Dual nature of $3d$ electrons in Yb$_2$Zn$_{20}$ ($T = \text{Co; Fe}$) evidenced by electron spin resonance

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Abstract. The electron spin resonance experiments were carried out in the single crystals YbFe$_2$Zn$_{20}$. The observed spin dynamics is compared with that in YbCo$_2$Zn$_{20}$ and Yb$_2$Co$_{12}$$P_7$ as well as with the data of inelastic neutron scattering and electronic band structure calculations. Our results provide direct evidence that $3d$ electrons are itinerant in YbFe$_2$Zn$_{20}$ and localized in YbCo$_2$Zn$_{20}$. Possible connection between spin paramagnetism of dense heavy fermion systems, quantum criticality effects, and ESR spectra is discussed.

1. Introduction
Competition between strong on-site Coulomb repulsion of $d$ or $f$ electrons leading to localization and orbital overlap with neighboring ligands (hybridization) causing a $d$-($f$-) electron itineracy is a long-standing challenging problem in the physics of strongly correlated electron materials. Usually, in the rare earth $4f$ compounds, the $4f$ orbitals are highly localized and hybridize only weakly with the conduction electrons ($ce$). Contrary, in uranium compounds, the $5f$ orbitals are spatially extended and form dispersive bands through strong hybridization with the neighboring $s$, $p$, and $d$ orbitals. Therefore, essential differences might be expected between the detailed behaviors of uranium- and rare-earth-based compounds. The spin dynamics derived from such methods as inelastic neutron scattering (INS) or electron spin resonance (ESR) are crucial for our understanding of these materials.

Both the $ce$ and localized magnetic moments can be microscopically studied by (ESR) method. This is especially important in the case of heavy fermion (HF) compounds with rare earth sublattices that display exotic behaviors at low temperatures such as quantum critical points (QCP) and superconductivity. Very recently, we have observed very unusual ESR properties of the YbCo$_2$Zn$_{20}$ single crystals [1]. The well-separated, strongly anisotropic ESR signals from the Co local magnetic moments and conduction electron spin resonance (CESR) have been detected in YbCo$_2$Zn$_{20}$. According to observed ESR spin dynamics, the YbCo$_2$Zn$_{20}$ compound behaves as a weak itinerant ferromagnet. The family of six closely related Yb-based HF systems YbT$_2$Zn$_{20}$ ($T = \text{Fe, Co, Ru, Rh, Os, Ir}$) with structures composed of cage-like units offers the possibility to study the interaction between $ce$ and $4f$ electrons in fully ordered compounds for relatively low concentrations of ytterbium.
Here, we report the temperature dependent ESR experiments in the YbFe$_2$Zn$_{20}$ single crystals, whose preparation, magnetic, thermodynamic, and transport measurements have been described elsewhere [2-4]. The YbT$_2$Zn$_{20}$ compounds with the highest mass renormalization observed up to now in strongly correlated electron systems crystallize in the cubic CeCr$_2$Al$_{20}$ (Fd3m space group) symmetry. In this structure, very small crystal electric field (CEF) splittings are related to every ytterbium atom which is surrounded by 16 zinc atoms in a nearly spherical array. In consequence, such systems can be considered as promising materials for understanding how the crossover from the itinerant to localized 4$f$ states may be realized. YbCo$_2$Zn$_{20}$ with the Kondo temperature $T_K \sim 1.5$ K is regarded to be located in the vicinity of a QCP because a magnetic transition at $T_M \sim 0.15$ K occurs at applying pressures more than 1 GPa [5]. On the other side, the pressure needed to bring YbFe$_2$Zn$_{20}$ ($T_K \sim 33$ K [2]) to a potential QCP (or at least quantum phase transition) is on the order of 9.8 GPa [6]. Very different HF properties of both YbFe$_2$Zn$_{20}$ and YbCo$_2$Zn$_{20}$ compounds with virtually identical crystal structures have been explained as the result of significantly different $T_K$ [2, 3].

2. Sample preparation and experimental

ESR measurements were performed with the X-band Bruker ESM/plus spectrometer (frequency $\nu \sim$9.4 GHz) coupled to a helium-gas-flux temperature controller system at $4.2 < T < 300$ K in magnetic fields up to 1.4 T. The high quality YbFe$_2$Zn$_{20}$ single crystals were cut into bars of 2-5 mg with typical length 2-4 mm. The powder X-ray and the low-temperature susceptibility measurements indicated little, or no local-moment-bearing impurities [2]. The ESR linewidth $\Delta H$ has been measured as the distance between two peaks in the plot of the first derivative of the absorption signal.

3. Results and discussion

An extremely weak and broad, nearly isotropic ESR lines could be resolved in YbFe$_2$Zn$_{20}$ at temperatures $T < 10$ K only. Their intensity was approximately one order of magnitude less than that in YbCo$_2$Zn$_{20}$ measured by the same conditions (Fig.1). The estimated value of the average ESR g-factor $g = h \nu / \mu_0 H_{res} \approx 3.5$, where $H_{res}$ is the resonance field position. The temperature dependence of $\Delta H$ can be well fitted by a linear increase in temperature $bT$ with a slope $b = 33$ Oe/K (Fig. 2). Similar temperature evolution of $\Delta H$ has been observed at low temperatures $T < 15$ K in YbRh$_2$Si$_2$ [7], YbRh$_2$P$_4$ [8], YbRh$_2$Pb [9], and YbNi$_2$ [10] and was associated with a Korringa law of local-moment relaxation of the Yb$^{3+}$ $(4f^{13})$ ions toward ce. The localization of the 4$f$ electrons in YbFe$_2$Zn$_{20}$ has been confirmed due to successful description of static and dynamic magnetic susceptibility, INS, and the specific heat measurements in the framework of the Kondo impurity model in contrast to the relevant data for URu$_2$Zn$_{20}$ and UCo$_2$Zn$_{20}$ [11]. Thus, the spin fluctuations in YbFe$_2$Zn$_{20}$ arise from localized 4$f$ electrons rather than itinerant 3$d$ electrons. Contrary, the corresponding g-factor values measured in YbCo$_2$Zn$_{20}$ in the range between 4.5 and 7.5 are too large in comparison with those of the Yb$^{3+}$ Kramers doublet and can be resolved up to room temperature. Moreover, for the external magnetic field $H$ aligned parallel to the crystallographic
direction [011], ESR spectrum in YbCo$_2$Zn$_{20}$ could be nicely fitted by two Dysonian components as shown at $T = 10$ K in the Fig. 3, the low-field peak 1 with the effective ESR g-factor $g \approx 6.6$ and the high-field peak 2 at $g \approx 2.05$. We have shown that both these lines ascribed to the cobalt local moments and CESR, respectively, coexist in the whole studied temperature interval from 4.2 to 290 K, differ by the character of their angular and temperature dependences of the ESR parameters, and that the extremely weak and distorted signal 3 at $g \approx 4.23$ which develops below 60 K is caused by cobalt clusters [1]. We can relate the strong low-field peak in the ESR spectrum of YbCo$_2$Zn$_{20}$ to the cobalt ions for the following reasons: (1) ESR spectra of very different properties have been found out only in two of six YbT$_2$Zn$_{20}$ alloys prepared in an identical manner. Hence, these signals cannot be attributed with some impurity phases. (2) An observed striking difference of ESR behavior in both isostructural Yb-based systems YbCo$_2$Zn$_{20}$ and YbFe$_2$Zn$_{20}$ can be caused by different behavior of the corresponding 3$d$ ions only. (3) The measured average values of the ESR g-factor in YbCo$_2$Zn$_{20}$ which are significantly larger than those for the Yb$^{3+}$-ion are very close to the typical g-values of cobalt ions in crystal fields.

Figure 2. Temperature dependence of ESR linewidth in YbFe$_2$Zn$_{20}$. Solid line is the linear fit which provides a Korringa slope $b = 33$ Oe/K as described in text.

Figure 3. ESR signals in the YbCo$_2$Zn$_{20}$ single crystal at 10 K for the constant magnetic field H aligned parallel to the crystallographic direction [011]. The dashed line indicates the fit by Dyson-type shape.
of different symmetries [12]. (4) As a rule, the Yb$^{3+}$-ESR cannot be detected at high temperatures $T > 120$ K. (5) Striking differences of spin dynamics in YbFe$_2$Zn$_{20}$ and YbCo$_2$Zn$_{20}$ can be explained by peculiarities of their electronic band structure. Calculations of the electron density of states performed in Ref. 13 showed that the $d$-$f$ hybridization in the YbFe$_2$Zn$_{20}$ is larger compared with that in the YbCo$_2$Zn$_{20}$, and the $d$ electrons from cobalt in YbCo$_2$Zn$_{20}$ are localized at energies below the Fermi level of the structure due to the contribution from the $f$ states in contrast to Fe $d$ states in YbFe$_2$Zn$_{20}$. It was also insisted that the $p$-$f$ hybridization plays an important role to delocalize the $f$ states in YbCo$_2$Zn$_{20}$ and in another itinerant isostructural Ul$_2$Zn$_{20}$ compound [14]. Recently, a complicated interplay between $4f/5f$ and $3d$ magnetism has been established in several reports. For example, polarized neutron and bulk magnetic measurements on a high-quality single crystal of UMn$_2$Al$_{20}$ indicated that the magnetic moments are present on the Mn sites only [15]. The FM ordering of Fe in Yb$_{0.88}$Fe$_4$Sb$_{12}$ [16] and the magnetized Mn sublattice in YbMn$_x$Ge$_{6-x}$Sn$_x$ ($x = 4.2$ and $4.4$) [17] have been evidenced by means of resonant X-ray emission spectroscopy due to a valence fluctuations of ytterbium and magnetic instability of iron or manganese ions, respectively. Magnetization, specific heat, and NMR studies in YbFe$_2$Al$_{10}$ have revealed contiguous $3d$ and $4f$ magnetism with the valence fluctuations from the $4f$ Yb ions in the high temperature range and the low temperature field dependent Kondo-like correlations associated to the $3d$ Fe ions [18]. Therefore, we argue that the configuration of the Yb moments in YbCo$_2$Zn$_{20}$ is strongly influenced by the cobalt magnetic moments and a weak itinerant ferromagnetism from the Co sublattice dominates an ESR spin dynamics at the microscopic level.

Most likely, a dominating role of the cobalt sublattice has been revealed also during our preliminary ESR experiments of the polycrystalline samples of the hexagonal, non-centrosymmetric compound Yb$_2$Co$_{12}$P$_7$. Previous specific heat and magnetization measurements down to $2$ K suggested disordered magnetism and a large density of states at the Fermi level associated with the Co $d$-electrons rather than from hybridized Yb $f$-electron states [19]. As can be seen in Fig. 4, below $60$ K, the X-band ESR
spectrum consists of the signal with the temperature independent resonance field position centered at \( g \approx 5.44 \) and the peak with the g-value which increases from 2.16 at \( T = 4.2 \) K up to \( g \approx 2.62 \) at \( T = 60 \) K. The measured g-values in \( \text{Yb}_2\text{Co}_{12}\text{P}_7 \) are very close to those reported for \( \text{YbCo}_2\text{Zn}_{20} \) [1] and can be also attributed with the localized Co moments and CESR, correspondingly. However, a detailed study of ESR spin dynamics in \( \text{Yb}_2\text{Co}_{12}\text{P}_7 \) will be issue of the forthcoming publication.

In spite of the present and previous ESR and INS studies in some undoped Yb-based HF intermetallics, we can present three main regimes of interest focusing on the interplay between the anisotropy of the CEF splitting \( \Delta_f \), \( f-ce \) hybridization strength with characteristic size \( V \), and quantum criticality:

1. Strong CEF anisotropy and weak hybridization (\( \Delta/V > 1 \)) observed in compounds without any QCP such as \( \text{YbFe}_2\text{Zn}_{20}, \text{YbRh}_2\text{P}_4 \) [8], \( \text{YbRh}_2\text{Pb} \) [9], \( \text{YbNi}_2 \) [10], and \( \text{YbCo}_2\text{Si}_2 \) [20]) lead to a very broad and weak ESR signals and to an INS spectra with sharp CEF levels which are associated with the well-localized Yb\(^{3+}\) ions. The Yb ion valence is very close to the integer value \( 3+ \).

2. Intermediate hybridization (\( \Delta/V \geq 1 \)) allows to observe the most intense and narrow ESR signals in the quantum critical systems \( \text{YbRh}_2\text{Si}_2 \) [7], \( \text{YbIr}_2\text{Si}_2 \) [21], and \( \beta\text{-YbAlB}_4 \) [22]. Electron spin relaxation processes are influenced by the Yb\(^{3+}\) spins. The INS spectra represent a set of extremely broadened ("smeared") CEF states. The Yb valence more or less strongly deviates from \( 3+ \).

3. Strong hybridization and small CEF splitting (\( \Delta/V < 1 \)) occur in \( \text{YbCo}_2\text{Zn}_{20} \) and \( \text{YbCuAl} \) [23, 1] which are close to a QCP. The positions of the CEF levels are of the orders of their broadening due to instability of the \( 4f \) shell and the associated valence instability of ytterbium. The \( f \) electrons can be fully or partially delocalized and strongly admixed with \( ce \) due to large \( d-f \) and \( p-f \) hybridization. The 3d sublattice forms a character of the electron spin dynamics. Furthermore, to our mind, the reported Yb\(^{3+}\)-ESR at \( g \sim 4.17 \) below 50 K in skutterudites \( \text{YbFe}_2\text{Sb}_{12} \) [24] belongs in fact, to the iron ions. These materials manifest magnetic instability of the Fe 3d electrons and valence instability of the Yb 4f electrons [16]. The value of the ESR g-factor and the observed temperature evolution of the ESR signal confirm that the latter arises from the Fe\(^{3+}\) (3d\(^f\)) rather than from the Yb\(^{3+}\) (4f\(^{13}\)) ions.

In conclusion, we have compared an ESR absorption in the dense HF systems \( \text{YbFe}_2\text{Zn}_{20} \) and \( \text{YbCo}_2\text{Zn}_{20} \). An analysis of their ESR spin dynamics showed that the Yb 4f electrons are well localized, and the Fe 3d electrons are itinerant in \( \text{YbFe}_2\text{Zn}_{20} \) in striking contradiction to the \( \text{YbCo}_2\text{Zn}_{20} \) compound which behaves as a weak itinerant ferromagnet with localization of the cobalt magnetic moments. A drastic difference in the ESR properties of both isostructural compounds can be associated with alternations of their \( f-ce \) hybridizations, CEF, and electronic band structures. Our findings suggest an idea about possible connection between the sharp narrowed ESR lines and the proximity to a QCP [25]. It would also be very interesting to examine whether 5f -based intermetallics with similar magnetic anisotropy and electron density of states such as \( \text{UT}_2\text{Zn}_{20} \) (\( \text{T} = \text{Co, Ir, Rh} \)) exhibit ESR signals.

4. Acknowledgments

This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities. Work at the Ames Laboratory was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. We wish also to thank B. Maple for furnishing the \( \text{Yb}_2\text{Co}_{12}\text{P}_7 \) samples.

References
[1] Ivanshin V A, Litvinova T O, Sukhanov A A, Ivanshin N A, Jia S, Bud’ko S L, Canfield P C 2014 JETP Lett. 99 153
[2] Torikachvili M C, Jia S, Mun E D, Hannahs S T, Black R C, Neils W K, Martien D, Bud’ko S L, Canfield P C 2007 PNAS 104 9960
