First order valence transition in Ce and YbInCu$_4$ in the $(B,T)$ - plane

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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 an 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 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.

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For years the isostructural $\gamma - \alpha$ transition in metallic Ce has been a classic example of the first order transition into a state with an intermediate valence ($\gamma - \text{Ce}^{3.67+} - \alpha - \text{Ce}^{3.67+}$). For the phase diagram of Ce, see [1]. Change in the valence state was judged by the change in the unit cell volume. Although a structural transition in a crystalline matter possessing a critical point in the $(P,T)$-plane is of a great interest by itself, the discovery of a non-integer valence in $\alpha - \text{Ce}$ has opened the field of the so-called intermediate or mixed valence (MV) states in the rare earths and actinides (both for elemental metals and intermetallic compounds).

The $(\gamma - \alpha)$ transition in Ce takes place in the pressure range $P \sim 10 \div 20$ kbar. Therefore, the isostructural transition in YbInCu$_4$ at $T_c \sim 40$ K and at ambient pressure, looking akin to the Ce “isomorphic” transition, has attracted recently a lot of interest due to the possibility of study of that phenomena in much greater details. The major experimental results are best summarized in [2].

In what follows we address the issue of the phase diagram of Ce and YbInCu$_4$ in the $(B,T)$-plane, where $B$ is a magnetic field, $T$ is a temperature. Indeed, among many interesting results of [2], 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 $(B/B_{c0}, T/T_{c0})$ the transition line separating the high temperature phase (paramagnetic, local moments) and the low temperature “metallic” phase is a perfect circle (where $T_{c0}$ 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 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. An origin of this phase however seems not to be important if this second phase is characterized by a larger energy scale. The same ideas applied to the $(\gamma - \alpha)$ transition in Ce predict similar behaviour in high magnetic fields with $B_{c0} \sim 200$ Tesla. This is the field range achievable for modern Megagauss magnetic field experiments.

The valence of Ce in the $\gamma$-phase is very close to the integer $f$-occupancy (see, e.g. review [3]), i.e., in the atomic configuration $(Xe + 4f^{14}6s^2)$ all $d$- and $s$-electrons of Ce go to the metallic bands. In accordance with the 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 $\Gamma_7$ doublet and a $\Gamma_8$ quartet (in the Ce $\gamma$-phase $\Gamma_7$ lies below $\Gamma_8$). Similarly, 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 ($\Gamma_6$) and two doublets ($\Gamma_6$ and $\Gamma_7$). Inelastic neutron studies [4] at $T> 45$ K reveal the crystal field scheme with $\Gamma_6$ and $\Gamma_7$ lying at 3.2 meV and 3.8 meV respectively above the ground state quartet $\Gamma_8$.

The first order transition line is determined by:

$$F_U(B,T) = F_L(B,T).$$

(1)

In (1) $F_L$ and $F_U$ stand for the free energies of the upper and lower phases. 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 center properties. For extensive discussion of the theoretical results for the degenerate Anderson models and the experimental results, see [5].

For YbInCu$_4$ $T_K^U \simeq 25$ K while $T_K^L \simeq 500$ K. With $T_v$, the temperature of the “valence transition”, for Yb and its alloys lying in the range of 10 – 100 K and $B_c \sim 50$ Tesla. The $F_U(B,T)$ 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:

$$F_U(B,T) = E_0 - T \cdot S(B,T)$$

(2)

with the band energy $E_0$ being actually temperature independent below $T_v$ (this assumption is discussed in more
details below). Correspondingly, the first order transition line in the \((B,T)\) plane is given by the equation:

\[
T \cdot S(B,T) = \text{const}, \quad (3)
\]

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

The magnetic susceptibility \(\chi(T)\) of YbInCu\(_4\) above \(T_{c0} = 42K\) follows the Curie-Weiss law with an effective moment only negligible (by 5\%) smaller than the whole \(J = 7/2\) ground state moment. Thus, we first neglect the crystal splitting and write:

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

where \(g_J\) is a g-factor (for \(J = 7/2\), \(g_J = 8/7\)). From these relations, \(a \mu_B B_{c0} = T_{c0}\) at zero field, is of the form:

\[
g_J \mu_B B_{c0} = T_{c0} \ln (2J + 1), \quad (5)
\]

which gives \(a \approx 1.9\) for \(J = 7/2\), a result which is remarkably close to the experimental value \(a \approx 1.8\).

We re-write the Eqs. (3,4) for the phase transition line using the new reduced variables \(\beta = B/B_{c0}\) and \(\tau = T/T_{c0}\) and with the help of (5) we obtain:

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

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

\[
\beta^2 + \tau^2 = \tau^2 \cos^{-2} \phi, \quad (7)
\]

one may re-write \((6)\) as:

\[
\beta^2 + \tau^2 = R(\phi), \quad (8)
\]

where

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

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

Since the deviation of \(R(\phi) - 1\) from zero does not exceed 0.06, we arrive to the main result of (9):

\[
\beta^2 + \tau^2 \approx 1. \quad (10)
\]

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 analyzed the relation:

\[
a \mu_B B_{c0} = T_{c0} \quad (11)
\]

in terms of the crystal field Hamiltonian:

\[
\hat{H} = \hat{H}_{\text{crystal}} + g \mu_B \hat{J} \cdot \hat{B} \quad (12)
\]

do we not stay on the results here, because \((11)\) must display some cubic anisotropy which was not experimentally studied yet (two components in \((12)\) do not commute with each other). We will limit ourselves with a comment that the energy levels’ scheme for \((12)\) follows straightforwardly from making use of the explicit wave functions \((5)\) for the representations \(\Gamma_6, \Gamma_7\) and \(\Gamma_8\). For the magnetic field, applied along the main cubic axis, it turns out that the experimental value \(a \approx 1.8\) is again closely reproduced in such analysis. We also would like to emphasize that the entropy:

\[
S(T_{c0}) \Rightarrow \ln \left\{ 4 + 2 \exp \left( -\frac{E_6}{T_{c0}} \right) + 2 \exp \left( -\frac{E_7}{T_{c0}} \right) \right\} \quad (13)
\]

with \(E_6, E_7\) taken from \((5)\), is rather close to its value 0.8 ln 8 as integrated through \(T_{c0}\) (see \((12)\)) 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 the most compositions studied in \((5)\) turns out to be really close to the Yb\(^{3+}\) trivalent state. This last fact, however, does not preclude yet that the upper phase may have developed pronounced Kondo effects with \(T_K \approx 25K\), as e.g. is stated in references \((13)\). On the other hand, it is not clear whether the existing data show considerable deviations from the free ion behavior for the upper phase. However, if it were so, \((13)\) would not have been correct at low temperatures. In such case, one may choose for \(F_{1/2}(B,T)\) another expression, say, the exact solution for the exchange model or for the degenerate Anderson model. In the non-magnetic phase the scale,
\( T_K \approx 500K \) is rather large and one may neglect the temperature dependence in \( F_\parallel (B, T) \) at temperatures below 50–100K. As for the conduction band electrons, typical energy scale for Ce would be of order of 1eV. Such a scale for YbInCu\(_4\) and its alloys comprises probably only \( \sim 0.1eV \), 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 Eqs.(12) or the result could be merely robust numerically. Unfortunately, the Anderson model 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 in [13]). To obtain the free energy expressions, one would need to integrate these data back, or solve the Bethe Anzats equations again.

![Phase Diagram](image)

**FIG. 2.** The line (solid) of the first order phase transition in the \((B, T)\)-plane for Ce \(\gamma - \alpha\) transition. In the reduced variables, deviations from the perfect circle (dashed line) would not exceed 6%.

In Fig. 2 the phase diagram in the \((B, T)\)-plane shows the first order phase transition line (solid), calculated for Ce according to [9] \((J = 5/2, gJ = 6/7)\). Its shape is again close to a circle in reduced variables (dashed line): the deviations from the circle do not exceed \(\sim 8\%\). The metamagnetic \(\gamma - \alpha\) transition in Ce has not been measured yet, to the best of our knowledge. One sees that the low temperature values of magnetic fields are in the experimentally accessible Megagauss range \((B^7 \sim 185\) Tesla\). The experiment presents a considerable interest and allows one to verify the free ion model we are using.

Finally, let us discuss the physics, which may be responsible for the transitions in Ce and YbInCu\(_4\). A first attempt to describe the Ce \((\gamma - \alpha)\) transition was the Falicov-Kimball-Ramirez (FKR) model [13]. Although the FKR model is capable to reproduce the appearance of the critical point on the \((\gamma - \alpha)\) transition line in the \((P, T)\)-plane, it does not reproduce such crucial feature of the \(\alpha\)-phase as its intermediate valence.

So far, the \((\gamma - \alpha)\) transition in Ce is usually interpreted in terms of the Kondo Volume Collapse (KVC) model [15, 22]. In the KVC model Ce atoms at the transition are treated as Ce\(^{3+}\)-ions in the both \(\alpha\) and \(\gamma\) phases (approximately one electron in the \(f\)-shell), although in the two different Kondo regimes. As it 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:

\[
T_K \propto \exp \left\{ -\frac{|\varepsilon_f^*|}{\Gamma} \right\},
\]

where \(|\varepsilon_f^*|\) 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 connects the first order transition with strong non-linear dependence of the Fermi level \(\varepsilon_F\) on the chemical potential \(\mu\). 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 (12) strongly depends on the parameters choice). 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 [12]. It is interesting, that although being somewhat sensitive to the choice of the model parameters, the elliptic shape of (11) for the phase transition line in the \((B, T)\)-plane is preserved in the calculation. 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 (12) strongly depends on the parameters choice).

Nevertheless, the KVC model seems not to be applicable in case YbInCu\(_4\), where the volume changes are extremely small [22]. On this reason, the FKR model has recently been revisited in [9]. It appears that although being somewhat sensitive to the choice of the model parameters, the elliptic shape of (11) for the phase transition line in the \((B, T)\)-plane is preserved in the calculation. 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 (12) strongly depends on the parameters choice).

For YbInCu\(_4\), the high temperature value \(T_K\) remains close to the low temperature value \(T_K\) in (14) and correct, the strong non-linearity in (14) comes from the rapid changes in the values of the DOS at the Fermi level [19]. Thus, the high temperature state (the one above \(T_{\alpha-b} \approx 42K\)) 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 [14].
to be Yb$^{2.8+}$ (an interaction term needs to be added to stabilize the valence).

The feature, which remains not well understood with the above explanation is that the Hall coefficient sharply decreases in the low temperature state, as if the number of carriers is getting 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 $\approx 0.2$. The energy scales involved and change in the Hall coefficient are also not consistent with the results of Eqs. (1,2). Indeed, $\Delta E$, the energy change per Yb using Eqs. (12) is:

$$\Delta E = T_0 \ln (2J + 1) \sim 90 K$$

(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 $T > T_0$ localized moments Yb$^{3+}$ are stable due to the entropy gain, and exist as the localized holes. (Yb$^{3+}$)CuIn$_4$ is a band-like semimetal with a small carriers concentration. Below $T_0$ the valence change is small because, unlike in the FKR model, only interactions with small electron-hole pockets are essential. 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 does not contradict to an emergence of a large $f$-like Fermi surface. An indirect support to these views may be found in the recent band structure calculations. From one may conclude that the change of the Yb valence $\sim 0.2$ at the 42K would just result in a shift of the chemical potential by $\sim 0.01$ eV inside the strongly featured DOS with a broader width of the order of 0.1eV (see Fig. 8 in ). This shift provides a correct magnitude for the energy change as estimated by (13). The band picture is also in a reasonable agreement with rather high value for the Sommerfeld coefficient in the linear term for the electronic specific heat, $\gamma \approx 55 mJ/mole \cdot K^2$.

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. Basing on similar calculations, we have suggested an experiment on the metamagnetic transition between the $(\gamma - \alpha)$ phases in cerrium. 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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1. D. C. Koskenmaki and K. A. Gschneider, in Handbook on the Physics and Chemistry of the Rare Earth, edited by K. A. Gschneider and L. Eyring (North-Holland, Amsterdam, 1978), p. 340.
2. I. Felner and I. Nowik, Phys. Rev. B33, 617 (1986).
3. J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawerence, D. Mandrus, and J. D. Thompson, Phys. Rev. B54, 12207 (1996).
4. J. L. Sarrao, Physica B259, 128 (1999).
5. A. L. Cornelius, J. M. Lawerence, J. L. Sarrao, Z. Fisk, M. F. Hundley, G. H. Kwei, J. D. Thompson, C. H. Booth, and F. Bridges, Phys. Rev. B56, 7993 (1997).
6. J. L. Sarrao, C. D. Immer, and Z. Fisk, in Physical Phenomena in High Magnetic Fields III, edited by Z. Fisk et al. (World-Scientific, Singapore, 1999), p. 166.
7. J. L. Sarrao, A. P. Ramirez, T. W. Darling, F. Freibert, A. Migliori, C. D. Immer, Z. Fisk, Y. Uwatoko, Phys. Rev. B58, 409 (1998).
8. Fritz Herlach, Jos A.A.J. Perenboom, Physica B211, 1 (1995); N. Mitura, H. Nojiri, Y. Shimamoto, Y. Imanaka, Physica B211, 23 (1995); H.-U. Müller, H. Scholz, N. Puhlmann, O. Portugall, M. Barczewski, I. Stolpe, M. von Ortenberg, Physica B246-247, 356 (1998).
9. J. M. Lawerence, P. S. Riseboroug, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).
10. L. D. Landau and E. M. Lifshitz, Quantum Mechanics, (Pergamon Press, Oxford, 1977).
11. A. Severing, E. Gratz, B. D. Rainford, and K. Yoshimura, Physica B163, 409 (1990).
12. P. Schlottmann, Phys. Rep. 181, 1 (1989).
13. C. D. Immer, J. L. Sarrao, Z. Fisk, A. Lacerda, C. Mielke, and J. D. Thompson, Phys. Rev. B56, 71 (1997).
14. K. R. Lea, M. J. M. Leask and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).
15. L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. 22, 997 (1969); R. Ramirez and L. M. Falicov, Phys. Rev. B 3, 2425 (1971).
16. J. W. Allen and R. M. Martin, Phys. Rev. Lett. 49, 1106 (1982).
17. L. Z. Liu, J. W. Allen, O. Gunnarson, N. S. Christensen, and O. K. Andersen, Phys. Rev. B45, 8034 (1992).
18. V. Zlatic and J. K. Freericks, preprint cond-mat/0006495.
19. E. Figuaora, J. M. Lawerence, J. L. Sarrao, Z. Fisk, M. F. Hundley, and J. D. Thompson, Solid State Comm. 106, 347 (1998).
20. K. Takegahara and T. Kasuya, J. Phys. Soc. Japan 59, 3299 (1990).
21. P. Monachesi and A. Contrenna, Phys. Rev. B54, 13558 (1996).
22. V. N. Antonov, M. Galli, F. Marabelli, A. N. Yaresko, A. Ya. Perlov, and E. Bauer, Phys. Rev. B62, 1742 (2000).