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Electron Spin resonance of Gd^{3+} in three dimensional topological insulator Bi_2Se_3

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Abstract. Bi_2Se_3 has been claimed to be a three dimensional topological insulator (TI) with topologically protected metallic surface states with exotic properties. We have performed electron spin resonance (ESR) measurements on Gd^{3+} doped ($x \approx 0.01$) Bi_2Se_3 single crystal grown from stoichiometric melt. For the studied crystals, our preliminary results revealed a partly resolved Gd^{3+} fine structure spectrum with Dysonian (metallic character) lines. At room temperature, the central line has a $g \approx 1.98$, a linewidth $\Delta H \approx 95$ G and the spectra have a overall splitting of roughly 1300 Oe. As the temperature is decreased, the Gd^{3+} ESR ΔH of the central line presents a very small Korringa-like behavior $b = \Delta H/\Delta T \approx 0.013$ Oe/K and nearly T-independent g-value. However, for $T \lesssim 40$ K, ΔH shows a stronger narrowing effect evolving to Korringa-like behavior ($b \approx 0.15$ Oe/K) for $T \lesssim 30$ K. Concomitantly with the change in ΔH behavior, the Gd^{3+} central line g value starts to decrease reaching a value of 1.976 at $T = 4.2$ K. The ESR results are discussed in terms of possible effects of protected topological surface states enlightened by complementary data from macroscopic measurements.

1. Introduction

Topological insulators are a type of condensed matter materials where a bulk insulator is coated by topologically protected metallic surface states which are robust to disorder[1]. These surface states have exotic properties which are claimed to be of interest to spintronics development. Usually, surface sensitive spectroscopic techniques such as ARPES (angle resolved photoemission spectroscopy) and STM (scanning tunneling microscopy) are used to probe this type of materials. However, to our knowledge, these materials were not studied by Electron Spin Resonance (ESR), which is a spectroscopic technique that can yield local information about the conduction electrons. Also, it is suggested that a periodic perturbation can affect the band topology[2, 3], such as microwave radiation in the ESR experiment. In this work, we have performed ESR measurements on Gd^{3+} doped Bi_2Se_3 single crystals. Our results indicate a non-trivial evolution of Gd^{3+} spectra at low-T (below 40 K) that we attempt to correlate to the presence the topological metallic surface states. Furthermore, our Gd^{3+} ESR data suggest that the studied samples show coexistence of both insulator and metallic behavior inside the microwave skin depth.

2. Experimental Details

$Bi_{2-x}Gd_xSe_3$ single crystals were synthesized from a stoichiometric melt of high purity elements in the ratio (Bi,Gd) : Se = 2 : 3. The materials were placed inside an alumina crucible and sealed in vacuum in a quartz tube. Then they were taken to a conventional furnace and heated to 800°C for 24 h, and slowly cooled down to room temperature over the period of a week. The crystals have a shiny surface and are easy to exfoliate. The hexagonal crystal structure and phase purity of the studied samples were determined by x-ray powder diffraction. Selected single crystals were submitted to elemental analysis using a commercial Energy Dispersive Spectroscopy (EDS) microprobe and a commercial Wavelength Dispersive Spectroscopy (WDS) equipment. Magnetization measurements were performed in a commercial SQUID magnetometer. ESR measurements were performed in a X-band (9.5 GHz) Bruker ELEXSYS-500 equipped with a goniometer and a He-flow cryostat.

3. Results and discussion

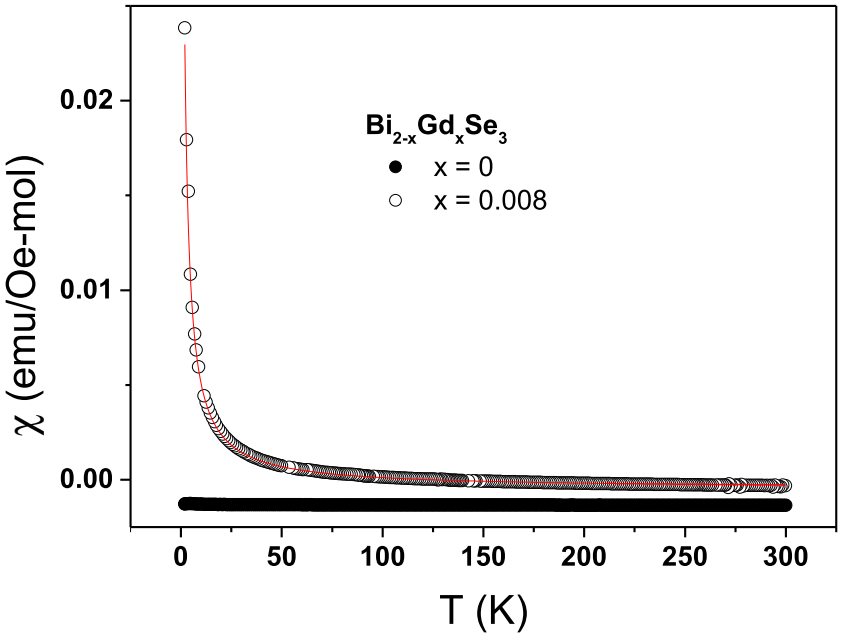

Figure 1. (Color online) Magnetic susceptibility of $Bi_{2-x}Gd_xSe_3$ single crystals as function of temperature. The line is a Curie fit to the data.

Fig. 1 shows the magnetic susceptibility as a function of temperature for single crystals of $Bi_{2-x}Gd_xSe_3$ ($x = 0$ and $x = 0.008$). For the pure sample, the sample is diamagnetic as expected for a bulk insulator, and with a susceptibility of $\chi_0 \approx -2.5 \times 10^{-5}$ emu/Oe-mol. From fits to the magnetic susceptibility data for the doped sample using a Curie-Weiss law, we extracted a Gd concentration of $x = 0.008$ and a very small Curie-Weiss temperature $\theta_{CW} = -0.5$ K consistent with a very diluted Gd^{3+} system.

Figure 2 presents the Gd^{3+} ESR spectrum at $T = 4$ K and microwave power $P = 2$ mW. The sample shows the partly resolved fine structure lines of Gd^{3+} up to room temperature, and the lineshape of each line is Dysonian (admixture of absorption and dispersion). The dysonian line is characteristic of metallic environments in a regime where the microwave skin depth (δ) is smaller than the sample size. Interestingly, this effect would not be expected considering the bulk conductivity of these materials. Yet the studied samples show insulating behavior in

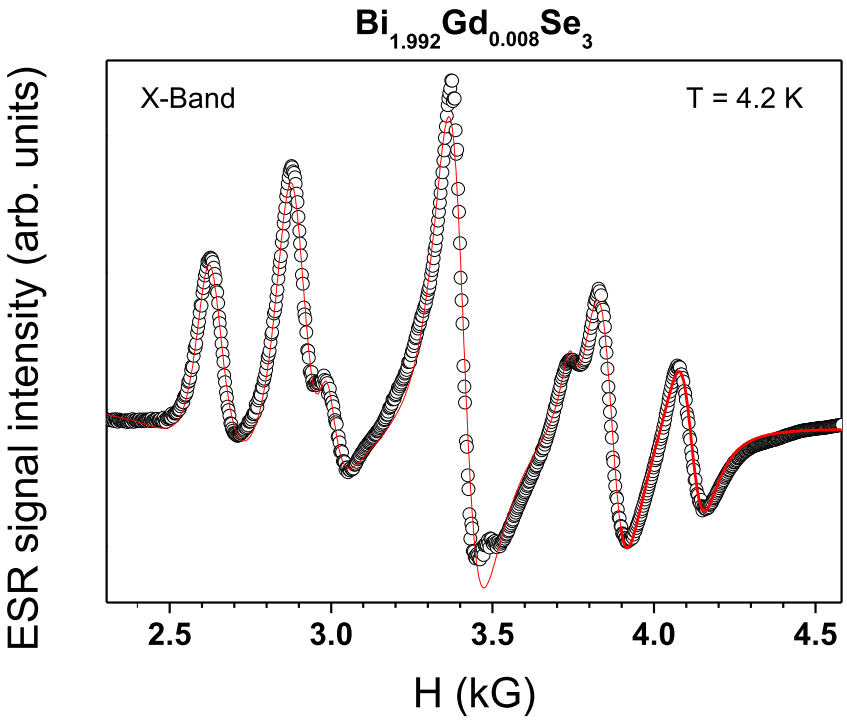

Figure 2. (Color online) Resolved Gd^{3+} ESR spectrum at 4,2 K for $Bi_{1.992}Gd_{0.008}Se_3$. The line is a fit of 7 dysonian lines to the data.

the magnetic susceptibility (Fig. 1) and in power dependence of the Gd^{3+} ESR lines intensity (saturation behavior (not shown))[4]. Regarding the fine structure lines of Gd^{3+}, for the studied samples, the Gd^{3+} spin-spin interactions are still strong enough to produce some overlap between the lines, which complicates angular and linewidth analysis of each individual line. By fitting seven dysonian lineshapes in each spectrum, we followed the evolutions of the g-shift Δg (using the g-value of Gd^{3+} central line - g-value of Gd^{3+} in insulators 1.993(2) [5]), and of the linewidths ΔH for each line as function of temperature. We focus our analysis on the results for Δg and ΔH for the central line which can be seen in Fig. 3a and 3b, respectively. One can see that, for higher temperatures ($T \gtrsim 40$ K), both Δg and ΔH are nearly constant but they show significant evolution at lower temperatures.

In order to analyze the temperature dependence of the Gd^{3+} ESR Δg and ΔH, one has to consider the exchange interaction, $J_{fs}\mathbf{S}.\mathbf{s}$, between a localized $4f$ electron spin ($\mathbf{S}$) on a solute atom (Gd^{3+}) and the free c-e's spin ($\mathbf{s}$) of the host metal.

In the simplest treatment, the ESR g-shift (Knight shift) [6] and the thermal broadening of the linewidth (Korringa rate) [7], when "*bottleneck*" and "*dynamic*" effects are not present [8], can be written as:

$$\Delta g = J_{fs}\, \eta\,(E_F)\,, \tag{1}$$

and

$$\frac{d\,(\Delta H)}{dT} = \frac{\pi k}{g\mu_B}\, J_{fs}^2\, \eta^2\,(E_F)\,, \tag{2}$$

where J_{fs} is the effective exchange interaction between the Gd^{3+} local moment and the c-e in the absence of c-e momentum transfer [9], $\eta(E_F)$ the "*bare*" density of states for one spin

direction at the Fermi surface, k the Boltzman constant, μ_B the Bohr magneton and g the Gd^{3+} g-value.

Equations 1 and 2 are normally used in the analysis of ESR data for highly diluted rare-earths magnetic moments in intermetallic compounds. As such, based on the small values Gd^{3+} ESR Δg and ΔH data displayed in Fig. 2 a) and b), the two equations suggest small values of the product $J_{fs} \cdot \eta(E_F)$ which are related to the dominant insulating character of the bulk of Bi_2Se_3, despite the fact that the Gd^{3+} spectra present Dysonian lines. At high-T, the temperature dependence of ΔH yields an upper limit for the Korringa rate of $\approx 0.013(3)$ Oe/K. In the same temperature range, the negative $\Delta g \approx$ - 0.013(2) indicates that the magnetic ions are interacting mainly with a small density of p-type conduction electron bands.[10–12].

Yet, when one considers the lower temperature range ($T \lesssim 40$ K) for both Δg and ΔH, there is a clear increase of the metallic-like behavior inside the microwave skin depth of $Bi_{2-x}Gd_xSe_3$ as seen by the Gd^{3+} probes at low-temperature. This is evident by the increase of one order of magnitude in the Korringa rate, becoming $b = 0.15(3)$ G/K below 40 K, and by the concomitant increase of the negative Δg. Puzzlingly, this crossover as a function temperatures is not accompanied by any change in behavior of the macroscopic properties (such as magnetic susceptibility (Fig.1, electrical resistivity and heat capacity (not shown)) as a function of temperature for the studied samples.

As such, we associated the temperature evolution of Gd^{3+} ESR Δg and ΔH in Fig. 2 a) and b) to subtle changes to the effective electronic local environment of Gd^{3+} probes that can only be detected by such microscopic technique.

In fact, the observation of a Gd^{3+} Dysonian lineshape even for materials with very large skin depth ($(\delta \gtrsim 1$ mm estimated from the bulk resistivity of Gd^{3+} doped Bi_2Se_3) concomitant with ESR intensity saturation effects and small values of Gd^{3+} ESR Δg and Korringa rate b suggests a non-trivial coexistence of metallic and insulating regions inside the actual microwave ((δ) of $Bi_{2-x}Gd_xSe_3$.

Since this system is a topological insulator, it is not unreasonable to speculate that the metallic surface states can give measurable contribution to the Gd^{3+} spin dynamics and local fields, and therefore affect the ESR spectra of the resonating Gd^{3+} ions inside the skin depth. As such, as the temperature is lowered and the resistivity of bulk increases dramatically, the relaxation channels and the polarization fields provided by the surface metallic state with very high conductivity dominate the temperature evolution of the whole spectra leading to a measurable increase of Δg and Korringa rate b.

In this scenario, if the surface metallic states dominate the behavior of the Gd^{3+} ESR lines at low temperature, the enhancement of the negative Δg implies that they have strong p-character. Hence, these surface electrons must be originated from either the Bi or Se p-bands. This results is in accordance to the band structure calculation of this material[13], since both bands cross at the Fermi level due to spin-orbit coupling.

Nonetheless, one point of concern of the present analysis of the Gd^{3+} ESR spectra is the fact the reported spectra is not completely resolved. As such, there is appreciable overlap between the seven lines of the Gd^{3+} spectra which can complicate the individual analysis of each line to extract a perfectly accurate ESR Δg and ΔH. To evaluate this possible artifact of our analysis, we plot in Figure 3c the difference between the resonance fields of the highest and lowest field lines $\Delta H_{7-1} \equiv H_{r7} - H_{r1}$ as a function of temperature. One can see in Figure 3c that ΔH_{7-1} starts near 1500 Oe at $T = 4.2$ K and is nearly temperature independent up to ≈ 25 K. Above 25 K, it decreases almost linearly, reaching the value $\Delta H_{7-1} \approx 1300$ Oe at 300 K. The difference ΔH_{7-1} is associated with the overall crystalline electrical field (CEF) splitting due to the CEF second order effect via excited states in Gd^{3+}[10]. This narrowing effect on the spectra Gd^{3+} with increasing temperature is very typical for insulators and it is related to the thermal expansion of the lattice parameters which modifies the CEF parameters.

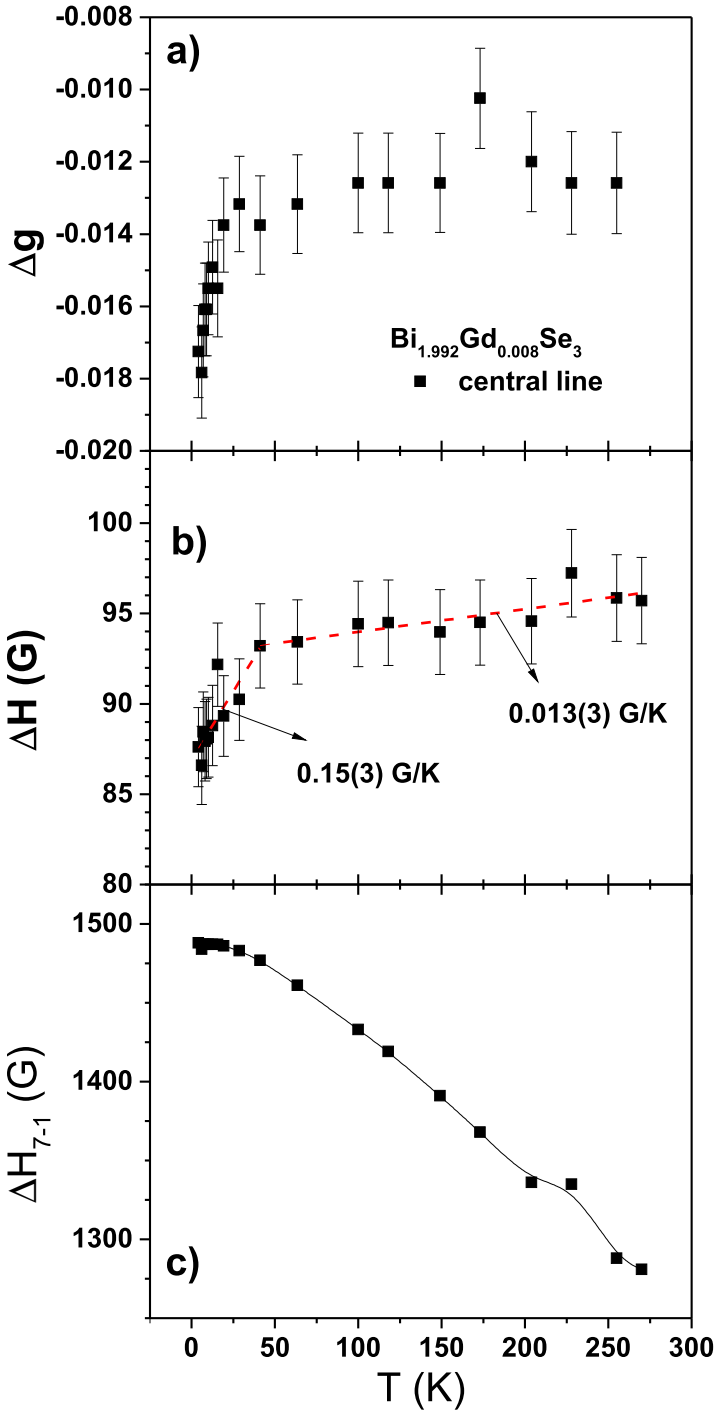

Figure 3. (Color online) Temperature dependence of: a) the g-shift (Δg) and b) the linewidth (ΔH) of the central line; and c) estimated overall splitting of Gd^{3+} ESR fine structure. The dashed lines are linear fits to the different temperature ranges. The values indicates in (b) are the Korringa rates for the low and high temperature regime.

However, on one hand, these narrowing effects on the spectra tend to increase the overlaps between the lines at high temperatures which suggests that the low-T evolution of the Gd^{3+}

ESR Δg and ΔH in Fig. 2 a) and b) cannot be attributed to artifact of our analysis. On the other hand, we are convinced that stronger claims about the results reported here can only be done after more detailed ESR work in very diluted $Bi_{2-x}Gd_xSe_3$ samples using different ESR frequencies bands.

It is worth to mention that the coexistence of metallic and insulator behavior within the microwave skin depth, as probed by Electron Spin Resonance experiments, was recently reported for diluted ($0.002 \lesssim x \lesssim 0.10$) Nd^{3+} ions in the claimed topological semimetal YBiPt. In this case, the X-band Nd^{3+} spectra at low temperature, 1.6 K $\lesssim T \lesssim$ 20 K, (9.4 GHz) show a g-value of 2.66(4) dysonian resonance lineshape which shows a remarkably unusual temperature, concentration, microwave power and particle size dependence. This unusual behavior was claimed to be associated with metallic surface states of YBiPt.[14].

4. Conclusions

In summary, we have observed a partly resolved Gd^{3+} ESR spectra in $Bi_{1.992}Gd_{0.008}Se_3$ from 4.2 K up to room temperature which are composed by dysonian resonance lines. This is in contrast to the insulator behavior (very large skin depth) shown by magnetic susceptibility and the occurrence of saturation in the ESR signal intensity as a function of microwave power for this sample. This behavior indicates a dual character in this material, where both insulator and metallic regions coexist within an effective skin depth. Furthermore, both Gd^{3+} ESR Δg and b of the central line show significant evolution below $T \approx 40$ K that we speculate to be associated with the presence of metallic surface states with p-character.

5. Acknowledgments

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