

Eu²⁺ spin dynamics in the filled skutterudites EuM₄Sb₁₂ (M = Fe, Ru, Os)F. A. Garcia,¹ C. Adriano,¹ G. G. Cabrera,¹ L. M. Holanda,¹ P. G. Pagliuso,¹ M. A. Avila,² S. B. Oseroff,³ and C. Rettori^{1,2}¹Instituto de Física “Gleb Wataghin,” UNICAMP, Campinas-SP, 13083-970, Brazil²Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André-SP 09210-170, Brazil³Department of Physics, San Diego State University, San Diego, California 92182, USA

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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 Eu²⁺ spins. The spin dynamics is probed directly by means of Eu²⁺ electron spin resonance (ESR), performed in both X-band (≈ 9.4 GHz) and Q-band (≈ 34 GHz) frequencies in the temperature interval $4.2 \text{ K} \lesssim T \lesssim 300 \text{ K}$. A comparative study with ESR measurements on the β -Eu₈Ga₁₆Ge₃₀ 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.

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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 is among the materials where this scenario is believed to take place.¹ 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 to as the “rattler atom” and its dynamics is fully characterized by a single parameter θ_E , the Einstein temperature.²

Filled skutterudite compounds have the general formula RM_4X_{12} , where R usually is a rare earth or actinide, M is a transition metal (Fe, Ru, Os, or Co), and X is a pnictogen (P, As, or Sb). These compounds crystallize in the LaFe₄P₁₂ structure with space group $Im\bar{3}$ and local point symmetry T_h for the R ions.³ This structure hosts a wide range of physical properties, including exotic strongly correlated ground states,⁴ and presents a promising potential for application in the construction of thermoelectric devices.²

The latter feature is argued to be closely related to the dynamics of the rattler R atom.⁵ 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 (noncorrelated) and localized (nondispersive) phonon modes.¹

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,^{6–8} which raises the question of the validity of the independent rattler approximation. It also raises the question of whether an “electron glass,” meaning a coupling between the guest ion dynamics and electronic degrees of freedom, could also be realized in these materials. Indeed, there are some recent theoretical proposals in this direction.^{9–11} In experiments, there is evidence for an interplay between the rattling motion and quadrupolar fluctuations with the unconventional superconductivity in PrOs₄Sb₁₂ (Ref. 12). Moreover,¹³ La nuclear magnetic resonance (NMR)

shows 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.¹⁴ We showed that the Yb³⁺ spectra in Ce_{1-x}Yb_xFe₄P₁₂ ($x \sim 0.002$) clearly reveal the R ion dynamical behavior. Taking advantage of this application of the ESR technique, here, we investigate the EuM₄Sb₁₂ ($M = \text{Fe, Ru, Os}$) skutterudites, to observe whether the Eu²⁺ ESR spectra are good probes for their rattling behavior. For comparison, we also present measurements on the β -Eu₈Ga₁₆Ge₃₀ clathrate compound, another well-known cage system inside which Eu²⁺ behaves as a rattler ion.

EuM₄Sb₁₂ ($M = \text{Fe, Ru, Os}$) are metallic systems that undergo a ferromagnetic transition around $T_C = 90 \text{ K}$, 4 K , and 9 K , respectively.¹⁵ Close investigation of the $M = \text{Fe}$ system indicates that, in fact, a ferrimagnetic transition takes place at $T_C = 90 \text{ K}$, as a consequence of an antiferromagnetic coupling of the Eu and Fe moments.^{16,17} The rattling behavior of the Eu²⁺ ions was studied by structure refinement of x-ray diffraction measurements¹⁵ and also by extended x-ray fine structure (EXAFS) measurements.¹⁸ The results obtained from both methods are in close agreement. The measurements gave, for $M = \text{Fe, Ru, and Os}$, $\theta_E = 84 \text{ K}$, 78 K , and 74 K , respectively, whereas EXAFS gave, for $M = \text{Ru and Os}$, $\theta_E = 81 \text{ K}$ and 78 K , respectively. In both measurements, no signs of static *off-center* displacement of the Eu²⁺ were found. X-ray absorption near edge spectroscopy (XANES) and also susceptibility measurements point to a predominant 2+ valence state of the Eu atoms, although a slightly mixed valence state cannot be completely excluded ($v \lesssim 2.1$).¹⁵ In particular, for EuM₄Sb₁₂ ($M = \text{Ru, Os}$), the susceptibility measurements are compatible with the full Eu²⁺ moment in the temperature interval $2 \lesssim T \lesssim 400 \text{ K}$.

The type I clathrate compound β -Eu₈Ga₁₆Ge₃₀ is a metallic compound which undergoes a ferromagnetic transition at $T_C = 35 \text{ K}$. 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.^{19,20}

In this work, we report a nontrivial evolution of the X-band ESR spectra of EuM₄Sb₁₂ ($M = \text{Ru, Os}$). We discuss that, in the low-temperature region ($4.2 \text{ K} \lesssim T \lesssim 150 \text{ K}$), the rattling motion couples with the Eu²⁺ spins. This gives rise to inhomogeneous spin dynamics, which manifests in the ESR linewidth (ΔH) behavior. We also discuss how our Q -band ESR spectra give support to these findings.

II. EXPERIMENT

For this work, we use single crystals of EuM₄Sb₁₂ ($M = \text{Fe, Ru, Os}$) grown in Sb flux as described in Ref. 15. 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 out on crushed small pieces of single crystals with high grain-size homogeneity. The ESR spectra were taken in an X-band and Q -band Bruker spectrometer using appropriate resonators coupled to a T controller of a helium gas flux system. The experiments covered the temperature interval $4.2 \text{ K} \lesssim T \lesssim 300 \text{ K}$. 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 sensitivity 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 line shape, described by equation

$$P(H) \propto \frac{\Delta H + \alpha(H - H_{\text{res}})}{(H - H_{\text{res}})^2 + \Delta H^2}. \quad (1)$$

This line shape 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.²¹ 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 line shape was completely symmetric ($D = 0$, no skin depth effects). This investigation was important to rule out any surface effect in our results.

III. RESULTS AND DISCUSSION

Figures 1, 2, and 3 present the relevant experimental results for the skutterudite compounds and Fig. 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 EuM₄Sb₁₂ ($M = \text{Ru, Os}$). It is well seen that the

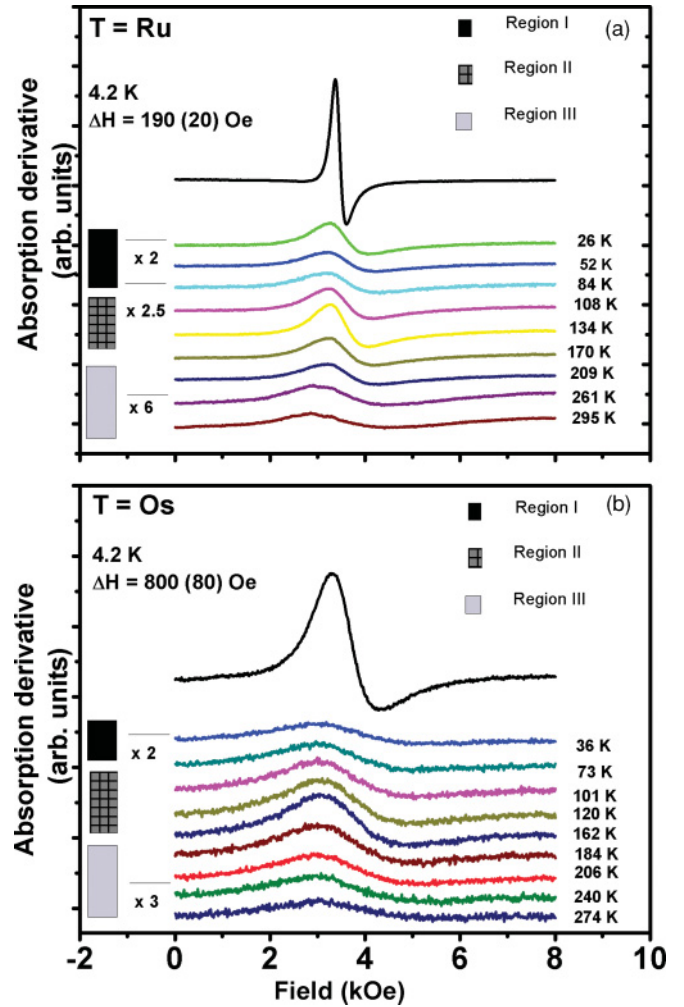


FIG. 1. (Color online) X-band ESR spectra of EuM₄Sb₁₂ ($M = \text{Ru, Os}$). Panels (a) and (b) give an overview of the spectra evolution in the temperature interval $4.2 \text{ K} \lesssim T \lesssim 300 \text{ K}$ and show in detail the spectrum for $T = 4.2 \text{ K}$. As the temperature increases, 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 ΔH as T increases further. We also indicate the magnifying factor for each region, in the lower left corner of the figures.

thermal activation induces a fast broadening of the spectra until $T \approx 75 \text{ K}$, when a narrowing process sets in up to $T \approx 150 \text{ K}$. Above this T , the spectra broaden as in a Korringa relaxation.^{21,22}

As pointed out in these figures, there are three regions inside which the spectra evolve with distinct characteristics. The behavior in Region III ($T \gtrsim 150 \text{ K}$) is expected to occur in any metal, but the behavior found in Regions I and II is unique. For $M = \text{Fe}$, only the ferromagnetic modes (for $T \lesssim T_c = 90 \text{ K}$) were observed for this compound (not shown). The nonobservation of the ESR signal in EuFe₄Sb₁₂ may be related to one or both of the following reasons: (i) as presented in Figs. 2(a) and 2(b) [and also in Figs. 3(a) and 3(b)] ΔH found in these compounds roughly scale with T_c ($\Delta H_{\text{Ru}}/\Delta H_{\text{Os}} \approx T_c^{\text{Ru}}/T_c^{\text{Os}}$). In an extrapolation, this would mean that ΔH_{Fe} would be of the order of several kOe,

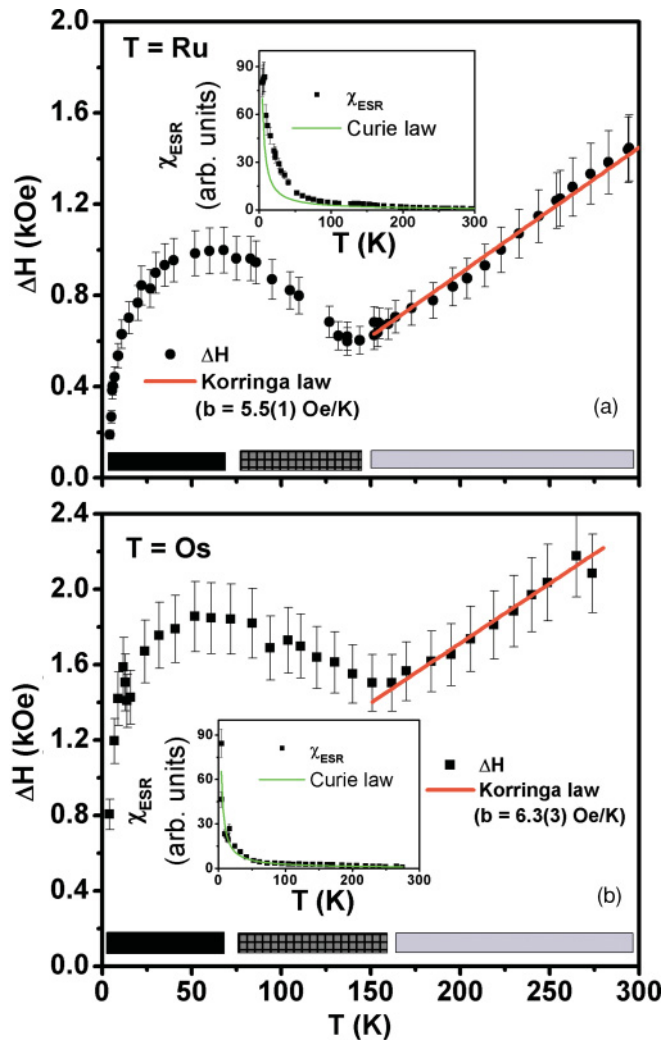


FIG. 2. (Color online) X -band ESR linewidth of $\text{EuM}_4\text{Sb}_{12}$ ($M = \text{Ru}, \text{Os}$). The same Regions I, II, and III discussed in Figs. 1(a) and 1(b) are indicated in the above figures. These data show clearly the existence of such distinct regions. In the insets of panels (a) and (b), we present the X -band ESR intensity (χ_{ESR}). It is shown that in all regions, χ_{ESR} closely follows a Curie-like behavior, which indicates that our resonance is due to localized electronic states.

which would prevent its observation; (ii) $\text{EuFe}_4\text{Sb}_{12}$ is a ferrimagnetic compound¹⁶ where the ordered Fe $3d$ orbitals partially compensate the Eu^{2+} moments. The effect of this local antiferromagnetic coupling between the Fe $3d$ moments and the Eu^{2+} $4f$ moment may result in 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 ΔH for both compounds. The behavior of ΔH resembles a coherence peak, as found in some NMR experiments,²² when a phase transition is approached. From Region I, for both compounds, as T increases, ΔH broadens by ≈ 800 Oe. Following this broadening, around $T \approx 75$ K, both spectra gradually narrow by ≈ 300 Oe (Region II). At $T \approx 150$ K, they broaden in a Korrington-like relaxation as evidenced by the fitting curve (Region III). The measured Korrington rates are $b = 5.5(1)$ Oe/K for $T = \text{Ru}$ and $b = 6.3(3)$ Oe/K for $T = \text{Os}$.

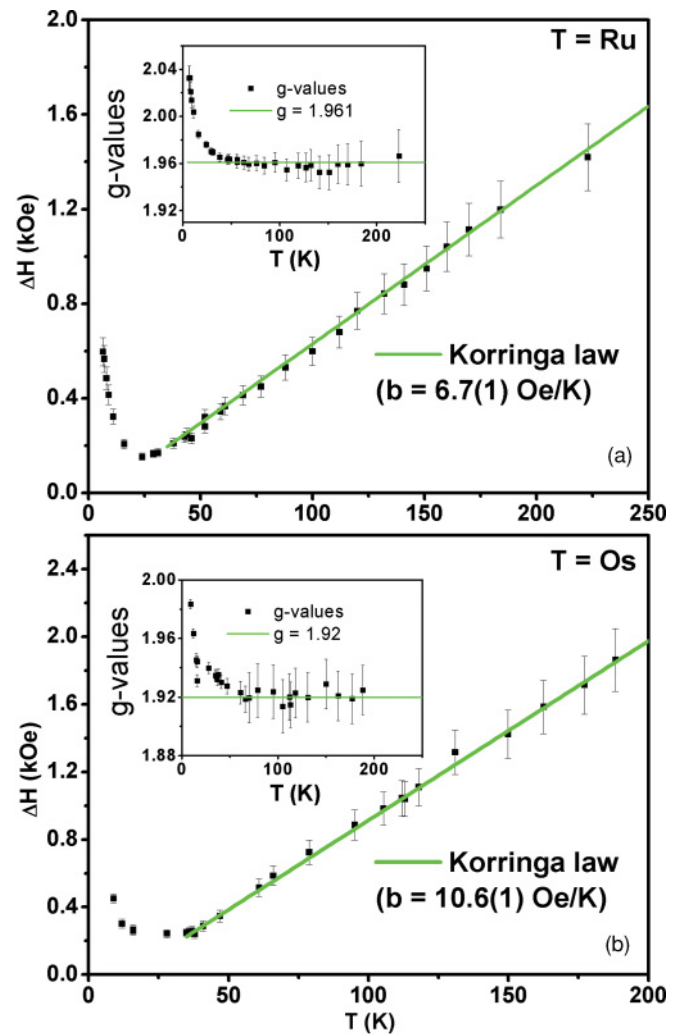


FIG. 3. (Color online) Q -band ESR linewidth of $\text{EuM}_4\text{Sb}_{12}$ ($M = \text{Ru}, \text{Os}$). Here no clear relation with the rattling modes is observed. For $T \gtrsim 30$ K, the spectra evolve as in a Korrington-like relaxation and the slowing down of the relaxation is seen below this temperature. The onset of the later phenomenon starts at a slightly higher temperature in the case $M = \text{Os}$. In the insets of panels (a) and (b), we present the Q -band ESR g values. It is shown that at $T \approx 35$ K and $T \approx 50$ K, for $M = \text{Ru}$ and $M = \text{Os}$, respectively, there is an increase of the g values reflecting the development of a ferromagnetic state.

The insets in these figures show the normalized ESR intensity [$\chi_{\text{ESR}}(T)/\chi(T = 300 \text{ K})$] 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 $\chi_{\text{ESR}}(T)$ 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.¹⁵ In the experiment with the powdered sample ($\text{EuRu}_4\text{Sb}_{12}$), where the skin depth is bigger than the size of grains, $\chi_{\text{ESR}}(T)$ also follows a Curie-like behavior.

The similarities between the broadening and narrowing phenomena in Regions I and II in both compounds indicate

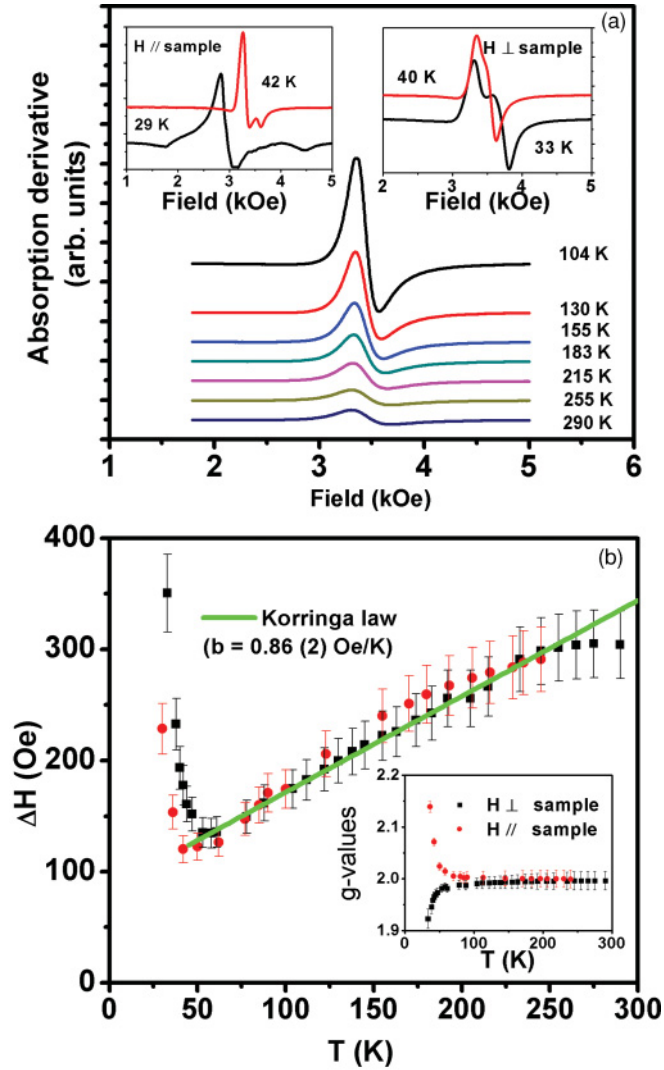


FIG. 4. (Color online) X-band ESR measurements of β - $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$. Panel (a) gives an overview of the spectra in the investigated temperature interval. At high temperatures, the spectra are isotropic and the ESR intensity (not shown) follows a Curie law. As the magnetic transition is approached, strong anisotropy develops, as demonstrated by the two insets. Panel (b) shows that above $T = 50$ K, a Korringa-like relaxation dominates the behavior of ΔH , whereas at low T , ΔH broadens due to magnetic fluctuations. The inset shows strong anisotropy reflected in the g values.

that these phenomena should have a common origin. In these compounds, the filler Eu atom is known to rattle with Einstein temperatures $\theta_E = 78$ K ($M = \text{Ru}$) and $\theta_E = 74$ K ($M = \text{Os}$).^{15,18} These temperatures are very similar to those where ΔH approaches its maximum before starting to narrow. We suggest that the thermal activation of the rattling motion gives rise to the behavior of ΔH in Regions I and II.

The thermal activation has its origin in the energy dispersion of an Einstein (harmonic) oscillator $E = (n + \frac{1}{2})\hbar\omega_E$ ($\omega_E = \frac{k_B\theta_E}{\hbar}$), 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 nonrattling resonating ions. At low T , the lines are relatively narrower due to

the spin-spin exchange interaction.²³ As T increases, the inhomogeneity of the spin dynamics, implied by the presence of rattling and nonrattling resonating centers, leads to the broadening of ΔH . In Region II, most of the ions are rattling, and an homogenization process ensues, leading to narrowing of ΔH . 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 ΔH , we referred to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which gives the exchange coupling between the localized spins in rare earth metals.²² 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 ΔH 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 similar to a spin glass, as probed by an ESR experiment²⁴ with a glass transition temperature $T_G^* \approx \theta_E$. For temperatures well below θ_E , the rattling is not activated, and the low- T ΔH 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 ΔH . In this sense, the peaks of ΔH , 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, Figs. 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 evolve as in a Korringa-like relaxation with $b = 6.7(1)$ Oe/K and $b = 10.6(1)$ Oe/K for $M = \text{Ru}$ and $M = \text{Os}$, respectively. In this T region, the relatively narrow ΔH allows for a precise determination of the g values. The results are $g = 1.961(3)$, for $M = \text{Ru}$, and $g = 1.92(1)$, for $M = \text{Os}$. In addition, at low, both values increase, reflecting the onset of the low- T ferromagnetic state previously reported for these compounds.¹⁵ These g values reflect a huge g shift ($g_{\text{experiment}} - g_{\text{insulator}}$), 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.²¹ This negative Δg is direct evidence for a covalent mixing between the $\text{Eu}^{2+} f$ orbitals and the conduction band d orbitals.

In a single-band picture,²¹ these Δg imply a Korringa rate of $b \approx 24$ Oe/K and $b \approx 124$ Oe/K for $M = \text{Ru}$ and $M = \text{Os}$, respectively. This strongly contrasts with the experimental results, reflecting the existence of a q dependency of the exchange coupling $J(q)$.²⁵ 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 Yb³⁺ resonance.¹⁴ In this work, however, the broadening of ΔH 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,²⁴ higher fields tend to quench the random anisotropy contribution. Our claim is that a field as high as 1 T is enough to suppress the small anisotropies implied by the Eu²⁺ dynamical behavior, thus suppressing the broadening of the spectra when T_G^* 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 ($T_C = 35$ K; Ref. 19). Above this low- T region ($T \gtrsim 70$ 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, ΔH broadens rapidly and continuously. The g values also reflect clearly the low- T anisotropy and magnetic transition.

No clear connection with the Eu²⁺ 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 Figs. 1(a) and 1(b) and 2(a) and 2(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 ($b = 0.86$ Oe/K), which agrees with previous results indicating that Eu₈Ga₁₆Ge₃₀ is a poor metallic system.¹⁹ This Korringa rate is compatible with the measured $\Delta g = 0.006(5)$, pointing to a q -independent J_{fs} constant and absence of multiband effects.

It is noteworthy that ΔH in the skutterudites and in the clathrates are of the same order of magnitude at low T (see Figs. 4 and 3 around $T \approx 50$ K). In general, ΔH in clean concentrated metallic systems will be determined by strong dipolar interactions, which broaden the line, and spin-spin exchange narrowing effects. Since the Eu²⁺ ions are slightly more apart from each other in the clathrates, one would expect dipolar interaction to be weaker in the clathrates and hence ΔH would be smaller, as it is verified. Since the latter two effects are temperature independent, the significant difference in ΔH at high T should be ascribed to the different Korringa rates of the Korringa-like relaxation,²¹ 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 ΔH 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,^{15,19} favor 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 studies²⁶ have shown that the Eu²⁺ rattling energy ($\theta_E \approx 25$ K) is lower than that of the magnetic ordering ($T_C = 36$ K). Hence, a spin-glass like behavior below θ_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 Δg analysis points 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 of temperature dependence of the valence state of the guest ion, as reported for the related compound YbFe₄Sb₁₂.²⁷ 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 YbFe₄Sb₁₂ was subsequently revised in the literature,²⁸ which determined that the Yb ions are in a stable divalent state. In our compounds, no significant fraction of Eu³⁺ was found for EuM₄Sb₁₂ ($M = \text{Ru, Os}$) nor any sign of temperature dependency of the Eu²⁺ fraction was found in these materials.¹⁵ In EuFe₄Sb₁₂, a fraction of 10%–15% of Eu³⁺ was reported. However, again, no sign for temperature dependency of this fraction was found, even in detailed studies of x-ray absorption spectroscopy.^{16,17} The insets of Figs. 2(a) and 2(b) show a Curie-like behavior for the ESR intensity, which should also be taken as another piece of evidence for a nearly stable Eu²⁺ configuration.

IV. CONCLUSION

In conclusion, we have provided evidence, from Eu²⁺ X -band ESR measurements, for inhomogeneous spin dynamics of the Eu²⁺ spins in the EuM₄Sb₁₂ ($M = \text{Ru, Os}$) skutterudites, triggered by the Eu²⁺ rattling modes. Our Q -band measurements were discussed in terms of presenting evidence for q -dependency of $J(q)$ exchange coupling and for covalent mixing between localized f and itinerant d orbital states. These two findings were related, respectively, to the inhomogeneous spin dynamics of the Eu²⁺ spins and to a stronger coupling between localized and itinerant states in the skutterudites than in the clathrate.

Our conclusion is that the behavior of ΔH 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 Figs. 2(a) and 2(b), the itinerant d orbital electronic states are coupled with oscillating and nonoscillating $4f$ 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 investigations 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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