Anomalous NMR Spin-Lattice Relaxation in SrB$_6$ and Ca$_{1-x}$La$_x$B$_6$

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We report the results of $^{11}$B nuclear magnetic resonance (NMR) measurements of SrB$_6$ and Ca$_{0.995}$La$_{0.005}$B$_6$ below room temperature. Although the electrical resistivities of these two materials differ substantially, their $^{11}$B-NMR responses exhibit some strikingly common features. Both materials exhibit ferromagnetic order, but their $^{11}$B-NMR spectra reveal very small hyperfine fields at the Boron sites. The spin lattice relaxation $T_1^{-1}$ varies considerably with external field but changes with temperature only below a few K. We discuss these unusual results by considering various different scenarios for the electronic structure of these materials.

Hexaboride compounds XB$_6$ (X = elements of the alkaline-earth and lanthanide series) have previously been studied [1], but they continue to reveal new and unexpected physical properties [2]. This is particularly true for the case of divalent hexaborides such as EuB$_6$ [3, 4], CaB$_6$ [5] and SrB$_6$ [6] whose physical properties seem to depend on subtle details of the electronic band structure, and are very sensitive to the presence of microscopic imperfections [7]. Recent research efforts involving these systems resulted in an unexpected discovery of ferromagnetic ordering of tiny magnetic moments in La-doped CaB$_6$ [8] with Curie temperatures of the order of 600 K. Subsequently, ferromagnetic order was also encountered in the nominally binary compounds SrB$_6$ and CaB$_6$, as well as La-doped BaB$_6$ [9-11].

In this letter we present and discuss NMR data obtained on ferromagnetic SrB$_6$ and Ca$_{0.995}$La$_{0.005}$B$_6$. The compounds XB$_6$ all crystallize by adopting the CaB$_6$ type structure with the space group $Pm\bar{3}m$. The Boron ions, directly probed by our NMR experiments, form a rigid network of interconnected Boron octahedra. The point symmetry of the B-sites is $4mm$ and allows for nonzero axially-symmetric electric-field gradients. Somewhat unexpectedly, the $^{11}$B-NMR response is largely insensitive to the magnitude of the electrical resistivities of these materials. At 1 K, the value of the electrical resistivity $\rho$ of the two samples differs by a factor of 30, but there is no appreciable difference in the spin-lattice relaxation rate $T_1^{-1}$ at this temperature. The $T_1^{-1}(T)$ data reflect neither a metallic nor a semiconducting behavior. Furthermore the data do not provide straightforward evidence for the ferromagnetism that is indicated by $M(H)$ measurements on the same samples [10,11]. However, the spin-lattice relaxation rate is orders of magnitude larger than what may be expected from a relaxation via itinerant electrons alone. We interpret this as evidence for the presence of weakly localized electronic states, with unusual dynamics. These states coexist with extended states responsible for the electrical transport and may be related to the unusual ferromagnetism observed in these materials.

For our NMR experiments we used standard spin-echo techniques. The samples consisted of collections of small single crystals, grown by the Al-flux method. The materials have extensively been characterized by measurements of thermal and transport properties [3-10].

In Fig. 1 we display examples of the recorded $^{11}$B NMR spectra for SrB$_6$, Ca$_{0.995}$La$_{0.005}$B$_6$ and LaB$_6$ measured at a fixed applied field of 5.195 T and at temperatures of 3.17, 3.12 and 1.53 K, respectively.

![Fig. 1](image-url)  
**Fig. 1.** $^{11}$B-NMR spectra for SrB$_6$, Ca$_{0.995}$La$_{0.005}$B$_6$ and LaB$_6$ measured at a fixed applied field of 5.195 T and at temperatures of 3.17, 3.12 and 1.53 K, respectively.
room temperature we found no substantial temperature-induced changes in the position of the NMR line for any of these materials. The width of the central line, FWHM = 23 kHz, is of the order of those of good metallic samples. No appreciable differences are found in the position and width of the central transition for LaB$_6$ with 1 conduction electron per unit cell and SrB$_6$ as well as Ca$_{0.995}$La$_{0.005}$B$_6$, with conduction electron concentrations $n_c \leq 5 \cdot 10^{-3}$ electrons per unit cell and exhibiting ferromagnetic ordering below 600 K. In ferromagnetic powders the NMR linewidth is largely determined by demagnetization factors, yielding a variation of the local magnetization factors, yielding a variation of the local fields of the order of the magnetization. In our case this implies a magnetic moment of $10^{-1}$ Bohr magnetons per unit cell, an upper limit consistent with our data. The actual ordered moment may be much smaller.

In Fig. 2a we display the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of SrB$_6$ for various applied magnetic fields. The dotted lines are guides to the eye. The solid line represents $T_1^{-1}(T)$ for LaB$_6$. (b) $T_1$ for SrB$_6$ as a function of the applied field at $T = 0.66$ K.

Next we consider the relaxation due to conduction electrons. It has been found that for LaB$_6$, above 30 K, $(T_1 T)^{-1} \approx 7 \cdot 10^{-4} K^{-1}s^{-1}$ \[15\]. This small value is consistent with the observed NMR lineshift and indicates a very weak coupling between the conduction electrons and the B nuclei in LaB$_6$. From a simple scaling of $(T_1 T)^{-1}$ by considering the differences in $n_c$, a three orders of magnitude weaker spin-lattice relaxation is expected for SrB$_6$ and La-doped CaB$_6$. However, as shown in Fig. 2,
\[(T_1 T)^{-1}\] of SrB\(_6\) below 30 K is larger than or equal to the values of LaB\(_6\) extrapolated from the results of the high-temperature measurements at 4.7 T \([10]\). Thus the direct relaxation rate \(T_1^{-1}\) due to conduction electrons is too small to be of relevance for the alkaline-earth hexaborides. Naturally, this poses the problem of identifying a source, other than the low-energy excitations of conduction electrons to account for the spin-lattice relaxation data. Below we consider three different scenarios that have recently been discussed in connection with the electronic structure of these materials \([11,12,21]\).

First we consider the case of a band overlap at the X point of the Brillouin zone for divalent hexaborides. For this case, as pointed out by Zhitomirsky and Rice \[21\], a Bose condensation of electron-hole pairs, excitons, is likely to occur, leading to ferromagnetic order among tiny moments below a high Curie temperature \(T_C\) upon doping. Little is known about the dynamic susceptibility of the excitonic condensate. On very general grounds, however, and drawing parallels with the case of superconductivity, at very low temperatures \((T \ll T_C)\) one may expect a very small, and rapidly decreasing relaxation rate upon decreasing temperature, which is not observed here for \(T_0 \leq T \ll T_C\).

Next we consider the case of a very small gap at the X point of the Brillouin zone, i.e., a gap of the order of the excitonic binding energy. The excitonic condensate mentioned in the previous scenario would not form, but for this case a novel spin-lattice relaxation mechanism has recently been suggested \[22\]. Under certain conditions the formation of “multiexciton molecules” containing several electron-hole pairs in SrB\(_6\) and CaB\(_6\) near impurities seems energetically favorable. The exciton molecules are expected to carry an uncompensated spin \(1/2\) and their thermally-induced spin flips are very effective in producing nuclear relaxation. The technical details of this interesting picture, in particular the temperature dependence of the spin-lattice relaxation, still have to be worked out.

Since a temperature independent \(T_1^{-1}\) is likely to be caused by localized magnetic moments, we finally consider yet another case. With a gap at the X point of the Brillouin zone that exceeds the excitonic binding-energy \([13]\), the conditions for the two previous cases are not fulfilled. Instead we consider a relaxation due to localized electronic states, as they occur in doped semiconductors close to the metal-insulator transition. Here the NMR relaxation is caused by thermally-induced spin-flips of weakly bound holes around vacancies on the alkaline-earth sites, and electrons below a certain mobility edge. We refer to both of them as weakly localized electronic states. Since the physical picture is relatively simple, we first check the consistency of such a scenario.

Weakly localized electronic states contribute very little to the electronic transport at low temperatures but, contrary to the extended electronic states may, as discussed below, cause a temperature independent relaxation. Mobile electrons and holes formed by conduction band states of Ca and Sr and by \(p\)-orbitals of B, respectively \([11]\) are, via the magnetic dipolar interaction, only weakly coupled to the B-nuclei. For a weakly localized state with a wave-function effective radius \(r\), however, the dipolar field at the B sites within the orbital is proportional to \(r^{-3}\). Its hyperfine coupling to the B-nuclei increases rapidly as \(r\) decreases. In doped semiconductors near the IMT, weakly localized and extended states coexist \[22\], and we assume the same to occur for SrB\(_6\) and Ca\(_{0.995}\)La\(_{0.005}\)B\(_6\). The extended electronic states induced by defects and doping contribute to the electronic transport and are only weakly coupled to the localized electrons. If localized states cause the experimental observations, they should have approximately the same concentration for various divalent hexaborides, near the critical concentration for delocalization. Judging from the \(\rho(T)\) data these states are of the order of 10 to 20 meV below the delocalization threshold \([13,14]\). Consider, for example, a single hole bound to a vacancy with an effective charge \(-2e\), at a Sr site in SrB\(_6\). The effective mass of the holes \([15]\) \(m^* = 0.24\) \(m_e\), with \(m_e\) as the free electron mass, and the dielectric constant \(\epsilon \approx 6\) \([24]\), yield for the \(H\)-type state an effective radius \(r_0 \approx 9\) lattice constants. Delocalization (i.e., the IMT) is expected for a concentration \(N_i \approx r_0^{-3} \approx 2 \cdot 10^{19}\) \(\text{cm}^{-3}\). The binding energy of a single \(H\)-type state \(E_b \approx 0.18\) eV is about one order of magnitude too large to match the \(\rho(T)\) data, but the energy needed for delocalization rapidly decreases from \(E_b\) as the IMT is approached from the insulating side. Of course the relatively large value of \(N_i\) should have measurable effects on the thermal and transport properties. This seems to be the case for SrB\(_6\), and Ca\(_{0.995}\)La\(_{0.005}\)B\(_6\), where anomalies in the temperature dependence of the specific heat have been found at low temperatures. For SrB\(_6\), e.g., the entropy associated with the excess specific heat below 7K saturates at 0.05% of \(R\cdot \ln 2\) at 7 K. For spin-1/2 particles this implies a concentration of \(0.7 \cdot 10^{19}\) \(\text{cm}^{-3}\), a value close to \(N_i \approx 10^{19}\) estimated above.

Following these arguments the \(T_1^{-1}\) data for \(T > T_0\) may qualitatively be understood. The NMR relaxation rate caused by localized electronic states interacting with the nuclei via dipolar coupling is given by \([24]\)

\[
\frac{1}{T_1} \approx \frac{2\gamma_S^2 \gamma_I^2 \hbar^2}{5 \pi \hbar^4} \cdot f(\omega) = C \cdot f(\omega) \tag{1}
\]

where \(\gamma_S\) and \(\gamma_I\) are the gyromagnetic ratios for electrons and \(^{11}\)B nuclei, respectively, \(S\) is the electron spin and \(f(\omega)\) is the spectral function describing the thermal fluctuations of the localized-electron system. The Larmor frequency \(\omega\) is proportional to the applied magnetic field. Most of the spectral weight of \(f(\omega)\) is assumed to be contained in a finite range of frequencies, from 0 up to
1/τ, where τ is the (electron) spin correlation time. Since it is not possible to calculate τ from first principles, except for very simple situations, one usually assumes the high-temperature approximation \( f(ω) = τ/(1 + ω^2τ^2) \).

To keep the arguments simple we neglect here complications due to spin diffusion \([22]\). Following the ideas of Gan and Lee \([23]\), the interaction between localized electrons near the IMT results in the formation of pairs with a broad distribution of singlet-triplet splittings \( J \). When \( J - 2μeH \approx 2μeH \) the random singlet-triplet transitions produce nuclear relaxation very effectively. The localized electron system is then characterized by a broad distribution \( P \) of correlation times \( τ \). The model is completed with

\[
 f(ω) = \int_{τ_{\text{min}}}^{τ_{\text{max}}} P(τ) \frac{τ}{1 + ω^2τ^2}, \quad ωτ_{\text{min}} \ll 1 \ll ωτ_{\text{max}}.
\]

Since in our case \( P(τ) \propto 1/τ \) \([24]\), \( f(ω) \propto (1/ω) \cdot \arctan(ωτ_{\text{max}}) \propto 1/ω \), which in Eq. 1 yields a temperature independent relaxation with \( T_{1}^{-1} \propto 1/H \). This behavior, as observed in our data above the crossover temperature \( T_0 \) and \( H > 1 \, \text{T} \), has previously been reported for doped semiconductors not far from the IMT \([25,26]\).

The different behavior of \( T_{1}^{-1}(T,H) \) below \( T_0 \) may be interpreted as evidence for changes in \( f(ω) \) at low temperatures. In particular our data for \( T \leq T_0 \) hints for a rapid increase of the minimum correlation time \( τ_{\text{min}}(T) \propto T^{-2} \) to values much larger than \( ω^{-1} \) and a drastic reduction of the range of active τ's. This yields \( f(ω) \propto 1/(ω^2τ_{\text{min}}) \) and \( T_{1}^{-1} \propto 1/(H^2T^{-2}) \).

In summary, we have shown that the \(^{11}\text{B}-\text{NMR}\) spin-lattice relaxation for \( \text{SrB}_6 \) and \( \text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6 \) is anomalous. In case of a large band gap at the \( X \) point of the Brillouin zone \([27]\) our \( T_{1}^{-1} \) data can be explained by postulating the coexistence of localized and extended electronic states with a very weak interaction between them. With this scenario we still face the problem concerning the origin of the weak but stable ferromagnetism in these materials. If the band gap is small, \( T_{1}^{-1} \) might be caused by spin-flips of "excitonic molecules" pinned to impurity or defect sites. Finally, we see no simple way to explain our \( T_{1}^{-1} \) data if there is a band overlap.

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