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NMR relaxation rates and Knight shifts in MgB_2

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We calculate *ab initio* the NMR relaxation rates and the Knight shifts in MgB_2. We show that the dominant relaxation mechanism at the ^{11}B nucleus is the interaction with the electronic orbital moment, and we give a simple explanation of that using a simple sp tight-binding model. When Stoner enhancement (also calculated *ab initio*) is accounted for, we obtain good agreement with reported experimental values. For the ^{25}Mg nucleus, we predict that the dominant relaxation mechanism is the Fermi-contact interaction, which also dominates the Mg Knight shift.

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Recent discovery[1] of superconductivity in MgB_2 created substantial interest. It was suggested that the underlying mechanism is electron-phonon interaction in the boron sublattice,[2] which was subsequently confirmed by observation of a sizeable boron,[3,4] but not magnesium[4] isotope effect. State of the art local-density approximation (LDA) calculations[5–7] produced electron-phonon coupling constants λ ranging from 0.75 to 0.87. Lacking single crystals, experimental determination of λ relies on the specific heat renormalization measurements.[8] Using the LDA density of states (DOS), these experiments give $\lambda \sim 0.6-0.8$; however, if there is any many-body renormalization of the LDA DOS, these experiments should be reanalyzed.

Nuclear magnetic resonance (NMR) is a common probe of the DOS. The measured quantities, the spin-lattice relaxation rate, $1/T_1$, and the Knight shift, K, are related to the spin susceptibility, and thus are not subject to a phonon renormalization. Measurements of the relaxation rates and the Knight shift of ^{11}B already exist.[9–12] From the electronic structure of MgB_2 one can conjecture[9,10] that the main source of relaxation should be the hyperfine coupling between the nuclear spin and conduction B p electrons. However, a full microscopic understanding of the NMR data (relaxation rates and Knight shifts) is still missing. While different sources[9,11,12] reasonably agree among themselves about the relaxation rates, reporting $1/T_1T$ between 5.6×10^{-3} and 6.5×10^{-3} 1/(K sec), there is considerable controversy about the Knight shifts. Some authors[11] report a small average shift $K=(K_z+2K_{xy})/3=0.0175\%$, and give an upper bound on its anisotropy, $K_{ax}=(K_z-K_{xy})/3<0.0030\%$. Other authors[9] report even smaller ($K=0.006\%$) shift and they attribute the shift to the Fermi-contact interaction. Note that the Korringa relation, $r=K^2(T_1T)(\gamma_n/2\mu_B)^2(4\pi k_B\hbar)\approx1$, where γ_n is the nuclear gyromagnetic ratio, is not satisfied here, as the measurements give $r\sim0.2$. Finally, a tiny negative shift ($K=-0.0005\%$) was measured by Tou *et al.*,[10] and attributed to core polarization. These discrepancies might arise from the difficulties in measuring the ^{11}B shift, due to its smallness, and, possibly, from the selection of the reference material.[9,10] Therefore, in order to clarify the microscopic origin of the NMR relaxation process and of the Knight shift, *ab initio* calculations are highly desirable.

In the present work we report LDA calculation of the relaxation rates and of the Knight shifts. We will show that for ^{11}B the relaxation is due to the p states, and the *orbital* relaxation rate is about 3 times larger than the *dipole* rate and 10 time larger than the *Fermi-contact* rate. After an appropriate Stoner renormalization is included, the agreement with the experiment is very good. On the other hand, the main source of Knight shift is the hyperfine coupling with s electrons. Also, the (yet unmeasured) relaxation on Mg is mainly due to the Fermi-contact interaction with the s states.

The hyperfine interaction $-\hbar\gamma_n\mathbf{I}\cdot\mathbf{H}$ is the coupling between the nuclear magnetic moment $\hbar\gamma_n\mathbf{I}$ and the hyperfine field $\mathbf{H}$ produced at the site of the nucleus by the conduction electrons. In order to discuss separately the different relaxation mechanisms, we neglect the small spin orbit coupling and split the hyperfine interaction into three terms, $-\hbar\gamma_n\mathbf{I}\cdot[\mathbf{H}^o+\mathbf{H}^d+\mathbf{H}^F]$. The first term is the coupling with the electronic orbital moment; the second and the third terms are, respectively, the dipole and the Fermi-contact interaction with the electronic spin. Thus the total hyperfine field is given by

$$\mathbf{H}=2\mu_B\left\{-\frac{\mathbf{l}}{r^3}+\left[\frac{\mathbf{s}}{r^3}-3\frac{\mathbf{r}(\mathbf{r}\cdot\mathbf{s})}{r^5}\right]-\frac{8\pi\mathbf{s}}{3}\delta(\mathbf{r})\right\},$$

where $\mathbf{r}$, $\mathbf{s}$, and $\mathbf{l}$ are the electronic position, spin, and angular momentum operator. In the case of ^{11}B, $I=3/2$ and $\gamma_n=0.89\gamma_N$, while in the case of ^{25}Mg $I=5/2$ and $\gamma_n=-0.17\gamma_N$, with $\gamma_N=e/m_pc$.

According to Fermi's golden rule, the relaxation rate, $1/T_1$, may be written as[13]

$$\frac{1}{T_1}=\frac{2\pi}{\hbar}\sum_{\mathbf{kk}'ss'mm'}f(\epsilon_{\mathbf{k}s})[1-f(\epsilon_{\mathbf{k}s'})]\delta(\epsilon_{\mathbf{k}s}-\epsilon_{\mathbf{k}'s'})\times|\langle\mathbf{k}sm|-\hbar\gamma_n\mathbf{I}\cdot\mathbf{H}|\mathbf{k}'s'm'\rangle|^2\times\frac{(\langle m|I_z|m\rangle-\langle m'|I_z|m'\rangle)^2}{\mathrm{Tr}I_z^2},\qquad(1)$$

where $f(\epsilon)$ is the Fermi-Dirac distribution, s is the spin index, and $|m\rangle$ are the eigenstates of I_z. Here $\mathbf{k}$ stands for both the wave vector and band index. Expansion of the Fermi

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TABLE I. Knight shift, K_α in %. Both unrenormalized and Stoner-enhanced values are included, as discussed in the text. The label $\alpha = xy,z$ indicates the direction of the external magnetic field.

	dipole (*xy*)	dipole (*z*)	orbital	Fermi-contact	core	Total (*xy/z*)	Total (renormalized)	Expt. [a]	Expt. [b]	Expt. [c]
Mg	0.0005	−0.0010	0	0.0260	0.0003	0.0271/0.0256	0.0361/0.0341			
B	−0.0004	0.0008	0	0.0027	−0.0007	0.0016/0.0028	0.0024/0.0042	0.0175	0.006	−0.0005

[a]Reference 11. [b]Reference 9. [c]Reference 10.

function and integration over the nuclear spin yields, for a polycrystalline sample, the following expression[15]

$$\frac{1}{T_1 T} = 2\pi k_B \hbar \gamma_n^2 \left[\mathrm{Tr}\frac{1}{3}|\mathbf{H}N|^2 \right],$$

where we introduced the density-of-states operator, $\langle \mathbf{k}\ s|N|\mathbf{k}'\ s'\rangle \equiv \delta_{ss'}\delta_{\mathbf{kk}'}\delta(\epsilon_{\mathbf{k}} - E_F)$. The prefactor is similar to that of the Korringa relation, $C = (4\pi k_B/\hbar) \times (\gamma_n/\gamma_e)^2$. In the present case $C \sim 1.4\times 10^4/(\mathrm{K\,sec})$ for ^{25}Mg and $C\sim 3.9\times 10^5/(\mathrm{K\,sec})$ for ^{11}B. The interaction cross terms in Eq. (1), i.e., the terms proportional to $\mathrm{Tr}[\mathbf{H}^o N \mathbf{H}^d N]$, $\mathrm{Tr}[\mathbf{H}^o N \mathbf{H}^F N]$ and $\mathrm{Tr}[\mathbf{H}^F N \mathbf{H}^d N]$ all vanish, the first two exactly, because $\mathrm{Tr}[\mathbf{s}]=0$ and the third vanishes exactly for polycrystals because $\mathrm{Tr}[s^2 - 3(\mathbf{s}\cdot\mathbf{r})^2]=0$, and approximately for single crystals, when the *d*-electron DOS is small [*cf.* Ref. 16, Eq. (24)]. Thus, without the core polarization, which will be discussed later, the relaxation rate has three contributions: the orbital, the dipole and the contact-field term. Note that in the terminology of Ref. 16, all cross terms, diagonal in interaction but off-diagonal in angular momentum, are included in the calculation. More details on this derivation can be found in Ref. 15.

In order to evaluate the relaxation rate, we adopt the tight binding LMTO-ASA method (LMTO47 Stuttgart code).[14] This method has been already used with success to calculate $1/T_1$, e.g., in A_3C_{60}.[15] Thus we express the Bloch function as $|i\mathbf{k}s\rangle = \Sigma_{RL}\langle \mathbf{r}|\chi^{\mathbf{k}}_{RL}\rangle c_{RLi,\mathbf{k}}|s\rangle$, with $|\chi^{\mathbf{k}}_{RL}\rangle = |\Phi_{RL}\rangle + \Sigma_{R'L'}|\dot{\Phi}_{R'L'}\rangle h^{\mathbf{k}}_{R'L',RL}$. Here $\langle \mathbf{r}|\Phi_{RL}\rangle = \phi_{Rl}(\epsilon_{\nu Rl}, r) Y_L(\hat{\mathbf{r}}_R)$, where ϕ_{Rl} is the radial solution of the Schrödinger equation at the energy $\epsilon_{\nu RL}$, $\dot{\phi}_{Rl'}$ is its energy derivative, Y_L is a spherical harmonic with $L = lm$. For simplicity, in the following we will write only the contributions from ϕ_{Rl}, although in the calculation we have, of course, included all terms. Thus the three contributions to $1/T_1$ can be expressed as a function of

$$N_{LL'} = \frac{V}{8\pi^3}\sum_i \int d^3k c_{L,i\mathbf{k}} \delta(\epsilon_{i\mathbf{k}}) c^*_{L',i\mathbf{k}}, \tag{2}$$

and of the radial integrals involving $\phi_{Rl}(\epsilon_{\nu Rl}, r)$

$$\langle r^{-3}\rangle_{l'l} = \int \phi_{Rl}(\epsilon_{\nu Rl}, r) r^{-3} \phi_{Rl'}(\epsilon_{\nu Rl'}, r) r^2 dr. \tag{3}$$

The Fermi-contact, the orbital, and the dipole contributions may then be written, respectively, as

$$Tr\frac{1}{3}|\mathbf{H}^F N|^2 = \frac{1}{2}\mu_B^2 \left(\frac{4}{3}\phi_s^2(\epsilon_{\nu Rl}, 0) N_{ss}\right)^2, \tag{4}$$

$$Tr\frac{1}{3}|\mathbf{H}^0 N|^2 = \frac{8}{3}\mu_B^2 \sum_{\mu=-1}^{1} \sum_{\Lambda\Lambda' LL'} \times \langle r^{-3}\rangle_{\lambda\lambda} D^{-\mu}_{LL'} N_{L'\Lambda'} \langle r^{-3}\rangle_{ll} D^{\mu}_{\Lambda'\Lambda} N_{\Lambda L}, \tag{5}$$

$$Tr\frac{1}{3}|\mathbf{H}^d N|^2 = 4\mu_B^2 \sum_{\mu=-2}^{2} \sum_{\Lambda\Lambda' LL'} \times \langle r^{-3}\rangle_{\lambda'\lambda} C^{2\mu}_{LL'} N_{L'\Lambda'} \langle r^{-3}\rangle_{ll'} C^{2\mu}_{\Lambda\Lambda'} N_{\Lambda L}. \tag{6}$$

Here $D^{\mu}_{LL'} = \langle L'|l_\mu|L\rangle$, $l_0 = l_z$, $l_{\pm 1} = l_{\pm}/\sqrt{2}$, and $C^{2\mu}_{LL'} = \sqrt{4\pi/5}\int Y_{2\mu}(\hat{r}) Y_L(\hat{r})^* Y_{L'}(\hat{r}) d^2\hat{r}$.

In the same way, the Knight shift can be written as $K_\alpha = 2\mu_B Tr\langle\uparrow|\mathbf{H}_\alpha N|\uparrow\rangle$ where α is the direction along which the external magnetic field is applied. As the relaxation rate, the relative shift may also be expressed as a function of the DOS matrix and the radial integrals, expanding the Bloch function in the LMTO basis set.

The DOS matrix was calculated by the linear tetrahedron method. We found that the results were already very well converged with a mesh of 370 irreducible **k** points. In order to minimize the linearization error and thus to obtain accurate wavefunctions at the Fermi level, the linear partial wave expansion was performed with $\epsilon_{\nu Rl} \equiv \epsilon_F$. The convergence of the sums over the angular momentum was also very good. We find that we can truncate after $l=2$. The reason is that the radial integrals $\langle (a_0/r)^3\rangle_{ll'}$ (a_0 is the Bohr radius) decrease quickly when l and l' increases. For Mg we find, e.g., $\langle (a_0/r)^3\rangle_{11} = 4.8$, $\langle (a_0/r)^3\rangle_{22} = 0.16$, and $\langle (a_0/r)^3\rangle_{33} = 0.09$, and in for B, $\langle (a_0/r)^3\rangle_{11} = 1.1$ and $\langle (a_0/r)^3\rangle_{22} = 0.2$.

What is the dominant mechanism that gives rise to the magnetic relaxation at B and Mg nuclei? In most metals it is the Fermi contact one, defined by the DOS of the *s* electrons at the Fermi level. However, in the case of MgB_2 the states near the Fermi level are mainly B *p*. We find that the ratio $N_{ss}(\mathrm{Mg})/N_{tot}(\mathrm{Mg}) \sim 1/4$, and $N_{ss}(\mathrm{B})/N_{tot}(\mathrm{B}) \sim 1/50$. Therefore, at least in the case of B, the ratio is very small, and the Fermi contact term could become comparable or even smaller than the dipole or the orbital term. We have calculated all three contributions for both elements and show the results in Tables I and II.

We also calculate *ab initio* the core polarization. For this purpose we applied in the calculations an external magnetic field *B*, and then calculated $m_n(0)$, the spin density of the *n*th core shell at the nucleus. Then the core polarization

Knight shift can be obtained as $K_{cp} = \mu_B(8\pi/3)\Sigma_n(m_n(0)/B)$, and the corresponding contributions to the relaxations rate can be computed from the Korringa relations for the core states.[18] For ^{25}Mg, the contribution of the core polarization is negligible and the Fermi-contact interaction dominates. For ^{11}B, we find that the contribution of the 1s shell is of the same order, but of opposite sign, as the the 2s shell contribution. Their total effect is thus small. Also, since the Fermi-contact contribution for B is much smaller than in Mg, the relative effect of the dipole term is larger, leading to a noticeable anisotropy of the Knight shift (about 30%), while the Mg Knight shift is essentially isotropic.

In order to understand the numerical results, we first calculate analytically the shifts and the relaxation rate for a model Hamiltonian which includes only B s and B p orbitals. We start with the contribution of s electrons, i.e., the contact term. The contact shift may be written as $K \sim \mu_B^2(4/3)|\phi_s(0)|^2 N_{ss}$, where N_{ss} is the s-projected DOS per atom per spin. We find $N_{ss}\sim 0.002$ states/eV per B atom. Using the free B atom value, $|\phi_s(0)|^2/(4\pi)\sim 1.64 a_0^{-3}$ ($2.16 a_0^{-3}$ in MgB_2) we find $K\sim 0.002\%$ and $1/T_1T\sim 0.15\times 10^{-3}$ 1/(K sec). Both numbers are very close to those obtained from the full calculations (Tables I and II).

We now consider the contribution of B p electrons. The states at the Fermi level are $\sim$70% B p-like. $N_{p_x,p_x}\sim 0.035$ states/(spin eV atom), and $N_{p_z,p_z}\sim 0.045$ states/(spin eV atom). Thus $N_{p_x,p_x}\sim N_{p_z,p_z}\sim N_p/3$, where N_p is the total p-projected DOS per spin per atom. Therefore we find the following approximate expression of the orbital contribution to the relaxation rate

$$\frac{1}{T_1T}\sim 4\pi k_B\hbar\gamma_n^2\frac{4\mu_B^2}{3}|\langle r^{-3}\rangle_{11}|^2 Tr_m[\mathbf{l}\cdot\mathbf{l}]\left(\frac{N_p}{3}\right)^2,$$

where $Tr_m[\mathbf{l}\cdot\mathbf{l}]=(2l+1)l(l+1)=6$. We find $N_p/3\sim 0.038$ states/eV per B atom and $\langle(a_0/r)^3\rangle\sim 0.82$ for the free B atom (1.14 in MgB_2), and therefore $1/T_1T\sim 1.6\times 10^{-3}/(\mathrm{K\,sec})$. The orbital part of the Knight shift is zero in this model because nondiagonal elements of the DOS matrix vanish.

In the same way the dipole term can be written as

$$\frac{1}{T_1T}\sim 8\pi k_B\hbar\gamma_n^2\mu_B^2|\langle r^{-3}\rangle_{11}|^2\sum_{\mu mm'}(C^{2\mu}_{1m,1m'})^2\left(\frac{N_p}{3}\right)^2,$$

where $\Sigma_{\mu mm'}(C^{2\mu}_{1m,1m'})^2=6/5$. Thus we find that the B p electron contribution to the dipole relaxation rate is $1/T_1T\sim 0.4\times 10^{-3}$ 1/(K sec). For the Knight shift we find $K_z^d\sim -2K_{xy}=2\mu_B^2\ C^{20}_{10,10}\langle r^{-3}\rangle_{11}(N_p/3)\sim 0.0011\%$. Again, all these numbers are rather close to the all-electron results shown in the Tables. The ratio $(T_1)_{dip}/(T_1)_{orb}\sim(2/3)Tr[\mathbf{1}\cdot\mathbf{l}]/\Sigma_{\mu mm'}(C^{2\mu}_{1m,1m'})^2\sim 3.3$. The reason for which the orbital term dominates over the dipole term is that all three p orbitals are present at the Fermi level, as opposed, for instance, to the fullerenes,[15] where only the p_z orbital has a sizable weight at the Fermi level, and thus the orbital term is strongly reduced.

In terms of the linear response theory, both the Knight shift and the relaxation rate are defined by the electronic spin susceptibility,[17] $\chi(\mathbf{q},\omega)$, specifically, $K\propto \mathrm{Re}\,\chi(\mathbf{0},0)$, and $1/T_1\propto \lim_{\omega\to 0}\Sigma_{\mathbf{q}}\mathrm{Im}\,\chi(\mathbf{q},\omega)/\omega$. Electron-hole excitations renormalized the spin susceptibility, and in the simplest possible approximation one writes

$$\chi(\mathbf{q},\omega)\approx\chi_0(\mathbf{q},\omega)/[1-I\chi_0(\mathbf{q},\omega)],$$

where χ_0 is the bare (noninteracting) susceptibility, I is the so-called Stoner factor, characterizing intraatomic exchange, and the calculations described above correspond to total neglect of the Stoner renormalization. One can estimate I from LSDA calculation with fixed total spin moment by fitting the total energy to the Stoner expression, $E_{tot}(M)=M^2/4N - M^2 I/4$, where M is the spin moment and N is the total DOS per spin. In this way, we found $IN\equiv I\chi(\mathbf{0},0)\approx 0.25$. Thus we can estimate renormalized Knight shift as $K\approx K_0/(1-IN)=1.33K_0$. The renormalized values are also shown in the Table I.

The renormalization of $1/T_1$ is somewhat more difficult to take into account, and it is, in principle, site dependent. It is easy to show[20] that in the Stoner approximation

$$\mathrm{Im}\,\chi(\mathbf{q},\omega)\approx \mathrm{Im}\,\chi_0(\mathbf{q},\omega)/[1-I\mathrm{Re}\,\chi_0(\mathbf{q},\omega)]^2, \qquad (7)$$

however, averaging this expression over $\mathbf{q}$'s requires knowledge of the $\mathbf{q}$-dependence of χ_0. Generally speaking, renormalization factor lies between $1/(1-IN)$ and $1/(1-IN)^2$. Using the Lindhard susceptibility ,and a sphere for the Fermi surface, Shastry and Abrahams[20] found that in the 3D case

$$\left\langle\frac{\mathrm{Im}\,\chi_0(\mathbf{q},\omega)}{[1-I\,\mathrm{Re}\,\chi_0(\mathbf{q},\omega)]^2}\right\rangle\approx\frac{\langle \mathrm{Im}\,\chi_0(\mathbf{q},\omega)\rangle}{(1-IN)(1-2IN/3)},$$

which is a good approximation for $IN\lesssim 0.7$. By integrating numerically Eq. (7) with the Lindhard function, we found a better approximation, good for essentially all IN, and preserving the correct small IN limit, namely $\langle \mathrm{Im}\,\chi_0(\mathbf{q},\omega)\rangle/(1-IN)^{5/3}$. Thus we used the factor $1.33^{5/3}$

TABLE II. Relaxation rate $1/T_1T$ in $10^{-3}/(\mathrm{K\,sec})$. Both unrenormalized and Stoner-enhanced values are included, as discussed in the text.

	orbital	dipole	Fermi-contact	core	Total	Total (renormalized)	Expt. [a]	Expt. [b]	Expt. [c]
Mg	0.02	0.01	1.0	0.0001	1.0	1.6			
B	2.6	0.8	0.28	0.02	3.7	4.3–5.9	5.6	6.5	6.1

[a]Reference 12. [b]Reference 11. [c]Reference 9.

$\approx$1.6 for $1/T_1$. For the 2D free electron gas, there is no $\mathbf{q}$ dependence in $\chi_0(\mathbf{q},\omega)$ for $q<2k_F$, and thus the renormalization factor is $1/(1-IN)^2$.

The many-body renormalization of the orbital susceptibility is even more complicated than that of the spin susceptibility. In the scalar-relativistic LDA it vanishes, however, the effects beyond LDA and the spin-orbit interaction enhance the χ_{orb}. While we cannot compute this renormalization within the methodology used in this paper, in order to get some idea of the scale of the renormalized relaxation rate, we show in the Table II a range of value, first neglecting the renormalization of χ_{orb} entirely, and then setting it to that of χ_{spin}.

The larger value of $1/T_1T$, namely 5.9×10^{-3} 1/(K sec), is in a good agreement with the reported experimental number. This means that the DOS, calculated within LDA, is a good approximation (maybe a slight underestimate) of the bare DOS, and thus the values for the electron-phonon coupling constant λ, obtained from the specific heat measurements, are reliable.

To the best of our knowledge, there are at present no experimental data for Mg. We predict that the magnetic shift is isotropic and that the principal relaxation mechanism is the Fermi-contact interaction, despite of the fact that $N_{ss}/\Sigma_{l>0}N_{ll}\sim1/3$. The reason is that the quantities that one has to compare are not the partial DOS N_{ss} and N_{ll} but rather the dimensionless couplings $(2\mu_B^2/3)|\phi_s(0)|^2N_{ss}$ and $\mu_B^2\Sigma_{l>0}\langle r^{-3}\rangle_{ll}N_{ll}$, and thus the relevant ratio is $R=(2/3)|\phi_s(0)|^2N_{ss}/(\Sigma_{l>0}\langle r^{-3}\rangle_{ll}N_{ll})$. In the case of Mg we find $|\phi_s(0)|^2/4\pi=4.54a_0^{-3}$, and $\langle r^{-3}\rangle_{11}=4.8a_0^{-3}$. Hence we find $R\sim5$. Instead, in the case of B, $|\phi_s(0)|^2/4\pi=2.16a_0^{-3}$ and $\langle r^{-3}\rangle_{11}=1.1a_0^{-3}$, and thus $R\sim0.35$. The coupling with non-s electron competes with or dominates over the coupling with s electrons when $R\leqslant1$.

Finally, we would like to mention that the presented values for $1/T_1T$ include contributions from both quasi-2D p_σ and 3D p_π bands. If, as suggested,[7] two different gaps open below T_c in these bands, the temperature dependence of $1/T_1T$ *at* low temperature should be computed taking the different character of these bands in the normal states. It is not obvious *a priori* that the corresponding weights will be just the densities of states. Calculations similar to those described above, but band decomposed are needed.

To summarize, we report first-principles calculations of the NMR relaxation rates and the Knight shifts on both sites in MgB_2. The results are in a good agreement with the experiment, provided that the dipole and the orbital hyperfine interactions are taken into account, as well as the Stoner renormalization of susceptibility. NMR relaxation at ^{11}B nucleus is dominated by the orbital interaction, and that at the ^{25}Mg nucleus by the Fermi-contact one. The Knight shift is dominated by the Fermi contact polarization on both B and Mg. After these calculations were completed, we learned about similar calculations from the Ames group,[19] with the results consistent with those reported here.

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