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NUCLEAR SPIN RELAXATION, HYBRIDIZATION, AND LOW-TEMPERATURE 4f SPIN FLUCTUATIONS IN INTERMEDIATE-VALENT SmB_6

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^{11}B spin-lattice relaxation measurements have been carried out in SmB_6 samples with large low-temperature resistivities. Above 15 K the relaxation is activated, with approximately the same gap (∿6 meV) as found previously in transport and optical measurements. 4f spin fluctuations apparently dominate the relaxation, so that these results give strong evidence for 4f-conduction band hybridization at the gap edge. An anomalous peak in the relaxation rate was observed at ∿5 K, which is tentatively attributed to fluctuations of "remagnetized" Sm^{3+} ions near Sm-site vacancies.

Highly-resistive intermediate-valent (IV) rare-earth compounds such as SmS under pressure, TmSe, and SmB_6 have recently been the subjects of considerable theoretical and experimental attention.[1] These materials exhibit large and poorly-understood departures from the Fermi-fluid behavior[2] which characterizes IV compounds with metallic resistivities. In SmB_6, for example, it is generally agreed that a gap of 5 to 10 meV describes transport,[3] optical,[4-5] and tunneling[5] properties. This gap has been ascribed to 4f-conduction band hybridization,[6] Anderson localization,[7] and Wigner lattice formation;[8] its presence makes SmB_6 a small-gap semiconductor.

Nuclear spin-lattice relaxation measurements in magnetic systems yield information on the strength and low-frequency fluctuation spectra of electronic spin excitations.[9] In metallic IV systems 4f spin fluctuations are effective and sometimes dominant relaxation mechanisms;[10] this effectiveness would also be expected in the highly-resistive IV materials. If relaxation is due to states at a gap edge, the relaxation rate $1/T_1$ should be activated: $1/T_1 \propto \exp(-E_a/k_BT)$, where E_a is the activation energy.

We report here ^{11}B NMR data obtained from a highly resistive, hence relatively defect-free SmB_6 specimen. Comparison of these and earlier NMR results[11] has enabled us to clarify the role of defects, and in particular to verify the defect independence of the activated behavior ($E_a = 5.6 \pm 0.5$ meV) previously observed above 15 K. Below this temperature $1/T_1$ exhibits an anomalous increase to a maximum at about 5 K. This feature was partially masked in previous measurements[11] by defect-induced inhomogeneous relaxation, which seems to be less evident in the present data.

The flux-grown specimen was obtained in the form of small single crystals. Four-probe resistance measurements yielded a residual resistance ratio (RRR) $\rho \equiv R(4.2K)/R(300K) = 1.9 \times 10^4$, which compares favorably to other specimens prepared in this manner.[3] NMR spectra and longitudinal relaxation functions were observed using a pulsed spin-echo spectrometer and standard techniques.[10,11] The large low-temperature resistivity of the sample allowed radiofrequency field penetration into the as-grown crystals below about 10 K; powdering of the sample, to permit NMR measurements at higher temperatures, had no effect on the relaxation rate at 4.2 K.

^{11}B field-swept spectra were obtained between 1.5 and 300 K on specimens with $10^3 \lesssim \rho \lesssim 2 \times 10^4$. The isotropic frequency shift K_i and the quadrupole coupling constant e^2qQ were found to be independent of temperature and ρ

within the above ranges: $K_i = -0.05 \pm 0.01$ %, and $e^2qQ/h = 1.185 \pm 0.010$ MHz.

The relaxation function $\Delta M_z(t)$, which describes the return of the longitudinal nuclear magnetization to equilibrium following saturation, was observed for several SmB_6 samples as well as for the isostructural nonmagnetic compound LaB_6. In the latter metallic system available data[12] are consistent with a Korringa law $T_1T \sim 10^3$ sec-K at 4.2, 77, and 300 K. The relaxation rates in SmB_6 are more than an order of magnitude faster than in LaB_6 at all temperatures, so that the Korringa mechanism appears to be negligible in SmB_6. Below 15 K $\Delta M_z(t)$ begins to exhibit a nonexponential character which, because of its temperature dependence, is not likely to be due to the quadrupole splitting of the ^{11}B resonance[11,13] but rather to a spatial distribution of relaxation rates in the sample due to defects.[10,11] Neither the degree of nonexponentiality nor the long-time asymptotic relaxation rate $1/T_1$ were observed to be very dependent on RRR within the range investigated, although some dependence of $1/T_1$ on applied magnetic field was seen in an imperfect sample ($\rho = 1.4 \times 10^3$). Such field dependence is a characteristic of defect-induced relaxation.[10,14]

The temperature, magnetic field, and sample dependence of $1/T_1$ are shown in Fig. 1, where it can be seen that, although data from the low-RRR sample are not accurate at low temperatures, there is little systematic dependence of $1/T_1$ on RRR. The two striking features of these measurements are the activated behavior at high temperatures, and the anomaly at 5 K. The former clearly indicates that the Sm spin fluctuations responsible for the relaxation are due to states at the edge of a gap in the excitation spectrum. The fact that approximately the <u>same</u> gap energy characterizes both 4f spin fluctuations and the itinerant electron states responsible for transport properties[3] strongly supports a 4f-conduction band hybridization model for the origin of the gap.[6] It is hard to see how this result would obtain for models in which low-temperature conduction is prevented by defects.[7,8]

The anomaly in $1/T_1$ is most clearly seen in the data for the purest sample (circles and dashed curve of Fig. 1). There is a suggestion of an anomaly in the specific heat in this same temperature range.[8] Since most explanations of the low-temperature transport properties invoke residual disorder,[6-8] it is natural to compare our NMR results with corresponding data from the well-characterized disordered semiconductor Si:P. Here no $1/T_1$ anomaly was observed either above or below the metal-insulator transition at $\sim 3 \times 10^{18}$ donors/cm^3.[14]

An increase in $1/T_1$ with decreasing temperature is often associated with a decrease in the rate of fluctuations of

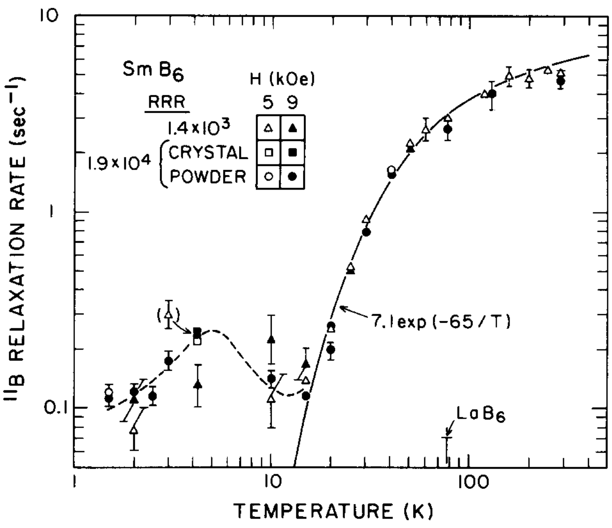

FIG. 1. Temperature dependence of the ^{11}B relaxation rate in SmB_6. Solid curve: high-temperature Arrhenius law describing activated relaxation. Dashed curve: low-temperature anomaly, seen most clearly in the data for residual resistance ratio $\rho = 1.9 \times 10^4$. An upper bound on $1/T_1$ for LaB_6 at 77 K is also shown; at 4.2 K $T_1(LaB_6) \gtrsim 250$ sec.

local fields at the nuclei.[9] If the fluctuation rate falls below the NMR precession frequency, the nuclear relaxation rate passes through a maximum and develops a field dependence at lower temperatures. This field dependence is not observed in the purest sample (Fig. 1), so that the maximum appears to be due to a decrease in fluctuation amplitude at low temperatures rather than an increase in fluctuation time.

Evaluation of models for the anomaly is hampered by lack of precise defect characterization in nearly pure SmB_6. One picture[7] attributes Sm^{3+} formation to the presence of neighboring Sm-site vacancies. These or other paramagnetic centers might then relax surrounding ^{11}B nuclei, with diffusion of spin energy between nuclei[15] smoothing out some of the inhomogeneity in T_1. We have used spin-echo decay measurements to estimate the spin-diffusion constant D crudely at 10^{-14} cm^2/sec at 4.2 K. This yields a homogeneous T_1 only if the average distance between impurities is less than $(DT_1)^{1/2} \sim 20$Å at 4.2 K, which corresponds to an impurity concentration of the order of 10^{-3} mole fraction or greater. Determination of impurity concentrations at this low level is difficult. Susceptibility measurements on our NMR samples have revealed low-temperature Curie-Weiss "tails" which, if attributed to Sm^{3+} spins as outlined above, yield impurity concentrations of the order of 10^{-2} mole fraction. This is larger than the crude lower limit established above, so that defect-induced spins could cause the anomaly. The maximum in $1/T_1$ might be explained by local spin ordering due to intracluster exchange, in which the temperature of the maximum would be of the order of the exchange constant and roughly independent of concentration as observed. The insensitivity of the magnitude of $1/T_1$ to changes in RRR remains puzzling.

Another candidate for the anomaly is hindered rotation of boron octahedra.[8,16] Even though these phonon modes, if fully excited, could give the observed order of magnitude of $1/T_1$,[9] such rotation would also give rise to temperature-dependent motional narrowing of the quadrupole-split NMR spectrum.[17] This is not observed. In addition the phonon spectra of SmB_6 and LaB_6 should be similar,[8] and the anomaly is not present in LaB_6 as noted above. This is not surprising: the phonon energies have been estimated[16] at $\sim$40 meV >> k_BT at 5 K.

To conclude, the activated spin-lattice relaxation above 15 K in SmB_6 demonstrates that Sm 4f states are found at the edge of an energy gap, as is also true of conduction states which govern transport properties. This is a positive indication of the role of hybridization in the formation of the gap.[6] The anomaly below 15 K is probably associated with impurities which, however, have remarkably little correlation with the RRR. It is tempting to speculate on the possible existence of intrinsic relaxation mechanisms, such as low-lying non-hybridizing 4f states,[10,18] although we know of no theoretical expectation or corroborating experimental evidence for low-frequency fluctuations associated with such states.

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