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LETTER TO THE EDITOR

First-order valence transition in $YbInCu_4$ in the (B, T)-plane

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Abstract. The puzzling properties of the first-order phase transition in $YbInCu_4$ and its alloys in the wide range of magnetic fields and temperatures are perfectly described in terms of a simple entropy transition for free Yb ions. In particular, it turns out that the transition line in the (B, T)-plane is very close to the elliptic shape, as it has been observed experimentally. Similar calculations are done, and the experiments are proposed for the $(\gamma$–$\alpha)$ phase transition in Ce in Megagauss fields. We speculate, that in the case of $YbInCu_4$ the first-order transition is a Mott transition between a higher temperature phase in which localized moments are stabilized by the entropy terms in the free energy, and a band-like non-magnetic ground state of the f-electrons.

For years the most famous example of the first-order transition into a state with an intermediate valence has been the isostructural γ–α transition in metallic Ce (for the phase diagram of Ce, see [1]). Changes in the valence state are usually judged by the change in the unit cell volume or by spectroscopic means, which strictly speaking do not always provide exact valence values. Although a structural transition in a crystalline matter possessing a critical point in the (P, T)-plane is of great interest by itself, an observation of the γ–α transition in Ce has created a new field of study: that of intermediate or mixed valence (MV) states in rare earths and actinides (both for elemental metals and intermetallic compounds).

While the $(\gamma$–$\alpha)$ transition in Ce takes place in the pressure range $P\sim$10–20 kBar, the isostructural transition in $YbInCu_4$ [2] is observed at $T_v\sim$40 K and at ambient pressure [3] (the major experimental results are best summarized in [4–6]). Looking similar to the Ce 'isomorphic' transition, it has recently attracted a lot of interest due to the possibility of studying that phenomenon in much greater detail.

In the following we first address the issue of the phase diagram of $YbInCu_4$ in the (B, T)-plane, where B is a magnetic field, T is a temperature. Indeed, among many interesting results of [5, 6], the most suprising one is the universality of the first-order transition line for $YbInCu_4$ and its alloys. Namely, being expressed in the reduced variables $(B/B_{c0}, T/T_{v0})$ the transition line separating the high-temperature phase (paramagnetic, local moments) and the low-temperature 'metallic' phase is a perfect circle (where T_{v0} is the structural transition temperature in the absence of the magnetic field and B_{c0} is the critical field at $T = 0$). We will show that these results are surprisingly well described in terms of an entropy first-order phase transition between the local f-moment phase and another phase probably of a less ordinary nature. The origin of this phase, however, seems not to be important if this second phase is characterized by a larger energy scale. If the same ideas were applied to the $(\gamma$–$\alpha)$ transition in Ce, it would have predicted similar behaviour in high magnetic fields with $B_{c0}\sim$200 T.

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This is the achievable field range for modern Megagauss magnetic field experiments [8]. A characterization of the (γ–α) transition in Ce not only in the (P, T)-plane, but also in the (B, T)-plane, thus looks feasible and is of great interest.

The valence of Ce in the γ-phase is very close to the integer f-occupancy [9], i.e., in the atomic configuration ($Xe + 4f5d6s^2$) [10] all d- and s-electrons of Ce go to the metallic bands. In accordance with Hund's rule the ionic ground state has the total angular momentum $J = 5/2$ which is split further in the cubic environment into a Γ_7 doublet and a Γ_8 quartet (in the Ce γ-phase Γ_7 lies below Γ_8). Correspondingly for Yb, the atomic configuration ($Xe + 4f^{14}6s^2$) results in the trivalent Yb^{3+} ionic configuration for the high-temperature $YbInCu_4$-C15b phase, leading, to a localized f-hole. The $f^{13}(J = 7/2)$ ground state is split by the crystal field into a quartet (Γ_8) and two doublets (Γ_6 and Γ_7). Inelastic neutron studies [11] at $T > 45$ K reveal the crystal field scheme with Γ_6 and Γ_7 lying at 3.2 meV and 3.8 meV respectively above the ground state quartet Γ_8.

The first-order transition line is determined by:

$$F_U(B, T) = F_L(B, T). \tag{1}$$

In (1) F_L and F_U stand for the free energies of the upper and lower phases. We emphasize once again, that the main assumption we use below is that the characteristic energies governing the behaviour of the two phases differ significantly. We denote these scales as T_K^U and T_K^L, two effective 'Kondo temperatures', in accordance with the existing tradition in the experimental literature to plot data versus the isolated Kondo centre properties [3, 5, 6] (for extensive discussion of the theoretical results for the degenerate Anderson models and the experimental results, see [12]).

For $YbInCu_4$ $T_K^U \simeq 25$ K while $T_K^L \simeq 500$ K, as estimated in [7, 13]. With T_v, the temperature of the 'valence transition', for Yb and its alloys lying in the range 10–100 K and $B_c \sim 50$ T [5, 6], the $F_L(B, T)$ in (1) can be taken as a constant (neglecting the magnetic susceptibility term), while for the $F_U(B, T)$ with the trivalent Yb^{3+} considered as a local free ion, one has:

$$F_U(B, T) = E_0 - T \cdot S(B, T) \tag{2}$$

where the temperature dependence of the energy E_0 of the itinerant band is neglected below T_v (this assumption is discussed in more detail below). Correspondingly, the first-order transition line in the (B, T) plane is given by the equation:

$$T \cdot S(B, T) = const \tag{3}$$

where the entropy is determined by the Yb^{3+} multiplet structure only.

The magnetic susceptibility $\chi(T)$ of $YbInCu_4$ above $T_{v0} = 42$ K follows the Curie–Weiss law with an effective moment only negligibly (by 5%) smaller than the whole $J = 7/2$ ground-state moment [6, 13]. Thus, we first neglect the crystal splitting and write:

$$T \cdot S(B, T) = -T \ln \left\{ \sum_{m=-J}^{J} \exp\left(-\frac{g_J \mu_B B}{T} m \right) \right\} \tag{4}$$

where g_J is a g-factor (for $J = 7/2$, $g_J = 8/7$). From (4) the relation $a\mu_B B_{c0} = T_{v0}$ between the critical field B_{c0} at $T = 0$ and the value of the structural transition temperature T_{v0} at zero field, is of the form:

$$g_J J \mu_B B_{c0} = T_{v0} \ln (2J + 1) \tag{5}$$

which gives $a \approx 1.9$ for $J = 7/2$, a result which is remarkably close to the experimental value $a \simeq 1.8$ [6].

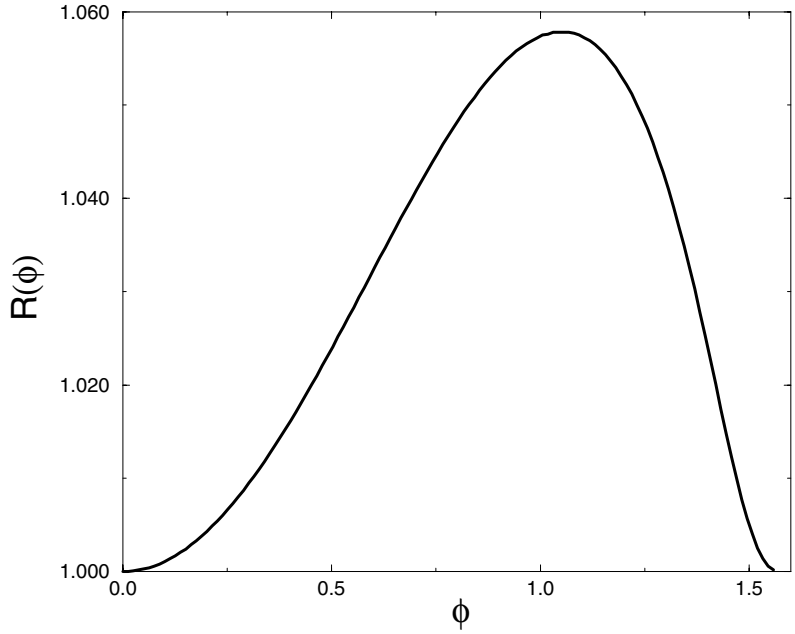

Figure 1. Function $R(\phi)$ (see text, equations (9) (10)) calculated for Yb^{3+} (J=7/2). Deviations of $R(\phi)$ from 1 do not exceed 6%.

We rewrite equations (3) and (4) for the phase transition line using the new reduced variables $\beta = B/B_{c0}$ and $\tau = T/T_{v0}$ and with the help of (5) we obtain:

$$\tau \ln \left\{ \sum_{m=-J}^{J} \exp \left[-m \left(\frac{\beta}{\tau J} \ln (2J+1) \right) \right] \right\} = \ln (2J+1). \tag{6}$$

Using the parametric form $\beta/\tau = \tan\phi$ and the identity:

$$\beta^2 + \tau^2 = \tau^2 \cos^{-2}\phi \tag{7}$$

one may re-write (6) as:

$$\beta^2 + \tau^2 = R(\phi) \tag{8}$$

where

$$R(\phi) = \ln^2 (2J+1) \left\{ \cos\phi \cdot \ln \left[\sum_{m=-J}^{J} \exp \left(\frac{-m \ln (2J+1) \tan\phi}{J} \right) \right] \right\}^{-2}. \tag{9}$$

The plot of the function $R(\phi)$ is shown in figure 1.

Since the deviation of $R(\phi) - 1$ from zero does not exceed 0.06, we arrive at the main result of [6, 13]:

$$\beta^2 + \tau^2 \simeq 1. \tag{10}$$

Postponing a detailed discussion for further publication, it is nevertheless necessary to highlight some essential features of our picture. The first interesting question is whether the account of crystal-field split-multiplets would improve the overall agreement with experiments. Although we have analysed the relation:

$$a \mu_B B_{c0} = T_{v0} \tag{11}$$

in terms of the crystal field Hamiltonian:

$$\hat{H} = \hat{H}_{crystal} + g_J \mu_B \hat{\boldsymbol{J}} \cdot \boldsymbol{B} \tag{12}$$

we do not focus on the results here, because (11) must display some cubic anisotropy which has not been experimentally studied yet (two components in (12) do not commute with each other). We will limit ourselves to a comment that the energy levels' scheme for (12) follows straightforwardly from making use of the explicit wave-functions [14] for the representations Γ_6, Γ_7 and Γ_8. For the magnetic field, applied along the main cubic axis, it turns out that the experimental value $a \simeq 1.8$ [6,13] is again closely reproduced in such analysis. Together with the contribution from the low-temperature paramagnetic phase susceptibility in equation (1), this value may change in the limits $a \simeq 1.9 \pm 0.1$. We also would like to emphasize that the entropy:

$$S(T_{v0}) \Rightarrow \ln \left\{ 4 + 2\exp\left(-\frac{E_6}{T_{v0}}\right) + 2\exp\left(-\frac{E_7}{T_{v0}}\right) \right\} \tag{13}$$

with E_6, E_7 taken from [11], is rather close to its value $0.8 \ln 8$ as integrated through T_{v0} (see [6,7,13]) for $YbInCu_4$, which indirectly confirms the applicability of an isolated crystal-field split-hole state for Yb^{3+} paramagnetic ion.

The Yb^{3+} hole occupation in the high-temperature state determined from Yb-L_3 x-ray absorption for most of the compositions studied in [5] turns out to be very close to the Yb^{3+} trivalent state. This last fact, however, does not yet preclude that the upper phase may have developed pronounced Kondo effects with $T_K \simeq 25$ K, as e.g., as stated in references [5,6,13]. On the other hand, it is not clear whether the existing data shows considerable deviations from the free-ion behaviour for the upper phase. However, if it were so, (2) would not have been correct at low temperatures. To verify that, one may choose for $F_U(B, T)$ another expression, say, the exact solution for the Kondo model or for the degenerate Anderson model. In the non-magnetic phase the scale, $T_K \approx 500$ K [13] is rather large and one may neglect the temperature dependence in $F_L(B, T)$ at temperatures below 50–100 K. As for the conduction band electrons, the typical energy scale for Ce would be of the order of 1 eV. Such a scale for $YbInCu_4$ and its alloys comprises probably only ~ 0.1 eV, as discussed below.

It would be interesting to check, of course, whether the circular shape (10) of the transition line in the (B, T)-plane is indeed due to the entropy transition in the free ion scheme of equations (2) and (3) or it could be that the result is merely numerically robust. Unfortunately, the Anderson model of thermodynamics in high magnetic fields has been studied in the Coqblin–Schriffer model limit (the charge is fixed) for Ce ($J = 5/2$) but not for Yb ($J = 7/2$). Even for Ce, there are published results only for magnetization and specific heat (see [12]). To obtain the free energy expressions, one would need to integrate these data back, or solve the Bethe–Ansatz equations again (we postpone this for future studies).

In figure 2 the phase diagram in the (B, T)-plane shows the first-order phase-transition line (solid), calculated for Ce according to (4) ($J = 5/2$, $g_J = 6/7$). Its shape is again close to a circle in reduced variables (dashed line): the deviations from the circle do not exceed $\approx 8\%$. The metamagnetic (γ–α) transition in Ce has not yet been measured, to the best of our knowledge. One sees that the low-temperature values of magnetic fields are in the experimentally accessible Megagauss range ($B^{\gamma} \sim 185$ T). The experiment is of considerable interest and allows one to verify the applicability of the free-ion model we are using also for the Ce case.

Finally, let us discuss the physics, which may be responsible for the transition in $YbInCu_4$. A first attempt to describe the Ce (γ–α) transition was the Falicov–Kimball–Ramirez (FKR) model [15]. Although the FKR model is capable of reproducing the appearance of the critical point on the (γ–α) transition line in the (P, T)-plane, it does not reproduce such crucial

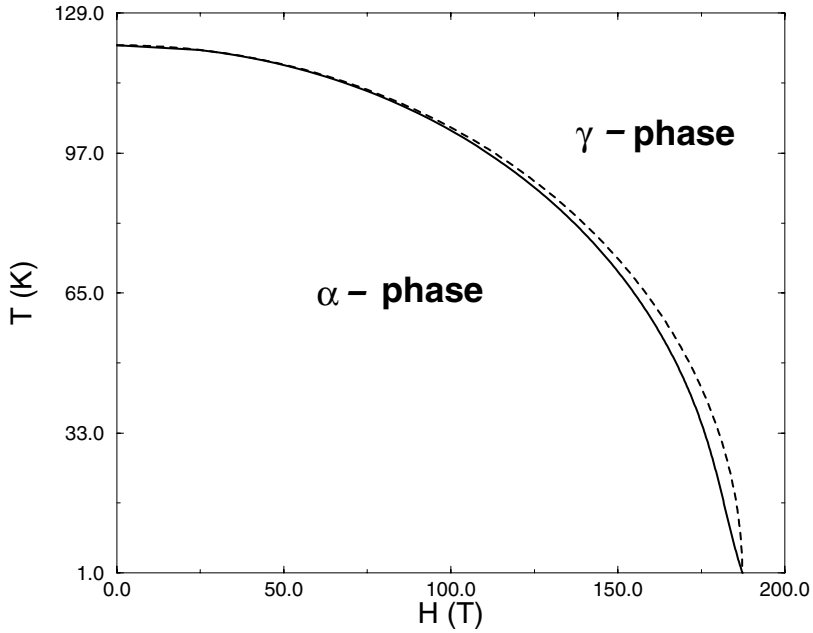

Figure 2. The line (solid) of the first-order phase-transition in the (B, T)-plane for Ce γ–α transition. In the reduced variables, deviations from the perfect circle (dashed line) would not exceed 6%.

features of the α-phase as its intermediate valence. Another approach in which the $(\gamma$–$\alpha)$ transition is ascribed to the Mott's first-order transition in a subsystem of f-electrons has first been discussed in [16].

Very often the $(\gamma$–$\alpha)$ transition in Ce is interpreted in terms of the Kondo volume collapse (KVC) model [17, 18]. In the KVC model Ce atoms at the transition are treated as Ce^{3+} ions in both α and γ phases (approximately one electron in the f-shell), although in the two different Kondo regimes. As is known, the Anderson impurity model reproduces the Kondo behaviour in the regime when charge fluctuations are fully suppressed, and provides for the T_K the expression:

$$T_K \propto \exp\left\{-\frac{\mid \varepsilon_f^* \mid}{\Gamma}\right\} \tag{14}$$

where $\mid \varepsilon_f^* \mid$ is the effective position of the localized level below the chemical potential and the level's width $\Gamma \propto V^2 \nu(\epsilon_F)$ depends on the hybridization matrix element,V, and the density of states at the Fermi level, $\nu(\epsilon_F)$.

The KVC model [17] connects the first-order transition with strong non-linear dependence of the Kondo scale (14) ($\mid \varepsilon_f^* \mid \ll \Gamma$) on the volume through the volume dependence of the hybridization matrix element (in Ce change in the unit cell volume is large, $\delta v/v \sim 20\%$!). Our arguments in the beginning of the paper, regarding the two different Kondo scales as needed for the applicability of (3), agree well with the values for Ce [18]:

$$T_K^{\alpha} \simeq 81.2 \pm 12.2 \text{ meV} \qquad T_K^{\gamma} \simeq 8.2 \pm 1.5 \text{ meV}.$$

Nevertheless, the KVC model seems not to be applicable in case $YbInCu_4$, where the volume changes are extremely small [3, 5–7]. For that reason, the FKR model has recently

been revisited in [19]. It is interesting that, although being somewhat sensitive to the choice of the model parameters, the elliptic shape of (10) for the phase-transition line in the (B, T)-plane is preserved in the calculations [19]. This is probably due to the same mechanism as above, i.e., due to large differences in the energy scales for the two phases (it seems however that the constant a in (11) strongly depends on the choice of parameters). Nevertheless, the FKR model can hardly be applicable for the $YbInCu_4$ compound. In addition to its well known drawbacks, such as an absence of hybridization, large changes in the n_f occupancy, it seems that the peculiarities of this compound may originate in somewhat unusual features of its non-magnetic analog $LuInCu_4$. This point has already been discussed in [20]. In [20] the authors suggested a mechanism based on the band structure calculations [21, 22] for the semimetallic state observed both in $LuInCu_4$ and $YbInCu_4$ (Yb^{3+}, the high-temperature phase!) [5,6]. In this state the ε_f level falls into a 'pseudogap' (or a dip in the DOS) at the choice of the chemical potential corresponding to the Yb^{3+} configuration. If the exponential form for T_K in (14) remains correct, the strong non-linearity in (14) would now come from the rapid changes in the values of the DOS at the Fermi level [20]. Thus, the high-temperature state (the one above $T_{v0} \simeq 42$ K) is stabilized by the entropy gain, while the phase with the higher DOS at the Fermi level is preferred at lower temperatures. The new state would, hence, correspond to a non-integer valence $Yb^{2.8+}$ as measured in [5].

The feature, which remains not well understood within the above explanation, is that the Hall coefficient decreases so sharply in the low-temperature state, that the number of carriers becomes comparable with the stoichiometric value for the divalent Yb ion (no hole in the f^{14}-shell). The increase is too large compared with the valence change ≈ 0.2 [5]. The energy scales involved and the change in the Hall coefficient are also inconsistent with the results of [21, 22]. Indeed, ΔE, the energy change per Yb using equations (1, 2) is:

$$\Delta E = T_{v0} \ln (2J + 1) \sim 90 \text{ K} \tag{15}$$

i.e. is too small to account for the large variation in the number of carriers. We propose another view on this problem, namely a weak Mott transition. At $T > T_{v0}$ localized moments Yb^{3+} are stable due to the entropy gain, and exist as the localized holes. Like $LuInCu_4$, $(Yb^{3+})InCu_4$ is a band-like semimetal with a small carrier concentration and accordingly screening is weak, favouring localization of the f-electrons. Below T_{v0} the valence change is small and occurs on the scale given by the volume of the electron-hole pockets. We speculate that after the transition into the low-temperature phase even the f-electrons form a band state, so that a small change in 'occupation' numbers would not contradict to an emergence of a large f-like Fermi surface. Thus, the mixed-valence transition is driven by the change in the electronic screening. This picture has similarities with ideas developed in [16] for Ce (note, however, that Ce is a metal in both phases).

An indirect support to these views may be found in the recent band structure calculations [23]. From [23], one may conclude that the change of the Yb valence ~ 0.2 at the 42 K would just result in a shift of the chemical potential by ~ 0.01 eV inside the strongly featured DOS with a broader width of the order of 0.1 eV (see figure 8 in [23]). This shift provides a correct magnitude for the energy change as estimated by (15). The band picture is also in reasonable agreement with rather high values for the Sommerfeld coefficient in the linear term for the electronic specific heat, $\gamma \approx 55$ mJ mole^{-1} K^2.

To summarize, we have shown that the entropy transition between the free-ion paramagnetic state and the low-temperature metallic state perfectly explains not only the elliptic shape of the transition line in the (B, T)-plane but also provides correct numerical results for its parameters. Based on similar calculations, we have suggested an experiment on the metamagnetic transition between the $(\gamma$–$\alpha)$ phases in cerium. As for the true nature of

the transition itself, we suggest that in $YbInCu_4$ it is a weak Mott transition between a f-band metal and the semimetallic phase with the localized Yb^{3+}-holes.

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