Eu$^{2+}$ spin dynamics in the filled skutterudites EuM$_4$Sb$_{12}$ (M=Fe, Ru, Os)

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We report evidence for a close relation between the thermal activation of the rattling motion of the filler guest atoms, and inhomogeneous spin dynamics of the Eu$^{2+}$ spins. The spin dynamics is probed directly by means of Eu$^{2+}$ electron spin resonance (ESR), performed in both X-band ($\approx 9.4$ GHz) and Q-band ($\approx 34$ GHz) frequencies in the temperature interval $4.2 \lesssim T \lesssim 300$ K. A comparative study with ESR measurements on the $\beta$-Eu$_4$Ga$_{12}$Ge$_{30}$ clathrate compound is presented. Our results point to a correlation between the rattling motion and the spin dynamics which may be relevant for the general understanding of the dynamics of cage systems.

I. INTRODUCTION

The discovery of localized phonon modes in metallic compounds opens an avenue for the study of electron-phonon and phonon-phonon interactions in solids. The family of the filled skutterudite compounds are among the materials where this scenario is believed to take place$^2$. These are cage systems inside which a guest, or filler, atom may perform relative large excursions. These excursions are described in terms of localized and isolated phonon modes (Einstein modes), usually called rattling modes. In this sense, the guest is referred as the rattler atom and its dynamics are fully characterized by a single parameter $\theta_E$, the Einstein temperature$^2$.

Filled skutterudite compounds have the general formula RT$_4$X$_{12}$, where usually R is a rare earth or actinide; T is a transition metal (Fe, Ru, Os or Co), and X is a pnictogen (P, As or Sb). These compounds crystallize in the LaFe$_4$P$_{12}$ structure with space group Im3 and local point symmetry $T_h$ for the R ion.$^3$ This structure hosts a wide range of physical properties, including exotic strongly correlated ground states$^2$ as well as presenting a promising potential for application in the construction of thermoelectric devices.$^4$

The latter feature is argued to be closely related to the dynamics of the rattler R atom.$^4$ The rattling modes seem to promote the dampening of the thermal conductivity mainly through the incoherent scattering of the Debye phonons. This leads to the concept of a phonon-glass type of heat conduction, which gives a fair picture of experimental results. Two important approximations to the rattler ion excursions are commonly adopted in this scenario: a description in terms of isolated (non correlated) and localized (non dispersive) phonon modes.$^5$

Extensions of this scenario have been a matter of intense discussion in the field. One may find strong experimental evidence for the dispersion of these modes.$^6$ which raises the question of the validity of the independent rattler approximation. It also raises the question of weather or not an “electron glass”, meaning a coupling between the guest ion dynamics and electronic degrees of freedom, could also be realized in these materials. In deed, there are some recent theoretical proposals in this direction.$^9$ In experiments, there is evidence for an interplay between the rattling motion and quadrupolar fluctuations with the unconventional superconductivity in PrOs$_4$Sb$_{12}$$^{12}$ Moreover, $^{139}$La nuclear magnetic resonance (NMR) show a correlation between the d band of transition metal and the rare earth rattling motion realized through electron-phonon coupling.$^{13}$ In this direction, the rattling modes may also have an important role in the strongly correlated electronic phenomena found in cage systems. For applications, a better understanding of the description of the rattling modes may possibly lead to a more efficient design of thermoelectric materials.

In a previous work, we presented electron spin resonance (ESR) as a probe for the guest ion dynamics.$^6$ We showed that the Yb$^{3+}$ spectra in Ce$_{1-x}$Yb$_x$Fe$_4$P$_{12}$ ($x \sim 0.002$) clearly reveal the R ion dynamical behavior. Taking advantage of this novel application of the ESR technique, here, we investigate the EuT$_4$Sb$_{12}$ ($T$ = Fe, Ru, Os) skutterudites, to observe whether the Eu$^{2+}$ ESR spectra is a good probe for their rattling behavior. For comparison, we also present measurements on the $\beta$-Eu$_4$Ga$_{12}$Ge$_{30}$ clathrate compound, another well-known cage system inside which Eu$^{2+}$ behaves as a rattler ion.

EuT$_4$Sb$_{12}$ ($T$ = Fe, Ru, Os) are metallic systems that undergo a ferromagnetic transition around $T_C = 90$ K, = 4 K and = 9 K, respectively.$^{13}$ Close investigation of the $T$ = Fe system indicates that, in fact, a ferrimagnetic transition takes place at $T_C = 90$ K, as a consequence of an antiferromagnetic coupling of the Eu and Fe moment.$^{13}$ The rattling behavior of the Eu$^{2+}$ ions was studied by structure refinement of x-ray diffraction measurement$^{13}$ and also by extended x-ray fine structure (EXAFS) measurement$^{13}$ The results obtained from both methods are in close agreement. The first measurements gave, for $T$ = Fe, Ru, Os, $\theta_E$ = 84, 78, 74 K respectively, whereas EXAFS gave, for $T$=Ru, Os $\theta_E$ = 81, 78 K respectively. In both measurements, no signs of static off-center displacement of the Eu$^{2+}$ were found. X-ray absorption near edge spectroscopy (XANES) and also susceptibility measurements, point to a predominant 2+ valence state of the Eu atoms, al-
though a slightly mixed valence state cannot be completely excluded ($v \lesssim 2.1$). In particular, for EuT₄Sb₁₂ (T = Ru, Os), the susceptibility measurements are compatible with the full Eu²⁺ moment in the temperature interval $2 \lesssim T \lesssim 400$K.

The type-I clathrate compound β-Eu₈Ga₁₆Ge₃₀ is a metallic compound which undergoes a ferromagnetic transition at $T_c = 35$ K. In type-I clathrates, one finds two distinct types of cages that eventually lead to different dynamical behaviors of the guest elements. In particular, in β-Eu₈Ga₁₆Ge₃₀, the majority of the guest Eu²⁺ ions are subjected to a potential with four symmetric off-center energy minima. In these cages, it was found that the dynamical behavior of the Eu²⁺ ions includes not only an off-center thermal activated rattling mode, but also quantum tunneling between the low temperature potential energy minima.

In this work, we report a non-trivial evolution of the X-band ESR spectra of EuT₄Sb₁₂ (T = Ru, Os). We shall discuss that, in the low temperature region ($4.2 \lesssim T \lesssim 150$ K), the rattling motion couples with the Eu²⁺ spins. This gives rise to inhomogeneous spin dynamics, which manifests in the ESR linewidth ($\Delta H$) behavior. We shall also discuss how our Q-band ESR spectra give support to these findings.

## II. EXPERIMENT

For this work, we use single crystals of EuT₄Sb₁₂ (T = Fe, Ru, Os) grown in Sb-flux as described in Ref. The resulting filled skutterudite structure was checked by X-ray powder diffraction. High filling rates were confirmed by refinement methods. The ESR experiments were carried on crushed small pieces of single crystals with high grain size homogeneity. The ESR spectra were taken in a X-band and Q-band Bruker spectrometer using appropriate resonators coupled to a T-controller of helium gas flux system. The experiments covered the temperature interval $4.2 \lesssim T \lesssim 300$ K. For comparison, X-band ESR experiments were performed on a single crystal of the clathrate compound β-Eu₈Ga₁₆Ge₃₀.

ESR detects the power P absorbed from the transverse magnetic microwave field as a function of the static magnetic field $H$. The sensitive of the instrument is improved by applying a lock-in technique with field modulation. As a result, it is the absorption derivative $\frac{dP}{dH}$ which is observed. In our experiments, the ESR spectra showed a single Dysonian lineshape, described by equation:

$$P(H) \propto \frac{\Delta H + \alpha(H - H_{res})}{(H - H_{res})^2 + \Delta H^2}$$

(1)

this lineshape contains an $\alpha = D/A$ parameter expressing the ratio between the dispersion ($D$) and absorption ($A$) of the microwave radiation when it probes a metallic material. This $D/A$ parameter appears due to skin depth effects. A small excess of EuRu₄Sb₁₂ was synthesized and the resulting crystals were crushed and sieved into fine powder. The powdered crystals were investigated in X-band and we obtained very similar results, but in this case the lineshape was completely symmetric ($D = 0$, no skin depth effects). This investigation was important rule out any surface effect in our results.

## III. RESULTS AND DISCUSSION

Figures 1(a)-(b) give an overview of the spectra evolution in the temperature interval $4.2 \lesssim T \lesssim 300$ K and show in detail the spectrum for $T = 4.2$ K. As the temperature increases, the spectra broaden (Region I) and then undergo a narrowing process (Region II), reaching temperatures (Region III) where a Korringa like relaxation process describes the behavior of $\Delta H$ as $T$ increases further. We also indicate the magnifying factor for each region, in the lower left corner of the figures.

Figures 1, 2 and 3 present the relevant experimental results for the skutterudite compounds and figure 4 gives a brief account of our results for the clathrate compound. In figures 1(a) and 1(b), we give an overview of the X-band ESR spectra obtained for EuT₄Sb₁₂ (T = Ru, Os). It is well seen that the thermal activation induces a fast broadening of the spectra until $T \approx 75$ K, when a narrowing process sets in up to $T \approx 150$ K. Above this $T$, the spectra broaden as in a Korringa relaxation.

As pointed out in these figures, there are 3 regions inside which the spectra evolve with distinct characteristics. The behavior in region III ($T \gtrsim 150$ K) is expected...
to occur in any metal, but the behavior found in regions I and II is unique. For $T = \text{Fe}$, only the ferromagnetic modes (for $T \lesssim T_c = 90$ K) were observed for this compound (not shown). The non-observation of the ESR signal in EuFe$_4$Sb$_{12}$ may be related to one or both of the following reasons: i) as presented in figures 2(a) and 2(b) (and also in 3(a) and 3(b)) $\Delta H$ found in these compounds roughly scale with $T_C$ ($\Delta H_{Ru}/\Delta H_{Os} \approx T_{C,Ru}/T_{C,Os}$). In an extrapolation, this would mean that $\Delta H_{Fe}$ would be of the order of several kOe, that would prevent its observation; ii) EuFe$_4$Sb$_{12}$ is a ferrimagnetic compound, where the ordered Fe 3d orbitals partially compensates the Eu$^{2+}$ moments. The effect of this local antiferromagnetic coupling between the Fe 3d moments and the Eu$^{2+}$ 4f moment may be a huge shift of the resonance that would also preclude its observation.

Figures 2(a) and 2(b) give a better view of the above cited regions by presenting the X-band ESR $\Delta H$ for both compounds. The behavior of $\Delta H$ resembles a coherence peak, as found in some NMR experiments, when a phase transition is approached. From region I, for both compounds, as $T$ increases, $\Delta H$ broadens by $\approx 800$ Oe. Following this broadening, around $T \approx 75$ K, both spectra gradually narrow by $\approx 300$ Oe (region II). At $T \approx 150$ K, they broaden in a Korringa like relaxation as evidenced by the fitting curve (region III). The measured Korringa rates are $b = 5.5(1)$ Oe/K for $T = \text{Ru}$, and $b = 6.3(3)$ Oe/K for $T = \text{Os}$.

The insets in these figures show the normalized ESR intensity $(\chi_{ESR}(T)/\chi(T = 300$ K)) for both compounds. A comparison with the Curie law shows that in all regions the spectra behave as a resonance arising from localized electronic states. This comparison also suggests that a small enhancement of $\chi_{ESR}(T)$ is in order at low temperatures. This could be ascribed to the proximity of ferromagnetic transition. The ESR intensity was also normalized taking into account the variation of the skin depth resulting from the $T$-dependency of resistivity. In the experiment with the powdered sample (EuRu$_4$Sb$_{12}$), where the skin depth is bigger than the size of grains, $\chi_{ESR}(T)$ also follows a Curie-like behaviour.

The similarities between the broadening and narrowing phenomena in regions I and II in both compounds indicate that these phenomena should have a common origin. In these compounds, the filler Eu atom is known to ratttle with Einstein temperatures $\theta_E = 78$ K ($T = \text{Ru}$) and $\theta_E = 74$ K ($T = \text{Os}$). These temperatures are very similar to those where $\Delta H$ approaches its maximum before starting to narrow. We suggest that the thermal activation of the rattling motion gives rise to the behavior of $\Delta H$ in regions I and II.

The thermal activation has its origin in the energy dispersion of an Einstein (harmonic) oscillator $E = (n + \frac{1}{2})\hbar \omega_E$ ($\omega_E = k_B \theta_E$) which, together with the proper statistical distribution, gives the number of active oscillators at a given temperature. Hence, in region I, there are rattling and non-rattling resonating ions. At low-$T$, the lines are relatively narrower due to the spin-spin exchange interaction. As $T$ increases, the inhomogeneity of the spin dynamics, implied by the presence of rattling and non-rattling resonating centers, leads to the broadening of $\Delta H$. In region II, most of the ions are rattling, and an homogenization process ensues, leading to narrowing of $\Delta H$. In region III, virtually all ions are rattling and the system has become quite homogeneous.

As a plausible scenario for the origin of this correlation between the rattling modes and $\Delta H$, we referred to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which gives the exchange coupling between the localized spins in rare earth metals. In skutterudites, the localized spins oscillate in their Einstein frequencies and this oscillation may give rise to random anisotropies in the exchange coupling $J$ of the RKKY interaction, resulting in an inhomogeneous spin dynamics of the Eu$^{2+}$ spins. Hence, in region I, the anisotropies of $J$ broaden the resonance lines and prevent the narrowing of the spectra to occur. Once the rattling is fully activated, a narrowing process takes place, giving rise to the behavior of $\Delta H$ in region II. In region III, the narrowed spectra relax as in a Korringa-like relaxation.

The above discussed behavior of the system is very sim-
Here, no clear relation with the rattling modes is observed. For $T \gtrsim 30$ K, the spectra evolve as in a Korringa-like relaxation and the slowing down of the relaxation is seem below this temperature. The onset of the later phenomenon starts at a slightly higher temperature in the case $T = Os$. In the insets of figures 3(a)-(b), we present the Q-band ESR $g$-values. It is shown that at $T \approx 35$ K and $T \approx 50$ K, for $T = Ru$ and $T = Os$, respectively, there is an increase of the $g$-values reflecting the development of a ferromagnetic internal field. Similar to a spin-glass, as probed by an ESR experiment, with a glass transition temperature $T^* \approx \theta_E$. For temperatures well below $\theta_E$, the rattling is not activated, and the low-$T \Delta H$ is only due to dipolar interactions and the spin-spin exchange narrowing. However, with increasing temperature, the spin-glass behavior manifests in the evolution of $\Delta H$. In this sense, the peaks of $\Delta H$, as shown in Fig. 2, are indeed coherence peaks, although we cannot claim that they express a phase transition to a true spin-glass state.

In contrast to the above described unique behavior of the X-band spectra, the Q-band measurements, figures 3(a) and 3(b), do not present this conspicuous influence of the Eu$^{2+}$ rattling behavior. For $T \gtrsim 45$ K, the spectra have a $\Delta H \approx 250$ Oe and evolves as in a Korringa-like relaxation with $b = 6.7(1)$ Oe/K and $b = 10.6(1)$ Oe/K for $T = Ru$ and $T = Os$, respectively. In this $T$-region, the relatively narrow $\Delta H$ allows for a precise determination of the $g$-values. The results are $g = 1.961(3)$, for $T = Ru$, and $g = 1.92(1)$, for $T = Os$. In addition, at low-$T$, both values increase, reflecting the internal fields of the low-$T$ ferromagnetic state previously reported for the compounds. These $g$-values reflect a huge $g$-shift ($\Delta g = g_{\text{insulator}} - g_{\text{experiment}}$), which is due to the Exchange interaction with conduction electrons (a polarization effect analogous to the Knight shift in NMR experiments), when compared to $g = 1.993(2)$ found in insulators. This negative $\Delta g$ is direct evidence for a covalent mixing between the Eu$^{2+}$ $f$ orbitals and the conduction band $d$ orbitals. In a single band picture, these $\Delta g$ imply a Korringa rate of $b \approx 24$ Oe/K and $b \approx 124$ Oe/K for $T = Ru$ and $T = Os$, respectively. This strongly contrasts with the experimental results, reflecting the existence of a $q$-dependency of the exchange coupling $J(q)$. This is evidence that the Eu-Eu interaction is not due to a constant $J$ exchange coupling, giving support to our claim of an inhomogeneous RKKY interaction.

An alternative scenario for a correlation of the rattling behavior with the ESR spectra would be related to crystal field inhomogeneities. In this picture, the Eu$^{2+}$ while performing its excursion within the cage would experience slightly different crystal field parameters and/or a crystal field environment of lower symmetry. This was
shown to be the case in our previous work on the Yb$^{3+}$ resonant. In this work, however, the broadening of $\Delta H$ in regions I and II, instead of being enhanced, is suppressed at higher fields. It appears that the rattling frequencies are too high, in comparison with the ESR frequencies, and the spatial inhomogeneities are completely averaged out.

We ascribe the lack of clear signatures of the rattling behavior in the Q-band ESR spectra to the relatively high fields ($H \approx 1$ T) used in the experiment. As observed in ESR experiments in a true spin-glass system, higher fields tend to quench the random anisotropy contribution. Our claim is that a field as high as 1T is enough to suppress the small anisotropies implied by the Eu$^{2+}$ dynamical behavior thus suppressing the broadening of the spectra when $T_C$ is approached.

Figure 4 shows that no comparable phenomenon takes place in the clathrate compound. Figure 4(a) shows that at low-$T$, the spectra are anisotropic due to the proximity of the magnetic transition ($T_C = 35 \text{ K}$). Above this low-$T$ region ($T \gtrsim 70 \text{ K}$), the spectra are isotropic with $g = 1.999(3)$ and broaden in a Korringa like relaxation. Figure 4(b) evidences the relatively narrow ESR line when compared to the skutterudite compounds. As the transition $T$ is approached, and below this temperature, $\Delta H$ broadens rapidly and continuously. The $g$-values also reflect clearly the low-$T$ anisotropy and magnetic transition.

No clear connection with the Eu$^{2+}$ rattling modes is observed in this experiment. Given the specific features of the behavior of the filler atom in this clathrate (off-center rattling), we would expect more signatures arising from crystal field inhomogeneities in this experiment than in the experiments with the skutterudites. This, and the Q-band measurements, lead us to rule out crystal field effects as the origin of the phenomena observed in figures 2(a)-(b) and 2(a)-(b). Both results considered together, give strength for our claim that the unique behavior of the ESR spectra of the skutterudites are due to the coupling between the rattling modes and electronic degrees of freedom.

Although we observe a metallic relaxation, the process is slow ($b = 0.86 \text{ Oe/K}$), which agrees with previous results pointing that Eu$_3$Ga$_{16}$Ge$_{30}$ is a poor metallic system. This Korringa rate is compatible with the measured $\Delta g = 0.006(5)$, pointing to a $q$-independent $J_{FS}$ constant and absence of multi-band effects.

It is noteworthy that $\Delta H$ in the skutterudites and in the clathrates are of the same order of magnitude at low-$T$ (see figures 4 and 3 around $T \approx 50 \text{ K}$). In general, $\Delta H$ in clean concentrated metallic systems will be determined by strong dipolar interactions, which broaden the line, and spin-spin Exchange narrowing effects. Since the Eu$^{2+}$ ions are slightly more apart from each other in the clathrates, one would expect dipolar interaction to be weaker in the clathrates and hence $\Delta H$ would be smaller, as it is verified. Since the latter two effects are temperature independent, the significant difference in $\Delta H$ at high-$T$ should be ascribed to the different Korringa rates of the Korringa-like relaxation discussed above. The exact nature of a relaxation process in a concentrated metallic system is very hard to determine. However, it should be related to an Exchange interaction with conduction electrons, and that is why we are careful to refer to the linear broadening of $\Delta H$ as a “Korringa-like” process. All the reported material parameters relevant to this coupling, such as the density of electronic states at the Fermi surface favors the idea that this coupling (and therefore the relaxation) should be stronger in the skutterudites.

Contrary to the skutterudites studied here, we note that for this compound, Raman scattering studies have shown that the Eu$^{2+}$ rattling energy ($\theta_E \approx 25 \text{ K}$) is lower than that of the magnetic ordering ($T_C = 36 \text{ K}$). Hence, a spin-glass like behavior below $\theta_E$ may also be prevented from occurring by the magnetically ordered state. Furthermore, the itinerant $d$ orbital contribution to the Fermi surface, in the case of the skutterudites, is most likely originated from the Ru (Os) $d$ atomic orbitals, indicating that the skutterudite cage is somehow stiffer (more correlated) than the clathrate cage. Indeed, the $\Delta g$ analysis point for a greater coupling of localized and itinerant states in the skutterudites, which should be important to correlate the rattling behavior with the Eu-Eu interaction.

In some skutterudites, there are earlier reports for temperature dependence of the valence state of the guest ion, as was reported for the related compound YbFe$_4$Sb$_{12}$[22]. This result raises the question about the valence state of the Eu ion on the compounds here investigated. We should point out, however, that the issue of the Yb valence state in YbFe$_4$Sb$_{12}$ was subsequently revised in the literature, determining that the Yb ions are in a stable divalent state. In our compounds, no significant fraction of Eu$^{3+}$ was found for Eu$_3$Ga$_{16}$Ge$_{30}$ ($T = \text{Ru, Os}$) nor it was found any sign for temperature dependency of the Eu$^{2+}$ fraction in these materials. In EuFe$_4$Sb$_{12}$, a fraction of $10-15\%$ of Eu$^{3+}$ was reported. However, again, no sign for temperature dependency of this fraction was found, even in detailed studies of X-ray absorption spectroscopy. The insets of figures 2(a)-(b) show a Curie-like behavior for the ESR intensity, that should also be taken as another piece of evidence for a nearly stable Eu$^{2+}$ configuration.

IV. CONCLUSION

In conclusion, we have provided evidence, from Eu$^{2+}$ X-band ESR measurements, for inhomogeneous spin dynamics of the Eu$^{2+}$ spins in the Eu$_3$Ga$_{16}$Ge$_{30}$ (T= Ru, Os) skutterudites, triggered by the Eu$^{2+}$ rattling modes. Our Q-band measurements were discussed in terms of presenting evidence for $q$-dependence of $J(q)$ exchange coupling and for covalent mixing between localized $f$ and itinerant $d$ orbital states. These two findings were related, respec-
tively, to the inhomogeneous spin dynamics of the Eu\(^{2+}\) spins and as an evidence for a stronger coupling between localized and itinerant states in the skutterudites than in the clathrate.

Our picture is that the behavior of ∆H in the X-band ESR measurements is due to an electron-phonon coupling between the rattling phonon modes and the electronic degrees of freedom. In regions I and II of figures \(2\)a) and \(2\)b), the itinerant d orbital electronic states are coupled with oscillating and non-oscillating 4f electronic states, which gives rise to random anisotropies of the exchange coupling and subsequently to the inhomogeneous spin dynamics found in these regions.

In analogy with the phonon-glass scenario discussed for cage systems, we discussed our findings in the framework of a spin-glass type of spin dynamics. In this sense, high fields tend to suppress the ESR line broadening when \(T_G\) is approached, by quenching the random anisotropies of these systems. We suggested that a similar effect takes place in our experiment, preventing the observation of inhomogeneous dynamics of the Eu\(^{2+}\) spins in Q-band. Further theoretical and experimental investigation may unravel the exact characteristics of this spin-glass like state and also explore the perspective of other phenomena emerging from the interaction between conduction electrons and the rattling phonon modes.

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