Contiguous 3d— and 4f—magnetism:
towards strongly correlated 3d—electrons in YbFe$_2$Al$_{10}$

P. Khuntia*,$^{1}$ P. Peratheepan,$^{2,3}$ A. Strydom,$^{1,2}$ F. Steglich,$^{1}$ and M. Baenitz$^{1}$

$^{1}$Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany
$^{2}$Physics Department, University of Johannesburg, P.O. Box 524, Auckland Park 2006, South Africa
$^{3}$Department of Physics, Eastern University, Vantharumooalai, Chenkalady 30350, Sri Lanka

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Abstract

We present magnetization, specific heat, and NMR investigations on YbFe$_2$Al$_{10}$ over a wide range in temperature and magnetic field. The magnetic susceptibility at low temperatures is strongly enhanced in weak magnetic fields accompanied by a $-\ln T$ divergence of the low $-T$ specific heat coefficient in zero field, which allows to attribute a ground state of correlated electrons. The system displays valence fluctuating behavior in the low to intermediate temperature range, whereas above 400 K, Yb$^{3+}$ carries a full and stable moment and Fe carries a moment of about 3.1 $\mu_B$. The enhanced value of the Sommerfeld Wilson ratio and the dynamic scaling of spin lattice relaxation rate by $T^{-27(1/T_1 T)}$ with static susceptibility suggest the presence of ferromagnetic correlations. $27(1/T_1 T)$ simultaneously tracks the valence fluctuations from the 4f -Yb ions in the high $T$ range and field dependent Kondo-like correlations among small Fe 3d moments (0.5 $\mu_B$) at low $T$ which evolve out of an Yb 4f admixed conduction band.

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Novel phases ranging from unconventional superconductivity and spin liquids, to quantum criticality in correlated electrons result from competing interactions between magnetic, charge, orbital and lattice degrees of freedom [1,2]. Competing interactions such as the mostly antiferromagnetic (AFM) Rudermann-Kittel-Kasuya-Yosida (RKKY) exchange and the Kondo effect on a localized spin leads to a magnetic instability which generates unusual temperature ($T$) and magnetic field ($H$) scaling behavior of bulk and microscopic observables. The competing magnetic interactions frequently produce generalized non-Fermi liquid (nFL) scaling in the thermal behavior of physical properties. If the RKKY spin exchange succeeds in overcoming the thermal energy of the spin system conducive to a paramagnetic-to-AFM transition, the addition of a competing Kondo spin exchange with the conduction electrons achieves a curbing effect on the phase transition. Moreover, under favorable conditions such as applied pressure or magnetic field the phase transition may become confined to temperatures arbitrarily close to zero, which in turn leads to remarkable thermal scaling in the realm of quantum criticality [3,7]. In exceptional cases quantum criticality presents itself under ambient conditions, such as in U$_3$Pt$_2$In [8,9] or in the superconductor $\beta$--YbAlB$_4$ [10]. Quantum criticality stemming from ferromagnetic exchange on the other hand is a rare occurrence, and has been discussed among 5f—electrons systems such as UGe$_2$ [11,12] or UCoGe [13,14], 4f systems like YbNi$_4$P$_2$ [15,16], CeRu$_{1-x}$Fe$_x$PO$_4$ [17,18], and in weak itinerant ferromagnets like ZrZn$_2$ [19] and NbFe$_2$ [20]. YFe$_2$Al$_{10}$, an isostuctural version of YbFe$_2$Al$_{10}$ with no 4f—electrons, is reported to be a plausible candidate for a FM quantum critical magnet [21,24,30].

The ternary orthorhombic aluminides of RT$_2$Al$_{10}$ type ($R =$ rare earth element, $T =$Fe, Ru, Os) have been the subject of considerable debate in view of a fascinating conundrum of physical properties. Most notable is the extremes of magnetic interactions found in the Ce series ranging from unpredictably high AFM order at 27 K in CeRu$_2$Al$_{10}$ [25,28] to the Kondo insulating state in CeFe$_2$Al$_{10}$ [29]. In the present study to further unravel the nature of 3d—electrons in this class of material, we assess the response of Fe-based magnetism in the presence of localized magnetism, namely the 4f$^{13}$ element Yb, and we use a combination of bulk and microscopic probes due to the anticipated complexity of an admixture of different types of magnetic exchange. A comparable situation can be found in CeFe$_2$Al$_{10}$ in which the confluence of the two types of magnetic species has the surprising effect of producing the non-magnetic Kondo insulating state [29], which is an extreme case of local-moment hybridization with conduction electrons. Recently, there has been a resurgence of research activities in intermediate valence systems following the discovery of superconductivity and quantum critical behavior in a mixed valence heavy fermion $\beta$--YbAlB$_4$ [10,31–38].

In this Letter, we present a comprehensive magnetic susceptibility, specific heat, and $^{27}$Al NMR investigations on polycrystalline YbFe$_2$Al$_{10}$. Magnetic susceptibility and specific heat display low temperature divergences, yet without any signature of magnetic ordering down to 0.35 K. In order to understand the low energy spin dynamics governing the underlying magnetism of the title compound, we have carried out NMR investigations with special attention to the spin lattice relaxation measurements. The low field spin lattice relaxation rate shows a divergence towards low temperatures, which is consistent with magnetization and specific heat data. The observed deviations
from the FL behavior is associated with correlated 3d Fe moments strongly coupled via Yb 4f derived conduction band.

Polycrystalline samples of YbFe$_2$Al$_{10}$ have been synthesized following a method discussed elsewhere [22, 27]. The dc magnetic susceptibility $\chi(T)$ ($=M/H$) and thermodpwer date were obtained using a QD PPMS.

In a recent work, a Kondo-like electrical resistivity accompanied by divergences in $\chi(T)$ and the Sommerfeld coefficient in zero field were reported [23] on YbFe$_2$Al$_{10}$. The magnetism of Yb in this compound was demonstrated [39] to be subject to an unstable valence and to recover its full trivalent state at $T > 400$ K, which is in agreement with the earlier report [40].

Shown in Fig. 1 (a) is the field dependent $\chi(T)$ of YbFe$_2$Al$_{10}$. The values of $\chi(T)$ are enhanced by one order of magnitude in comparison with the non-4f electron homologue YFe$_2$Al$_{10}$ [21], which indicates a strong hybridization of Yb 4f states with the conduction electron states. A modified band structure is expected therefore with subsequent effects on the bands of conduction electrons. Towards higher temperatures, Yb tends to reach its full trivalent state and this temperature-driven evolution is appropriately reflected in the thermodpwer $S(T)$ illustrated in Fig. 1(d), at a broad peak centered at $T^*$ which we use to denote the temperature scale of the valence conversion of Yb. $S(T)$ is a very sensitive probe for changes of the electronic density of states at the Fermi energy. Such a peak is typical for intermediate valent (IV) Yb compounds. At the high temperature end, the consequence of this peak is played out by a change in the sign of $S(T)$ at about 300 K, which implies a temperature-driven change in the relative weights and participation of both holes and electrons in the underlying bandstructure. However, the negative sign in $S(T)$ of YbFe$_2$Al$_{10}$ signals stable and local-moment magnetic character of Yb above 300 K, because $S(T)$ native to the weakly hybridized 4f$^{13+2}$ state of Yb is expected to be negative [41]. Positive $S(T)$ values in correlated Yb compounds may be found in cases where severe hybridization with conduction electrons drives the Yb into the near-divalent, nonmagnetic state. Such behavior can be found for example in YbFe$_2$Sb$_{12}$ [42], even in the temperature range where Yb carries $\simeq$ 75% of its full moment [43]. A positive $S(T)$ may also result when a weak negative signal from Yb hybridized magnetism is masked by a stronger positive band contribution, such as was demonstrated [44] for YbPdCu$_4$, when compared to the overall negative $S(T)$ of its homologues YbAuCu$_4$ and YbAgCu$_4$, while an underlying semi-metallic lattice may also conceiv Kondo type hybridization in $S(T)$ [45]. However, the observed trend seems to be that hybridization effects on Yb$^{3+}$ when band electrons play a minor role such as in YbB$_{12}$ for example are manifest in a negative $S(T)$ [46].

A small upturn in $S(T)$ below 10 K is consistent with the incoherent Kondo like resistivity $\rho(T)$ [23]. A peak in resistivity $\rho(T)$ at $T \simeq 4.5$ K (see supplemental) is reminiscent of Kondo-lattice behavior [23]. The Kondo type upturn in $\rho(T)$ as well as the low-$T$ divergence in $\chi(T)$ is quenched by applying magnetic fields of a few teslas. However, the initial susceptibility $\chi(H \rightarrow 0)$ at 2 K as well as the high-field magnetization $M(H)$ yield extremely small values of the magnetic moment (\mu$_{3d}$ $\simeq$ 0.5 \mu$_B$) in YbFe$_2$Al$_{10}$. Following a weak curvature in the $M(H)$ in low fields, there is however no saturation achieved in $M(H)$ at 2 K even up to 7 T, Fig. 1(c), where a quasi-linear in field magnetization is found. The high-field magnetic susceptibility is thus both field- and $T$ independent, from Fig. 1(c) and (a), respectively, and this is the susceptibility response composed of quenched 3d correlations plus the Pauli spin susceptibility of the conduction electrons. To put this in context, we draw a comparison with the susceptibility of YbRu$_2$Al$_{10}$ [47] in which there are 4f $-$ electrons of Yb as the sole magnetic species and no unpaired $d$ $-$ electrons. This compound achieves a $\chi(T)$ value only about one half the value obtained for the Fe-containing compound YbFe$_2$Al$_{10}$ in comparable conditions.

A detailed analysis of $\chi(T)$ (see Fig 1b) reveals an intermediate valence (IV) state of Yb at low and intermediate $T$, but Yb recovers its full moment with a high spin state Fe at $T>400$ K with predominant AFM correlations at high $T$. This could be ascribed to the role of Fe (3.1 \mu$_B$) in addition to Yb (4.54 \mu$_B$) on the underlying magnetism of this system since Yb is in the IV state (see supplemental) at high $T$. A similar scenario has been
discussed in the IV Yb-based skutterudites YbFe$_2$Sb$_{12}$ [48] and YbFe$_2$P$_{12}$ [49]. The deconvolution of the Fe−3$d$ contribution and the more localized Yb−4$f$ contribution is a daunting task and beyond the scope of this manuscript. Nonetheless, based on the model of Rajan [50], for the Yb−4$f$ part a constant and $T$-independent susceptibility could be expected towards low temperatures. Therefore, based upon interpretation of the magnetism in YbFe$_2$Al$_{10}$ we assign the low $T$ divergences in this compound to correlations among small Fe−3$d$ moments.

Shown in Fig.2(a) is the specific heat coefficient ($C_p(T)/T$) in different magnetic fields measured using $^3$He option of QD PPMS. The value of $C_p/T$ is enhanced towards low temperatures and follows a $-\ln T$ behavior in zero field, which suggests a correlated behavior of electrons. This may be attributed to entropy of unquenched spin degrees of freedom, or to impending cooperative behavior at much lower temperatures. Applied magnetic fields achieve a suppression and eventual saturation into a constant value of $C_p/T$ and thus the recovery of the Fermi liquid ground state. The ratio of the enhanced $\gamma_0$ value at zero field to the fully quenched value $\gamma_{1f}$ in 9 T at 0.35 K is about 2.5. Surprisingly, this enhancement factor is qualitatively similar to that of the non-4$f$ compound YFe$_2$Al$_{10}$ [39]. Despite the fact that the relative enhancements $\Delta\gamma/\gamma_{1f} = (\gamma_0 - \gamma_{1f})/\gamma_{1f}$ are similar, it should be mentioned that the $T$ dependence of $C_p/T$ are dissimilar (−$\ln T$ for YbFe$_2$Al$_{10}$ and power law behavior in case of YFe$_2$Al$_{10}$). For YbFe$_2$Al$_{10}$ the magnetic entropy at low $T$ amounts to only 0.063$R\ln 8$, or $\sim 6.3\%$ of the $J = 7/2$ multiplet value appropriate for Yb [51]. Therefore, we relate the low temperature divergence of the Sommerfeld coefficient to the emergence of correlations among Fe moments amplified by the strong hybridization between Yb−4$f$ states and $s$+$d$ conduction band states at the Fermi level. The field dependence of the Sommerfeld coefficient at 0.5 K follows a $H^{-0.35}$ behavior (Fig. 2b) and the transition to a constant in $T$ regime provides the crossover scale between FL and nFL behavior (inset of Fig. 2b).

The residual quenched Sommerfeld coefficient of $\gamma_{1f} = 75$ mJ/mol K$^2$ in YbFe$_2$Al$_{10}$ exceeds that of the La equivalent [29] by a factor $\sim 3$, which indicates that the Fermi level in YbFe$_2$Al$_{10}$ is occupied predominantly by the electrons of a heavy Fermi liquid. An enhanced value of the Sommerfeld-Wilson ratio $R_w = \pi^2k_B^2/\mu_0\mu_{eff}(\chi/\gamma) \approx 12$ at 2 K indicates the presence of FM correlations, which is in contrast to the high $T$ regime. It is also important to mention that there is a striking similarity of our specific heat data in Fig. 2a to those of $\beta$−YbAlB$_4$ [11]. $\beta$−YbAlB$_4$ is a rare example of an IV system with local moment low $T$ electron correlations [32]. Another prominent example in that context is the IV system YbAl$_3$ [52].

$^{27}$Al-NMR ($I = 5/2$) measurements have been performed using a standard Tecmag NMR spectrometer in the temperature range $1.8 \leq T \leq 300$ K and in the field range $0.98 \leq \mu_0 H \leq 7.27$ T. The orthorhombic crystal structure of YbFe$_2$Al$_{10}$ hosts five inequivalent Al sites. Usually this results in rather broad NMR spectra with a clear central transition and superimposed first order satellite transitions. Surprisingly, we found a rather well-resolved central transition with a small field dependent anisotropy, which implies that the different Al sites are rather equal in their magnetic environment. There are no sharp features assigned to the first order quadrupolar transitions [39] and no appreciable shift observed in the $^{27}$Al-NMR line (Fig. 3), but instead a broadening of the central transition with decreasing temperatures is found. The line width (FWHM) increases with decreasing temperature and scales with the bulk susceptibility yielding a Curie-Weiss like behavior. At the lowest $T$ and in small magnetic fields the scaling of FWHM with $\chi(T)$ breaks down, which is in-line with the expected behavior at the onset of electronic correlations.

The sharp central transition enables us to perform $^{27}$Al spin-lattice relaxation rate (SLRR) measurements consistently following saturation recovery method with suitable $rf$ pulses and the results are shown in Fig. 4. The relaxation rate divided by $T$, i.e. $1/T_1$, shows a divergence towards low temperatures (Fig. 4a) with a proportionality $\chi(T)/\sqrt{T}$ in the lowest magnetic fields. Such a dynamic scaling is frequently found in heavy fermion systems with AFM correlations and even with admixed FM correlations like in CeFePO [53,57]. In addition, the relative change $[(\gamma_0 - \gamma_{1f})/\gamma_{1f}] \approx 1.7$ underestimates the SLRR enhancement found in the experiment ($\approx 4.6$). The stronger enhancement in the SLRR points towards the presence of dominant $q = 0$ contributions, as a response to FM correlations. Usually the specific heat is more sensitive to finite $q$ excitations which explains the difference in the enhancement factors. In contrast with the discrepancy in the $T$ enhancement, the field dependence of the SLRR is in agreement with the Fermi liquid theory exhibit-
The spin fluctuation spectra and \( H^0.7 \) in the SLRR of the Al nuclei at high temperatures. The inset shows the simulation of the 4.3 K spectra.

Independent of the magnetic field a peak (Fig. 4a) in the SLRR probes the valence fluctuations from the \( 4f \) ion, \( A_{hf} \) is the uniform bulk susceptibility. It has to be mentioned that in case of large valence variations (like in Eu systems where the valence could vary between 2+ and 3+) the electronic structure may be perturbed which changes \( A_{hf} \), but we omit this detail for YbFe\(_2\)Al\(_10\) and assume that \( A_{hf} \) is not varying with temperature. The beauty of these results is that \( ^{27}\text{Al} \) NMR simultaneously senses the valence fluctuations from the \( 4f \)-related Yb ions in the high \( T \) range and the low \( T \) field dependent Kondo-like correlations associated to the \( 3d \)-Fe ions. Upon the application of high magnetic fields these fluctuations are quenched (here \( \tau_{3d} \ll \tau_{af} \) for all \( T \)). Therefore, the relaxation rate at 7.27 T allows for the determination of the effective fluctuation time \( \tau_{af} = 1/\Gamma_{af} \), which is plotted as a function of temperature in Fig. 4(c). The step like change of \( \tau_{af} \) at about 100 K signals more a charge gap scenario (like in Kondo insulators) than an intermediate valence system with a smooth variation in \( \tau_{af} \). With the knowledge of the \( T \) dependent (but not \( H \)-dependent) relaxation time \( \tau_{af} \), we now proceed to fit the \( 1/T_1T \) vs. \( T \) results in low magnetic field. Surprisingly, the assumption of \( \tau_{3d} = 1/\sqrt{T} \approx \chi \) results in a very good agreement with the experimental data (red line in Fig. 4(a)), which also explains the \( ^{27}(1/T_1T) \propto \chi^2 \) behavior at \( T = 0 \) limit. With this approach we have convincingly shown that NMR is able to probe both energy regimes; i) the high-temperature \( IV \) regime where \( \Gamma_{4f} \) is changing strongly and ii) the low-\( T \) regime where \( \Gamma_{4f} \) is constant and \( \Gamma_{3d} \) shows a local moment behavior with \( \Gamma_{3d} \propto \sqrt{T} \).

In summary, our comprehensive investigation provides compelling evidence for low-temperature \( 3d \)-electron correlations evolving out of an intermediate valent Yb density of states and reveals the dual (local and itinerant) nature of Fe magnetism in YbFe\(_2\)Al\(_10\). The spin lattice relaxation rate is in convincing agreement with the local moment metal (FL) scenario and unveils the persistence of \( \Gamma_{4f} \) at 7.27 T.

![Graph showing \( ^{27}(1/T_1T) \) vs. \( T \) in fields.](image)

![Graph comparing magnetic field dependence of \( \tau_{af} \) at 2.5 K.](image)
dilute the 3 contiguous Fe magnetism. It would be of great interest to electron transfer could not be maintained because of the edges support from SA-NRF (78832). We thank C. Klausnitzer for technical support concerning specific heat measurements. We thank the DFG for financial support (project OE-511/1-1). AMS acknowledges support from SA-NRF (78832).

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*pkhuntia@gmail.com

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