Quantum Critical Kondo Quasiparticles Probed by ESR in $\beta$-YbAlB$_4$


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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 superconductor $\beta$-YbAlB$_4$ [S. Nakatsuji et al., Nature Phys. 4, 603 (2008)] which behaves as a CESR at high temperatures and acquires characteristics of the Yb$^{3+}$ 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 may favor the appearance of this dual character of the ESR signal in $\beta$-YbAlB$_4$.

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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 quasiparticles 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 Yb$^{3+}$ or Ce$^{3+}$ would broaden dramatically at low-$T$ avoiding their observation. Contrarily, an ESR signal was found in the intermediate valence YbCuAl [1] and in the Kondo lattice antiferromagnetic (AFM) heavy-fermion (HF) YbRh$_2$Si$_2$ [2] compounds. After the latter observation, ESR lines were reported for few others HF systems [3,4] and theoretical models [5,6] were proposed to explain the origin of such unexpected signals. However, the remarkable ESR signal reported here for $\beta$-YbAlB$_4$ comes to challenge any previous understanding that was believed to exist so far.

$\beta$-YbAlB$_4$ ($T_c = 80$ mK) is the first reported Yb-based HF superconductor (HFS). It is a new morphology of the known $\beta$-YbAlB$_4$ phase which is a paramagnetic metal at low-$T$ [7]. In contrast, for the $\beta$-YbAlB$_4$ phase, the low-$T$ superconducting state emerges from a non-Fermi-liquid (NFL) normal state associated to quantum criticality [8]. Not coincidentally, YbRh$_2$Si$_2$ that shows an ESR signal [2,9] also presents pronounced NFL behavior when its AFM state ($T_N = 70$ mK) is tuned towards a quantum critical point (QCP) by magnetic field [10,11].

Single crystals of $\beta$-(Yb, Lu)AlB$_4$ compounds were grown from Al flux as described previously [7,8]. The typical crystals size for both compounds was $\sim 0.5 \times 0.5 \times 0.05$ mm$^3$ and their mass were less than $\sim 0.1$ 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 plateletlike single crystals were glued on flat plastic surfaces and mounted in a form of sandwiches with the crystal’s $c$ axis perpendicular to the surface (total mass of the used crystals $\sim 4.0$ mg).

The ESR spectra were taken in a Bruker X-band (9.5 GHz) spectrometer. Dysonian ESR line shapes were observed for both samples in the whole $T$ range which corresponds to a skin depth smaller than the size of the crystals [12]. The ESR signal was calibrated at room $T$ using a strong pith standard with $4.55 \times 10^{15}$ 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 $\beta$-YbAlB$_4$ and $\beta$-LuAlB$_4$ compounds and Fig. 1(b) shows the high-$T$ and low-$T$ X-band ESR spectra for fine powder of $\beta$-YbAlB$_4$. The solid thick lines in Fig. 1 are fits to the spectra using a Dysonian line shape. The best fits for $\beta$-LuAlB$_4$ yield $g = 2.1(1)$ and linewidth $\Delta H = 800(50)$ Oe at high $T$. For $\beta$-YbAlB$_4$, 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.
value found for hyperfine lines of symmetry systems [14,15]. The observation of these spectra found for hyperfine lines is an irrefutable indication that the ESR -/C12 we obtain the hyperfine constant position of the batches; however, the ESR line reaches \( g \) of the order of typical values found for \(^{171}\)Yb. In contrast, the ESR -/C12 to the spectra using a Dysonian line shape. In the spectra of \(^{171}\)Yb -/C12 figures \( I = \frac{1}{2} \) at low-\( T \) values, \( \Delta H(T) \) decreases, i.e., the resonance shift toward lower fields [see Fig. 1(b)] 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 \(^{171}\)Yb\(^{3+} \) Kramers doublets in different crystal symmetries [2,3,9,14,16]. In contrast, the ESR line of \(^{173}\)Yb presents a nearly \( T \)-independent \( g \sim 2.1 \) down to \( T = 4.2 \) K.

A striking difference between the \( T \) dependence of \( \Delta H \) is also verified for the \( \beta \)-(Yb,Lu)\( \text{AlB}_4 \) compounds [see Fig. 2(b)]. For \( \beta \)-Yb\( \text{AlB}_4 \), \( \Delta H(T) \) shows a weak nonmonotonic behavior as a function of temperature. At high \( T \), \( \Delta H(T) \) is nearly constant but for \( T \leq 70 \) K, it shows a broadening of \( \approx 3 \) Oe/K as temperature increases. This rate has the same order of magnitude that the linear Korringa rate found for the ESR line observed at low \( T \) for the most high quality samples of Yb\( \text{Rh}_2\text{Si}_2 \) [2,9]. In contrast, for \( \beta \)-Lu\( \text{AlB}_4 \) \( \Delta H(T) \) is much broader at room \( T \) and it increases weakly with decreasing \( T \) down to \( T = 4.2 \) K.

Last, Fig. 2(c) 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 Yb\( \text{Rh}_2\text{Si}_2 \) [2,9] [Curie-like behavior, see Fig. 2(c)]. Thus, these results show that the ESR signal found in the HFS \( \beta \)-Yb\( \text{AlB}_4 \) 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 \( \beta \)-Lu\( \text{AlB}_4 \) presents an ESR signal that behaves as CESR in the whole studied...
low $T$, associated to the ESR results found for the reference compound $\beta$-LuAlB$_4$, allow us to propose a qualitative scenario that may explain the origin of the unprecedented ESR signal in $\beta$-YbAlB$_4$.

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 Er$^{3+}$ and Dy$^{3+}$ ESR $4f$/$C$ in their Kramers doublet ground states [19]. 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 ($g = 7.6$ for Dy$^{3+}$) and the CESR line ($g = 2.4$) 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 $T$ [19].

In the case of Kondo ions such as Yb$^{3+}$ 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 Dy$^{3+}$ and, in some compounds, these two spin systems ($4f$ and CE) may be strongly hybridized [20]. 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 quasi-particles spin resonance (KQSR). The KQSR is a new ESR response that possesses 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 [20] 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, YbInCu$_4$, [22] and YbAgCu$_4$, [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 $T$ (e.g., YbRh$_2$Si$_2$, YbIr$_2$Si$_2$, 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 or dynamic effects), crystal field excited states, phonons, and magnetic correlations. In particular, the strong bottleneck regime may favor the observation of LM-like KQSR [2-4,9].

The striking $T$-independent intensity of the KQSR in $\beta$-YbAlB$_4$ 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 $\beta$-YbAlB$_4$ it is important to rely on the observance of a standard CESR in $\beta$-LuAlB$_4$. 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, MgB$_2$ and Mg$_{1-x}$Al$_2$B$_2$, [24,25] highly oriented pyrolytic graphite (HOPG) [17,26], intercalated AlCl$_3$-HOPG [27] and C$_6$ [28]. However, the observance of a CESR in $\beta$-LuAlB$_4$ 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 $\beta$-LuAlB$_4$ is explained by its crystal structure and the resulting electronic band structure. For $\beta$-LuAlB$_4$, 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 [24,27,28]. 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 $R$ = rare-earth $\beta$-RAIB$_4$ compounds, and therefore it is not surprising that a CESR signal is found in $\beta$-YbAlB$_4$. On the other hand, due to the Kondo coupling between the 4$f$ and the CE in $\beta$-YbAlB$_4$, we argue that the amazing CESR signal observed in $\beta$-YbAlB$_4$ evolves as a function of $T$, from a CESR signal at high-$T$ to a KQSR arising from 4$f$-CE coupled Kondo quasiparticles 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 4$f$-CE quasiparticles that captures the Yb$^{3+}$ ionic characteristic at low $T$, suggests that the scenario of local quantum criticality more properly describes the behavior of the 4$f$ electrons near a QCP [20,30].

In this regards, it is elucidating to compare the ESR signal of $\beta$-YbAlB$_4$ with that of YbRh$_2$Si$_2$. YbRh$_2$Si$_2$ is also at the vicinity of a QCP, however, located on the AFM side. The ESR signal found in YbRh$_2$Si$_2$ shows all the characteristics of a LM-like KQSR in a strong bottleneck-like regime [9]. According to the analysis of the field dependent resistivity and heat capacity data for $\beta$-YbAlB$_4$ and YbRh$_2$Si$_2$, these two Yb-based compounds show different quantum critical exponents, however, other compelling similarities suggest that $\beta$-YbAlB$_4$ may be just like YbRh$_2$Si$_2$ but with higher temperatures scales (e.g., coherence temperature $T^*$) [8]. As such, $\beta$-YbAlB$_4$ 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 $\beta$-LuAlB$_4$, the ESR signal is just a pure CESR (see Fig. 2). Finally, the fact that the two Yb compounds, $\beta$-YbAlB$_4$ and YbRh$_2$Si$_2$, are prototypical of quantum critical behavior arising from opposite sides of a QCP and that both systems present ESR signal with prominent characteristics of Yb$^{3+}$ LM, is an indication that the Yb 4$f$ electron possesses localized character at the QCP. In summary, we report a remarkable ESR signal in the HFS $\beta$-YbAlB$_4$ phase which has the unique behavior of a CESR at high $T$ that acquires characteristics of a LM Yb$^{3+}$ ESR at low $T$. This unprecedented dual nature was not found in the reference compound $\beta$-LuAlB$_4$.

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[18] The anisotropy $g_{||} - g_{\perp} \approx 0.4$ should imply in a powder spectra with $\Delta H \approx 0.4$ kOe at X band. This suggests that the data of Figs. 1 and 2 have a strong contribution of $H||c$ orientation due to the lack of perfect random orientation of the plateletlike microcristals.