An excellent probe to study the influence of the Al sub-
stition on the electronic structure of electron doped MgB$_2$ is nuclear magnetic resonance (NMR). Knight shift, $K$, and nuclear spin-lattice relaxation (NSLR) rate $1/T_1$ measurements, give us the possibility to determine experimentally $N(E_F)$ through the static and fluctuating parts of the hyperfine field, induced at the position of the resonating nuclei from electrons at the Fermi surface. This allows to estimate the contribution of different atoms to $N(E_F)$ as well as and the anisotropy of electronic states at the Fermi level.

The Hamiltonian describing the magnetic interaction of the nucleus with the atomic electrons can be written as

$$\mathcal{H} = 2\left(8\pi/3\right)\mu_B\gamma_n\hbar\mathbf{I} \cdot \mathbf{S}(r)\delta(r) - 2\mu_B\gamma_n\hbar\mathbf{I} \cdot \left[\mathbf{S}/r^3 - 3\mathbf{r}\cdot\mathbf{S}/r^5\right] - \gamma_n\hbar(e/mc)[\mathbf{I} \cdot \mathbf{r}]/r^3,$$

where $\mu_B$ is the Bohr magneton, $\gamma_n$ the gyromagnetic ratio, $\mathbf{I}$ and $\mathbf{S}$ the nuclear and electron spins respectively, and $r$ is the radius vector of the electron with the nucleus at the origin. In the formula above, the first term describes the Fermi contact interaction, the second term the spin dipolar interaction between nuclear and electron spins, and the third term the coupling with the electronic orbital moment.

In the simplest case, where only contribution from the Fermi contact term is considered, the first term can be rewritten as $\mathcal{H}_{KS} \approx -V\left(8\pi/3\right)\gamma_n\hbar\langle \Psi(0)|\mathbf{S}|\Psi(0)\rangle k_B T$. A similar dependence on $N_2(E_F)$ holds if the nuclear Hamiltonian is dominated by the nuclear-electron orbital interaction.

Until now, $^{11}$B, $^{27}$Al, and $^{25}$Mg NSLR and Knight shift measurements have been reported for pure MgB$_2$ and AlB$_2$. Several of these measurements are in agreement with the theoretical predictions. These results, in conjunction with ab initio calculations, have shown that in MgB$_2$ the $^{11}$B NSLR is dominated by orbital relaxation, whereas in AlB$_2$ the $^{11}$B NSLR is overruled by the Fermi-contact interaction. On the other hand, $^{27}$Al and $^{25}$Mg NSLRs, as well as the Knight shift on all three $^{11}$B, $^{27}$Al, and $^{25}$Mg sites was shown to be controlled by the Fermi-contact polarization. Besides, $^{11}$B-NMR NSLR relaxation rate measurements on mixed Mg$_{1-x}$Al$_x$B$_2$, $0 \leq x \leq 0.2$, have shown a rapid decrease of $1/(T_1 T)$ with doping that was attributed to reduction of the total $N(E_F)$.

The purpose of this work is to report a systematic study of $^{11}$B and $^{27}$Al NSLR rates $1/T_1$, as well as of $^{27}$Al Knight shifts, as a function of Al doping for Mg$_{1-x}$Al$_x$B$_2$, $0 \leq x \leq 1$. $^{11}$B Knight shift measurements were not considered, because the isotropic $^{11}$B Knight shift is small ($+40$ ppm for MgB$_2$ and $-10$ ppm for AlB$_2$), and of the same order of magnitude with the dipolar and the second order quadrupolar split in the NMR fields 2.35, and 4.7 Tesla that have been used in this work. Our measurements show an excellent agreement between the experimental boron $^{11}(1/T_1 T)$ plot with that obtained from local density-functional methods, and the dominance of the orbital relaxation up to $x \approx 0.55$, where $T_1(x)$ vanishes. This is a convincing evidence that up to this doping the hole-type $2 - D$ cylindrical sheets (from bonding $2p_{x,y}$ boron orbitals) of the Fermi surface play an essential role in the $^{11}$B NSLR. The slight decrease of both $27$K and $^{27}(1/T_1 T)$ for $x \leq 0.55$, and their abrupt increase above this doping value are in support of this conclusion.

Polycrystalline samples of nominal composition Mg$_{1-x}$Al$_x$B$_2$ for $0 \leq x \leq 1$ were prepared by reaction of Al and Mg powders with amorphous B at temperatures between 700$^\circ$C and 910$^\circ$C as described elsewhere. We notify that: According to the available literature, and our data, the temperature where the reaction (preparation temperature) takes place, defines the shape of the (00l) diffraction peaks in the region.
0.05 ≤ x ≤ 0.5. The existence of significant broadening or/and splitting in these peaks manifest the existence of some kind of phase separation in this doping range. (ii) Carefully prepared samples in the region around x = 0.5 display a broad superlattice peak (001/2) which means that ordering of Mg and Al occurs [36].

27Al NMR line shape measurements of the central transition (−1/2 → 1/2) were performed on two spectrometers operating in external magnetic fields H0 = 2.35 and 4.7 Tesla. Spectra were obtained from the Fourier transform of half of the echo, following a typical π/2 − τ − π/2 solid spin-echo pulse sequence. The 11B T1 of the central line was determined by applying a saturation recovery technique, and fitting with the two exponential relaxation function that is appropriate for I = 3/2 nuclei [29]. Correspondingly, 27Al T1 was determined by applying the three-exponential relaxation law that is appropriate for I = 5/2 nuclei [31, 33].

Figure 3 shows the boron 11(1/T1T) as a function of x, in the normal state. In all cases a single component of T1 was found to fit satisfactorily the magnetization recovery curves. Besides, a 1/T1T = constant relation was fitting the experimental data from room temperature down to 80K. Our measurements reveal that by increasing doping, 11(1/T1T) decreases rapidly up to x = 0.55, and subsequently exhibits a slight increase for x ≥ 0.55. For reasons of comparison, we have plotted the calculated 11(1/T1T) values from Ref. [8] for all three orbital, dipole-dipole, and Fermi contact term contributions. Clearly, the orbital term dominates in the 11B relaxation rates for x ≤ 0.55. In case of pure MgB2 the 11B orbital hyperfine interaction of 2p-holes with the nuclear magnetic moments is about 3 times larger than the dipole-dipole, and the Fermi contact interaction. This is due to the fact that the boron px and py bands are all at the Fermi level (Npx=Npy ≈ 0.035, Npz ≈ 0.045 states/eV/spin/B), whereas only a few s boron electrons are close to the Fermi level (Ns ≈ 0.002 states/eV/B) [8]. This gives a ratio between the Fermi-contact and the orbital/dipole-dipole coupling constants, F ≈ 0.35 [8], and 11T1−1 is mainly proportional to N2p(EF)2. It may thus be inferred that the rapid decrease of the 11B relaxation rate is due to decrease of the DOS in the 2−D hole-type sheets, while a minimum 1/T1 value is obtained at 0.55 ≤ x ≤ 0.60, where the 2−D sheets appear to collapse. We also notice the discrepancy between the theoretical and experimental values for x > 0.6. Most probably, calculations tend to overestimate the Fermi contact interaction at the position of the B nucleus in this doping range [8].

Figure 4 demonstrates 27Al NMR line shapes of Mg1−xAlxB2 at room temperature in field 4.7 Tesla. A completely similar picture was obtained in field 2.35 Tesla. The spectra for x = 0.0125, and 0.025, were extremely weak, and therefore were acquired with 100,000 signal accumulations (for comparison, signals for x ≥ 0.1 were acquired with 512 accumulations). In all samples the spectra consist of a central transition line, ≈ 20 kHz wide, which shifts with doping, and a broad powder pattern from the satellite transitions. The low doping spectra exhibit a spurious weak peak at +1700 ppm that was produced by the probe. The strong peak at the same frequency for x = 0.80, 1.0 is produced by free Al that inavoidably remains during sample preparation at high doping concentrations.

In Figure 4 we show the shift of the central line peak as a function of x, in fields 2.35 and 4.7 Tesla. The sig-
nal of a standard aqueous solution of AlCl$_3$ was used as reference. The coincidence of the curves in both fields is a clear evidence that the obtained spectral shift corresponds solely to the $^{27}$K shift. In typical metallic shifts of $I = 5/2$ nuclei like $^{27}$Al, in addition to the Knight shift, the center-of-gravity position of the NMR signal should include the second-order quadrupole shift given by $\Delta \nu = (25\nu_0^2)/(18\nu_L)$ [23]. However, recent experiments on AlB$_2$ have shown that the quadrupolar coupling constant is $\nu_Q \approx 80$ kHz [29], thus giving a negligibly small second order quadrupolar shift, $\Delta \nu \approx 14$ ppm. According to Figure 3, by increasing $x$ the $^{27}$K decreases rapidly, whereas for $x \geq 0.55$, i.e. at the doping value where the superconductive phase disappears [22], it increases sharply becoming $\approx +900$ ppm for pure AlB$_2$. As previously shown, by Al doping of MgB$_2$ the $\sigma$ hole bands are filled [2, 4, 24], and their contribution to $N(E_F)$ becomes zero at $x \approx 0.55$ [24]. Evidently, the gradual decrease of $^{27}$K for $x \leq 0.55$ reflects, (i) the initial slight decrease of $N_s(E_F)$ in this doping range [3], and (ii) the reduction of the Stoner enhancement by filling the $\sigma$ hole bands, due to decrease of the total $N(E_F)$. We notice that the Stoner enhancement renormalizes both K and $1/T_1$ by a factor $S = 1/(1 - IN(E_F))^{\alpha}$, with $\alpha = 1$ for K, and $1 \leq \alpha \leq 2$ for $1/T_1$ [3, 8]. On the other hand, the sharp increase of the Knight shift for $x \geq 0.55$, may be attributed to the rapid increase of $N_s$ by further doping, after completely filling the $2p_{x,y}$ hole bands ($N_s$(Mg) in MgB$_2$ is $\approx 0.0092$ states/eV/spin, whereas $N_s$(Al) in AlB$_2$ is $\approx 0.0362$ states/eV/spin [3]). A similar behaviour is observed in Figure 4, which exhibits the $^{27}(1/T_1T)$ vs. $x$ plot. This is expected as the $^{27}$Al relaxation rate is dominated by the Fermi contact interaction, and therefore is proportional to $N_s^2$(Al) [29].

In conclusion, $^{11}$B and $^{27}$Al NMR NSLR rate and Knight shift measurements have been employed in order to investigate the structure and the variation of the Fermi surface in MgB$_2$ upon Al (i.e. electron) doping. Our results are completely consistent with calculations predicting a strongly anisotropic Fermi surface that is comprised from hole-type $\sigma$-bonding $2 - D$ cylindrical sheets, and a hole-type and electron-type, $3 - D \pi$-bonding tubular network. The collapse of the $2 - D$ sheets at $x \simeq 0.55$, as predicted by theory, is experimentally verified by the fast decrease of the $^{11}$B NSLR rate for $x \leq 0.55$ and the sharp increase of both the $^{27}$K, and $^{27}$NSLR rates for $x \geq 0.55$. The latter indicates a strong reshaping of the Fermi surface towards the electronic structure of AlB$_2$, due to interplane electron contribution. Our results concur with both experimental and theoretical evidence that indicate anisotropic pairing and multi-gap superconductivity in MgB$_2$.

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