

NMR in the normal and in the superconducting state of MgB$_2$ and comparison with AlB$_2$

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11$^\text{B}$ NMR measurements have been performed in $^{11}$B enriched MgB$_2$ powder samples in external fields of 0.813, 1.55, 4.7, and 7.2 T both in the normal phase and in the superconducting phase. A previously unreported dipolar pair doublet has been observed in the quadrupole perturbed NMR spectrum. The Knight shift can thus be accurately determined by narrowing the line with the Magic Angle Spinning (MAS) technique. Results of Knight shift ($K$) and relaxation rates ($1/T_1$) for both $^{11}$B and $^{27}$Al nuclei are reported also for AlB$_2$. The comparison of the data in the two compounds shows the dramatic drop of the density of states at the boron site in AlB$_2$ with respect to MgB$_2$. The experimental values for $K$ and $1/T_1$ in the normal phase are in most cases in good agreement with the theoretical values obtained from first principles calculations. The recovery of the nuclear magnetization below $T_c$ in random powder samples is non-exponential due to the anisotropy of the upper critical field. The exponential drop of $1/T_1$ in the superconducting phase observed by Kotegawa et al. is confirmed here but not the coherence peak.

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I. INTRODUCTION

After the discovery of superconductivity in MgB$_2$ with $T_c$ $\sim$ 39 K and subsequent observation of boron isotope effects confirming that MgB$_2$ is a phonon-mediated BCS superconductor, much effort have been devoted to this intermetallic compound up to date due to its remarkably high $T_c$ among BCS superconductors.

Nuclear Magnetic Resonance (NMR) is a suitable microscopic tool to investigate the electronic structure in the normal state, the structure of the gap and the flux line lattice in the superconducting state. This justifies the large number of studies by both $^{11}$B and $^{25}$Mg NMR in MgB$_2$ which have already appeared in the literature.

Regarding the $^{11}$B NMR, there is substantial agreement about the measurements of the quadrupole coupling constant $\nu_Q$ and about the nuclear spin-lattice relaxation rate, $1/T_1$, in the normal phase. On the other hand there is considerable controversy concerning the $^{11}$B Knight shifts in the normal phase and about the temperature dependence of $1/T_1$ in the superconducting phase. In the present paper, we report new results for the $^{11}$B NMR spectrum in the normal phase and an accurate determination of the Knight shift by using the Magic Angle Spinning (MAS) technique. We also find an explanation for the discrepancies in the results of $1/T_1$ below $T_c$ reported by different authors, based on the strong anisotropy of the upper critical field in MgB$_2$.

Since NMR in metals probes the density of states (DOS) at the Fermi level, we have performed measurements of both $^{11}$B and $^{27}$Al NMR in AlB$_2$ in order to compare the DOS in the two compounds. Finally the experimental results for Knight shifts and relaxation rates in both MgB$_2$ and AlB$_2$ have been compared with *ab initio* calculations.

II. EXPERIMENTAL DETAILS AND SAMPLE PREPARATION

MgB$_2$ crystallizes in the hexagonal AlB$_2$ type structure, which consists of alternating hexagonal layers of Mg atoms and graphite-like honeycomb layers of B atoms. Powder samples were prepared with the method described in Ref. 1. X-ray powder diffraction measurements confirmed the hexagonal unit cell of MgB$_2$. Magnetization measurements done at $H = 2.5$ mT yield a transition temperature $T_c = 39.2$ K with a shielding volume fraction close to 100 %.

We have investigated several samples from different batches of polycrystalline $^{11}$B enriched MgB$_2$ in order to check the reproducibility of the data. Also we have performed measurements in samples from the same batch both in bulk and in powder ground to different particle size. No substantial differences were observed in the NMR measurements in the different samples. The onset of superconductivity was also determined by monitoring the detuning of the NMR circuit occurring at the irreversibility temperature, $T_{\text{irr}}$. This type of measurement corresponds to probing the temperature dependence of the radio frequency (rf) surface resistance. Thus, as the magnetic field is increased the transition region broadens due to the dissipation associated with flux line motion below $T_c$, and at 7.2 T no detuning can be observed although the magnetization measurements indicate a $T_c = 23$ K at 7 T. The transition temperature at 4.7 T was found to be $T_c = 27.5$ K and at 1.55 T, $T_c = 34$ K.

$^{11}$B and $^{27}$Al NMR and spin-relaxation measurements were performed with home built Fourier transform (FT)
pulse spectrometers operating at variable frequencies. The \( \pi/2 \) radio frequency (rf) pulse length was typically 6 \( \mu s \). The Magic Angle Spinning (MAS) experiment was performed with a home built spinning probe with a maximum spinning frequency of about 10 kHz.

III. \(^{11}\text{B} \) NMR IN MgB\(_2\) IN THE NORMAL STATE

The \(^{11}\text{B} \) NMR spectrum in MgB\(_2\) powder samples is complicated by the simultaneous presence of first and second order quadrupole interactions, anisotropic Knight shift and a previously unnoticed dipolar splitting which is particularly evident in \(^{11}\text{B} \) isotopically enriched samples. In the following we analyze the different spectral features, a necessary step in order to extract reliable NMR parameters.

A. Quadrupole interactions

The complete \(^{11}\text{B} \) NMR spectrum was determined in a 7.2 T external field by performing the Fourier transform of half of the solid echo following a \( (\pi/2)_0 - \tau - (\pi/2)_90 \) pulse sequence. In order to cover the whole spectrum three separate frequencies were recorded at resonance frequencies centered at the three lines and added together. The result is shown in Fig. 1. Each rf pulse has a bandwidth of about 100 kHz. Since the spectrum is the result of irradiation at only three different frequencies, the parts of the spectrum in between the peaks may be distorted but this does not affect the conclusions. The separation of the symmetric satellite lines is due to first and second order quadrupole interactions, anisotropic Knight shift and a previously unnoticed dipolar splitting which is particularly evident in \(^{11}\text{B} \) isotopically enriched samples. In the following we analyze the different spectral features, a necessary step in order to extract reliable NMR parameters.

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B. Dipolar doublet

As shown in Fig. 2(a) at high fields, where the second order quadrupole effects become negligible, the \(^{11}\text{B} \) NMR spectrum is formed by a doublet. At low fields one can clearly resolve two doublets, one for each singularity in the quadrupole powder pattern. The splitting is temperature and field independent and results from the nearest neighbor nuclear dipolar interaction of \(^{11}\text{B} \) nuclei in the planar honeycomb lattice structure. In such a structure each \(^{11}\text{B} \) nucleus is strongly coupled to three nearest neighbors resulting in three equivalent Pake pairs. A single dipolar pair gives rise to a Pake doublet in the NMR spectrum with frequencies:

\[
\nu_\pm = \nu_L \pm \nu_D (3\cos^2 \theta’ - 1)
\]
FIG. 2: (a) Central line transition of $^{11}$B NMR spectrum for powder sample of MgB$_2$ at several representative magnetic fields. (b) Spectrum at 0.813 T. The distance between the middle point of each doublet corresponds to the second order quadrupole splitting, $\delta \nu$.

with

$$\nu_D = \frac{3}{2} \frac{\gamma \mu}{2\pi a^3}$$  \hspace{1cm} (4)

where $\theta'$ is the angle formed by the magnetic field with the vector joining the two interacting nuclei, $\mu$ is the nuclear magnetic moment and $a$ is the internuclear distance.

In the presence of three interacting pairs one has to sum over the different angles and take the powder average including the second order quadrupole interaction and the anisotropic Knight shift interaction. The situation was analyzed previously in connection with measurements in intermetallic compounds of the C32 (AlB$_2$) structure. The conclusion was reached that in the C32 structure the resonance line in the presence of all the above interactions can be described in terms of the angle $\theta$ formed by the magnetic field and the $c$ axial symmetry axis perpendicular to the B plane. Thus it was predicted that the $\theta = 90^\circ$ singularity in the quadrupole pattern should be split into two lines separated by $\Delta \nu_{90} = 3\nu_D$ while the intermediate angle singularity should be split into two lines separated by $\Delta \nu_1 = 2\nu_D$. From the inspection of Fig. 2(b) one can see that the ratio of the two splittings is in reasonable agreement with the above prediction. Furthermore, by using in Eq. 4 $\gamma = 13.66 \times 2\pi$ MHz/T, $\mu = I\gamma h/2\pi$ and the measured value $\nu_D = 4.00 \pm 0.50$ kHz (at 0.813 T), one obtains the B-B nearest neighbor distance $a = 1.72 \pm 0.08$ Å in agreement with the known value of 1.782 Å.

C. Knight shift

In order to determine the Knight shift, both isotropic and anisotropic parts, measurements should be made at very high magnetic fields ($H \gg 10$ T) where the second order quadrupole effects are negligible, and the anisotropic Knight shift may be inferred from the asymmetric broadening of the NMR line. Since our measurements are limited to a maximum field of 7.2 T no measurable anisotropic Knight shift could be detected. The isotropic Knight shift, $K$, is measurable but very small. Its measurement is further complicated by the dipolar splitting discussed above. In order to obtain a reliable value of $K$ we performed a magic angle spinning (MAS) experiment at room temperature in a field of 4.7 T. As shown in Fig. 3 the dipolar splitting is totally removed for a spinning frequency of 8 kHz as well as part of the dipolar broadening and of the quadrupole broadening. From the resulting narrow line we obtain $K = 80$ ppm with respect to a reference solution of NaBH$_4$. If the Knight shift is referred to the BF$_3$ solution, which is the compound used by chemists as the “zero chemical shift” one obtains $K = 40 \pm 10$ ppm.

D. Nuclear spin-lattice relaxation rate

For the case of saturation of the central line of the $^{11}$B NMR spectrum with a single rf pulse (or short sequence of pulses) and for magnetic relaxation mechanism, the recovery of the nuclear magnetization after a time $t$ following saturation is given by

$$\frac{M(\infty) - M(t)}{M(\infty)} = 0.1 \exp(-2Wt) + 0.9 \exp(-12Wt)$$  \hspace{1cm} (5)

where we define the nuclear spin lattice relaxation rate as $1/T_1 = 2W$. The results for the temperature dependence of $1/T_1$ are shown in Fig. 4. As can be seen, a field independent linear temperature dependence is observed in the normal phase yielding $T_1 T = 170$ kK.
FIG. 4: Temperature dependence of $1/T_1$ for $^{11}$B in MgB$_2$ at external fields 1.55, 4.7 and 7.2 T. The line is the Korringa law with $T_1 T = 170$ sK. The three arrows indicate the superconducting transition temperatures at each field which are 23, 27.5 and 34 K respectively. In the inset, $(T_1 T)^{-1} 10^3$ is plotted against temperature.

IV. $^{11}$B AND $^{27}$Al NMR IN AlB$_2$

The room temperature $^{11}$B NMR spectrum on the powder sample of AlB$_2$ is very similar to the one shown in Fig. 3 for MgB$_2$. From the separation of the satellite lines one derives a quadrupole coupling frequency $\nu_Q = 540 \pm 10$ kHz somewhat smaller than the one in MgB$_2$. The central transition linewidth at room temperature is about 19 kHz and it hides the dipolar splitting discussed for the case of MgB$_2$ due to the stronger dipolar interaction with the $^{27}$Al nuclei present in AlB$_2$. By spinning the sample at 10 kHz we obtain a MAS NMR line 2 kHz wide. The Knight shift value with respect to a reference solution of BF$_3$ measured from the MAS spectrum is found to be $K = -10 \pm 5$ ppm. Finally, the $1/T_1$ measurements as a function of temperature shown in Fig. 4 yield a Korringa law with $T_1 T = 1400$ sK i.e. almost one order of magnitude greater than in MgB$_2$.

The room temperature $^{27}$Al ($I = 5/2$) NMR spectrum in AlB$_2$ is composed of a central transition line 23 kHz wide and a poorly-resolved powder pattern originating from the two satellite pairs over a spectral distribution of about 200 kHz. From the fit of the NMR spectrum to a computer simulated spectrum with a Gaussian dipolar width of 7.5 kHz one can derive a quadrupole coupling constant $\nu_Q = 80 \pm 10$ kHz. It is assumed that the electric field gradient has axial symmetry as for the $^{11}$B site. The Knight shift was measured from the position of the central line transition (which has a negligible second order quadrupole broadening). The Knight shift with respect to a AlCl$_3$ aqueous solution is $K = 880 \pm 20$ ppm.

The $^{27}$Al $1/T_1$ results as a function of temperature are shown in Fig. 5 together with the $^{11}$B results. The linear temperature dependence yields for $^{27}$Al $T_1 T = 3.5$ sK which is 400 times smaller than the value for $^{11}$B.

The various NMR parameters for both MgB$_2$ and AlB$_2$ are summarized in Tab. I. The constant $S$ listed in Tab. I is given by $S = (\gamma_e/\gamma_n)^2 h/(8\pi^2 k_B)$ and the Korringa ratio $R$ is defined as $R = K^2 T_1 T/S$.

V. COMPARISON OF THEORY AND EXPERIMENTS IN MgB$_2$ AND AlB$_2$

In order to understand the microscopic origin of the relaxation, and thus also the differences between AlB$_2$ and MgB$_2$, a comparison between experimental and \emph{ab-initio} calculated values of Knight shifts and relaxation rates is highly desirable. Recently, first principles calculation of the relaxation rates were performed for MgB$_2$. In Ref. [22] the relaxation rates were calculated for AlB$_2$ as well. In the present work we calculate $K$ and $1/T_1 T$ for AlB$_2$ by using the method described in Ref. [21], and compare the results for MgB$_2$ and AlB$_2$. Our calculations are based on density functional theory (DFT) in the local density approximation (LDA). We adopt the tight binding linear-muffin-tin-orbital (LMTO) method in the atomic-spheres-approximation (LMTO47 Stuttgart code). The density of states matrix (Eq. 2 of Ref. [21]) and the partial density of states, $N_L$, (with $L = lm$, where $l$ is the orbital angular momentum quantum number, and $m = -l, \ldots, l$) were calculated by using the linear tetrahedron method. We found that the results already converged very well with a mesh of 481 irreducible $k$ points. In order to obtain accurate wavefunctions at the Fermi level, the linear partial wave expansion was performed with $e_\nu \equiv e_F$, where $e_F$ is the Fermi level and $e_\nu$ the expansion energy. Further details about the method employed can be found
TABLE I: Summary of the various NMR parameters for both MgB2 and AlB2. The Korringa ratio, \( R \), is defined as \( R = K^2T_1T/S \). Results for \( ^{25}\text{Mg} \) NMR were taken from Ref. [21].

|       | \( ^{25}\text{Mg} \) [Ref. 21] | \( ^{11}\text{B} \) | \( ^{27}\text{Al} \) | \( ^{11}\text{B} \) |
|-------|-------------------------------|-----------------|-----------------|-----------------|
| \( K \) (ppm) | \( 242 \pm 4^a \) | \( +40 \pm 10^b \) | \( +880 \pm 20^c \) | \( -10 \pm 5^c \) |
| \( T_1T \) (sK) | 1090 | 170 | 3.5 | 1400 |
| \( S \) (sK) | \( 7.03 \times 10^{-5} \) | \( 2.57 \times 10^{-6} \) | \( 3.88 \times 10^{-6} \) | \( 2.57 \times 10^{-6} \) |
| \( R \) | 0.95 | 0.102 \( \pm 0.05 \) | 0.7 \( \pm 0.03 \) | 0 \( \pm 0.12 \) |
| \( \nuQ \) (kHz) | 222 (1.5) | 835 (10) | 80 (10) | 540 (10) |

\( ^a \)Reference solution MgCl2
\( ^b \)Reference solution BF3
\( ^c \)Reference solution AlCl3

in Ref. [21].

In Tab. I and Tab. [11], we show the calculated \( K \) and \( 1/T_1T \). The results for MgB2 are taken from Ref. [21].

Let us discuss first the case of MgB2. The \( ^{11}\text{B} \) orbital relaxation rate is about 3 times larger than the dipole-dipole, and about 10 times larger than the Fermi-contact term. As explained in Ref. [21], the reason is the following. In MgB2 the B \( p_\tau \) and B \( p_z \) bands are all at the Fermi level: the partial density of states \( N_{p_\tau,N} (\sigma \text{ bands}) \) and \( N_{p_z} (\pi \text{ bands}) \) are, respectively, \( N_{p_z} = N_{p_\tau} \sim 0.035 \) states/eV/spin/B, and \( N_{p_z} \sim 0.045 \) states/eV/spin/B. On the contrary, there are very few B s electrons close to \( e \) (\( N_s \sim 0.002 \) states/eV/B). An approximate formula for the ratio between the Fermi-contact and the orbital/dipole-dipole coupling constants is given by [21]

\[
F = \frac{2}{3} \frac{\langle \phi_s(0) \rangle^2 N_s}{\sum_{r>0} (\langle r^{-3} \rangle)^2/N_l}.
\]

Here \( \phi(r) \) is the \( l \) radial solutions of the Schrödinger equation at energy \( e_l \) and \( N_l = \sum_{m=-l}^{l} N_{m} \). In addition \( \langle r^{-3} \rangle_{l,l} \equiv \int \langle \phi(r) \rangle \langle r^{-3} \rangle \phi(r) \rangle dr \) and \( \phi(l) = \phi(0) = 0 \), where \( r=0 \) is the position of the nucleus. In the case of B it was found \[21\] \( F \sim 0.35 \). Thus \( F \) is considerably smaller than 1, and the Fermi contact interaction (which usually dominates over the orbital and dipole-dipole mechanisms) gives only a small contribution to the relaxation rate. Moreover, it was found [21] that \( N_{p_z} = N_{p_\tau} \sim N_{p_\tau} \). For a model Hamiltonian which includes only B \( p \) orbitals and for which \( N_{p_\tau} = N_{p_z} = N_p/3 \), one can show analytically [21] that the ratio between orbital/dipole-dipole relaxation rate is about 3.3. This explains the numerical results obtained for B in MgB2.

The case of \( ^{25}\text{Mg} \) is different: the ratio \( F \) is considerably larger than one (\( F \sim 5 \)) and thus the Fermi contact interaction is expected to dominate. Tab. [11] shows that this actually happens: the orbital and the dipole-dipole terms are much smaller than the Fermi contact contribution.

With a Stoner enhancement factor of about 1.33 (calculated ab-initio in Ref. [21]), the following results were found for the total Knight shifts: \( K(\text{Mg}) \sim 361/341 \) ppm and \( K(\text{B}) \sim 21/37 \) ppm. For the relaxation time, it was shown [21] that the Stoner enhancement factor is about 1.6. Thus the total relaxation times are: \( T_1T(\text{Mg}) \sim 625 \) sK and \( T_1T(B) \sim 169 \) sK. These results are in quite good agreement with experimental data.

Let us now discuss the case of AlB2. In this compound the B \( p_\tau \) bands are fully occupied, and only B \( p_\tau \) bands are at the Fermi level. In addition \( \langle \phi_s(0) \rangle^2/4\pi \sim 2.87 a_0^3 \) and \( N_s \sim 0.003 \) states/eV/spin/B, \( (r^{-3})_{11} \sim 1.45 a_0^3 \) and \( N_p \sim 0.0216 \) states/eV/spin/B. With these numbers we find \( F \sim 2.3 \); terms with \( l > 1 \) give a small contribution to \( F \), because the radial integrals decrease quickly when \( l \) increases and because, in the case of B, \( N_s \) is very small for \( l > 1 \). Thus \( F \) is considerably larger than 1, and the Fermi contact interaction is the dominant mechanism of relaxation for \( ^{11}\text{B} \) (see Tab. [11]). The same happens for \( ^{27}\text{Al} \), for which we find \( \langle \phi_s(0) \rangle^2/4\pi \sim 2.96 a_0^3 \) and \( N_s \sim 0.0362 \) states/eV/spin, \( (r^{-3})_{11} \sim 1.74 a_0^3 \) and \( N_p \sim 0.0325 \) states/eV/spin/B, and therefore \( F \sim 16 \).

In order to understand better the numerical results for AlB2, we calculate analytically the contact shift and relaxation rates for a model Hamiltonian which includes only B \( s \) and Al \( s \) states. Within this model, the Knight shift is given by \( K \sim \mu_B^2 (4/3) \langle \phi_s(0) \rangle^2 N_s \), and the relaxation rate can be obtained from the Korringa relation. We find \( K(\text{Al}) \sim 645 \) ppm, \( K(\text{B}) \sim 52 \) ppm and \( 1/T_1T(\text{Al}) \sim 107 \cdot 10^{-3}/(s\text{K}) \), \( 1/T_1T(\text{B}) \sim 1.05 \cdot 10^{-3}/(s\text{K}) \), in very good agreement with the first principle values of Tab. [11] and Tab. [11].

The \( ab\text{-initio} \) total Knight shifts (Tab. [11]) are \( K(\text{Al}) \sim 644/647 \) ppm and \( K(\text{B}) \sim 42/66 \), and the total relaxation times (Tab. [11]) are \( T_1T(\text{Al}) \sim 9 \) sK and \( T_1T(B) \sim 602 \) sK. The agreement between first principle results and experimental data is quite good for Al. In the case of B the calculated relaxation time is about 2 times smaller than the experimental data. Similar results were found in Ref. [22]. This discrepancy could suggest that, in the case of AlB2, LDA tends to slightly overestimate the Fermi-contact interaction at B nucleus.

Finally, we point out that in AlB2 the density of states in the B plane is strongly reduced with respect to MgB2. The reason is that in AlB2 the \( \sigma \) bands are well below
TABLE II: Knight shifts in ppm in MgB$_2$ and AlB$_2$ (without Stoner factor). The label $\alpha = x, y, z$ indicates the direction of the external magnetic field. Results for MgB$_2$ are taken from Ref. [21].

| MgB$_2$ | dipole (xy) | dipole(z) | orbital | Fermi contact | core | Total (xy/z) | Experiment |
|---------|-------------|-----------|---------|---------------|------|--------------|------------|
| B       | -4          | 8         | 0       | 27            | -7   | 16/28        | 40 ± 10    |
| Mg      | 5           | -10       | 0       | 260           | 3    | 271/256      | 242 ± 4    |

| AlB$_2$ | dipole (xy) | dipole(z) | orbital | Fermi contact | core | Total (xy/z) | Experiment |
|---------|-------------|-----------|---------|---------------|------|--------------|------------|
| B       | -8          | 16        | 0       | 61            | -11  | 42/66        | -10 ± 5    |
| Al      | 1           | -2        | 0       | 660           | -15  | 644/647      | 880 ± 20   |

TABLE III: Relaxation rates in $10^{-3}$/sK in MgB$_2$ and AlB$_2$ (without Stoner factor). Results for MgB$_2$ are taken from Ref. [21].

$\epsilon_F$, while in MgB$_2$ they cross the Fermi level. We find $N_{p_x} + N_{p_y} \sim 0.0046$ and $N_{p_z} \sim 0.017$ states/eV/spin/B, while for MgB$_2$ $N_{p_x} + N_{p_y} \sim 0.07$ and $N_{p_z} \sim 0.045$ states/eV/spin/B was found.[2]

VI. $^{11}$B NMR IN MgB$_2$ IN THE SUPERCONDUCTING PHASE

Although the main emphasis of the present paper is on the electronic properties of MgB$_2$ in the normal phase, it is worthwhile to present and discuss here the $^{11}$B NMR results obtained in the superconducting phase mostly to point out the limitations incurred in the NMR experiments in polycrystalline samples.

Regarding the Knight shift, one can conclude that no meaningful measurements of $K$ can be performed below $T_c$ in a powder sample. In fact the Knight shift is very small compared to the line broadening due to the magnetic field distribution of the flux line lattice.[2] Furthermore the correction for the shift due to the diamagnetic shielding in the superconducting phase cannot be estimated accurately in a powder sample as a result of the distribution of shapes of the particles e.g. distribution of demagnetization factors.

The temperature dependence of $1/T_1$ below $T_c$ allows in principle to obtain information about the pairing symmetry and the structure of the superconducting gap.[3] In fact the ratio of the relaxation rates in the superconducting phase and the normal phase, $(1/T_{1s}/(1/T_{1n}))$, is related to the density of states in the superconducting phase and should decrease below $T_c$ either exponentially or with a power law depending on the pairing symmetry and/or the structure of the gap.[3] As can be seen in Fig. 6 a decrease of the relaxation rate below $T_c$ can be observed in the data taken in an external field of 1.55 T but not in the data at 4.7 T and 7.2 T. The explanation for this is easily found in the strong anisotropy of the upper critical field, $H_{c2}$. The powders utilized in the present experiment have $H_{c2 \max}^s/H_{c2 \min}^s = 2 \approx 6$ whereby the maximum critical field pertains to the particles with the field in the $ab$ plane.[2] In a detuning experiment one detects the superconducting transition of the particles which have the higher upper critical field (see arrows in Fig. 4). On the other hand in the NMR experiment the stronger signal arises from the particles which are oriented in such a way as to have the lower upper critical field. This is a consequence of the strongly reduced rf penetration length and consequently reduced NMR signal, in the superconducting particles. Thus the results
Recent resistivity measurements in MgB$_2$ have a much smaller anisotropy of the upper critical field. It is noted that the samples used in Kotegawa’s experiments could be of different quality. The magnetization is the superposition of curves, Eq. 5, with different $W$ values. Therefore it is very difficult to infer the presence of a coherence peak in $1/T_1$ just below $T_c$ as claimed by Kotegawa et al.\cite{Kotegawa}. More detailed measurements as a function of magnetic field are needed to elucidate this point.

\textbf{VII. SUMMARY AND CONCLUSIONS}

From the analysis of the $^{11}$B NMR spectrum in the normal phase of isotopically enriched MgB$_2$, we have found evidence for a field independent splitting of the line due to the nuclear dipolar interaction (Pake doublet). By averaging out the dipolar interaction with Magic Angle Spinning, we have obtained reliable values for the Knight shifts for $^{11}$B in both MgB$_2$ and AlB$_2$. Both the decrease of $K$ and more so of $(T/T_1)^{-1}$ for $^{11}$B in AlB$_2$ with respect to MgB$_2$ is in qualitative agreement with a drastic drop of the DOS at the Fermi level at the B site in AlB$_2$. The ab-initio calculated values in Tab. II and III are in excellent agreement with the experimental ones in MgB$_2$ provided the theoretical results are multiplied by a Stoner enhancement factor of 1.33 for the Knight shift and 1.6 for the relaxation rates.

For the case of AlB$_2$ the ab-initio calculated values are in good agreement with the experiments only for the $^{27}$Al data considering that the theoretical results in Tab. II and III are still to be multiplied by the Stoner factor. However, for the B site in AlB$_2$ the theoretical values for both $K$ and $(T/T_1)^{-1}$ are a factor of two bigger than the experimental values indicating that the LDA calculations overestimate the Fermi contact interaction at the B nuclear site.

Regarding the superconducting phase in MgB$_2$, we conclude that it is very difficult to obtain reliable information for the NMR parameters (particularly the relaxation rates) from polycrystalline samples due to the random orientation with respect to the applied field and the strong critical field anisotropy. In particular, we could confirm qualitatively the exponential drop of $1/T_1$ vs $T$ below $T_c$ reported by Kotegawa et al.\cite{Kotegawa} but we could not detect any enhancement of $1/T_1$ just below $T_c$ (coherence peak).

One issue which remains to be investigated is the effect on the nuclear relaxation rate of the flux line lattice and flux line fluctuations in the superconducting phase which was detected qualitatively in the enhancement of $T_1T$ below $T_c$ (see the inset of Fig. 4) but which would require aligned powder samples or single crystals to be investigated quantitatively.
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1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature 410, 63 (2001).
2. S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. 86, 1877 (2001).
3. D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature 411, 457 (2001).
4. A. Rigamonti, F. Borsa, and P. Carretta, Rep. Prog. Phys. 61, 1367 (1998).
5. J. K. Jung, S. H. Baek, F. Borsa, S. L. Bud’ko, G. Lapertot, and P. C. Canfield, Phys. Rev. B 64, 012514 (2001).
6. A. V. Tsvyashchenko et al., Solid State Comm. 119, 153 (2001).
7. M. Mali, J. Roos, A. Shengelaya, H. Keller, and K. Conder, Cond-Mat/0111022 v2 (2001).
8. G. Papavassiliou, M. Pissas, M. Fardis, M. Karayanni, and C. Christides, Cond-Mat/0107511 (2001).
9. H. Kotegawa, K. Ishida, Y. Kitaoka, T. Muranaka, and J. Akimitsu, Phys. Rev. Lett. 87, 127001 (2001).
10. A. Gerashenko, K. Mikhaliev, S. Verkhovskij, T. D’yachova, A. Tyutyunnik, and V. Zubkov, Cond-Mat/0102421 (2001).
11. H. Tou, H. Ikejiri, Y. Maniwa, T. Ito, T. Takenobu, K. Prassides, and Y. Iwasa, Cond-Mat/0103484 (2001).
12. D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett 86, 2420 (2001).
13. P. C. Canfield, D. K. Finnemore, S. L. Bud’ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. 86, 2423 (2001).
14. A. Abragam, Principles of Nuclear Magnetism (Academic Press, London, 1961).
15. F. Borsa and A. Rigamonti, J. of Magnetic Resonance 20, 232 (1975).
16. G. E. Pake, J. Chem. Phys. 16, 327 (1948).
17. D. R. Torjeson, R. G. Barnes, and R. B. Creel, J. Chem. Phys. 56, 4178 (1972).
18. E. Fukushima and S. B. W. Roeder, Experimental Pulse NMR (Addison-Wesley Pub. Co, 1981).
19. T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, J. Phys. Chem. 63, 1533 (1959).
20. E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. London 78, 1 (1961).
21. E. Pavarini and I. I. Mazin, Phys. Rev. B 64, 140504(R) (2001).
22. K. D. Belashchenko, V. P. Antropov, and S. N. Rashkeev, Phys. Rev. B 64, 132506 (2001).
23. O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B 34, R5253 (1986).
24. L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959).
25. L. C. Hebel, Phys. Rev. 116, 79 (1959).
26. S. L. Bud’ko, V. G. Kogan, and P. C. Canfield, Phys. Rev. B 64, 180506(R) (2001).
27. F. Simon et al., Phys. Rev. Lett 87, 047002 (2001).
28. S. Lee, H. Mori, T. Masui, Y. Eltsev, A. Yamamoto, and S. Tajima, J. Phys. Soc. Japan 70, 2255 (2001).
29. Y. Kitaoka, Private communication.