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Quantum critical Kondo quasiparticles probed by ESR in β -YbAlB₄

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Electron Spin Resonance (ESR) can probe conduction electrons (*ce*) and local moment (LM) spin systems in different materials. A *ce* spin resonance (CESR) is observed in metallic systems based on light elements or with enhanced Pauli susceptibility. LM ESR can be seen in compounds with paramagnetic ions and localized *d* or *f* electrons. Here we report a remarkable and unprecedented ESR signal in the heavy fermion (HF) superconductor β -YbAlB₄[1] which behaves as a CESR at high temperatures and acquires characteristics of the Yb³⁺ LM ESR at low temperature. This dual behavior strikes as an *in situ* unique observation of the Kondo *quasiparticles* in a quantum critical regime. The proximity to a quantum critical point (QCP) may favor the appearance of this dual character of the ESR signal in β -YbAlB₄.

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An important and heavily studied problem in condensed matter physics involves the microscopic understanding of how localized *f*-electrons at high-*T* evolve to itinerant heavy quasi-particles in a low-*T* metallic state. The fundamental mechanism of this evolution lies at the heart of heavy-electron physics and depends on the Kondo coupling between the localized *f*-electrons and the conduction electrons (*ce*).

In principle, ESR would be one of the main techniques to bring insights to this problem since it could probe directly the *f*-electrons of Kondo ions and their interaction with the *ce*. However, for many years, it was generally accepted that the ESR lines of a Kondo ion such as Yb³⁺ or Ce³⁺ would broaden dramatically at low-*T* avoiding their observation. Contrarily, a ESR signal was found in the intermediate valence YbCuAl[3] and in the Kondo lattice antiferromagnetic (AFM) heavy-fermion (HF) YbRh₂Si₂[4] compounds. After the latter observation, ESR lines were reported for few others HF systems[5, 6] and theoretical models[7, 8] were proposed to explain the origin of such unexpected signals. However, the remarkable ESR signal reported here for β -YbAlB₄ comes to challenge any previous understanding that was believed to exist so far.

β -YbAlB₄ (*T*_c = 80 mK) is the first reported Yb-based HF superconductor (HFS). It is a new morphology of the known α -YbAlB₄ phase which is a paramagnetic metal at low-*T*. [9] In contrast, for the β -YbAlB₄ phase, the low-*T* superconducting state emerges from a non-fermi-liquid (NFL) normal state associated to quantum criticality.[1] Not coincidentally, YbRh₂Si₂ that shows an ESR signal[4, 10] also presents pronounced NFL behavior when its AFM state (*T*_N = 70 mK) is tuned towards a quantum critical point (QCP) by magnetic field.[13, 14]

Single crystals of β -(Yb,Lu)AlB₄ compounds were grown from Al-flux as described previously.[1, 9] The typical crystals size for both compounds was $\sim 0.5 \times$

$0.5 \times 0.05 \text{ mm}^3$ and their mass were less than ~ 0.1 mg. Most of the ESR data were taken in powdered crystals to increase the signal-to-noise ratio. To evaluate the anisotropy of the ESR spectra of the studied crystals, several oriented platelet-like single-crystals were glued on flat plastic surfaces and mounted in a form of sandwiches with the crystals *c*-axis perpendicular to the surface (total mass of the used crystals ~ 4.0 mg).

The ESR spectra were taken in a Bruker X-band (9.5 GHz) spectrometer. Dysonian ESR lineshapes were observed for both samples in the whole *T*-range which corresponds to a skin depth smaller than the size of the crystals.[15] The ESR signal was calibrated at room-*T* using a strong pith standard with 4.55×10^{15} spins/cm. For both samples, the calibrated number of resonating spins were of the same order of the estimated number of Yb atoms within the samples skin depth.

Figure 1 a) presents the room-*T* X-Band ESR spectra for fine powder of β -YbAlB₄ and β -LuAlB₄ compounds and b) shows the high-*T* and low-*T* X-Band ESR spectra for fine powder of β -YbAlB₄. The solid thick lines in Fig.1 are fits to the spectra using a Dysonian lineshape. The best fits for β -LuAlB₄ yield $g = 2.1(1)$ and linewidth $\Delta H = 800(50)$ Oe at high-*T*. For β -YbAlB₄, we obtain $g = 2.34(8)$ and $\Delta H = 260(20)$ Oe at high-*T* and $g = 2.98(6)$ and $\Delta H = 150(10)$ Oe at *T* = 4.2 K and $g = 2.90(8)$ and $\Delta H = 170(10)$ Oe at *T* = 11 K.

In the spectra of β -YbAlB₄ at *T* = 4.2 K, the arrows clearly indicate the presence of the hyperfine lines associated with the ¹⁷¹Yb (*I* = 1/2) isotope. Using the field position of the ¹⁷¹Yb hyperfine lines, extracted from the low-*T* spectra of Fig. 1b and the Breit-Rabi formula[16], we obtain the hyperfine constant ¹⁷¹A ≈ 1300 Oe which is of the order of typical values found for ¹⁷¹Yb in low symmetry systems.[17, 18] The observation of these hyperfine lines is an irrefutable indication that the ESR spectra found for β -YbAlB₄ acquires the characteristic

of the Yb^{3+} ions at low- T . We should mention that the hyperfine lines could not be observed for $T \gtrsim 10$ K. Furthermore, the appearance of the hyperfine at $T = 4.2$ K were confirmed for samples from three different batches, however the ESR ΔH for both isotopes were found to be strongly sample dependent.

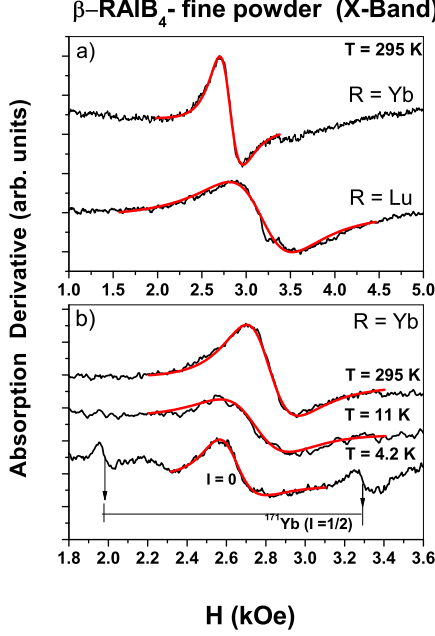


FIG. 1: (color online) X-Band ESR spectra for fine powder of $\beta\text{-(Yb,Lu)AlB}_4$ at various temperatures. The solid lines are fits to the spectra using a Dysonian lineshape. In the spectra of $\beta\text{-YbAlB}_4$ at $T = 4.2$ K in panel b), the arrows indicate the presence of the hyperfine lines associated with the ^{171}Yb ($I = 1/2$) isotope. Natural Yb has $\sim 70\%$ of ^{170}Yb ($I = 0$), $\sim 14\%$ of ^{171}Yb ($I = 1/2$) and $\sim 16\%$ of ^{173}Yb ($I = 5/2$) isotopes. The hyperfine lines of ^{173}Yb are more than 2 times less intense than the lines of ^{171}Yb ($I = 1/2$) and they are not obviously observable in the spectra of Fig. 1b).

The T -dependence of the ESR parameters, g -value, ΔH and intensity, for a fine powder of both $\beta\text{-YbAlB}_4$ and $\beta\text{-LuAlB}_4$ compounds are shown in Figure 2. For $\beta\text{-YbAlB}_4$ and $T \lesssim 100$ K Fig 2a shows that the g -value increases as T -decreases, i.e., the resonance shift toward lower fields (see Fig. 1b) and at $T = 4.2$ K the ESR line reaches $g \sim 3.0$. This g -value is close to the g -value found for Yb^{3+} Kramers doublets in different crystal symmetries.[4, 5, 10, 17, 19] In contrast, the ESR line of $\beta\text{-LuAlB}_4$ presents a nearly T -independent $g \sim 2.1$ down to $T = 4.2$ K.

A striking difference between the T -dependence of ΔH is also verified for the $\beta\text{-(Yb,Lu)AlB}_4$ compounds (see Fig. 2b). For $\beta\text{-YbAlB}_4$, $\Delta H(T)$ shows a weak non-monotonic behavior as a function of temperature. At high- T , $\Delta H(T)$ is nearly constant but for $T \lesssim 70$ K, it shows a broadening of ≈ 3 Oe/K as temperature increases. This rate has the same order of magnitude that the linear Korringa-rate found for the ESR line ob-

served at low- T for the most high quality samples of YbRh_2Si_2 [4, 10] In contrast, for $\beta\text{-LuAlB}_4$ $\Delta H(T)$ is much broader at room- T and it increases weakly with decreasing- T down to $T = 4.2$ K.

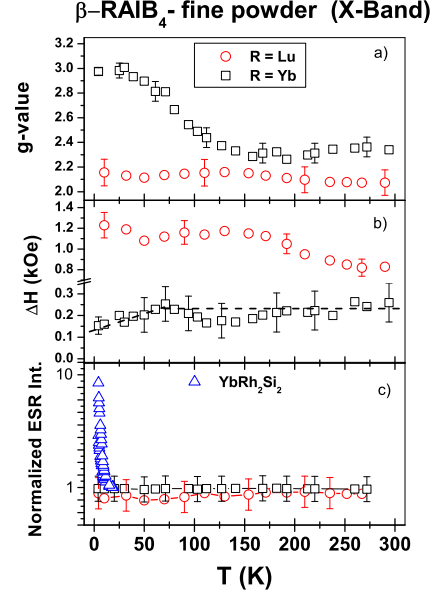


FIG. 2: (color online) The T -dependence of the ESR a) g -value, b) ΔH and c) normalized intensity for fine powder of $\beta\text{-(Yb,Lu)AlB}_4$. The open triangles show this data for YbRh_2Si_2

Lastly Figure 2c displays a very important and conclusive result. The ESR intensity obtained from the double integral of the ESR spectra is nearly T -independent in the whole studied T -range for both samples. This is a typical behavior of a Conduction Electron Spin Resonance (CESR) since the ce present a T -independent Pauli magnetic susceptibility and it is in dramatic contrast to what is expected for the T -dependence of a local moment (LM) ESR intensity as in YbRh_2Si_2 [4, 10] (Curie-like behavior, see Fig 2c). Thus, these results show that the ESR signal found in the HFS $\beta\text{-YbAlB}_4$ displays the typical behavior of a CESR which acquires at low- T characteristics of Yb^{3+} LM resonance (Kramer doublet g -value, korringa-like behavior and hyperfine splitting) in spite of the fact that no Curie-like behavior is observed in the ESR intensity. On the other hand, the Pauli paramagnetic metal $\beta\text{-LuAlB}_4$ presents an ESR signal that behaves as CESR in the whole studied T -range (T -independent g -value and ESR intensity) apart from the weak line broadening at low- T and the g -value ~ 2.1 reasonably larger than $g = 2$ for free electrons. This broadening may occur in CESR lines due to the presence of fluctuations in the spin-orbit effective field[11] and/or due to spin-spin ce interaction in the FL regime of the $\beta\text{-LuAlB}_4$. The dual behavior of the ESR spectra of $\beta\text{-YbAlB}_4$ is further confirmed when the anisotropy of the ESR spectra is investigated.

Figure 3 display the angular dependence of the g -

values for crystals of both β -YbAlB₄ and β -LuAlB₄ at different temperatures. The g -value is isotropic and T -independent for β -LuAlB₄, as expected for a CESR. However, for β -YbAlB₄, the g -value is isotropic at room- T but becomes clearly anisotropic[12] at $T = 4.2$ K, as it would be expected for an ESR signal arising from a Yb³⁺ LM Kramers doublet in orthorhombic symmetry. Furthermore, the observed anisotropy at $T = 4.2$ K for β -YbAlB₄ shows the largest g -value when H is applied along the c -axis, consistent with the largest magnetic susceptibility measured for this field orientation.[1, 9] Interestingly, the g -value anisotropy of the β -YbAlB₄ phase is in contrast to that found for YbRh₂Si₂,[4, 10] where the largest g -value is found for H perpendicular to the c -axis. This change in the single ion anisotropy is probably associated with a change in the symmetry of the Yb³⁺ crystal field ground state wave functions.

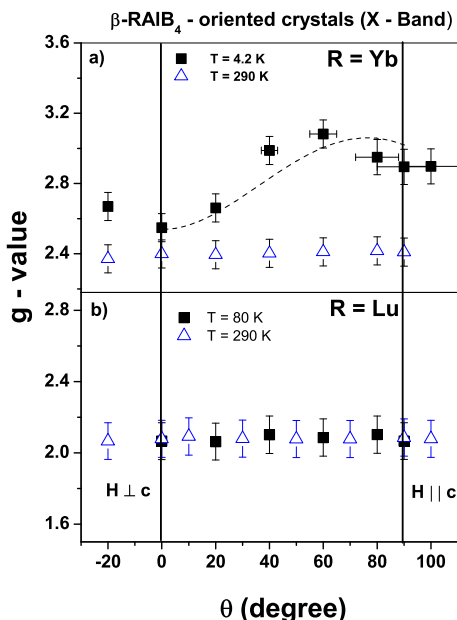


FIG. 3: (color online) g -values as a function of angle for oriented crystals of β -(Yb,Lu)AlB₄ at different temperatures. The dashed line is a guide to the eye. We should clarify that the set of crystals aligned to perform these experiments were not the same crystals used to prepare the powder measured in Fig.1

The striking and unique dual behavior observed in the same ESR spectra of β -YbAlB₄, which behaves as a CESR at high- T and acquires characteristics of Yb³⁺ LM at low- T , associated to the ESR results found for the reference compound β -LuAlB₄, allow us to propose a qualitative scenario that may explain the origin of the unprecedented ESR signal in β -YbAlB₄.

To build up such a scenario one has to go back to the classical transmission ESR (TESR) experiments in Ag:Dy and Ag:Er alloys that, respectively, allowed the simultaneous observation at low- T of the CESR and the Er³⁺ and Dy³⁺ ESR 4f LM in their Kramers doublet ground states.[20] In these experiments, it was shown

that, as T -decreases, the CESR shifts to lower field showing an increase in the g -value which was proportional to the dc -magnetic susceptibility of the LM. The LM ESR showed a T -independent g -shift proportional to the ce Pauli susceptibility (Knight-shift). However, at $T = 1.5$ K it was possible to observe that the LM ESR ($g \approx 7.6$ for Dy³⁺) and the CESR line ($g \approx 2.4$) were well separated ESR signals. Furthermore, as a function of T the two signals evolved accordingly to their individual characteristics. For instance, the intensity of the LM Kramers doublet ESR decreases dramatically with increasing- T while the CESR could be followed to much higher- T . [20]

In the case of Kondo ions such as Yb³⁺ it is known that the exchange coupling between the 4f and the ce , J_{fs} , is much stronger than that for non-Kondo rare-earth ions such as Dy³⁺ and, in some compounds, these two spin system (4f and ce) may be strongly hybridized.[2] Thus, it is entirely possible that for HF systems, the two independent ESR responses mentioned above become a unique 4f- ce strongly coupled ESR mode that we named *Kondo quasiparticles spin resonance* (KQSR). The KQSR is a new ESR response that possess dual nature, a CESR and/or LM ESR, depending on the strength of J_{fs} . For instance, HF systems with large Kondo energy scale (T_K) situated in the Fermi liquid (FL) region of a Doniach-like phase diagram[2] would tend to present a CESR-like KQSR that may be observable depending on the material properties, e.g., metals with low ce spin-flip scattering (light metals with small *spin-orbit* coupling) and/or metals with enhanced Pauli magnetic susceptibility.[21] Typical FL HF are, for instance, YbInCu₄, [22] and YbAgCu₄, [23]. In these systems the KQSR would be expected to be CESR-like and should not be observed due to the large ce spin-flip scattering expected for the In, Cu and Ag elements.

On the other hand, HF systems with small T_K which may show magnetic ordering at low- T (eg. YbRh₂Si₂, YbIr₂Si₂ and CeRuPO) would present in their paramagnetic state a LM-like KQSR that may be observable depending on the f -electrons spin-lattice relaxation rate involving the ce (Korringa-rate, bottleneck/dynamic effects), crystal field excited states, phonons and magnetic correlations. In particular, the strong bottleneck regime may favor the observation of LM-like KQSR.[4–6, 10]

The striking T -independent intensity of the KQSR in β -YbAlB₄ shows that the statistics of the KQSR is reminiscent of that of the CESR. Thus, this behavior suggests that the density of itinerant KQ at the Fermi level increases as T -increase. Nevertheless, our results propose that further theoretical works are required to model the T -dependence of the KQ density at the Fermi level.

To understand the characteristics of the ESR signal in β -YbAlB₄ it is important to rely on the observance of a standard CESR in β -LuAlB₄. The ce spin-flip scattering is normally expected to be small for the light B and Al elements. As such, standard CESR have been found in many compounds based on these or other light elements, for instance, MgB₂ and Mg_{1-x}Al_xB₂, [24, 25]

highly oriented pyrolytic graphite(HOPG),[11, 27] intercalated AlCl_3 -HOPG[26] and C_6 . [28] However, the observance of a CESR in β -LuAlB₄ would not be expected, in principle, due to presence of the heavy atom, Lu. We argue that the observance of a pure CESR signal in the reference compound β -LuAlB₄ is explained by its crystal structure and the resulting electronic band structure. For β -LuAlB₄, Lu atoms are suspended between two planes of boron heptagons and surrounded in-plane by a distorted rectangles of Al atoms.[29] The two-dimensional layers of boron are similar to the two-dimensional layers of intercalated graphite compounds and MgB_2 where CESR signal has been observed.[24, 26, 28]. As such, it is plausible that the *ce* in the Boron layers are only weakly scattered by suspended Lu atoms allowing the observation of a broad CESR signal. In this scenario, the CESR signal would be expected for any $\text{R} = \text{rare-earth}$ β -RAlB₄ compounds, and therefore it is not surprise that a ESR signal is found in β -YbAlB₄. On the other hand, due to the Kondo coupling between the *4f* and the *ce* in β -YbAlB₄, we argue that the amazing ESR signal observed in β -YbAlB₄ evolves as a function of *T*, from a CESR signal at high- *T* to a KQSR arising from *4f-ce* coupled Kondo quasi-particles at low-*T*, which shares the nature of both, the LM-like and CESR-like ESR signals. The fact that this ESR signal presumably arises from Kondo *4f-ce* quasi-particles that captures the Yb³⁺ ionic characteristic at low-*T*, suggests that the scenario of local quantum criticality more properly describes the behavior of the *4f* electrons near a QCP.[2, 30]

In this regards, it is elucidative to compare the ESR

signal of β -YbAlB₄ with that of YbRh₂Si₂. YbRh₂Si₂ is also at the vicinity of a QCP, however, located on the AFM side. The ESR signal found in YbRh₂Si₂ show all the characteristics of a LM-like KQSR in a strong bottleneck-like regime.[10] According to the analysis of the field dependent resistivity and heat capacity data for β -YbAlB₄ and YbRh₂Si₂, these two Yb-based compounds show different quantum critical exponents, however, other compelling similarities suggest that β -YbAlB₄ may be just like YbRh₂Si₂ but, with higher temperatures scales (e.g. coherence temperature T^*). [1] As such, β -YbAlB₄ is at the vicinity of a QCP from the paramagnetic metal side (being in fact a HFS), showing the dual behavior in the ESR signal. Going away from the QCP, as in the FL-like reference compound β -LuAlB₄, the ESR signal is just a pure CESR (see Fig. 2). Finally, the fact that the two Yb-compounds, β -YbAlB₄ and YbRh₂Si₂, are prototypical of quantum critical behavior arising from opposite sides of a QCP and that both systems present ESR signal with prominent characteristics of Yb³⁺ LM, is an indication that the Yb *4f* electron posses localized character at the QCP. In summary, we report a remarkable ESR signal in the HFS β -YbAlB₄ phase which has the unique behavior of a CESR at high-*T* that acquires characteristics of a LM Yb³⁺ ESR at low-*T*. This unprecedented dual nature was not found in the reference compound β -LuAlB₄. We thank FAPESP, CNPq and CAPES (Brazil); NSF (USA); Grant No. 21684019 from the JSPS and Grant No. 17071003 from MEXT Japan for financial support and P. Coleman, M. Continentino and E. Miranda for valuable discussions.

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