La doping effects in the coupling between localized and itinerant electronic states in EuFe$_2$As$_2$ probed by Eu$^{2+}$ ESR.

FA Garcia$^1$, EM Bittar$^1$, C Adriano$^1$, TM Garitezi$^1$, C Rettori$^1$, PG Pagliuso$^1$

$^1$Instituto de Física “Gleb Wataghin”, UNICAMP, Campinas-SP, 13083-970, Brasil.
E-mail: fgarcia@ifi.unicamp.br

Abstract. In this work we present an Electron Spin Resonance (ESR) study on La-doped EuFe$_2$As$_2$ aiming to further understand the coupling of localized spin states and itinerant electrons in these systems. The temperature dependence of the Eu$^{2+}$ ESR linewidth, g-value and intensity was investigated for both monocrystalline and powdered samples. Our results confirm the suggestion of previous ESR experiments on the pure compound [1], that the SDW transition dramatically changes the coupling between localized and itinerant states. In addition, we found a peculiar dome like shape in the Eu$^{2+}$ ESR linewidth temperature dependence for temperatures between $T_{SDW}$ and $T_N$.

1. INTRODUCTION

The discovery of superconductivity in Fe-based pnictides [2] gave rise to a series of experimental and theoretical work on this field. As previously speculated in the case of cuprates, magnetic fluctuations appears to be of great importance on the onset and stabilization of the superconducting state. It makes the study of related magnetic non-superconducting compounds an important tool to understand the role and interplay of these fluctuations with superconductivity.

Among these compounds, EuFe$_2$As$_2$ calls attention of the community since it can be tuned to a superconducting state upon doping on any of the Eu, Fe and As sites [3, 4, 5] and also by applying pressure, which leads to the appearance of a re-entrant superconducting state [6]. Its electronic and magnetic properties are the subject of several recent studies [7, 8].

Electron Spin Resonance (ESR) is a very sensitive microscopic probe to local spin fluctuations and magnetic interactions [9]. Moreover, it can also extract, in some cases, information about the superconducting state of unconventional superconductors as it has been shown recently for Fe-based pnictides superconductors [3, 10].

This work discuss the La doping effects on the coupling between the localized Eu$^{2+}$ and itinerant electronic states as probed by ESR. In general, our results are in qualitative agreement with a previous work done on the pure compound [1]. Some peculiarities, however, exist and are reported in this paper, being the most interesting a conspicuous dome-like shape in the ESR linewidth in the temperature interval between $T_N$ and $T_{SDW}$.
2. METHOD AND RESULTS

Single crystals of $Eu_{0.6}La_{0.4}Fe_2As_2$ were grown in a molten Sn flux according to the method described in Ref. [11]. The crystal structure (space group $I4/mmm$) and phase purity were checked by X-ray powder diffraction. The La content is the stoichiometric nominal value used in the synthesis. The ESR experiments were carried on both powdered and single crystal samples. The powdered sample was obtained from crushed single crystals with high grain size homogeneity and for the single crystal experiment a platelet ($\approx 0.5 \text{mm} \times 0.2 \text{mm} \times 0.01 \text{mm}$) shaped sample was chosen.

The ESR spectra were taken in a X (9.48 GHz)-band Bruker spectrometer using appropriate resonators coupled to a T-controller of helium gas flux system for $4.2 \leq T \leq 300 \text{ K}$. For the single crystals, the ESR lines usually showed a Dysonian lineshape. This asymmetric lineshape reflects the skin depth effects due to the penetration of the microwave on a metallic surface, in a regime that the skin depth is smaller than the sample size. For the powdered sample, a Lorentzian lineshape was observed. At low temperatures, close to the reported $T_N$ for the parent compound, substantial lineshape deformation was observed.

Figures 1a and 1b show some representative spectra for the powdered and single crystal samples, respectively. All the experimental data were fitted to a Dysonian lineshape to extract the ESR linewidth ($\Delta H$), resonance field (converted to $g$-value), intensity (double integration of the resonance spectrum) and the absorption/dispersion relation ($D/A$, that express the lineshape asymmetry, being 0 for a Lorentzian lineshape.) In figure 1a we show a comparison between the fitting and experimental results and a very good agreement is achieved for all $T$-interval. Figure 1b shows that above the magnetic transition ($T_N \approx 20 \text{K}$ ) no significant anisotropy was found in the spectra.

Figure 2 presents the ESR linewidth as a function of temperature. At high temperatures $(T > 200 \text{K})$, the linewidth increases linearly with temperature in a Korringa-like relaxation with $b = 3(1) \text{ Oe/K}$ (powdered sample), a value significantly lower than the one previous reported of $\approx 8 \text{ Oe/K}$ [1]. Below this temperature, this relaxation ceases and the linewidth start to increase until reaching a maximum at $T \approx 100 \text{K}$. Then it decreases again down to $T \approx 25 \text{K}$, where magnetic fluctuations become important resulting in strong anisotropy (single crystal) and broadening (powder) of the resonance lines. The inset in this figure, shows that, within experimental error, the $g$-value is isotropic and temperature independent for $T > 25 \text{K}$. The $g$-value of 1.96(9) is consistent with a $Eu^{2+}$ $g$-value and this same value was reported earlier.
The described dome-like shape in the linewidth is a robust result that was not reported in this previous work.

Figure 2. X-Band ESR linewidth behavior in the temperature interval 4.2 ≤ T ≤ 300K for all experiments. In the inset, the calculated g-values are presented as a function of temperature.

Figure 3 presents the normalized ESR intensity for temperatures well above (T > 50K) the magnetic transition at T ≈ 25K. The experimental results follow closely a Curie law confirming that our resonance arises from a localized electronic state. The absorption/dispersion relation is plotted in the inset. Away from the magnetic transition, this quantity is closely constant, with a variation smaller than 10%. Both results are in contrast to those previously reported for the pure compound [1].

Figure 3. X-Band ESR normalized intensity as a function of temperature. The intensities are normalized for T > 50K since due to the proximity to the magnetic transition at T ≈ 25K, and also low temperature spin-spin interaction, the ESR intensity may deviate from the expected Curie behavior. The inset shows that the absorption/dispersion ratio is nearly constant in a broad T-interval.

3. DISCUSSION
The key aspects of the magnetic ordering phenomena in EuFe₂As₂ and similar compounds are reflected in changes of the ESR parameters. In particular, appearance of SDW ordering is reported to be related to changes in the linewidth (EuFe₂As₂ [1], EuFe₂₋ₓCoₓAs₂ [3]) g-value (EuFe₂₋ₓCoₓAs₂ [3]) and intensity (EuFe₂₋ₓCoₓAs₂ [3]) behavior.

In the linewidth, the reported changes are the appearance of anisotropic linewidth and modification in the relaxation regime, where the linewidth is closely constant below T_{SDW}. It is usually thought that the SDW transition leads to nesting of the Fermi surface that greatly reduces the exchange interaction of the conduction electrons with the localized Eu²⁺ states. This exchange interaction dominates the spin dynamics above T_{SDW} leading to the observed Korringa relaxation. All these experiments were done on concentrated Eu²⁺ systems.

Qualitatively, it is expected that the La-doping dilutes the Eu²⁺ ions reducing the localized spin-spin interaction. At the same time, it may also affect the local density of itinerant electronic
states at a given Eu$^{2+}$ site and/or change the localized-itinerant spin $J_{fs}$ exchange coupling. Localized spin-spin interaction leads to deformation and broadening of the resonance line. Inspection of figures 1(a)-(b) and the inset of figure 3 indicates that, for all temperature interval (above $\approx 25$K), the broadening effects of the Eu$^{2+}$ spin-spin interaction remains strong but no significant lineshape deformation appears. This is in contrast to the previous results where lineshape deformation was observed.

On figure 2, the reduction of the Korringa relaxation at high temperatures may be attributed to one, or both, of the cited putative La-doping effects. This is so because its value is direct connected to the values of the density of states and $J_{fs}$ ($J_{fs} = g_{f} B \frac{\mu_{B}}{\pi k_{B}} J_{fs} \eta_{F}$). The regime between $25 \lesssim T \lesssim 195$K, however, is unique and different from the previous report.

An anisotropy was found in the pure compound and was attributed to CF effects reflecting the low symmetry of the system. These effects were absent at high temperatures due to interaction with the conduction electrons, which was turned off at $T_{SDW}$. Figure 2 shows that, within experimental error, the linewidth and $g$-values are the same for the field applied perpendicular and parallel to the plane of the sample. This leads us to believe that the anisotropy observed for the pure compound is not due to CF effects but to localized Eu$^{2+}$ spin-spin interaction, which is weakly suppressed in our case due to the La-doping. This point is based upon the fact that the CF effect is a single ion effect which would remain in the Eu$^{2+}$ ion in the La-doped sample.

Another interesting distinct behavior of our doped system, is that in EuFe$_{2}$As$_{2}$ [1] (and also EuFe$_{2-x}$Co$_{x}$As$_{2}$ [3]) the linewidth is nearly constant in this $T$-interval. In our case, a conspicuous dome like shape appears in this region. The strange behavior of ESR linewidth in the temperature region below $T_{SDW}$ is usually ascribed to intricate Fermi surface nesting characteristics, and may resemble the coherence peak usually found in NMR data near a gap opening transition. A systematic study as a function of La-doping may elucidate this issue.

For EuFe$_{2}$As$_{2}$, a correction of the intensity values due to change of the lineshape (expressed by change in the $A/D$ ration), was needed to adjust the intensity to a Curie law. Figure 3 shows that this is not necessary in our case. Our intensity naturally follows a Curie law above the low-$T$ magnetic transition. We claim that it is further evidence that localized Eu$^{2+}$ spin-spin interaction is affecting the lineshape analysis in the results for EuFe$_{2}$As$_{2}$.

In conclusion, ESR proved to be an important tool to further investigate magnetic and electronic ordering properties of Fe-based pnictide compounds. We expect that a systematic ESR study with different La-doping, and possible other dopings at both the Fe and As sites, may reveal interesting new physics of these materials.

ACKNOWLEDGMENTS

This work was supported by FAPESP and CNPq, Brazil.

4. REFERENCES

[1] E. Dengler, J. Deseinhofer, H.-A. Krug von Nidda, Seunghyun Khin, J. S. Kim, Kee Hoon Kim, F. Casper, C. Felser, and A. Loidl, 2010, Phys Rev B 81, 024406.

[2] Kamihara Y, Watanabe T, Hirano M , Hosono H, 2008 J.Ame.Chem.Soc. 130, 11.

[3] H. S. Jeevan, et al, 2008, Phys Rev B 78, 692406.

[4] Z. Ren, et al, 2009, Phys Rev Letters 102, 137002.

[5] J. J. Ying, et al, 2010, Phys Rev B 81, 052503.

[6] C. F. Miclea, et al, 2009, Phys Rev B 79, 212509.

[7] Y. Xiao, et al, 2009, Phys Rev B 80, 174424.

[8] B. Zhou, et al, 2010, arXiv : 1001.4537v1.

[9] A. Abragam and B. Bleaney, EPR of Transition Ions, (Clarendon Press, Oxford, 1970).

[10] Pascher N, et al, 2010, arXiv : 1001.1302v1.

[11] Z. Fisk and J. P. Remeika, Handbook on the Physics and Chemistry of Rare Earths (Elsevier, North-Holland, Amsterdam, 1989), Vol. 12, p. 53.