Different Gd$^{3+}$ sites in CaB$_6$: an ESR study

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The local environment of Gd$^{3+}$ (4$f^7$, $S = 7/2$) ions in single crystals of Ca$_{1-x}$Gd$_x$B$_6$ (0.0001 $\lesssim x \lesssim 0.01$) is studied by means of Electron Spin Resonance (ESR). The spectra for low concentration samples ($x \lesssim 0.001$) show a split spectrum due to cubic crystal field effects (CFE). The lineshape of each fine structure line is lorentzian, indicating an insulating environment for the Gd$^{3+}$ ions. For higher concentrations (0.003 $\lesssim x \lesssim 0.01$), the spectra show a single resonance ($g = 1.992(4)$, $\Delta H_{1/2} \approx 30 - 60$ Oe) with no CFE and dysonian lineshape indicating metallic environment for the Gd$^{3+}$ ions. For intermediate concentrations, a coexistence of spectra corresponding to insulating and metallic regions is observed. Most of the measured samples show the weak ferromagnetism (WF) as reported for Ca$_{1-x}$La$_x$B$_6$ ($x \approx 0.005$), but, surprisingly, this WF has no effect in our ESR spectra either for metallic or insulating environments. This result suggests that the ferromagnetism in these systems may be isolated in clusters (defect-rich regions) and its relationship with metallicity is nontrivial.

The weak ferromagnetism (WF) and Curie temperature of roughly 600 K recently reported by Young et al. in lightly-La doped calcium hexaborides (Ca$_{1-x}$La$_x$B$_6$ ($x \sim 0.005$) has fueled interest from theorists and experimentalists. It has, for example, revived interest in the physics of the so called "excitonic insulators", vigorously discussed in the 60's and 70's. However, recently, controversial experimental results have been reported creating extensive discussion. For example, Vonlanthen et al. reported that CaB$_6$ sample close to stoichiometry does not show WF but instead one deficient in Ca is magnetic. Moriwaka et al. argued that FM is induced by Ca vacancies in CaB$_6$ and speculated that a lowering of the crystal symmetry may play a role in its origin. Monnier et al. claimed that a neutral B$_6$ vacancy would be more effective to induce FM. Gianò et al. suggested that the defects are predominantly donors, providing partly itinerant and partly localized electrons. Terashima et al. reported that the data in Ca$_{0.995}$La$_{0.005}$B$_6$ is sample dependent. Kuwii observed a highly anisotropic ferromagnetic resonance (FMR) line in Ca$_{0.995}$La$_{0.005}$B$_6$ and concluded that the spins are confined within a surface layer of $\sim 1.5$ um thick, which leads to a magnet moment several orders of magnitude larger than that obtained for the bulk. Dengler et al. measured photoemission spectroscopy and found a large difference between the electronic structure of the surface and that expected for the bulk. All these results have raised many questions about the remarkable properties of these hexaborides compounds, such as: i) Is the WF in the bulk or just in the surface of the material? ii) What kind of defects are present in these compounds, and how do they dope these materials? iii) Is there a FMR in Ca$_{0.995}$La$_{0.005}$B$_6$? iv) Is there is a reduction in the cubic symmetry of the crystal or change in the EPR spectra at the ordering temperature? and v) What kind of correlation exist between magnetic and transport properties in these hexaborides?

Despite the experimental controversies, recent ambitious theoretical communications using different approaches have tried to explain the WF in these materials. In particular, Tromp et al. suggest that CaB$_6$ is a semiconductor with a band gap of 0.8 eV and that the magnetism in the La doped hexaborides occurs on the metallic side of a Mott transition in the La-induced impurity band. However, earlier models rely on electronic structure calculations, which claimed that CaB$_6$ is a semimetal with a small overlap of the conduction and valence bands at the X point of the Brillouin zone. However, a complete and conclusive modeling of this phenomenon that includes all of the experimental results is still missing.

In this letter we present ESR, magnetization and resistivity results in Ca$_{1-x}$Gd$_x$B$_6$ (0.0001 $\lesssim x \lesssim 0.01$). ESR is a powerful local experimental technique that can used to probe the microscopic properties of these materials. Our main findings are: i) an unusual CFE is observed in the ESR spectra of diluted Gd$^{3+}$ in CaB$_6$; coexistence of Gd$^{3+}$ sites with and without crystal field (CF) splitting is found, ii) the ESR spectra of Gd$^{3+}$ are not affected by the presence of WF in these systems, iii) We found no evidence for a reduction of the cubic symmetry in these compounds, and iv) the WF in these materials is a bulk property which is strongly sample and doping dependent with nontrivial correlation with metallicity. As we will discuss, these results serve to substantially constrain the range of models applicable to the WF in these materials.

More than fifty single crystalline Ca excess/deficient/stoichiometric samples of Ca$_{1-x}$R$_x$B$_6$ (0.0001 $\lesssim x \lesssim 0.01$, R = La, Gd,
Er) were grown as described in ref. [1]. The structure
and phase purity were checked by x-ray powder diffraction
and the orientation was determined by Laue x-ray diffraction.
The ESR experiments were carried out in a Bruker X-band spectrometer, using a TE$_{102}$ room-$T$ cavity and a helium gas flux (4.2 K – 300 K) temperature controller. The magnetization measurements between 2 K and 800 K were made in a Quantum Design SQUID dc-magnetometer. Electrical resistivity was measured using a low-frequency $ac$-resistance bridge and 4-contact configuration. The concentration for all the samples reported in this work was deduced from Curie-Weiss fits of the low-$T$ susceptibility data.

Results shown here span the full range of properties observed among the more than fifty samples studied. Figures 1a, 1b, and 1c show the ESR, $M_{dc}(T)$, and $M_{ac}(H)$ data for three of our $\text{Ca}_{1-x}\text{Gd}_x\text{B}_6$ samples ($x = 0.0003, 0.003, 0.01$). Electrical resistivity, $\rho(T)$, for the data for $x = 0.0003$ and $x = 0.003$ are also shown in Fig. 1. All these samples show a WF component and $T_C$ between 600 K and 800 K. The data are qualitatively similar to that of $\text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6$ reported by Young et al. [4]. However, the WF component (saturation magnetic moment) for the $x = 0.0003$ and $x = 0.003$ samples is estimated to be $\sim 3$ and $\sim 0.16 \mu_B/\text{Gd}$, respectively, which are much larger than that reported in ref. 1 and there is no clear systematic between $x$ and the WF component.

For $X$-band measurements on insulators, the Gd$^{3+}$ ions in a cubic-site symmetry usually show a characteristic CF split ESR spectrum with fine structure of seven lorentzian lines of well defined relative intensities due to their transition probabilities and population Boltzmann factor. [4] The different Gd$^{3+}$ spectra of Fig. 1 show that there are two different Gd$^{3+}$ sites. For samples of low concentration ($x \lesssim 0.0003$, Fig. 1a) the spectra show the typical fine structure due to cubic CF of insulators. The high concentration samples ($0.003 \lesssim x \lesssim 0.01$, Fig. 1c) show a single resonance with a dysonian lineshape ($A/B \approx 2.2$) characteristic of skin depth smaller than the size of the sample. [7] No CFE were observed in this resonance. Absorption/dispersion lineshape analysis of this resonance between 4.2 and 50 K yields a $T$-independent $g$-value ($g \approx 1.990(6)$) and linewidth ($\Delta H_{1/2} \approx 80 \text{ Oe}$). For samples of intermediate concentration ($0.0003 \lesssim x \lesssim 0.003$, Fig. 1b) the ESR spectra show the coexistence of both Gd$^{3+}$ sites. In addition, $\rho(T)$ data for $x = 0.0003$ and $x = 0.003$ taken on different crystals from the same batches (with the same measured WF component) show metallic-like behavior and comparable absolute values for both $x = 0.0003$ and $x = 0.003$ samples.

Figures 2a and 2b show the ESR spectra for a set of samples similar to those of Fig. 1. Although the ESR spectra show similar features ($g$-values, linewidths, and two Gd$^{3+}$ sites) all of them presented smaller saturation magnetic moment ($\lesssim 0.5 \text{ emu/mole f.u.}$) than those of Fig. 1. Also, we found that some of the undoped Ca excess/deficient/stoichiometric samples presented an even smaller, but measurable, saturation magnetic moment ($\lesssim 0.1 \text{ emu/mole f.u.}$). In this case, samples are found consistently to be insulator-like by ESR and resistivity. See data for $x = 0.0001$ in Fig. 2a. Hence, it is clear from the results of Figs. 1 and 2 that the Gd-doping contributes to the WF in these systems, but it is also true that the WF is strongly sample dependent.

In some of the as grown crystals we also observed an extra isotropic resonance at $g = 2.0028(6)$ with a lorentzian lineshape and linewidth of $\Delta H_{pp} \approx 7 \text{ Oe}$. This resonance could be eliminated by gently etching and/or polishing the crystal surfaces (see Fig. 2a for $x = 0.0001$). We associate this resonance with an unidentified ESR active center on the surface of the crystals. Surface etching and/or polishing did not affect the ESR spectra or $M_{dc}(T, H)$ data shown in Figs. 1 and 2. Fig. 2b shows the ESR spectra for one of the lowest Gd concentration samples ($x \lesssim 0.00005$). This spectrum shows, besides the small resonances of Gd$^{3+}$, the typical spectrum due to natural impurities of Eu$^{2+}$ in cubic symmetry with fine and hyperfine structure ($4f^7$, $S = 7/2$, $^{151}\text{Eu}^{2+}$ and $^{153}\text{Eu}^{2+}$ isotopes, $I = 5/2$).

Figure 3a presents the angular dependence in the (110) plane of the ESR spectra of Figure 3b. This angular dependence corresponds to that expected for Gd$^{3+}$ ions, ($4f^7$, $S = 7/2$), with cubic site symmetry. [10] The solid lines are fits obtained from the Spin Hamiltonian, $\mathcal{H} = g_\mu_B HS + b_4 O_4 + b_6 O_6$, to the data assuming cubic CF and an isotropic $g$-factor. [10] The different intensity between the transitions $-5/2 \leftrightarrow -7/2$ and $7/2 \leftrightarrow 5/2$ at low-$T$ leads to a negative value for $b_4$ (see Fig. 3b). The Gd$^{3+}$ fitting parameters are: $g = 1.992(4)$, $b_4 = -13.3(4) \text{ Oe}$, and $b_6 < 1(1) \text{ Oe}$. The simulation of the Gd$^{3+}$ spectrum for $H//[001]$ is shown in Fig. 3b. It is clear from this spectrum that two Gd$^{3+}$ sites are coexisting in this material for intermediate Gd concentrations, one with CF splitting and another with no CF splitting. The Spin Hamiltonian parameters were concentration independent, within the accuracy of the measurements.

The results obtained in the 0.5% co-doped La and Ca excess/deficient $\text{Ca}_{1-x} (\text{Gd,Er})_x \text{B}_6$ samples showed the general behavior and features described in Figs. 1-3. For the sake of simplicity, these data are not included in the figures. We want to mention that ESR in $\text{Ca}_{1-x} \text{La}_x \text{B}_6$ for $x = 0$ and $x \approx 0.005$, showing saturation magnetic moment of $\sim 0.1$ and $\sim 1-2 \text{ emu/mole f.u.}$, respectively, did not show any traces of other-R natural impurities.

The observation of a coexistence of different Gd$^{3+}$ sites, with ESR spectra of different lineshape and structure, suggest that there are distribution of doping levels along these samples. The presence of Gd$^{3+}$ resonances with lorentzian (insulator) and dysonian (metallic) lineshapes and different CFE lead us to conclude about the coexistence of low and highly doped regions in the samples. Also, crystals from the same batch (with similar WF) were found to be metallic-like by $\rho(T)$ and...
insulator-like by ESR (see $x = 0.0003$ in Fig. 1) confirming strong doping inhomogeneity for these range of concentration ($0.0003 \lesssim x \lesssim 0.003$). An explanation for the observed sample dependency and doping inhomogeneity is probably related to the presence of defects in the sample. Defects can either dope the sample with carriers or serve as deep local traps capturing local moments on the order of $1 \mu_B$. Vacancies of Ca or neutral $B_0$ have been suggested as the origin for these effects. Consistently, for more concentrated samples, $0.003 \lesssim x \lesssim 0.01$ (where the effective doping is probably more spatially homogeneous), the ESR results (single dysonian resonance) were only slightly sample dependent and always consistent with metallic $\rho(T)$ data.

The absence of Gd$^{3+}$-shift (Knight shift), thermal broadening of the linewidth (Korringa rate), and long estimates for $T_1$ (spin-lattice relaxation time) in these metallic regions suggest that the exchange interaction between the rare-earth localized magnetic moments and conduction electrons may be negligible in these regions. Therefore, the absence of CFE in the Gd$^{3+}$ spectra of these metallic regions is unlikely to be due to CF exchange narrowing mechanisms. Also, the relatively low Gd concentration used in this work ($x \lesssim 0.01$) and the observed $T$-independent $g$-value and linewidth suggests that these metallic region cannot be associated with clusters of Gd$^{3+}$ ions. As such, the absence of CFE in the Gd$^{3+}$ ESR spectra is an unexpected result that, to the best of our knowledge, has only been previously reported in one system, YBiPt, which perhaps was coincidentally a small gap semiconductor. Since the Er$^{3+}$ resonance remains a $I_g$ crystal field ground state even in these metallic regions (not shown), the absence of CFE in the Gd$^{3+}$ ESR spectra of these materials should be intrinsically associated with the basic mechanisms that lead to the observation of fine structure in a S-state ground state. It is clear from our data that these mechanisms must be reviewed.

An alternative speculation about our findings would come from the comparison of the phase separation predicted in refs. 11 and 12 with the insulating/metallic regions reported here, suggesting that the samples of Fig. 1 and 2 present SDW (triplet) and CDW (singlet) excitonic condensate ground states, respectively. However, concerns about the excitonic picture arose after WF was also in defect doped hexaborides. This result would seem to rule out the idea that the $d$-electrons of La atoms play a fundamental role to the magnetism in this compounds.

In this work we employed ESR, one of the most powerful local experimental technique, to investigate the microscopic properties of the Ca$_{1-x}$Gd$_x$B$_6$ ($0.0001 \lesssim x \lesssim 0.01$) system. The systematic ESR, $M_{dc}(T)$, $M_{dc}(H)$ and $\rho(T)$ study of more than fifty samples reveals that the relative strong WF observed in these materials is a bulk property resulting from a subtle combination of R-doping and sample preparation methods. In agreement with previous work, we find that some of the R-undoped samples prepared by different methods also showed the presence of WF, presumably due to defect self-doping. The ESR experiments show that for $x \lesssim 0.003$ the samples are inhomogeneous presenting a coexistence of insulating and metallic regions. We believe this happens when doping is dominated by defects. Further, ESR, $M_{dc}(T,H)$ and $\rho(T)$ data are extremely sample dependent, and as far as the doping is concerned Gd ions behave like La ions. Within the accuracy of our experiments ($\sim 10\%$ of the measured linewidths, $\sim 10$ Oe), we found no evidence for a WF-induced $g$-shift in the Gd$^{3+}$ ESR spectra. Moreover, although the resonances in the metallic regions are broader than in the insulating regions, no correlation between the ESR linewidth and WF component was found even for high concentrated metallic samples, which suggest that WF in these compounds might be associated with coupled local moments isolated in clusters. Nevertheless, the striking results showing coexistence of microscopic regions insulator/with and metallic/without CFE in the Gd$^{3+}$ ESR spectra suggest that the interplay between CF, self-doping, R-doping, conductivity and magnetism is very subtle, and it is at the moment far from understood in these systems. In particular, the origin and nature of the self-doping defects need to be clarified and included in the models.

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FIG. 1. ESR, $M_{dc}(T)$, and $M_{ac}(H)$ data for three samples of Ca$_{1-x}$Gd$_x$B$_6$: a) $x = 0.0003$, b) $x = 0.003$, and c) $x = 0.01$. $\rho(T)$ data for the $x = 0.0003$ and $x = 0.003$ are also shown.

FIG. 2. Gd$^{3+}$ ESR spectra for four samples of Ca$_{1-x}$Gd$_x$B$_6$: a) $x = 0.0016$, $x = 0.0013$, $x = 0.0001$ (as grown and etched) and $\rho(T)$ and $M_{ac}(H)$ data for the $x = 0.0016$ and $x = 0.0001$. b) $x = 0.00005$ (as grown). This sample shows the ESR spectrum of natural impurities of Eu$^{2+}$. 

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FIG. 3. ESR data for Ca$_{1-x}$Gd$_x$B$_6$ ($x = 0.0013$): a) angular dependence of the field for resonance in the (110) plane and, b) Experimental (open circles) and simulated (solid line) ESR spectrum of Gd$^{3+}$ for $H//[001]$. 