Novel Function of the Boron Icosahedron; a New Mediator of Magnetic Interaction

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ABSTRACT

Rare earth borides containing the B_{12} icosahedron display surprisingly strong magnetic interactions although they are magnetically dilute insulating materials with localized f-electrons. A microscopic local probe, ESR, was utilized to investigate the mechanism of the interaction. From detailed analysis of the spectra of a ladder-like Gd borosilicide, it was indicated that the Gd atoms are coupled along the 1D infinite chain of the atomic ladder rather than between the rungs which is actually the shorter metal-metal spacing. The 1D atomic chain is along an infinite chain of B_{12} icosahedra and this result is consistent with the idea that the boron icosahedra clusters are functioning as a new mediator of magnetic interaction.

Keywords: borides, f electron, antiferromagnetic, icosahedra, ESR

1 Introduction

Intensive research is being carried out on carbon nanostructures. The neighbor to carbon in the elemental table, boron, has also been known to form nanostructures of atomic clusters, but due to the electron deficiency they are usually found as structural units of strongly covalent compounds. We have been able to find striking phenomena in which it is indicated that the boron cluster as a nanostructural unit is supplying a novel function to the compound as a whole.

As background, we have previously discovered unusual magnetic behavior in rare earth boron compounds containing the B_{12} boron icosahedron [1]–[7]. Although they are magnetically dilute insulating materials with localized f-electrons, they display surprisingly strong magnetic interactions. A wide range of magnetic behavior ranging from dimer-like magnetic behavior in REB_{50}-type compounds [1], [2], 2D spin glasses in a homologous series of compounds $REB_{17}CN$, $REB_{22}C_2N$, $REB_{28.5}C_4$ [3]–[6], and 3D long range order in $GdB_{18}Si_5$ [7] have been observed for rare earth B_{12} icosahedral compounds. Despite these systems being magnetically dilute insulating systems, surprisingly strong magnetic interactions (e.g. T_f = 29 K for $HoB_{17}CN$) have been observed [1]–[7].

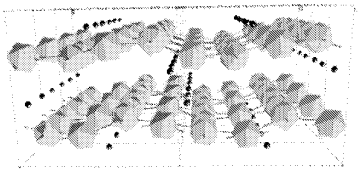

Figure 1: View of the crystal structure of $GdB_{44}Si_2$. The polyhedra indicate B_{12} icosahedra and the large dark circles indicate Gd. For visual clarity, among the five structurally independent B_{12} icosahedra, only the two nearest to the RE atoms are plotted.

Regarding a related topic of novel magnetism in borides, the high temperature ferromagnetism reported in Nature and Science for semiconducting CaB_6 and CaB_2C_2 systems has attracted great interest. We have clearly demonstrated that they are indicated to be non-intrinsic phenomena originating from iron impurities [8], [9].

In this work, a microscopic local probe, ESR, was utilized to investigate the mechanism of the interaction in these novel systems. ESR was performed on a Gd borosilicide compound, the REB_{50}-type $GdB_{44}Si_2$ in which the rare earth atoms are arranged in a ladder-like array (Fig. 1).

2 Experimental

In order to perform ESR measurements we tried to prepare a Gd phase compound of the REB_{50} phase because it is $^8S_{7/2}$ and convenient for ESR analysis. As has been pointed out previously [10], the GdB_{50} compound will not form because of the large size of the gadolinium atoms. However, the addition of a small amount of silicon was found to increase the lattice constants and an isotypic gadolinium borosilicide was formed [10].

ESR measurements at the X band were performed using a JEOL JES-TE100 spectrometer with an ES-CT470 helium liquid transfer refrigerator for 4 - 300 K. As a standard we used Mn^{2+} in MgO.

The structure of $GdB_{44}Si_2$ is orthorhombic (space group Pbam). The lattice constants of $GdB_{44}Si_2$ are a = 16.746 Å, b = 17.731Å, and c = 9.565 Å. The rare earth atoms form infinite ladders in the direction of the c-axis. Within the ladder the chains have alternating

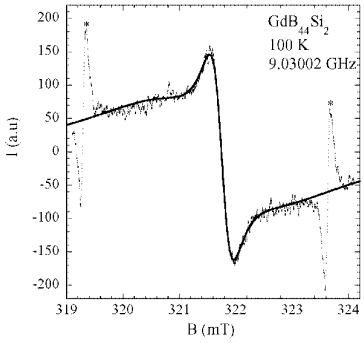

Figure 2: Typical ESR absorption line of $GdB_{44}Si_2$ at 100 K. The line depicts the fit as 2 Lorentzian curves which are described by Eq. 1. Astericks indicate the standard MgO:Mn^{2+} signals.

bonds, with separation of 4.39 Å and 5.18 Å. These chains are separated from one another in the a-b plane by 3.98 Å to form the ladder.

3 Results and Discussion

First of all, we review the basic magnetic properties of $GdB_{44}Si_2$. From the magnetic susceptibility a Curie-Weiss temperature of θ =-7.2 K was determined, but due to a large low temperature tail a drop in the susceptibility was not clearly observed [10]. The magnetic specific heat C_m exhibits a broad peak at T ∼4 K.

A typical ESR line obtained for $GdB_{44}Si_2$ is shown in Fig. 2. Since modulation field is applied, we obtain a derivative of the absorption. It is obvious that there appear to be two signals comprising the ESR absorption line, a narrow signal and broad one. The signals were analyzed by fitting with two Lorentzian curves, broad and narrow, which gave a relatively good fit.

The Lorentzian lineshape is given by the form

$$I_0/((B - B_0)^2 + B_1^2), \quad (1)$$

where I_0 is proportional to the intensity, B is the magnetic field, B_0 is the resonance field proportional to the g factor, and B_1 is proportional to the peak to peak linewidth. The signals we obtain here are the derivative of the above equation. We do not observe any fine structure such as has been observed for Gd^{3+} doped CaB_6, for example [11]. This can be attributed to the higher concentration of Gd and relatively strong coupling in $GdB_{44}Si_2$ which apparently results in exchange narrowing of the ESR spectra. This agrees with the Lorentzian shape observed.

The origin of two signals, narrow and broad, appearing in this Gd^{3+} $^8S_{7/2}$ system is not so clear. Because of the distinctness of the narrow signal compared to the broad signal, we discuss in detail the temperature dependence of the parameters determined for the narrow

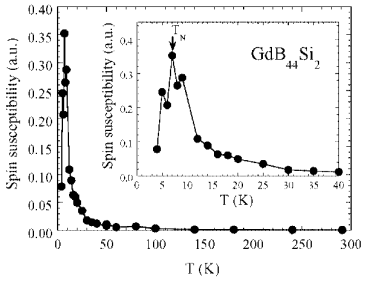

Figure 3: Temperature dependence of the ESR spin susceptibility (closed circles) of the distinctive narrow component of $GdB_{44}Si_2$ determined as $\sigma \propto I_0 B_1^4$.

signal. The broad signal parameters had more error but a simulation showed that such variations do not largely affect the parameters of the distinct narrow signal. As will be seen later, the temperature dependence definitely indicates that our ESR spectra originating from Gd^{3+} rather than coming from the low temperature tail observed in the static susceptibility, for example. Furthermore, crystal field effects are not large in our system based on $\mu_{\rm eff}$/Gd atom = 7.87 μ_B [10] which agrees well with free Gd^{3+} values, and therefore the g factors of ∼2 that we obtain for our signals are reasonable for Gd^{3+}. Regarding the origin of 2 signals appearing, we note that Zorko et. al similarly observed 2 signals, narrow and broad, for a low dimensional dimer system [12]. From input from inelastic neutron scattering measurements they were able to assign the 2 signals as isolated and correlated triplet excitations. We are unable to carry out such an analysis at present, but in any case, the following parameters obtained from our spectra will be seen to give important information on the intrinsic magnetism of the system.

From the ESR absorption resonance intensity areas we can determine the temperature dependence of the spin susceptibility. We note that for the area to be actually proportional to the susceptibility, either linewidth should be much narrower than the center field of the resonance line or the response of the spin system should be described by Bloch's equation. Our X band ESR measurements satisfy the former condition and furthermore, the signals could be fit well with Lorentzian shapes which are characteristic of solutions to Bloch's equation.

In Fig. 3 is plotted the temperature dependence of the spin susceptibility determined for the narrow signal. We calculate the spin susceptibility as $\sigma \propto I_0 B_1^4$. The striking feature of the data is the drop below 7 K. As noted, we were previously unable to discern clearly a transition from the magnetic susceptibility results [10] but the microscopic ESR results indicate a transition occurring at $T_N = 7$ K. The peak in C_m at T_* is sizably lower than T_N ($T_* \sim 0.6T_N$) and a model to analyze the specific heat should be formulated next. Another

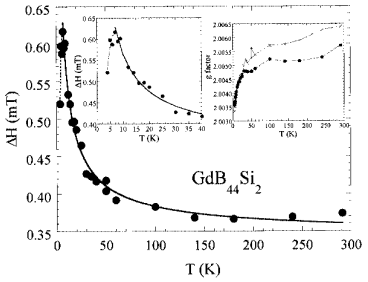

Figure 4: Temperature dependence of the ESR linewidth ΔH of the distinctive narrow component of $GdB_{44}Si_2$. The solid line describes the fit to $\Delta H = aT^{-p} + \Delta H_0$, with a =1.2 p =0.72 and ΔH_0=0.34 mT. The insets show an enlarged view and also the temperature dependence of the g factors of the narrow (circles) and broad (crosses) signals.

important point is that we can see that the susceptibility appears to go to 0 as T $\rightarrow$ 0. The spin susceptibility for an S=1/2 antiferromagnetically coupled dimer can be given by [13]

$$\chi = Ng^2\mu_B^2/k_BT1/(3 + exp[-2J/k_BT]), \qquad (2)$$

which does not fit our data well but unfortunately we were unable to obtain an expression for an S=7/2 system.

The g factors of the narrow and also the broad signal are plotted in the inset of Fig. 4. At room temperature the g factors are 2.0057 and 2.0064, respectively. At high temperatures there is a small temperature dependence, but strikingly, a large decrease in the g factors of both signals are observed below $\sim$30 K. This points to the growth of short range correlations and supports the fact of a magnetic transition occurring in this system.

The temperature dependence of the linewidth defined as the width between the derivative peaks (in the case of a Lorentzian; $1.15B_1$) is shown in Fig. 4. The linewidth increases monotonically with increasing temperature and shows a peak at T = 7 K. In 3D antiferromagnets the ESR linewidth diverges critically as the temperature is lowered toward the transition temperature T_N. Behavior of the linewidth near the transition has been calculated theoretically by Kawasaki [14], to be

$$\Delta H \propto (T - T_N)^{-p}. \qquad (3)$$

This divergent behavior has been qualitatively observed for other gadolinium borides like GdB_6 and GdB_4 which have 3D antiferromagnetic transitions [15]. We note the behavior of the linewidth in $GdB_{44}Si_2$ in Fig. 4 is strikingly different from a 3D antiferromagnetic system. There is no divergence as the transition temperature is approached but rather a drop in the magnitude of linewidth. We first consider theoretical aspects of the linewidth of ESR. In general, many contributions to the linewidth should be taken into account, such as inhomogeneous broadening, broadening due to spin-phonon relaxation, dipole-dipole interaction, hyperfine interaction etc., and motional exchange narrowing of these effects. Kubo [16] has shown that if relaxation is governed by a random process the Fourier transform of the lineshape, namely the relaxation function, has the form

$$\phi(t) = exp\left[-\omega_d^2 \int_0^t (t-\tau)\psi(\tau)d\tau\right], \qquad (4)$$

where $\omega_d^2 = \langle\, \omega(0)^2\rangle$ is the second moment of the resonance line and $\psi(\tau)$ is the spin correlation function.

Kubo and Tomita [17] originally derived that the exchange narrowing of the dipolar linewidth due to exchange-induced fluctuations rapidly averaging the dipolar field (motional narrowing) is given by

$$\Delta\omega \sim \omega_d^2/\omega_e, \qquad (5)$$

where $\Delta\omega$ is the observed linewidth and ω_e is the exchange frequency with $\omega_e \gg \omega_d$, with the spin correlation function falling off exponentially as $\exp(-\omega_e^2 t^2/2)$. Later it was realized that at times long compared to $1/\omega_e$, the spin correlation function is governed by spin diffusion. The diffusive process gives a decrease of the spin correlation function as $t^{-d/2}$ [18], where d is the dimensionality of the system. Therefore, the Fourier transform of the correlation function, which defines the spectral density $\phi(\omega)$ (contributing to the linewidth), diverges as $\omega^{-1/2}$ in 1 dimensional and as -lnω in 2 dimensional systems, with no frequency dependence for 3 dimensional system. Using this theoretical framework Cheung et. al has calculated the temperature dependence of exchange narrowing in a 1D antiferromagnet with classical spins [19]. Since it is a numerical study it is difficult to directly compare our results but we observe a similar increase toward T=0 (nondivergent for T$\neq$0) and a sharp drop at low temperatures near θ. This 1D model can explain the unusual characteristic features of ΔH(T) of $GdB_{44}Si_2$ which is obviously also a classical spin system.

Previously, we have found upon non-magnetically diluting $TbB_{44}Si_2$ samples that the critical field H_C of the metamagnetic transition does not vary even up to a dilution of 50 % [2]. The critical field H_C is a measure of the strength of the magnetic coupling. The doping has also been observed to result in a correlated increase of free Tb spins. These results indicate the antiferromagnetic transition in $TbB_{44}Si_2$ is of dimer-like nature, where non-magnetic substitution leads to broken pairs resulting in free spins.

There are two possible configurations for the magnetic pairs to be formed. Looking at close metal-metal separation, pairs are likely to be formed (a) between the rungs of the rare earth ladder (3.98 Å separation) or (b)

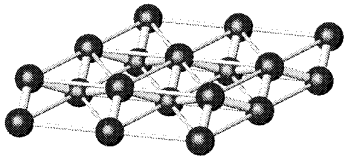

Figure 5: Arrangement of only RE atoms of the homologous RE-B-C(N) compounds [3]-[6].

along the ladder and the c-axis (an alternating 4.39 Å and 5.18 Å separation). We disregard other possible pairings since the distances are sizably larger. The former situation is persuasive due to the short separation, but the latter is also likely since the rare earths form an alternating-bond chain along the c-axis which is favorable for forming dimers. The present ESR results are compatible with the 1D model which indicates that the magnetic ions are forming pairs along the c-axis in a one dimensional arrangement.

In a phenomenological treatment of the linewidth, Ajiro et. al observed for a 1D S=1/2 system the line width increases with decreasing temperature in the form; $\Delta H \propto T^{-1.2\pm0.2}$ at low temperatures [20]. For our $GdB_{44}Si_2$ compound we can empirically obtain the power law as $\Delta H = 1.2T^{-0.72} + 0.34$ as is described by the solid line in Fig. 4. The exponent of our S=7/2 $GdB_{44}Si_2$ is lower than the S=1/2 system, but we note that for a more classical spin of S=5/2, Fernandes et. al has observed $\Delta H \propto T^{-0.46}$ for the 1D $MnMgB_{25}$ system [21] and the agreement is better. It would be of worth to systematically compare 1D systems with different spin value to see whether this simple empiric relation has intrinsic meaning.

Regarding the mechanism of interaction we consider the following. From our recent work on the homologous RE-B-C(N) 2D spin glasses [3]–[6], it has been indicated that the B_{12} icosahedra are mediating the magnetic interaction between the rare earth ions. This is because the strongest interaction is indicated to occur along a metal-metal separation (5.62 Å, e.g. $HoB_{22}C_2N$) which is in proximity to B_{12} icosahedra. A shorter metal-metal separation (3.54 Å, e.g. $HoB_{22}C_2N$) which is not along B_{12} icosahedra is indicated to give much weaker coupling (as normally expected for a dilute insulating f-electron system) despite the much shorter distance (Fig. 5).

The idea that the boron icosahedra clusters are mediating the magnetic interaction is further supported by the present results. The interaction has been indicated to be dominant along the infinite rare earth atomic chain along the c-axis. This rare earth chain is adjacent to B_{12} icosahedral infinite chains and therefore, it is indicated that the B_{12} icosahedra play a role to mediate the interaction.

The author is grateful to Mr. Y. Yajima for performing chemical analyses on the samples.

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