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NMR and spin/charge fluctuations in intermediate-valent SmB$_6$

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Information on spin and charge fluctuations in the non-metallic intermediate-valent compound SmB$_6$ has been obtained via ^{10}B and ^{11}B NMR between 2 and 300 K. Both the isotropic shift and the quadrupole coupling constant are temperature independent over this range, as expected if the fractional valence mixing is also temperature independent. Below 4.2 K the boron spin-lattice relaxation rate T_1^{-1} varies linearly with temperature, and yields a spin fluctuation rate $\tau_{sf}^{-1} \sim 10^{13}$ sec^{-1}, which corresponds to a spin fluctuation temperature $T_{sf} \sim 50$ K if characteristic of the stoichiometric compound. An increase of T_1^{-1} above 20 K indicates the onset of Sm-spin relaxation by thermal excitations. The results are also consistent with relaxation by impurity-band states associated with vacancies, but the Korringa constant obtained on this assumption is unrealistically small. Comparison between data obtained from ^{10}B and ^{11}B resonances yields no indication of a contribution from electric field gradient fluctuations to the relaxation; an upper bound on the charge fluctuation time $\tau_{cf} \lesssim 3\tau_{sf}$ is obtained. It is shown that correlations between Sm spin and charge fluctuations, if present, do not affect the nuclear relaxation in the extreme narrowing limit.

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INTRODUCTION

The intermediate-valent compound SmB$_6$ is unique in exhibiting a very high low-temperature resistivity and intermediate valence (IV) at atmospheric pressure, and has been extensively studied [1-4]. Central questions concerning this compound are: (i) whether the resistivity behavior arises from a small number of carriers and an energy gap due to hybridization [1] or from localization or other effects within an otherwise normal d-like conduction band [4]; (ii) how to reconcile the near temperature independence of the susceptibility and Mössbauer isomer shift [5] with the resistivity variation of more than four orders of magnitude [6] and the corresponding Hall-effect behavior [1,3]; (iii) whether or not the 4f spin and charge fluctuations behave similarly to those in the more common metallic IV compounds such as CePd$_3$ [7] and YbCuAl [8].

We have undertaken a study of boron NMR spectra and relaxation rates in SmB$_6$, since a number of NMR properties are sensitive to characteristics of the IV state [8-10]. We report here studies of ^{10}B and ^{11}B spin-lattice rates, which in principle permit the determination of both hyperfine field and electric field gradient fluctuation rates via standard techniques [11]. These in turn are related to Sm spin and charge fluctuations, respectively. Our work also confirms a previous characterization of the NMR shift and quadrupole coupling above 100 K [9], and extends measurements to 2 K.

Our results indicate that (i) intermediate valence in SmB$_6$ is indeed a dynamic and not a static phenomenon (i.e. not due to a static configuration of Sm^{2+} and Sm^{3+} ions), in agreement with other studies [1]; (ii) under the assumption that the data are representative of the stoichiometric compound, a IV spin fluctuation time $\tau_{sf} \sim 10^{-13}$ sec, corresponding to a spin fluctuation temperature $T_{sf} = \hbar/k_B\tau_{sf} \sim 50$ K, is found below 4.2 K; and (iii) the unobservability of quadrupole contributions to the spin-lattice relaxation rates puts an upper limit $\tau_{cf} \lesssim 3\tau_{sf}$ on the charge fluctuation time τ_{cf}.

The possibility cannot be dismissed that lack of stoichiometry in our sample gives rise to an impurity band [1] which dominates the NMR behavior, but this interpretation leads to an unreasonbly small value for the NMR Korringa constant [11] and raises as well the question of why IV effects from the majority of the SM ions should not be observable.

Finally, the effect of correlated Sm spin and charge fluctuations on nuclear relaxation is examined and shown to vanish at least in the extreme narrowing limit appropriate to SmB$_6$.

EXPERIMENTAL RESULTS

The specimen was prepared as a number of small single crystals in aluminum flux. These were powdered to allow rf field penetration in the high-temperature region (resistivity < 10^{-3} Ω-cm); a few crystals were saved for four-probe resistance measurements. The residual resistance ratio RRR = R(4.2K)/R(300K) was 1.2 × 10^3, which indicates good but not perfect stoichiometry [1]; RRR values of up to 3.6 × 10^4 have recently been reported [6]. Imperfect stoichiometry is thought to give rise to an impurity band associated with Sm ions near Sm site vacancies [1,4] which might influence NMR behavior as discussed below.

NMR spectra and relaxation rates were obtained using standard spin-echo techniques [8,10]. The isotropic NMR shift K_i, obtained from the center of gravity of the (1/2 ↔ -1/2) ^{11}B transition after correction for a quadrupolar contribution [11], was sensibly constant at the value -0.07(2)% between 2 and 300 K. This value is in slight disagreement with the result of Bose et al. [9], who obtained K_i = -0.03(1)%. Although different reference compounds were used (triethyl borate [11] in our case), it is unlikely that reference chemical shifts can account for all of the difference. We shall adopt the value K_i = -0.05(2)%; uncertainty in the shift value is the most important source of error in the subsequent analysis.

From the usual relation [11]

$$K_i = (H_{hf}/N\mu_B)\chi \qquad (1)$$

for the shift in terms of the hf field H_{hf} and the bulk molar susceptibility χ (N is Avogadro's number), the value $H_{hf} = -0.84(33)$ kOe/μ_B is obtained assuming shift and susceptibility are due to a unique mechanism. This value is comparable to transferred hf fields in a number of metallic rare-earth compounds. The quadrupole coupling constant $e^2qQ/h = 1.15(1)$ MHz obtained from first-order satellites was found to be independent of temperature and in good agreement with previous work [9]. Measurements on a poorly characterized but considerably less stoichiometric sample (Alfa Ventron, supplier) yielded the same values of K_i and e^2qQ/h within errors.

Nuclear magnetization recovery after a string of saturating pulses was monitored to measure spin-lattice relaxation rates. Measured recovery functions $M_z(t) - M_z(\infty)$ were nonexponential at all temperatures between 2 and 300 K. Some representative data are shown in Fig. 1. The nonexponentiality at 77 K and above can be accounted for by the multiple-rate solutions of the master relaxation equation in the presence of quadrupole splitting [12], but at 4.2 K and below the nonexponentiality increases and is no longer well described by the master-equation solutions. ^{11}B relaxation times $T_1(11)$ were obtained from the long-time asymptotic behavior of the magnetization recovery at all temperatures, and are given in Fig. 2. A field dependence is evident at 4.2 K and below, which disappears above 77 K. Above 20 K the relaxation rate fits an Arrhenius law with an activation energy of 62 K. ^{10}B relaxation measurements at 4.2 K and 10 kOe applied field yielded $T_1^{-1}(10) = (\gamma^2_{10}/\gamma^2_{11})T_1^{-1}(11)$ to within 10%, where the γ's are the nuclear gyromagnetic ratios. This ratio is expected from purely magnetic relaxation, so that no evidence was found for a contribution by fluctuating electric field gradients to the relaxation.
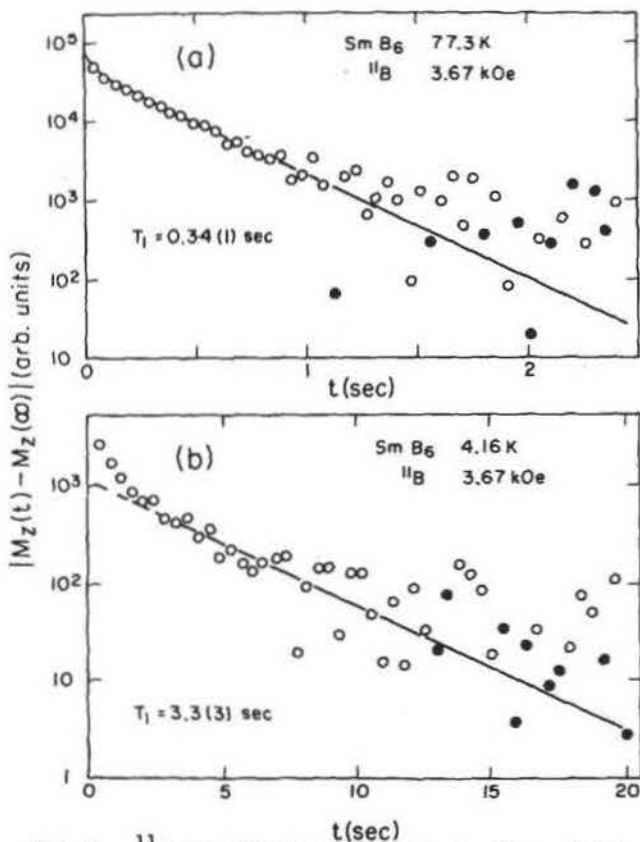

Fig. 1. ^{11}B magnetization recovery functions $M_z(t) - M_z(\infty)$ in SmB$_6$ at 3.67 kOe and (a) 77.3 K and (b) 4.16 K. The filled circles denote points below the baseline. Note the pronounced initial nonexponentiality in (b).
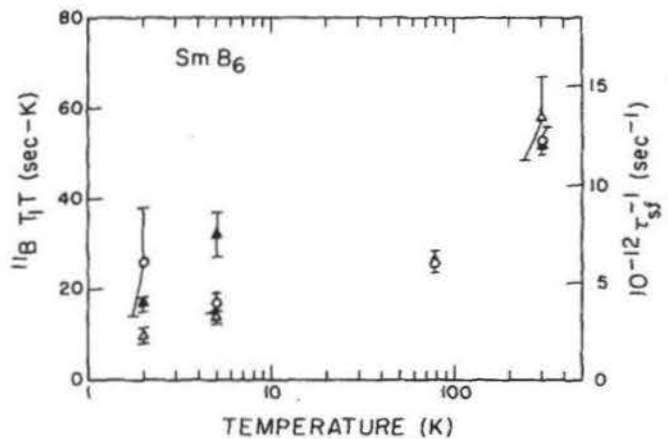

Fig. 2 Temperature dependence of ^{11}B spin-lattice time-temperature product T_1T (left-hand ordinate) and Sm-ion spin fluctuation rate τ_{sf}^{-1} (right-hand ordinate). Open triangles: H = 3.67 kOe. Circles: H = 5.0 kOe. Filled triangles: H = 9.0 kOe. The spin fluctuation rate was calculated using Eq. (2), with $K_i = 5 \times 10^{-4}$ and $n_{eff} = 4$ (see text).

DISCUSSION

Under the assumption that K_i and T_1 are characteristic of stoichiometric SmB$_6$, and are dominated by transferred hf coupling from the Sm ions, a NMR estimate of the IV spin fluctuation rate τ_{sf}^{-1} can be obtained [8,10]:

$$n_{eff}\tau_{sf}^{-1} = 2N\gamma_n^2 k_B(K_i^2 T_1 T/\chi), \qquad (2)$$

where n_{eff} is the effective number of Sm neighbors to a boron nucleus [10], and γ_n is the nuclear gyromagnetic ratio. At 4.2 K and 10 kOe this yields $\tau_{sf}^{-1} = 2.5-13 \times 10^{12}$ sec^{-1}, depending on the value of K_i used and assuming $n_{eff} = 4$, the nearest-neighbor coordination number. The corresponding spin fluctuation temperature is $T_{sf} = 20-100$ K, which is of the order of magnitude found in metallic IV systems [7,8]. The temperature dependence of τ_{sf}^{-1} tracks that of T_1T (Fig. 2); the increase with increasing temperature is to be compared with near temperature independence in CePd$_3$ [7] and a decrease with increasing temperature in YbCuAl [8]. The persistance of fluctuations to low temperatures in this model implies that even though there is a gap against excitations [1] the Sm spin is not a quantum number of the IV ground state; the fluctuations are a form of zero-point motion.

The "characteristic temperature" $T_\chi = C/\chi(T=0)$, where C is the Sm^{3+} Curie constant, is often used as a measure of the spin fluctuation temperature [13]. Its value in SmB$_6$ is 27 K, which is in order-of-magnitude agreement with the NMR estimate at 4.2 K.

An alternate hypothesis, that the observed low-temperature relaxation originates from impurity-band states associated with Sm ions in the neighborhood of vacancies, has been alluded to above. In this model the boron relaxation is dominated by fermion excitations in the impurity band. Inhomogeneity associated with the band offers an explanation of the increased nonexponentiality in the magnetization recovery at low temperatures (Fig. 1), as well as the field dependence of T_1. The latter is in analogy with results in heavily doped Si:P [14].

A certain amount of evidence exists, however, which indicates that the band-relaxation model may not fully explain the data. First, the bulk susceptibility [15] and the ^{11}B shift data show only a weak dependence on stoichiometry. Second, for shift and relaxation rate determined by band excitations one expects a Korringa relation of the form

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$$K_i^2 T_1 T = S_o \equiv \hbar(\gamma_e^2/\gamma_n^2)4\pi k_B, \qquad (3)$$

where γ_e is the free-electron gyromagnetic ratio, to hold to within an enhancement factor of the order of unity [11]. Experimental values of the ^{11}B Korringa constant $(K_i^2 T_1 T)_{exp}/S_o$ range in fact between 1.5 and 8 depending on the value of K_i used. But if the measured K_i is not very dependent on stoichiometry, then the impurity-band contribution to K_i is much smaller than the measured value, and the Korringa constant (assuming T_1 to be dominated by the impurity band) is much smaller than unity. This argument must be used with care, since data on the stoichiometry dependence of the shift (and relaxation) are scarce. In any event ^{29}Si NMR in Si:P [14] (10^{19} impurities/cm^3, T = 0.55 K) yields a Korringa constant of 1.7 as expected.

The data therefore do not decide unambiguously in favor of either model. Roughly equal contributions of IV and impurity-band fluctuations may also determine relaxation in our specimen. Clearly measurements on more nearly stoichiometric samples are required to resolve this point.

The large increase in relaxation rate above 20 K is probably a reflection of additional Sm relaxation by the same thermal excitations (conduction-band electrons in a gap model) which restore metallic conduction at high temperatures.

QUADRUPOLE RELAXATION AND CHARGE FLUCTUATIONS

We consider a crude model for the combined effect of magnetic and quadrupolar relaxation on the ith boron isotope (i = 10,11). Expressions for the separate relaxation rates T_{1M}^{-1} and T_{1Q}^{-1} are given by Abragam [16]; we add these to obtain the total rate T_{1i}^{-1}:

$$T_{1i}^{-1} = \frac{2}{3}(\gamma_i H_{hf})^2 \tau_{sf} + \frac{3}{40}\frac{2I_i+3}{I_i^2(2I_i-1)}\left(\frac{e^2 qQ_i}{\hbar}\right)^2 \tau_{cf} \qquad (4)$$

where I_i is the nuclear spin and τ_{sf} and τ_{cf} are the spin and charge fluctuation times respectively. We estimate the amplitude of the fluctuating component of $e^2 qQ/h = 0.17$ MHz from the NMR studies of quadrupole interactions in a series of 2+ and 3+ rare-earth hexaborides by Aono and Kawai [17]. Then the absence to within 10% of quadrupolar contributions to the measured T_{1i} described above puts an upper bound of $\sim 2.8\tau_{sf} \sim 10^{-12}$ sec on the charge fluctuation time τ_{cf}. One expects τ_{sf} to be longer than τ_{cf} due to Coulomb correlation effects [18]; the experimental bound is consistent with this expectation.

In the presence of correlated spin and charge fluctuations, which might be expected from IV ions [18], the possibility of a cross term in the nuclear relaxation must be examined. In the extreme narrowing limit appropriate to SmB$_6$ and in the spin temperature approximation, the following expression for the nuclear relaxation rate can be obtained [19]:

$$T_1^{-1} = -\overline{\text{tr}[H_o, H_1(t)]^2}\, \tau/\text{tr}(H_o^2). \qquad (5)$$

Here H_o is the time-independent term in the nuclear hamiltonian, $H_1(t)$ is the fluctuating coupling to the lattice, and τ is a suitably defined correlation time. The traces are over nuclear spin operators, and the bar indicates an ensemble average. If $H_o \propto I_z$ describes a Zeeman coupling to the applied field, and $H_1(t) = H_1^{(M)} + H_1^{(Q)}$ is the sum of a magnetic and a quadrupolar term, then it can easily be shown that the cross-term commutator trace

$$\text{tr}[I_z, H_1^{(M)}(t)][I_z, H_1^{(Q)}(t)]$$

vanishes. Therefore the potentially informative correlated nature of the spin and charge fluctuations has no effect on nuclear relaxation.

In conclusion, we suggest that theoretical models of valence fluctuations in SmB$_6$ should be investigated for predictions of ground-state Sm moment lifetimes and for the effect of thermal excitations, to be compared with the results of this study.

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