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Gd^{3+} rattling triggered by a "weak" M–I transition at 140–160 K in the $Ce_{1-x}Gd_xFe_4P_{12}$ ($x \approx 0.001$) skutterudite compounds: An ESR study

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In this work we report electron spin resonance (ESR) measurements in the semiconducting $Ce_{1-x}Gd_xFe_4P_{12}$ ($x \approx 0.001$) filled skutterudite compounds. Investigation of the temperature (T) dependence of the ESR spectra and relaxation process suggests, that in the T-interval of 140–160 K, the onset of a "weak" metal–insulator (M–I) transition takes place due to the increasing density of thermally activated carriers across the semiconducting gap of ≈ 1500 K. In addition, the observed low-T fine and hyperfine structures start to collapse at $T \approx 140$ K and is completely absent for $T \gtrsim 160$ K. We claim that the increasing carrier density is able to trigger the rattling of the Gd^{3+} ions which in turn is responsible, via a motional narrowing mechanism, for the collapse of the ESR spectra.

1 Introduction The filled skutterudite RT_4X_{12} compounds, where R is a rare-earth or actinide, T is a transition metal (Fe, Ru, Os), and X is a pnictogen (P, As, Sb) have attracted great attention due to their broad range of physical properties. They are of interest for those seeking more efficient thermoelectric materials [1, 2] and also for those investigating the basic issues of strongly correlated electron systems [3–5].

These compounds crystallize in the $LaFe_4P_{12}$ structure with space group $Im3$ and local point symmetry T_h for the R ions. The R ions are guests in the oversized rigid cages constituted by the $(T_2X_3)_4$ atoms [6]. The dynamics of these guest R ions is believed to be of great importance in dampening the thermal conductivity [7, 8] as observed in the filled compounds of this family and it may also play an important role on the appearance of heavy fermion behavior and superconductivity [3, 9].

Electron spin resonance (ESR) is a sensitive and powerful microscopic tool to provide information about crystal field (CF) effects, site symmetries, valency of paramagnetic ions, g-values, and fine and hyperfine parameters [10]. In our recent work [11], ESR was found to be a useful tool to probe the dynamics of the R ions. The temperature (T)-dependence of the guest R ions localization lead the ions to experience slightly different symmetry environments causing a distribution of g-values that was detected by our ESR experiment. In addition, a remarkable reduction of the hyperfine parameters was observed in the ESR spectra being attributed to a motional narrowing mechanism [12] caused by the rattling of the R ions. In our previous ESR experiments on Yb^{3+} impurities in $Ce_{1-x}Yb_xFe_4P_{12}$ [11], these two effects were analyzed and the coexistence of two distinct sites were determined.

Ogita et al. [13], performing Raman scattering experiments on several metallic skutterudite compounds of RT_4X_{12} (T = Fe, Ru, Os; X = P, Sb), found resonant 2nd order phonon modes associated with the vibration that change the bond length of R–X (stretching mode). However, in the semiconducting $CeFe_4P_{12}$ the 2nd order phonon modes were found to be non-resonant. Based on these results the authors conclude that there should be a strong coupling between the R–X stretching modes and the conduction

electrons. Thus, in $CeFe_4P_{12}$ a weak stretching mode-conduction electron coupling should be expected.

In this work, to further investigate these ideas, we have studied the T-evolution of the ESR spectra of the Gd^{3+} ion in the $Ce_{1-x}Gd_xFe_4P_{12}$ ($x \approx 0.001$) filled skutterudite compounds.

2 Experimental Single crystals of $Ce_{1-x}Gd_xFe_4P_{12}$ ($x \lesssim 0.001$) were grown in Sn-flux as described in Ref. [14]. The cubic structure ($Im3$) and phase purity were checked by X-ray powder diffraction. The Gd concentrations were determined from the H- and T-dependence of the magnetization, $M(H,T)$, measured in a Quantum Design SQUID dc-magnetometer. The ESR experiments used crystals of $\sim 2 \times 2 \times 2\,mm^3$ of naturally grown crystallographic faces. The ESR spectra were taken in Bruker X (9.48 GHz)-band spectrometer using appropriated resonators coupled to a T-controller of a helium gas flux system for $4.2\,K \lesssim T \lesssim 300\,K$.

The low-T ESR spectra show the full fine structure of Gd^{3+} and its angular variation was studied at $T = 4.2, 20$, and 300 K with the applied field, H, in the (110) plane. The experimental arrangement was set up in a way that $\theta = 0$ corresponds to the [001] direction. The complete results of this work will be the subject of a more extended manuscript [15]. In this work we will discuss measurements in the T-interval $110\,K \lesssim T \lesssim 160\,K$ for various directions of H. In this interval, the fine structure collapses in one single broad line and its lineshape changes from Lorentzian (insulator) to Dysonian (metallic). These features were confirmed for three different batches.

3 Results and discussion Figure 1 presents the normalized low-T ESR spectra ($T \approx 4.2\,K$) taken for H along the [001] direction (Fig. 1a) and at $\theta \approx 30°$ from [001] in the (110) plane (Fig. 1b). The $^{155,157}Gd^{3+}$ ($I = 3/2$) isotopes hyperfine structure close to the central $(1/2 \leftrightarrow -1/2)$ transition is clearly observed in the inset of Fig. 1a, where a zoom of the spectra around this transition is shown. The measured hyperfine parameter is $A = 5.5(2)$ Oe. This structure is also observed (not so clearly) for the other fine structure components and it is almost completely hidden on Fig. 1b, due to the overlap with the other fine structure transitions. The inset of Fig. 1b shows that some structure remains, distorting the lineshape of the observed single line due to a crystal misorientation of $\approx 1°$.

Figure 2 shows the T-evolution of the above resonances in the T-interval $140\,K \lesssim T \lesssim 160\,K$. In Fig. 2a, for H along the [001] direction, the fine structure starts to collapse at $T \approx 140\,K$ and is completely absent above $T \approx 160\,K$. The spectra turn into a single broad line which broadens even further as T-increases. In addition, the resonance lineshape throughout this T-interval changes from Lorentzian (insulator) to Dysonian (metallic). Furthermore, an isotropic (not shown) near linear T-dependence of the linewidth of about 1.1 Oe/K is observed above $T \approx 200\,K$ (see Fig. 2b). Notice that below $\simeq 140\,K$ there is no T-dependence of the

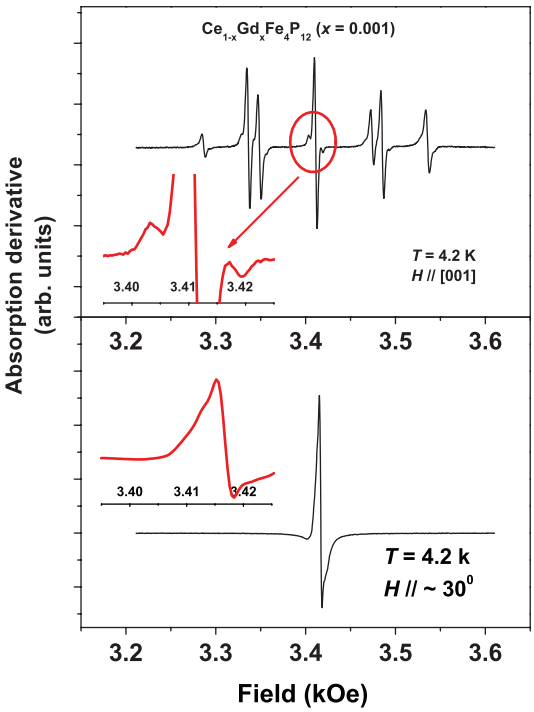

Figure 1 (online color at: www.pss-b.com) (a) X-band ESR spectra ($T = 4.2\,K$) for H along the [001] direction. The inset shows a zoom of spectra that put in evidence the hyperfine structure of the $^{157}Gd^{3+}$ ($I = 3/2$) isotope. (b) X-band ESR ($T = 4.2\,K$) for H along $\theta = 30°$ from [001] in the (110) plane. The inset presents details of the single line around this angle.

linewidth. These results suggest that above $T \simeq 160\,K$ the localized magnetic moment of the Gd^{3+} ions may be relaxing through an exchange interaction with the conduction electrons, i.e., Korringa relaxation mechanism [16].

Figure 3 presents the T-dependence of the hyperfine structure for the $(1/2 \leftrightarrow -1/2)$ transition. These data show that the collapse of the hyperfine structure is observed at $T \approx 10\,K$ below the collapse of the fine structure and that the ESR lineshape changes dramatically from Lorentzian (insulator) to Dysonian (metallic).

The above results may be associated with the increasing metallic character of $CeFe_4P_{12}$ due to the thermally activated carriers across its semiconducting gap of $\approx 1500\,K$ [17]. Thus, we suggest that the collapse of the fine and hyperfine structure, change of the ESR lineshape and the Korringa-like relaxation are a consequence of this increase in the carrier concentration. Following the Raman experiments in metallic skutterudites [13], we also suggest that the increase in the metallic character of $CeFe_4P_{12}$ may activate the Gd–X stretching mode and, in turn, trigger the rattling of the Gd^{3+} ions. The Gd^{3+} rattling inside the oversized $(Fe_2P_3)_4$ cage, via a motional narrowing mechanism [12], may be responsible for the collapse of the fine and hyperfine structure into a single broad and isotropic line [11], whereas the Korringa-like relaxation for the observed linear T-dependence of the linewidth [16].

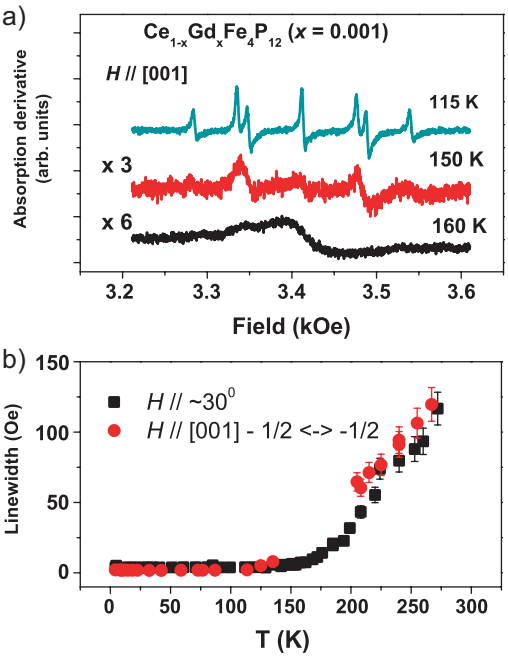

Figure 2 (online color at: www.pss-b.com) (a) X-band T-dependence ESR spectra ($115 \lesssim T \lesssim 160$ K) for H along the [001] direction. (b) T-dependence of the linewidth for H along $\theta = 30°$ from [001] in the (110) plane.

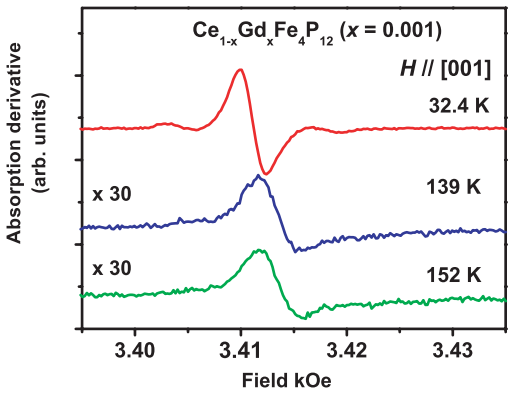

Figure 3 (online color at: www.pss-b.com) ESR spectra in the interval $32.4\ \text{K} \lesssim T \lesssim 155$ K, showing the narrowing of the hyperfine structure for the $^{155,157}Gd^{3+}$ ($I = 3/2$) isotopes and the change in the lineshape of the ESR spectra.

4 Conclusions In general the T-dependence of the dc-resistivity in $CeFe_4P_{12}$ presents a semiconducting-like behavior. However, it is strongly sample dependent and in some cases it shows a metallic behavior between ~50 and ~200 K [17]. Nevertheless, a common behavior for all the samples is that above ~200 K predominate the thermally activated conductivity mechanism.

In this work we have presented experimental evidences that in the T-interval of $140\ \text{K} \lesssim T \lesssim 160$ K there are three dramatic changes in the ESR spectra: (a) the collapse of the hyperfine and fine structures; (b) the ESR lineshape goes from Lorentzian (insulating media) to Dysonian (metallic media); and (c) the T-dependence of the ESR linewidth changes from a T-independent to a nearly linear T-dependence behavior which resembles the Korringa-like relaxation process in a metallic host [16]. These results indicates that around ~160 K, and at the microwave frequency, there is a clear change in the ac-conductivity of the material. We associate this change to a "weak" metal–insulator (M–I) transition which could be detected by our highly sensitivity ESR experiment.

These observations, together with the Raman results on these compounds, lead us to suggest that this "weak" M–I transition presumable triggers the rattling (stretching mode) of the Gd^{3+} ions in the oversized $(Fe_2P_3)_4$ cage and that this rattling may be responsible for the collapse of the hyperfine and fine structures via a motional narrowing mechanism [11, 12]. The present study gives further insights for the subtle interaction that in general exists between the localized vibration modes (Einstein oscillators) of the R ions and the conduction electrons in the filled skutterudite compounds. In particular, our work supports the idea that some metallic character is always needed to set up the necessary conditions for the rattling of the R ions in these materials.

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