Anisotropy of $p$ states and $^{11}$B nuclear spin-lattice relaxation in Mg$_{1-x}$Al$_x$B$_2$

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We calculated the nuclear spin-lattice relaxation rate in the Mg$_{1-x}$Al$_x$B$_2$ system and found that the orbital relaxation mechanism dominates over the dipolar and Fermi-contact mechanisms in MgB$_2$, whereas in AlB$_2$ due to a smaller density of states and strong anisotropy of boron $p$ orbitals the relaxation is completely determined by Fermi-contact interaction. The results for MgB$_2$ are compared with existing experimental data, whereas our results for the doped alloy and AlB$_2$ can be used in future experiments to verify the theoretical predictions about the electronic structure of this system.

The discovery of superconductivity in MgB$_2$ has stimulated a significant interest in the electronic structure of these intercalated boron compounds. For the superconductivity, one of the most important parameters is the value $N(E_F) \equiv N$ of the electronic density of states (DOS) at the Fermi level in the normal state. Several groups have performed local density-functional (LDA) calculations of this quantity and the results scatter around 0.7 states/(eV-f.u.). Experimentally $N$ can be determined in many different ways but the nuclear spin-lattice relaxation (NSLR) rate $1/T_1$ measurements represent an excellent opportunity to check experimentally not only the total $N$ and its partial components but also their anisotropy, i.e., the distribution between the in-plane and out-of-plane $p$ orbitals. Experimental numbers have been reported in Refs. 3, 4 where values of $TT_1$ = 180, 155 and 165 K-sec for MgB$_2$ on $^{11}$B ($\mu = 2.689\mu_N$) were obtained. These authors interpreted the relaxation rates in terms of dipolar and orbital contributions due to the corresponding Korringa ratio and the already known theoretical total $N$. Below by using the general formulas for $T_1$ in the hexagonal crystal we evaluate the relaxation rates for MgB$_2$ and AlB$_2$ compounds using an LDA calculation. We will show that in MgB$_2$ the orbital relaxation rate is about three times larger than the dipolar and the Fermi-contact rates with all other contribution being much smaller, whereas the Fermi-contact mechanism is dominating in AlB$_2$. Our calculated total rates are in fair agreement with those measured, thus indicating that the calculated $N$ in MgB$_2$ is basically correct, whereas in AlB$_2$ due to an unusually high anisotropy of $p$ states, we predict a much smaller relaxation rate fully determined by Fermi-contact mechanism.

The standard technical details of the LMTO-ASA calculations are similar to those described in Refs. 2. In addition, we carefully checked the sensitivity of ASA results to the parameters of calculations. We used different exchange-correlation potentials and inputs with different radii of the B sphere (both with and without empty spheres). Our values of DOS for s and p orbitals $N_i$ for the B site in MgB$_2$ and AlB$_2$ are listed in Table I. One can see that in MgB$_2$ all p orbitals on the B site have a sizeable DOS, while in AlB$_2$ only $p_z$ orbital is significant with $N_{pz} \approx 0.1N_{pz}$. The $s$ component in AlB$_2$ becomes relatively more important compared to MgB$_2$ resulting in the dominance of the Fermi-contact NSLR, as we will show below. In both materials the contribution of d states to NSLR is very small. As for the Mg site, the $s$ component of $N$ is the most important, and we expect that the NSLR on $^{25}$Mg is controlled by the Fermi-contact mechanism. However, in this paper we will focus on the $^{11}$B NSLR.

To calculate $T_1$ according to a general prescription one has to estimate the $\langle r^{-3}\rangle_t$ expectation values for different orbitals and the electronic density at the nucleus $\varphi_n^2(0)/4\pi$. These parameters (properly normalized with the densities of states) are the largest source of uncertainty in our calculation due to the notable dependence of $\langle r^{-3}\rangle_t$ on the chosen radius of the B sphere $r_B$ (from $r_B = 2.15a_0$ to $r_B = 2.34a_0$ it decreases by $\approx 11\%$). In our calculations we used the largest $r_B$ that were possible without a significant distortion of the band structure, $2.4a_0$ for MgB$_2$ and $2.1a_0$ for AlB$_2$. For these radii we have $\langle (a_0/r)^3\rangle_t = 1.11$ in MgB$_2$ and 1.37 in AlB$_2$. Although due to the poor convergence these averages probably still have a considerable inaccuracy of about 10-15% (which is close to the experimental error bar), we believe that they are the most accurate that may be obtained in ASA. For comparison, the atomic value for $\langle (a_0/r)^3\rangle_t$ in B is 0.78. The electronic densities on the nucleus $a_0^3\varphi_n^2(0)/4\pi$ for MgB$_2$ and AlB$_2$ were, respectively, 2.68 and 3.02.

The contributions to the $^{11}$B relaxation rate for the polycrystalline sample calculated using the formulas of Ref. 5 are given in Table II. The in-plane and out-of-plane $p$ orbitals in MgB$_2$ have similar densities of states, and hence the relative magnitude of orbital and dipolar contributions to NSLR is similar to the 3/10 rule for $p$ states in a cubic crystal described by Ohashi. The Fermi-contact contribution is also important and amounts to 30% of the orbital term. The contributions from the $d$ partial waves to the dipole and orbital relaxation rates were small (at the order of 1%) due to the low diagonal and off-diagonal densities of states $(N_d/N_p)^2 \sim 0.02$ and $(N_{pd}/N_p)^2 \sim 0.05$. The quadrupole contribution to NSLR is negligible due to a rather small $^{11}$B quadrupole moment.
The values of $T_1$ obtained in such manner correspond to the theoretical ‘bare’ $N$ which does not include the exchange-correlation enhancement. We have estimated the effective Stoner exchange parameter to be $I = \Delta E/m = 1.7$ eV from the splitting of the bands at the $\Gamma$ point in the external magnetic field. The corresponding Stoner enhancement of the uniform susceptibility (which enters the $T_1^{-1}$) can be written as $S = 3/[\{1 - NI\} (3 - 2IN)] \approx (1 - IN)^{-\alpha}$, where $\alpha \approx 1.62$ in the 3D case and in the 2D case $\alpha = 2$. In our case due to the mixed 2D and 3D character of the bands it is not clear what value of $\alpha$ should be used in our simple estimation. We used $\alpha = 1.9$, resulting in the enhancement of $T_1^{-1}$ by approximately 60% (Table II). The total calculated relaxation rate $81 \cdot 10^{-4}$ K·sec for MgB$_2$ should be compared with the experimental rates of $56 - 64 \cdot 10^{-4}$ (K·sec)$^{-1}$ measured at temperatures slightly above $T_c$. The fact that such simple estimate gives a faster relaxation compared to experiments, even without taking into account any other mechanisms of susceptibility enhancement, may serve as a manifestation of a possible importance of unusual effects resulting in the lowering of the effective $N$.

We obtained a very different relation between the different mechanisms of NSLR in AlB$_2$ where no traces of superconductivity have been found and where no NMR data are available. According to our theoretical estimation, due to the sharp decrease of the $p$ component of $N$ compared to MgB$_2$, the orbital and dipolar contributions to NSLR become very small, and the total NSLR in AlB$_2$ is completely dominated by the Fermi-contact mechanism. The resulting NSLR rate is more than two times smaller than in MgB$_2$ (see Table II). Corresponding numbers for the anisotropy parameter at the Fermi level $N_{px}/N_{pz}$ are 0.1 for AlB$_2$ and 0.73 for MgB$_2$. This specific feature of AlB$_2$ on this stage is completely theoretical prediction and more experimental information needed to check it. We also performed the rigid band calculations of $T_1$ in Mg$_{x}$Al$_{1-x}$B$_2$. From Fig. 1 one can see how different mechanisms of NSLR are progressing as a function of doping. The sharp decrease of $N$ in the 2D sheets of the Fermi surface leads to a corresponding lowering of all contributions to NSLR, and at the point of the structural transition we expect a very large $T_1$. We expect that the new NMR experiments for this alloy will be a crucial test of our understanding of the electronic structure of this system. Simultaneously with the nuclear quadrupole resonance data on this material (which is related to the anisotropy of total charges on different $p$ orbitals) the general picture of anisotropy of $p$ orbitals in normal states can be build.

The above calculations have been done for a polycrystalline material. Because single crystals are becoming available, we include our estimations of the anisotropy in the angular dependence of NSLR rate $A + B \sin^2 \theta$. For MgB$_2$ we obtained $B/A \approx -0.06$, so that the NSLR is nearly isotropic.

In conclusion, we have performed LDA calculations for the NSLR rate in the Mg$_{x}$Al$_{1-x}$B$_2$ system. We find that the orbital mechanism of relaxation dominates over the spin-dipolar and Fermi-contact mechanisms in MgB$_2$, because the boron $p$ orbitals at the Fermi level are distributed nearly isotropically and have a large DOS. With the values of 0.7 st. /eV for the bare DOS at the Fermi level for MgB$_2$ and 1.7 eV for the effective Stoner exchange parameter, reasonable agreement is obtained with the experimental relaxation rates. We estimate the overall error of our $T_1$ calculations in MgB$_2$ as 15%. Strong anisotropy of $p$ states at the Fermi level and different leading mechanism of relaxation in AlB$_2$ compared to MgB$_2$ is predicted.

When this paper was completed we became aware that similar results for NSLR in MgB$_2$ were independently obtained in Ref. [10] where the $T_1$ on $^{25}$Mg and the Knight shifts were also computed, as well as the small core polarization term for $^{11}$B.

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**TABLE I. Partial DOS for $s$ and $p$ orbitals at B site, $10^{-3}$ (eV-spin-atom)$^{-1}$**

|        | $s$  | $p_z$ | $p_x$ |
|--------|------|-------|-------|
| MgB$_2$ | 3.4  | 50    | 36    |
| AlB$_2$ | 3.3  | 19    | 1.9   |

**TABLE II. Contributions to $(TT_1)^{-1}$ [10$^{-4}$/(K·sec)]**

|        | Fermi-contact | Orbital | Dipole | Total | Stoner-enhanced |
|--------|---------------|---------|--------|-------|----------------|
| MgB$_2$ | 12            | 30      | 9      | 51    | 81             |
| AlB$_2$ | 21            | 1       | 1      | 23    | 26             |
FIG. 1. Different contributions to the total $^{11}$B relaxation rate in Mg$_{1-x}$Al$_x$B$_2$. Thick solid line, orbital; dashed, dipolar; thin solid, Fermi-contact.
$(T_1 T)^{-1}, 10^{-4} \text{ K} \cdot \text{sec}$