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Authors
Duque, JGS
Urbano, RR
Pagliuso, PG
et al.

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Electron spin resonance study of the local environment for the Gd^{3+} and Eu^{2+} ions in $Ca_{1-x}R_xB_6$ (R = Gd, Eu) $(0.0001 \leqslant x \leqslant 0.30)$

J.G.S. Duque[a,*], R.R. Urbano[a], P.G. Pagliuso[a], C. Rettori[a], P. Schlottmann[b], Z. Fisk[c], S.B. Oseroff[d]

[a]Instituto de Fisica "Gleb Wataghin", UNICAMP, Campinas-SP 13083-970, Brazil
[b]Department of Physics, Florida State University, Tallahassee, FL 32306, USA
[c]UC Davis, Physics Department, CA 95616, USA
[d]San Diego State University, San Diego, CA 92182, USA

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Abstract

The environment of Gd^{3+}/Eu^{2+} ($4f^7, S=\frac{7}{2}$) in $Ca_{1-x}R_xB_6$ (R = Gd, Eu; $0.0001 \leqslant x \leqslant 0.30$) is studied by electron spin resonance (ESR). For $x \lesssim 0.001$ the spectra show Lorentzian shape (insulating phase). As x increases, the spectra present a superposition of Lorentzian and Dysonian resonances (coexistence of insulating and metallic phases). For $x \gtrsim 0.01$, the line shape becomes pure Dysonian (metallic phase). Thus, the intermediate concentration regime of $Ca_{1-x}R_xB_6$ is intrinsically inhomogeneous. These compounds show no weak ferromagnetism.

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Keywords: ESR; Dysonian Line shape; CaB_6

1. Introduction

The cubic system $Ca_{1-x}R_xB_6$ (R = rare earths; space group 221, Pm3m), specially La, was extensively investigated since the reported weak-ferromagnetism (WF) at $T_C \sim 600$–800 K by Young et al. [1]. Later reports on strong sample dependent WF [2] and doubts about its intrinsic nature were raised [3]. It was argued that the intrinsic WF could be hidden by the FM of Fe and Ni impurities [4] and that CaB_6 is a ~1 eV-gap semiconductor. Hence, an ESR study, probing the local R = Gd^{3+}/Eu^{2+} environment is of great interest to understand the magnetic/non-magnetic and metallic/non-metallic properties in $Ca_{1-x}R_xB_6$.

2. Experiments

Single crystals of $\sim 1 \times 0.5 \times 0.3\,mm^3$ of $Ca_{1-x}R_xB_6$ (R = Gd, Eu) $(0.0001 \leqslant x \leqslant 0.30)$ were grown as described in Ref. [1]. The structure, phase purity and orientation were checked by powder and Laue X-ray diffraction. The ESR experiments were done in a Bruker X-band (9.479 GHz) spectrometer with a TE_{102} room-T cavity coupled to a T-controller of helium gas flux system for $4.2 \leqslant T \leqslant 300$ K. The Gd^{3+}/Eu^{2+} concentration was obtained from Curie–Weiss fits of $\chi(T)(2 \leqslant T \leqslant 300\,K)$ measured in a Quantum Design SQUID DC-magnetometer.

3. Experimental results

Fig. 1 shows the room-T Eu^{2+} ESR for H∥[0 0 1], $x=0.023$, 0.07 and 0.30 crystals. The spectra for $x=0.023$ and 0.07 were simulated by the superposition of two Eu^{2+} spectra: a resolved fine structure of Lorentzian resonances (fsL) corresponding to Eu^{2+} ions in an insulating phase [5] and a single Dysonian (D) resonance associated to Eu^{2+} ions in a metallic phase [6]. For $x=0.30$ the spectrum was simulated with a D resonance. The insets show the spectra for (a) three crystals of the same $x=0.03$ batch, and (b) an as-grown and 950 °C five days annealed/

*Corresponding author. Tel.: +55 19 37885504; fax: +55 19 37884146.
E-mail address: jduque@ifi.unicamp.br (J.G.S. Duque).

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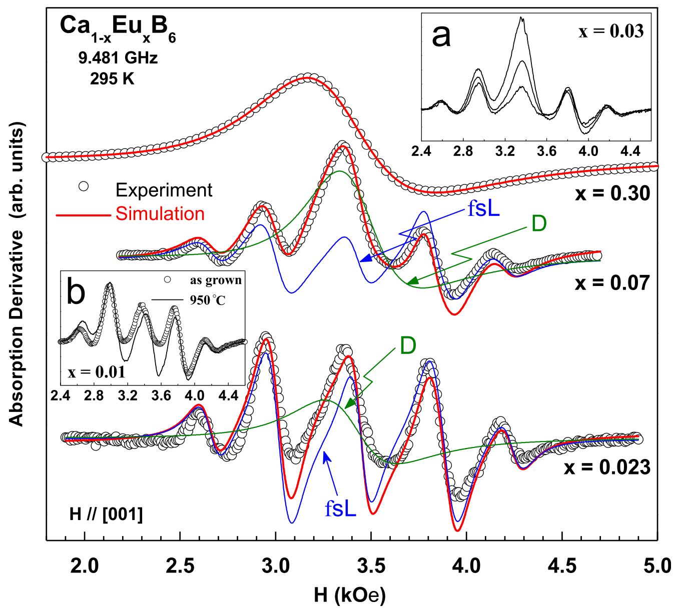

Fig. 1. ESR of Eu^{2+}. The fsL (blue) spectrum corresponds to the seven resonances in a cubic insulating phase. The D resonance corresponds to the metallic phase. For $x = 0.023$ and 0.07, S (red) are the superposition of fsL and D. For $x = 0.30$ S is given by a D resonance. Insets: spectra for (a) three crystals of the same $x = 0.03$ batch, and (b) an as-grown and 950 °C five days annealed/liquid N_2 quenched $x = 0.01$ crystal.

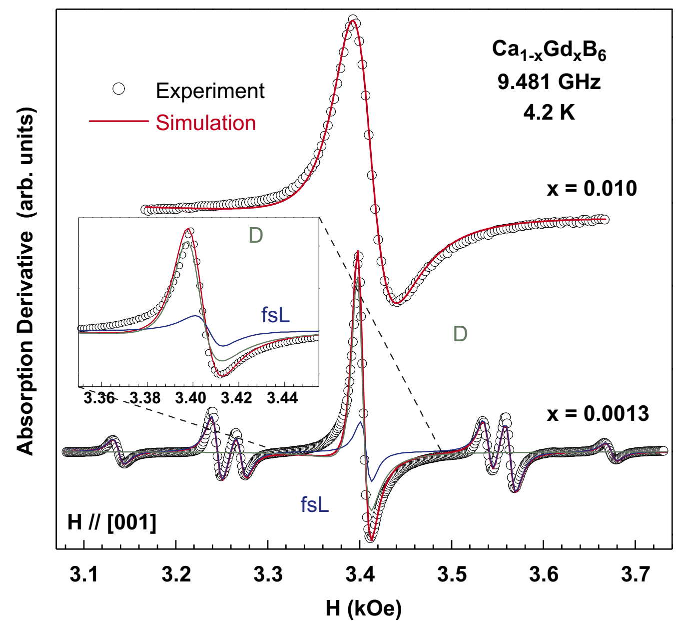

Fig. 2. ESR of Gd^{3+}. The fsL (blue) spectrum corresponds to the seven resonances in a cubic insulating phase. The D (green) resonance corresponds to the metallic phase. For $x = 0.0013$, S (red) are the superposition of fsL and D. For $x = 0.01$, S is given by a D resonance. The inset is a blow up of the central part of the spectrum.

liquid N_2 quenched $x = 0.01$ crystal. These results confirm the highly metastable inhomogeneous coexistence of two different local environments for the Eu^{2+} ions in the range of $0.023 \lesssim x \lesssim 0.15$.

Fig. 2 displays the Gd^{3+} ESR at 4.2 K for $H \| [0\,0\,1]$, $x = 0.0013$ and 0.01 crystals. The spectra were simulated by the superposition of two Gd^{3+} spectra: a resolved fsL resonances corresponding to Gd^{3+} ions in an insulating phase and a single D resonance associated to Gd^{3+} ions in a metallic phase. For $x = 0.01$ the spectrum was simulated with a D resonance. Similarly to the Eu doped crystal, these results confirm the coexistence of two different local environments for the Gd^{3+} ions in the range of $0.001 \lesssim x \lesssim 0.003$.

4. Analysis and discussion

The ESR of $R = Gd^{3+}/Eu^{2+}$ in $Ca_{1-x}R_xB_6$ show three concentration regimes. For low x the line shapes are Lorentzian, thus, the environment for Gd^{3+}/Eu^{2+} ions is insulating and the fine structure can be resolved. The isotropic g-value and anisotropy of the fine structure [7,8] indicate that the Gd^{3+}/Eu^{2+} local symmetry is cubic. For intermediate x the ESR present a superposition of fsL and D resonances. The line shape starts to show Dysonian shape (metallic phase), i.e., the microwave skin-depth is comparable to the size of our crystals. For higher x the resonance is Dysonian (metallic phase) and the fine structure can no longer be resolved. The g-value and line width are T-independent down to $\sim$10 K [8], indicating that there are no direct/indirect magnetic interactions between the R ions. For small x each Eu^{2+} in $Ca_{1-x}R_xB_6$ gives rise to an impurity bound state in the semiconductor gap which is localized within about one unit cell. As x increases the number of impurity states increases, starts to overlap, and eventually form a percolative network. Our data indicate coexistence of insulating and metallic phases for Gd and Eu concentrations of $x \approx 0.001$ and 0.02, respectively. These values are well bellow the percolation threshold for nearest neighbor (nn), next-to-nearest neighbors (nnn) and next to nnn in a simple cubic lattice ($x = 0.307$, 0.137 and 0.099). The Dysonian line shape indicates that the size of the Eu/Gd rich regions should be of the order of the skin-depth which is about 1 μm for the resistivity of pure EuB_6 and GdB_6. According to Ref. [9] we may associate the fsL and D spectra with regions rich in Ca^{2+} and Eu^{2+}, respectively.

5. Conclusions

In $Ca_{1-x}R_xB_6$ ($R = Eu/Gd$), as a function of x, an evolution from insulating to a metallic character of the compound is verified from the change of the Eu^{2+}/Gd^{3+} ESR line shapes. The percolative transition between these two regimes is estimated at $x \sim 0.14$ for Eu doped samples, indicating that nnn bounds contribute to the percolative network. For lower x, a highly metastable inhomogeneous coexistence of insulating and metallic phases is observed. This coexistence was also found in $Ca_{1-x}Gd_xB_6$, however, due to the Gd^{3+} doping extra electron, the percolative interval is found at a much lower level of Gd concentration ($x \sim 0.0015$). All measured $Ca_{1-x}R_xB_6$ ($R = Eu, Gd$) crystals presented a WF $\leqslant 0.5$ emu/mol, i.e., much smaller than that of La doped CaB_6 [1].

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