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Experimental evidence for off-center rattling of Yb^{3+} in the skutterudite compounds of $Ce_{1-x}Yb_xFe_4P_{12}$.

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Abstract. Electron Spin Resonance (ESR) experiments in the filled $Ce_{1-x}Yb_xFe_4P_{12}$ ($x \lesssim 0.0023$) skutterudite compounds of T_h cubic symmetry ($Im3$) 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 $(Fe_2P_3)_4$-cages of the $Ce_{1-x}Yb_xFe_4P_{12}$ 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_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) crystallize in the $LaFe_4P_{12}$ structure with space group $Im3$ 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 $(T_2X_3)_4$-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

$$H_{CF} = B_4^c(O_4^0 + 5O_4^4) + B_6^c(O_6^0 - 21O_6^4) + B_6^t(O_6^2 - O_6^6), \quad (1)$$

where the last term is not allowed in the ordinary cubic symmetry O_h. This new term may strongly mix the former Γ_6 and Γ_7 ground states of ordinary cubic symmetry, giving rise to some appreciably different eigenfunctions and eigenvalues [8].

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Garcia *et al.* [10] have measured the low-T ESR of $Ce_{1-x}R_xFe_4P_{12}$ (R = Nd, Dy, Er, Yb; $x \lesssim 0.005$). 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 $Ce_{1-x}Yb_xFe_4P_{12}$ ($x \lesssim 0.0023$) were grown in a molten Sn flux according to the method described in Ref. [11]. The cubic structure (space group $Im3$) 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 $4.2 \lesssim T \lesssim 45$ K. The resonances usually showed a metallic lineshape associated to the thermally activated conductivity ($\simeq 10^{-4}$ $(\Omega\text{cm})^{-1}$) reported for this material at low-T [11].

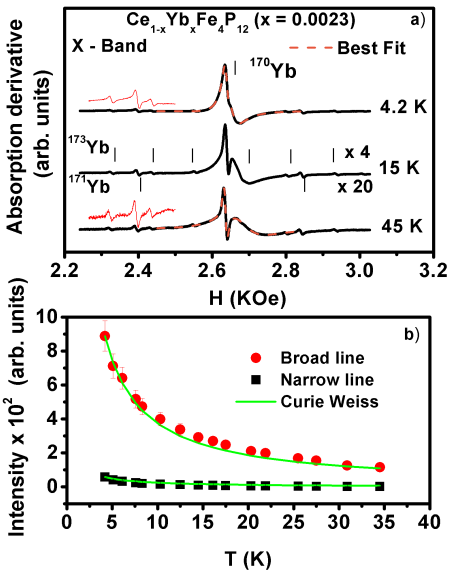

Figure 1. a) T-evolution of the normalized Yb^{3+} X-band ESR spectra in a $Ce_{1-x}Yb_xFe_4P_{12}$ ($x \simeq 0.0023$) single crystal. b) X-band T-dependence of the ESR intensity for the two resonances of the $^{170}Yb^{3+}$(I=0) isotope.

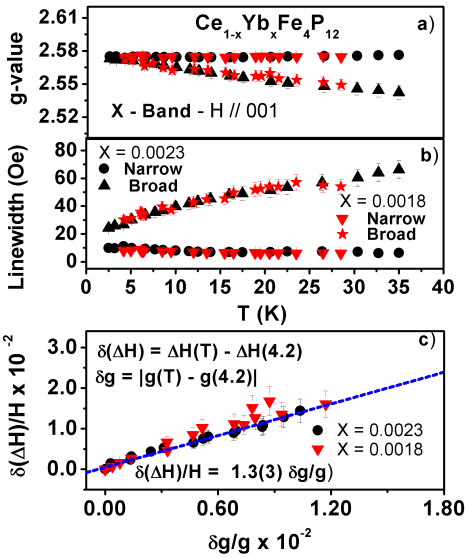

Figure 2. X-band T-evolution ($4.2 \lesssim T \lesssim 40$ K) of: a) g-value and b) ΔH for the *narrow* and *broad lines* of Yb^{3+} in $Ce_{1-x}Yb_xFe_4P_{12}$ ($x \simeq 0.0023$ and $x \simeq 0.0018$) single crystals. c) the high correlation between $\delta(\Delta H)/H$ and $\delta g/g$.

Figure 1a presents the T-evolution ($4.2 \lesssim T \lesssim 45$ K) of the X-band ESR spectra for a Kramers doublet of the $^{170}Yb^{3+}$(I=0) isotope in a $Ce_{1-x}Yb_xFe_4P_{12}$ ($x \cong 0.0023$) 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 presents 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 $Ce_{1-x}Yb_xFe_4P_{12}$ 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, ΔH, 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 ΔH are T-independent; *b*) for those of the *broad line* the g-value and ΔH are T-dependent. Figure 2c shows that for both batches the relative change of the linewidth of the *broad line* , $\delta(\Delta H)/H$, scales at all-T with the relative change of the g-value, $\delta g/g$, *i.e.*, $\delta(\Delta H)/H \simeq 1.3(3)\delta g/g$. 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.

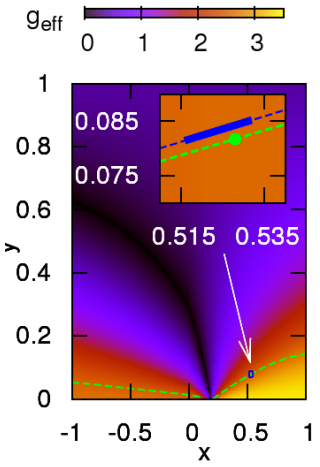

Figure 3. Ground state g-values for Yb^{3+} ($J = 7/2$; $g_J = 8/7$; $W > 0$) as a function of (x,y). The green dashed line indicates the set of (x,y) values corresponding to $g = 2.57$. In the inset of this figure the area between and limited by the green dashed line and the thick blue line next to 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 $g_J\mu_B\mathbf{H}\cdot\mathbf{J}$ it is written as:

$$H_{CFZ} = W\left\{(1-|y|)\left[x\frac{O_4^c}{F_4^0}+(1-|x|)\frac{O_6^c}{F_6^0}\right]+y\frac{O_6^t}{F_6^2}\right\}+g_J\mu_B\mathbf{H}\cdot\mathbf{J}, \quad (2)$$

the x variable, which describes the relative ratio between the O_4^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^t 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 Γ_6 and Γ_7 ($y = 0$) ground states.

Our early work [10] allowed us to obtain the values x = 0.54 and y = 0.08 for Yb^{3+}. These (x,y) values correspond to the Yb^{3+} resonance observed at $T \simeq 4.2$ K and $g \simeq 2.57$ and are related to *on-center* Yb^{3+} ions. However, from Figs. 1 and 2, we see that the spectrum evolves to display another coexisting Yb^{3+} site whose g-values are explained with a different set of (x,y) values. This site is originated from *off-center* 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* Yb^{3+} ions inside the ($\phi \simeq 5\mathring{A}$) $(Fe_2P_3)_4$-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* Yb^{3+} ions. A minimum rattling frequency of ∼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 $\lesssim 0.1$ $\mathring{A}$ [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 Yb^{3+} sites were determined. We associate the homogeneous *narrow line*, corresponding to the low occupied sites, to *on-center* ≃1 GHz rattling 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 ∼20 GHz rattling *off-center* 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].

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