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Journal
Journal of Physics Conference Series, 200(1)

ISSN
1742-6588

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Publication Date
2010

DOI
10.1088/1742-6596/200/1/012045

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Peer reviewed
Experimental evidence for off-center rattling of Yb$^{3+}$ in the skutterudite compounds of Ce$_{1-x}$Yb$_x$Fe$_4$P$_{12}$.

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Abstract. Electron Spin Resonance (ESR) experiments in the filled Ce$_{1-x}$Yb$_x$Fe$_4$P$_{12}$ ($x \lesssim 0.0023$) skutterudite compounds of T$_h$ cubic symmetry ($Im\bar{3}$) reveal the coexistence of two distinct Yb$^{3+}$ sites with large difference in their site occupation, hyperfine interaction and temperature dependence of the ESR parameters. These results suggest a scenario where the oversized (Fe$_2$P$_3$)$_4$-cages of the Ce$_{1-x}$Yb$_x$Fe$_4$P$_{12}$ compounds are occupied with small number of on-center-Yb$^{3+}$ ions and a distribution of highly occupied off-center-Yb$^{3+}$ ions, rattling at $\sim$1 GHz and above $\sim$20 GHz, respectively.

The filled skutterudite RT$_4$X$_{12}$ 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) crystallize in the LaFe$_4$P$_{12}$ structure with space group $Im\bar{3}$ and local point symmetry T$_h$ for the R ions [1]. The dynamics of the guests R ions is a topic of great importance related to the physics of the skutterudite compounds. Intense discussions exist about whether the R ions are sited at the on and/or off-center site in the oversized rigid (T$_2$X$_3$)$_4$-cages [2, 3] and also about the possibility that these ions may rattle as free Einstein oscillators inside these cages. This behavior may lead to a phonon-glass type of heat conductivity, [4, 5] and also play an important role in the wide range of strongly correlated phenomena [3, 6, 7] exhibited by these materials.

Takegahara et al. [8], studied their electric crystal field (CF) and noticed that an appropriate description of such CF should be done in terms of point groups T and T$_h$, which requires an extra sixth order term to be associated to a new CF parameter. Therefore, in terms of the Steven’s operators [9] $H_{CF}$ is written as

$$H_{CF} = B'^{5}_4 (O^4_4 + 5O^0_4) + B'^{5}_6 (O^6_6 - 21O^4_6) + B'^{2}_6 (O^2_6 - O^0_6), \quad (1)$$

where the last term is not allowed in the ordinary cubic symmetry $O_h$. This new term may strongly mix the former $\Gamma^6_6$ and $\Gamma^7_7$ ground states of ordinary cubic symmetry, giving rise to some appreciably different eigenfunctions and eigenvalues [8].
Garcia et al. [10] have measured the low-\(T\) ESR of Ce\(_{1-x}\)R\(_x\)Fe\(_4\)P\(_{12}\) (R = Nd, Dy, Er, Yb; \(x \leq 0.005\)). This ESR data was explained using the \(H_{CF}\) given in Eq. (1) and the full set of CF parameters could be determined. The present work deals with the evolution of the Yb\(^{3+}\) ESR data with temperature, which results in the appearance of a second resonance, corresponding to another coexisting and distinct Yb\(^{3+}\) site. The presence of the last term in Eq. (1) turned to be essential to explain the behavior of this second Yb\(^{3+}\) resonance.

Single crystals of Ce\(_{1-x}\)Yb\(_x\)Fe\(_4\)P\(_{12}\) \((x \leq 0.0023)\) were grown in a molten Sn flux according to the method described in Ref. [11]. The cubic structure (space group \(I\overline{m}3\)) and phase purity were checked by x-ray powder diffraction. The Yb concentrations were determined from \(M(H,T)\) measurements obtained in a SQUID \(dc\)-magnetometer.

For the ESR experiments we used single crystals with perfect natural crystallographic grown faces. The ESR spectra were taken in a Bruker X (9.48 GHz)-band spectrometer using appropriate resonators coupled to a \(T\)-controller of a helium gas flux system for \(4.2 \leq T \leq 45\) K. The resonances usually showed a metallic lineshape associated to the thermally activated conductivity \((\sim 10^{-4} \ (\Omega cm)^{-1})\) reported for this material at low-\(T\) [11].

![Figure 1](image1.png)

**Figure 1.** a) \(T\)-evolution of the normalized Yb\(^{3+}\) X-band ESR spectra in a Ce\(_{1-}\)Yb\(_{2}\)Fe\(_4\)P\(_{12}\) \((x \simeq 0.0023)\) single crystal. b) X-band \(T\)-dependence of the ESR intensity for the two resonances of the \(^{170}\)Yb\(^{3+}\) \((I=0)\) isotope.

![Figure 2](image2.png)

**Figure 2.** X-band \(T\)-evolution \((4.2 \leq T \leq 40\) K) of: a) \(g\)-value and b) \(\Delta H\) for the narrow and broad lines of Yb\(^{3+}\) in Ce\(_{1-x}\)Yb\(_x\)Fe\(_4\)P\(_{12}\) \((x \simeq 0.0023\) and \(x \simeq 0.0018)\) single crystals. c) the high correlation between \(\delta(\Delta H)/H\) and \(\delta g/g\).

Figure 1a presents the \(T\)-evolution \((4.2 \leq T \leq 45\) K) of the X-band ESR spectra for a Kramers doublet of the \(^{170}\)Yb\(^{3+}\) \((I=0)\) isotope in a Ce\(_{1-x}\)Yb\(_x\)Fe\(_4\)P\(_{12}\) \((x \cong 0.0023)\) single crystal. The figure shows that as \(T\) increases a second resonance is clearly separated from the main line observed at \(T = 4.2\) K. The ESR spectra of the \(^{170}\)Yb\(^{3+}\) isotope becomes two slightly separated lines, a narrow and a displaced broad one, which we associate to two different Yb\(^{3+}\) sites.

Also in Fig. 1a, one can see the ESR full hyperfine spectra, associated with the narrow line, for the various Yb isotopes, \(^{170}\)Yb\(^{3+}\) \((I=0)\), \(^{171}\)Yb\(^{3+}\) \((I=1/2)\) and \(^{173}\)Yb\(^{3+}\) \((I=5/2)\). From its analysis the hyperfine parameters \(^{171}A = 440(10)\) Oe and \(^{173}A = 120(3)\) Oe were obtained.
These values present a reduction of $\sim 20\%$ in comparison with the ones usually measured for these isotopes in other cubic compounds [9]. Even more noteworthy (see low field part of Fig. 1a) is that the two hyperfine structure corresponding to the broad line were not observed.

Figure 1b displays the $T$-dependence of the above ESR intensity for the broad and narrow lines of the $^{170}$Yb$^{3+}$($I=0$). From their relative intensities we estimate that the broad and narrow lines correspond, respectively, to $\sim 95\%$ and $\sim 5\%$ of the Yb$^{3+}$ ions occupying the available sites in the Ce$_{1-x}$Yb$_x$Fe$_2$P$_{12}$ compounds. Furthermore, the comparison with the Curie-Weiss law indicates that the $^{170}$Yb$^{3+}$ ions carry localized magnetic moment and that the resonances arise from a Kramers doublet ground state of the CF split $J = 7/2$-multiplet.

Figures 2a and 2b show, respectively, the $T$-evolution ($4.2 \lesssim T \lesssim 40$ K) of the $g$-values and linewidths, $\Delta H$, for the observed narrow and broad lines of Fig. 1 and these same results for another batch. These data show the following features: a) for the sites corresponding to the narrow line the $g$-value and $\Delta H$ are $T$-independent; b) for those of the broad line the $g$-value and $\Delta H$ are $T$-dependent. Figure 2c shows that for both batches the relative change of the linewidth, $\delta g/g$, i.e., $\delta(\Delta H)/\Delta T = 1.3(3)$, scales at all $T$ with the relative change of the $g$-value, $\delta g/g$. The angular dependence of the spectra was tested at various $T$ and it was found to be isotropic.

A comparative analysis of the behavior for these two resonances allowed us to conclude that the narrow line is a homogeneous resonance and the broad line an inhomogeneous one, and that the origin of the inhomogeneity is a distribution of $g$-values which is of the order of the change in the $g$-value. The results are nearly the same for all measured batches.

![Figure 3](image)

Figure 3. Ground state $g$-values for Yb$^{3+}$ ($J = 7/2$; $g_J = 8/7$; $W > 0$) as a function of $(x,y)$. The green dashed line indicates the set of $(x,y)$ values corresponding to $g = 2.57$. In the inset of this figure the area between and limited by the green dashed line and the thick blue line next to the $(x=0.54,y=0.08)$ point shows the sets of possible $(x,y)$ values appropriated to the $g$-value of the broad line (see text).

Working on the basis of the framework proposed by Takegahara et al. [8], we give a new parametrization to Eq. (1) [10]. Adding the Zeeman term $g_J\mu_BH \cdot J$ it is written as:

$$H_{CFZ} = W \left\{ (1 - |y|) \left[ x \frac{O_5^c}{F_4^2} + (1 - |x|) \frac{O_6^c}{F_6^2} \right] + y \frac{O_6^c}{F_6^2} \right\} + g_J\mu_BH \cdot J, \quad (2)$$

the $x$ variable, which describes the relative ratio between the $O_5^c$ and $O_6^c$ terms, was already included in the work by Lea, Leask and Wolf (LLW) [12]. The above equation now includes an extra variable $y$, to account for the effects of the new $O_6^c$ sixth order term in $H_{CF}$ (Eq. 1).

From this Hamiltonian and for small $H$ the ground state $g$-value as a function of $x$ and $y$ can be calculated. Fig. 3 shows the $x$ and $y$ dependence of the $g$-value for the Kramers doublet ground state of Yb$^{3+}$ ($J = 7/2$; $g_J = 8/7$; $W > 0$) in a color scale. The measured $g$-value of 2.57 obtained at $T \simeq 4.2$ K corresponds to a mixing of the $\Gamma_6$ and $\Gamma_7$ ($y = 0$) ground states.
Our early work [10] allowed us to obtain the values \( x = 0.54 \) and \( y = 0.08 \) for \( \text{Yb}^{3+} \). These \((x,y)\) values correspond to the \( \text{Yb}^{3+} \) resonance observed at \( T \simeq 4.2 \) K and \( g \simeq 2.57 \) and are related to on-center \( \text{Yb}^{3+} \) ions. However, from Figs. 1 and 2, we see that the spectrum evolves to display another coexisting \( \text{Yb}^{3+} \) site whose \( g \)-values are explained with a different set of \((x,y)\) values. This site is originated from off-center \( \text{Yb}^{3+} \) ions.

We argue that the reduced hyperfine constant of the narrow line spectra results from a motional narrowing mechanism [13, 14] due to the rattling, in a frequency of about 1 GHz, of on-center \( \text{Yb}^{3+} \) ions inside the \((\phi \simeq 5 \text{\degree}) (\text{Fe}_2\text{P}_3)_4\)-cages. Since the hyperfine structure due the broad line spectra was not observed, we claim that it has been collapsed by the rattling of the off-center \( \text{Yb}^{3+} \) ions. A minimum rattling frequency of \( \sim 20 \) GHz [14] would be enough to produce the needed 90 to 95% reduction of the hyperfine constant leading to the observed spectra. It is important to mention that the usual reported amplitudes for the rattling modes are \( \lesssim 0.1 \) \AA{} [15].

This work presents the experimental results that introduces ESR measurements as an useful and unexpected probe of the dynamics of the guest \( R \) ions in the skutterudite compounds. These results were checked for several different batches (two presented). The coexistence of two distinct \( \text{Yb}^{3+} \) sites were determined. We associate the homogeneous narrow line, corresponding to the low occupied sites, to on-center \( \simeq 1 \) GHz rattling \( \text{Yb}^{3+} \) ions at exactly the \((x=0.54,y=0.08)\) point, whereas the inhomogeneous broad line, corresponding to the highly occupied sites, to a distribution of \( \sim 20 \) GHz rattling off-center \( \text{Yb}^{3+} \) ions covering all the \((x,y)\) values within the area next to the \((x=0.54,y=0.08)\) point described above. In addition, this distribution yields the observed broadening of the inhomogeneous line. This is a simple approximation since we used the same \( x \) and \( y \) parameters connected to the \( T_h \) crystal field symmetry. In fact, the off-center ions are experiencing, during its excursion in the oversized cages, slightly deformed environments breaking the cubic \( T_h \) symmetry. Nevertheless, this simple picture captures the main issues of our results. Our detailed discussion will be published elsewhere [16].

ACKNOWLEDGMENTS

This work was supported by FAPESP and CNPq, Brazil.

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