Revisiting the Possible $4f^7\ 5d^1$ Ground State of Gd Impurities in SmB$_6$ by Electron Spin Resonance

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The search for topological states in strongly correlated electron systems has renewed the interest in the Kondo insulator SmB$_6$. One of the most intriguing previous results was an anomalous electron spin resonance spectrum in Gd-doped SmB$_6$. This spectrum was attributed to Gd$^{2+}$ ions because it could be very well described by a model considering a change in the valence from Gd$^{3+}$ to Gd$^{2+}$, a dynamic Jahn-Teller effect and a $4f^7\ 5d^1$ ground state in the Hamiltonian. In our work, we have revisited this scenario using electron spin resonance and energy dispersive X-ray spectroscopy measurements. Our results suggest that the resonance is produced by Gd$^{2+}$ ions; however the resonance stems from an extrinsic oxide impurity phase that lies on the surface of the crystal.

INTRODUCTION

The mixed-valence ground state, the nature of the hybridization gap and the saturation of the resistivity below $\approx 4$ K have been puzzling features of SmB$_6$ for a long time [1]. Since the theoretical prediction of a topological Kondo insulating phase in SmB$_6$ [2], this system has renewed the interest of the community to understand all of the puzzling open questions. One important aspect we emphasize here is the necessity of diagnosing extrinsic effects in this system [3].

One of the remaining questions is the possible existence of a formal Gd$^{2+}$ ground state ($4f^7\ 5d^1$) of Gd-doped SmB$_6$. The extra electron brought by Gd$^{2+}$ to the lattice may be bound in a singlet state which should be relevant for understanding the low-temperature Kondo physics [4, 5]. Furthermore, a putative existence of a Gd$^{2+}$ state may be relevant in interpreting the suppression of surface states in Gd-doped SmB$_6$ [6]. Clearly, the role of magnetic impurities on topological and Kondo insulators is essential to understand their fundamental mechanism.

G. Wiese, H. Schäffer and B. Elschner reported an electron spin resonance (ESR) study [7] in which a Hamiltonian including a $4f^7\ 5d^1$ ground state and a dynamic Jahn-Teller effect was employed. This was investigated in great detail within a Diploma thesis [8], in which ESR measurements at 9.25 GHz (X-band) and various theoretical models were also reported. Wiese et al. measured samples of Sm$_{1-x}$Gd$_x$B$_6$ in the range of $0.0002 \leq x \leq 0.003$ that were grown by an aluminum flux technique [9]. The authors claimed that the anomalous spectra were observed in all concentrations, but they mainly focused on the analysis of $x = 0.003$ due to a better signal-to-noise ratio. Furthermore, floating zone grown crystals did not present this supposedly anomalous Gd$^{2+}$ ESR spectra, which was interpreted as an indication that only high quality samples would show such effect.

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etched samples to investigate whether the signal was due to some impurity on the surface that could be etched away. The etching process was done using a dilute mixture of hydrochloric and nitric acids (aqua regia), and the crystals were etched for two minutes in each session. ESR measurements were performed in a X-band (9.4 GHz) spectrometer equipped with a goniometer and a He-flow cryostat, in the temperature range of $2.5 \, \text{K} \leq T \leq 20 \, \text{K}$. The studied samples ranged in mass from 0.4 mg to 1.5 mg. We performed our experiments on 10 different crystals from seven different batches.

RESULTS AND DISCUSSION

Figure 1a) displays the ESR spectra of Gd in SmB$_6$ at 4.2 K with the external magnetic field applied along the [100] and [111] directions obtained by G. Wiese and reported in his Diploma [8]. Figures. 1b) and c) show the Gd ESR spectra we obtained for two different crystals (samples S1 and S2) with $x \approx 0.004$ at 4.5 K and within the same field range $H \leq 10\, \text{kOe}$. Both measurements were performed using crystals that were not etched. Sample S2 was aligned with the magnetic field parallel to the [100] direction, whereas S1 was aligned with the magnetic field parallel to the [110] direction. It is evident from our Gd ESR spectra that we could reproduce the same results obtained by G. Wiese et al. [7, 8].

We also performed ESR experiments as a function of temperature and field orientation (not shown). The ESR Gd anomalous spectra has a Curie-Weiss behavior and the intensity for $T \geq 6\, \text{K}$ is reduced drastically, which confirms previous reports [7, 8]. The angle dependence of the anomalous ESR spectra is extremely anisotropic, with no clear cubic symmetry. This is another hint that this anomalous spectrum could be connected with extrinsic phases, and not with the Gd ESR in SmB$_6$.

The fine structure for SmB$_6$ crystals with 200 ppm and 400 ppm Gd shows a clear cubic symmetry [13] in angle-dependent ESR experiments, which confirms that the probe is in the cubic SmB$_6$ matrix. In the case of the anomalous Gd spectra, even variations of two degrees had a major impact on the spectrum, with lines vanishing and new ones appearing (not shown). Moreover, the appearance of the anomalous Gd spectra was sample dependent. G. Wiese pointed out [8] that SmB$_6$ Gd-doped floating zone crystals grown by Kunii et al. [14] did not show the anomalous Gd spectrum and explained this result in terms of the quality of the crystals used.

Therefore, we searched for any kind of impurities using optical microscopy. Figure 2a) shows an image taken by optical microscopy of the Gd-doped SmB$_6$ sample S1. We observe a clear difference: there is one region with a more smooth, mirror-like surface, and a white pocket region with a more pronounced roughness. The pattern was also observed for sample S2, as shown in Fig. 2b). This white region could not be etched away, even by etching the samples for one session, as shown in Figure 2c), or three sessions, as shown in Fig. 2d), increasing the aqua regia concentration after each step. This is a clear indication that such regions could be connected with an oxide extrinsic phase.

After etching the crystals, we performed ESR experiments again in the Gd-doped SmB$_6$ samples S1 and S2. As it is shown for S2 in Fig. 2a), when we compare the normalized (by the Gd$^{3+}$ resonance intensity) Gd anomalous ESR spectra, we do not observe a clear change in the Gd anomalous spectra.

As the Gd-doped SmB$_6$ crystals are thin and small it is challenging to polish the samples and obtain an ESR
signal due to the intensity of the signal. Furthermore, the white region could be found on different facets of the same crystal, which dashes any hope to improve a crystal surface treatment by just polishing the samples. In order to avoid such challenge, we intentionally broke a Gd-doped SmB$_6$ sample in three different pieces, as it is shown in Figure 2c, and performed ESR experiments on piece 1 and piece 2 with different surface coverage by white regions. Piece 1 had a larger surface area covered by this rough region compared with piece 2 and the ratio of the areas with white region from piece 1 to piece 2 was $\approx 3.0$, whereas the ratio of the total area was $\approx 1.3$ and the mass ratio was $\approx 1.2$.

![Graphs and images]

**FIG. 3:** Normalized Gd ESR spectra at $T = 4.5$K for Gd-doped SmB$_6$ samples a) S2 before and after etching and b) two different pieces from S1. c) and d) EDX images of piece 1 from sample S1. The crystals were not etched or polished after the ESR measurements. e) Two distinct points of EDX analysis done in sample S1. The region I corresponds to the red spectrum and the region II to the blue spectrum in f). The Ni and Fe peaks are due to contamination while preparing the sample to perform EDX measurements.

Figure 3b) shows the Gd ESR spectra, normalized by the Gd$^{3+}$ intensity from two different pieces - see inset. It is important to emphasize that all the pieces together reproduced the results obtained by G. Wiese et al. 3, 4, as shown in Fig. 4. If the Gd anomalous spectrum were coming from the bulk of the crystal, it would be expected that the comparison of the normalized Gd ESR spectra would be very similar, which is not the case. There is a clear reduction in the intensity of the Gd anomalous spectra as measured on piece 2, which is a very convincing hint that the Gd anomalous spectra is not related with the bulk of the Gd-doped SmB$_6$ crystal.

By choosing an isolated peak, which is featured in the gray region of Fig. 3b), we calculated the ratio of the intensity of the same resonance peak for pieces 1 and 2 of sample S1. The ratio was $\approx 2.5$, which is closer to the ratio of the white regions of these two pieces than to the ratio of the total area or mass. All these results are in agreement with our scenario that such Gd anomalous signal is closely connected with this rough, white surface.

In order to investigate the origin of this white surface, we performed EDX experiments on piece 1 of the sample S1 of Gd-doped SmB$_6$ after the ESR measurements reported in Fig. 3a) and b) to investigate the crystal surface. From a morphological point of view, as shown in Figs. 4c) and d), the two regions are easily distinguishable: while the gray region is much more flat and smooth, the white region is more rough and irregular. The amplified image shown in Fig. 3d) clarifies even more the difference between these two regions in the Gd-doped SmB$_6$.

Finally, we tried to differentiate, in a semi-quantitative approach, the elements from these two regions of the same crystal. We analyzed the smooth surface (region I) of piece 1 from the sample S1 of Gd-doped SmB$_6$, shown in figure 3e), and compared it with the white surface (region II). Figure 3f) shows the comparison between the obtained spectra, where the red spectrum was obtained for the smooth surface and the blue for the rough surface.

Comparing the two spectra, there is a clear increase of Al and O peaks. The Fe- and Ni-peaks are due to a contamination when we were preparing the sample to measure EDX - they were not observed in previous measurements. We did not observe a Gd peak due to the small concentration (the EDX detection limit for Gd is approximately 0.2 at %).

This observation reinforces the notion that the white surface is, most likely, an aluminum oxide impurity phase grown at the top of the Gd-doped SmB$_6$ crystals. Since this impurity could be an aluminum oxide, etching the sample should not remove it and, as a consequence, should not affect the anomalous spectra. Our result also reinterprets the reasoning behind the lack of anomalous Gd spectra in Gd-doped SmB$_6$ floating zone grown 14 crystals: there is no impurity phase due to the growing process, hence the obtained Gd ESR spectrum is the expected one for a Gd$^{3+}$ ion in an cubic environment.

Measurements in SmB$_6$ Eu$^{2+}$ (x = 0.01 and 0.0004) and Er$^{3+}$ (x = 0.007) 13 doped samples also do not show such kind of anomalous spectrum, even with the experiments being done in similar doping ranges. If the signal only appears in Gd doped samples, the signal should be related with the Gd doping. As the intensity scales well with the area of the oxide on the surface, this oxide may contain Gd and the signal could be related to Gd$^{2+}$.

Recently the synthesis of a molecular complex, containing Gd$^{2+}$ ions, was reported 10. They demonstrated that an electronic ground state 4f$^7$ 5d$^1$ for Gd$^{2+}$ exists, which goes into the direction of theoretical predictions reported by G. Wiese et al. 3, 4. They also performed ESR experiments for $T \geq 77$ K. They did not, however, observe any trace of an anomalous Gd spectrum, which is expected for this temperature range and for molecular complexes. Another recent report 11 explored the origin of shallow electrons trapped in Ce-doped Gd$_3$Al$_2$Ga$_3$O$_{12}$. Using infrared absorption and first-principles calculations, the authors showed that de-
fect complexes of antisite Gd$^{2+}$ ions adjacent to oxygen vacancies exist.

The above reported results point out that the Gd$^{2+}$ anomalous spectra observed is likely due to an extrinsic oxide impurity on the surface of Al-flux grown Gd:SmB$_6$. Such valence has been shown to be possible in oxides, especially due to defect complexes.

**CONCLUSION**

In summary, we were able to reproduce the ESR spectra reported by G. Wiese et al. [7, 8]. The ESR anomalous spectrum is highly anisotropic, is reduced for $T \geq 6$ K and is sample dependent, as was also pointed out previously [7]. All the crystals that showed this ESR spectrum had a white region on the surface. We analyzed two pieces of the same crystal that showed the Gd anomalous spectrum. The ratio between intensities of the Gd anomalous spectra scales well with the ratio of the white region areas from the two pieces. EDX experiments showed that the white region, most likely, is due to an extrinsic Al oxide impurity phase that lies on the surface of the crystals. Finally, recent reports from literature [10, 11] demonstrated the existence of a Gd$^{2+}$ ion in the electronic ground state $4f^{7} 5d^1$. This could be formed in an oxide which contains Gd and Al. Our results show that, most likely, the Gd anomalous ESR spectra in Gd-doped SmB$_6$, first seen by G. Wiese and confirmed by our work, may be coming from a Gd$^{2+}$ ion that lies in an extrinsic oxide phase on the surface of the crystal.

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