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Kirill D. Belashchenko
University of Nebraska-Lincoln, kbelashchenko2@unl.edu

V.P. Antropov
Ames Laboratory, Ames, Iowa

S.N. Rashkeev
Vanderbilt University, Nashville, Tennessee

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Anisotropy of conducting *p* states and ^{11}B nuclear spin-lattice relaxation in $Mg_{1-x}Al_xB_2$

K. D. Belashchenko,[1] V. P. Antropov,[1] and S. N. Rashkeev[2]
[1]*Ames Laboratory, Ames, Iowa 50011*
[2]*Vanderbilt University, Nashville, Tennessee 37235*
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We calculated the nuclear spin-lattice relaxation rate in the $Mg_{1-x}Al_xB_2$ 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. To validate the theory, nuclear resonance experiments for the studied diboride alloy system are needed.

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The discovery of superconductivity in MgB_2 (Ref. 1) has stimulated a significant interest in the electronic structure of 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.).[2–4] 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 values of $TT_1 = 180$, 155, and 165 K sec for ^{11}B ($\mu = 2.689\mu_N$) were reported.[5–7] These relaxation rates were interpreted in terms of dipolar and orbital contributions due to the corresponding Korringa ratio and the already known[2–4] theoretical total N. In this paper we perform a more careful theoretical analysis of NSLR in MgB_2. However, the direct numerical comparison with experiment for one single system may not be sufficient to verify the theory, and studies of trends in a sequence of related systems are usually much more credible. Therefore, we also studied the NSLR in $Mg_{1-x}Al_xB_2$ that is the only known diboride alloy with substitution in the Mg sublattice and a rather wide range of solubility.[8] In addition, earlier studies[2–4] have shown that in this system the two-dimensional (2D) boron bands are gradually filled with Al doping. Hopefully, the studies of NSLR in this system may provide valuable information about the genesis of anisotropy of electronic states at the Fermi level.

Below we evaluate the relaxation rates for MgB_2 and AlB_2 compounds using an LDA calculation, and for the intermediate concentrations we used the rigid band approximation with MgB_2 bands. We will show that in MgB_2 the orbital mechanism is the leading term in NSLR, whereas the Fermi-contact mechanism is dominating in AlB_2. Our calculated total relaxation rate in MgB_2 is in fair agreement with experiments,[5–7] thus indicating that the calculated N in MgB_2 is basically correct, whereas in AlB_2, due to high anisotropy and low DOS of boron *p* states, we predict a much smaller relaxation rate fully determined by the Fermi-contact mechanism.

The standard technical details of the Linear muffin-tin orbital calculations are similar to those described in Refs. 2 and 3. In addition, we carefully checked the sensitivity of the 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 on 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 sizable DOS, while in AlB_2 only p_z orbital is significant with $N_{px} \approx 0.1 N_{pz}$. The *s* component in AlB_2 becomes relatively more important compared to MgB_2 resulting in the dominance of the Fermi-contact NSLR in AlB_2, 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 $\langle r^{-3} \rangle_l$ expectation values for different orbitals and the electronic density at the nucleus $\varphi_s^2(0)/4\pi$. We found that the convergence of the total NSLR rate with respect to the boron sphere radius in this *sp* system is worse compared to *d* metals (from $r_B = 2.3a_0$ to $r_B = 2.4a_0$ the total T_1^{-1} decreases by $\sim 15\%$). The uncertainty is mostly related to the value of $\langle r^{-3} \rangle_p N_p$.

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 $\langle (a_0/r)^3 \rangle_p = 1.11$ in MgB_2 and 1.37 in AlB_2. For comparison, the atomic value[9] for $\langle (a_0/r)^3 \rangle_p$ in *B* is 0.78. The electronic densities on the nucleus $a_0^3 \varphi_s^2(0)/4\pi$ 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 general formulas[10] for the hexagonal crystal are given in Table II. The in-plane and

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

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

	Fermi contact	Orbital	Dipole	Total	Stoner enhanced	Experiments
MgB_2	12	30	9	51	81	56[5],64[6],61[7]
AlB_2	21	1	1	23	26	

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 close to the 3/10 rule for p states in a cubic crystal described by Obata.[10] 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 are 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^{-1} obtained in such manner correspond to the theoretical 'bare' partial boron N whereas the actual T_1^{-1} contains different terms enhanced according to the corresponding susceptibilities. To estimate the possible range of enhancement, we calculated the total enhancement coming from the spin susceptibility only (which is the case for AlB_2). We estimated the effective Stoner exchange parameter $I \equiv \Delta E/m = 1.7$ eV from the splitting of the bands at the Γ point in the external magnetic field. The corresponding Stoner enhancement of the uniform susceptibility in the 3D case may be written[11] as $S = 3/[(1-NI)(3-2IN)] \approx (1-IN)^{-\alpha}$ with $\alpha \approx 1.62$, while in the 2D case the enhancement is described by the same formula with $\alpha = 2$. In our case due to the mixed 2D and 3D character of the bands it is not clear what value of α should be used, but the difference in the result for $\alpha = 1.62$ and 2.0 is less than 10%. We used $\alpha = 1.9$ resulting in the enhancement of T_1^{-1} by approximately 60% (Table II). The obtained 'bare' and enhanced values provide a range of possible NSLR rates for MgB_2 that should be compared with the experimental rates[5–7] of 56×10^{-4}–64×10^{-4} $(\mathrm{K\,sec})^{-1}$. The fact that such simple estimate may give a faster relaxation compared to experiments suggests a possible importance of unique effects resulting in the lowering of the effective boron N.

The roles of the three NSLR mechanisms are very different in AlB_2 where no traces of superconductivity have been found and where no experimental data are available. According to our theoretical estimation, due to the sharp decrease of the boron p component of N compared to MgB_2 and its very strong anisotropy (see Table I), the orbital and dipolar contributions to NSLR become very small, and the NSLR in AlB_2 is completely dominated by the Fermi-contact mechanism. This conclusion may be verified experimentally by studying the Korringa ratio. The resulting Stoner-enhanced NSLR rate in AlB_2 is more than three times smaller than in MgB_2 (see Table II). We should note that the strong anisotropy of boron p states in AlB_2 on this stage is a theoretical prediction and more experimental information is needed to confirm it.

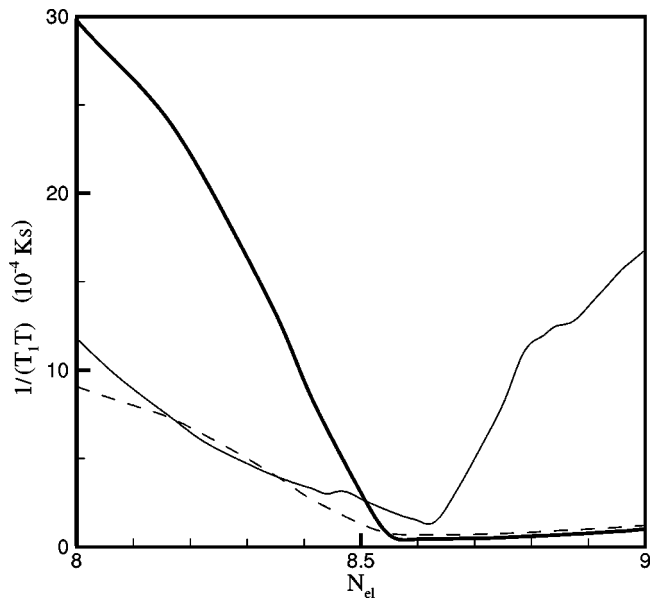

FIG. 1. Different contributions to the total ^{11}B relaxation rate in $Mg_{1-x}Al_xB_2$. Thick solid line, orbital; dashed, dipolar; thin solid, Fermi contact.

We also calculated the NSLR rate in $Mg_{1-x}Al_xB_2$ in the rigid band approximation with MgB_2 bands. From Fig. 1 one can see how the roles of different mechanisms of NSLR change with doping. The sharp decrease of N in the 2D sheets of the Fermi surface with doping[3] leads to the corresponding lowering of all contributions to NSLR, and at the point of the complete filling of these 2D bands we expect a very large T_1. Experimental verification of this sharp dependence of T_1 on doping in this alloy may be a crucial test of our understanding of the electronic structure of this system and is highly desirable. Together with the nuclear quadrupole resonance data (which is related to the anisotropy of total charges on different p orbitals) such measurements should help to build a general picture of anisotropy of p orbitals.

The above calculations have been done for a polycrystalline sample. Because single crystals are becoming available, we include our estimations of the anisotropy in the angular dependence of NSLR rate[10] $A + B\sin^2\theta$. For MgB_2 we obtained $B/A \approx -0.06$, so that the NSLR is nearly isotropic. The NSLR rate in AlB_2 is isotropic because it is determined by isotropic Fermi-contact mechanism.

In conclusion, we have performed LDA calculations for the NSLR rate in the $Mg_{1-x}Al_xB_2$ system. We found that the orbital mechanism of relaxation dominates over the spin-dipolar and Fermi-contact ones in MgB_2, because the boron p orbitals at the Fermi level are distributed nearly isotropically and have a large DOS. Strong anisotropy and low density of p states at the Fermi level in AlB_2 results in the dominance of the Fermi-contact NSLR mechanism. With the values of 0.7 (0.5) st./eV for the bare total (boron partial) 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 NSLR rates. However, we emphasize a relatively weak radial convergence of the NSLR rate in this system compared to the well-studied d metals,

and a common uncertainty related to the estimate of the enhancement factor. Still, we strongly believe that the obtained results related to the relative importance of different NSLR mechanisms are qualitatively correct. According to our calculation, the NSLR rate strongly depends on the concentration in the $Mg_{1-x}Al_xB_2$ system, and the experimental studies of this dependence are highly desirable for the understanding of the anisotropy of boron p states.

When this paper was completed we became aware that similar results for NSLR in MgB_2 were independently obtained in Ref. 12, where the T_1 on ^{25}Mg and the Knight shifts were also computed. We believe that the discrepancy in the Fermi-contact term is mainly due to the significantly larger boron sphere radius used in our calculations.

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