Crystal-field effects in the first-order valence transition in YbInCu$_4$ induced by an external magnetic field

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As it was shown earlier [Dzero, Gor’kov, and Zvezdin, J. Phys.:Condens. Matter 12, L711 (2000)] the properties of the first-order valence phase transition in YbInCu$_4$ in the wide range of magnetic fields and temperatures are perfectly described in terms of a simple entropy transition for free Yb ions. Within this approach, the crystal field effects have been taken into account and we show that the phase diagram in the $B-T$ plane acquires some anisotropy with respect to the direction of an external magnetic field.

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As it is well known, YbInCu$_4$ undergoes a first-order valence transition at 42 K, accompanied by a small change in volume of the order of 0.5%. This transition is quite similar to the $\gamma - \alpha$ transition in metallic Ce (for the phase diagram of Ce, see\[\ref{f:phase}]). It turns out, that YbInCu$_4$ is the only stoichiometric compound known in which an isostructural valence transition at ambient pressure has been observed\[\ref{f:phase}]. However, as it was pointed out in\[\ref{f:phase}\], the isostructural valence transition is just the extreme limit of the very common competition that occurs between local-moment and itinerant behavior in many strongly correlated compounds.

The valence transition induced by an external magnetic field in YbInCu$_4$ and its alloys has been studied in\[\ref{f:phase}\]. The most interesting result obtained is that the data extracted from the resistance measurements can collapse all of the pressure dependent data, as well as that from doped variants of YbInCu$_4$ at ambient pressure, onto a universal $B-T$ phase diagram (here $B$ is a magnetic field, $T$ is a temperature).

The physics which can be responsible for the transition in YbInCu$_4$ has been discussed by several authors. One of the first attempts to describe the transition in metallic Ce, the one which is similar to the transition in YbInCu$_4$, was the Falicov-Kimball-Ramirez (FKR) model\[\ref{f:phase}\]. 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\[\ref{f:phase}\].

Very often the ($\gamma - \alpha$) transition in Ce is interpreted in terms of the Kondo Volume Collapse (KVC) model\[\ref{f:phase}\]. 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 behavior in the regime when charge fluctuations are fully suppressed, and provides for the $T_K$ the expression:

$$T_K \propto \exp \left\{ - \frac{|\varepsilon_f^\gamma|}{\Gamma} \right\},$$

where $|\varepsilon_f^\gamma|$ is the effective position of the localized level below the chemical potential and the levels 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\[\ref{f:phase}\] connects the first order transition with strong non-linear dependence of the Kondo scale $|\varepsilon_f^\gamma|$ on the volume through the volume dependence of the hybridization matrix element (in Ce change in the unit cell volume is large, $\delta v/v \sim 20\%$).

Nevertheless, the KVC model seems not to be applicable in case of YbInCu$_4$, where the volume changes are extremely small\[\ref{f:phase}\]. On that reason, the FKR model has recently been revisited in\[\ref{f:phase}\]. It is interesting, that although being somewhat sensitive to the choice of the model parameters, the elliptic shape for the phase transition line in the ($B T$)-plane, observed in\[\ref{f:phase}\], is preserved in the calculations\[\ref{f:phase}\]. 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\[\ref{f:phase}\] strongly depends on the parameters choice).

As it was discussed in\[\ref{f:phase}\] the universality of the first-order transition line for YbInCu$_4$ and its alloys in the $B-T$ plane can be described in terms of an entropy first-order transition between the local $f$-moment phase and another phase with a compensated moment. It was also suggested in\[\ref{f:phase}\] that the mixed-valence transition is driven by the change in the electronic screening: high-temperature phase can be described as a band-like semimetal with a small carrier concentration and accordingly screening is weak, what favors to localization of the $f$-electrons. At lower temperatures after a phase transition occurred, 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.

In this paper we would like to address the issue of how the phase diagram of YbInCu$_4$ in the $B-T$ plane is affected by taking into account the crystal field effects and, as a consequence, an appearance of anisotropy of a phase diagram with respect to the direction of an applied field. We also would like to analyze the relation,
experimentally obtained in [3]:

\[ a_{\mu B} B_{\epsilon 0} = T_{\epsilon 0} \]  

(2)

in terms of the crystal field Hamiltonian:

\[ \hat{H} = \hat{H}_{\text{crystal}} + g_{J} \mu_{B} \mathbf{J} \cdot \mathbf{B}. \]  

(3)

When magnetic ion is placed in a cubic environment, the spatial degeneracy of its angular momentum is removed by the electrostatic field due to the neighboring charges. For example, the \( J = 5/2 \) multiplet for a Ce ion is split into a \( \Gamma_{7} \) doublet and \( \Gamma_{8} \) quartet while the \( J = 7/2 \) multiplet of an Yb ion is split into a \( \Gamma_{6} \) doublet, \( \Gamma_{7} \) doublet and \( \Gamma_{8} \) quartet.

For the \( J = 7/2 \) the wave functions for representations \( \Gamma_{6}, \Gamma_{7} \) and \( \Gamma_{8} \) are given by [3]:

\[
\Gamma_{6} : \begin{cases} 
\psi_{1} = \sqrt{\frac{5}{12}} | \frac{7}{2} \rangle + \sqrt{\frac{7}{12}} | \frac{5}{2} \rangle - \frac{1}{2} | \frac{1}{2} \rangle + \frac{1}{2} | \frac{3}{2} \rangle \\
\psi_{2} = \sqrt{\frac{5}{12}} | \frac{7}{2} \rangle - \sqrt{\frac{7}{12}} | \frac{5}{2} \rangle + \frac{1}{2} | \frac{1}{2} \rangle - \frac{1}{2} | \frac{3}{2} \rangle 
\end{cases}
\]

(4)

\[
\Gamma_{7} : \begin{cases} 
\psi_{3} = \sqrt{\frac{3}{7}} | \frac{7}{2} \rangle + \frac{3}{7} | \frac{5}{2} \rangle - \frac{1}{7} | \frac{1}{2} \rangle + \frac{3}{7} | \frac{3}{2} \rangle \\
\psi_{4} = \sqrt{\frac{3}{7}} | \frac{7}{2} \rangle - \frac{3}{7} | \frac{5}{2} \rangle + \frac{1}{7} | \frac{1}{2} \rangle - \frac{3}{7} | \frac{3}{2} \rangle 
\end{cases}
\]

(5)

\[
\Gamma_{8} : \begin{cases} 
\psi_{5} = \sqrt{\frac{2}{7}} | \frac{7}{2} \rangle + \frac{2}{7} | \frac{5}{2} \rangle - \frac{1}{7} | \frac{1}{2} \rangle + \frac{2}{7} | \frac{3}{2} \rangle \\
\psi_{6} = \sqrt{\frac{2}{7}} | \frac{7}{2} \rangle - \frac{2}{7} | \frac{5}{2} \rangle + \frac{1}{7} | \frac{1}{2} \rangle - \frac{2}{7} | \frac{3}{2} \rangle \\
\psi_{7} = \frac{1}{2} | \frac{7}{2} \rangle + \frac{1}{2} | \frac{5}{2} \rangle + \frac{1}{2} | \frac{3}{2} \rangle + \frac{1}{2} | \frac{1}{2} \rangle \\
\psi_{8} = \frac{1}{2} | \frac{7}{2} \rangle - \frac{1}{2} | \frac{5}{2} \rangle - \frac{1}{2} | \frac{3}{2} \rangle - \frac{1}{2} | \frac{1}{2} \rangle 
\end{cases}
\]

(6)

According to [3] the first-order transition line in the \((B, T)\) plane is determined by the equation:

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

(7)

The entropy is determined by the Yb\(^{3+}\) multiplet structure only. Taking the crystal splitting effects into account, the entropy is given by:

\[ T \cdot S(B, T) = -T \ln \left\{ \sum_{n=1}^{8} \exp \left( -\frac{\lambda_{n}}{T} \right) \right\}, \]  

(8)

where \( \lambda_{n} \) are the eigenvalues, obtained by a solution of an eigenvalue problem for \( \hat{H} \) on wavefunctions \( \{\psi_{n}\} \).

Now we have to find eigenvalues \( \lambda_{n} \). Re-writing the last term in (3) as:

\[ g_{J} \mu_{B} \mathbf{J} \cdot \mathbf{B} = \hat{J}_{z} \beta_{z} + \hat{J}_{+} \beta_{+} + \hat{J}_{-} \beta_{-}, \]  

(9)

where \( \hat{J}_{\pm} = \hat{J}_{x} \pm i \hat{J}_{y} \) and \( \beta_{\pm} = \frac{g_{J} \mu_{B}}{2} (B_{z} \pm i B_{y}) \), \( \beta_{z} = g_{J} \mu_{B} B_{z} \), matrix elements \( H_{ij} \) of (3) are given by:

\[
H_{ij} = \begin{pmatrix}
E_{6} + \frac{7}{6} \beta_{z} & \frac{7}{3} \beta_{-} & 0 & 0 & \frac{\sqrt{35}}{3} \beta_{z} & -\frac{7}{3} \beta_{-} & \frac{\sqrt{35}}{4} \beta_{z} & 0 \\
\frac{7}{6} \beta_{z} & E_{6} - \frac{7}{6} \beta_{z} & 0 & 0 & -\frac{\sqrt{35}}{3} \beta_{z} & -\frac{7}{3} \beta_{-} & -\frac{\sqrt{35}}{4} \beta_{z} & 0 \\
0 & 0 & E_{7} + \frac{7}{2} \beta_{z} & -3 \beta_{+} & 3 \beta_{-} & 0 & \sqrt{3} \beta_{z} & \sqrt{3} \beta_{+} & \sqrt{3} \beta_{-} \\
0 & 0 & -3 \beta_{-} & E_{7} - \frac{7}{2} \beta_{z} & 0 & \frac{\sqrt{35}}{3} \beta_{z} & \sqrt{3} \beta_{-} & -\sqrt{3} \beta_{+} & 0 \\
\frac{\sqrt{35}}{3} \beta_{z} & -\frac{\sqrt{35}}{3} \beta_{-} & 3 \beta_{+} & 0 & E_{8} + \frac{11}{6} \beta_{z} & \frac{\sqrt{35}}{4} \beta_{z} & \sqrt{35} \beta_{+} & 0 & -\sqrt{35} \beta_{-} \\
-\frac{\sqrt{35}}{3} \beta_{z} & \frac{\sqrt{35}}{3} \beta_{-} & 0 & \sqrt{35} \beta_{+} & \sqrt{35} \beta_{-} & -\frac{\sqrt{35}}{4} \beta_{z} & -\sqrt{35} \beta_{+} & 0 & 0 \\
0 & \sqrt{35} \beta_{z} & \sqrt{35} \beta_{+} & -\sqrt{35} \beta_{-} & 0 & \sqrt{35} \beta_{z} & 3 \beta_{+} & E_{8} - \frac{1}{2} \beta_{z} & 3 \beta_{+} \\
0 & \sqrt{35} \beta_{-} & \sqrt{35} \beta_{+} & -\sqrt{35} \beta_{-} & 0 & \sqrt{35} \beta_{-} & 3 \beta_{-} & E_{8} + \frac{1}{2} \beta_{z} & 3 \beta_{+} \\
\end{pmatrix}
\]  

(10)

where the matrix elements of \( \hat{H}_{\text{crystal}} \) are defined as:

\[ \langle \Gamma_{6} | \hat{H}_{\text{crystal}} | \Gamma_{6} \rangle = E_{6}, \quad \langle \Gamma_{7} | \hat{H}_{\text{crystal}} | \Gamma_{7} \rangle = E_{7}, \quad \langle \Gamma_{8} | \hat{H}_{\text{crystal}} | \Gamma_{8} \rangle = E_{8}, \]  

(11)

As it turns out, the secular equation:

\[ \text{det} \left| H_{ij} - \lambda \delta_{ij} \right| = 0, \]

with Hamiltonian matrix, given by (10) can not be solved exactly in its general form, but there exist the exact solutions for particular cases, such as \( \mathbf{B} = (0, 0, B_{z}) \). The eigenvalues in that case are:

\[ \lambda_{1,2}(\beta_{z}) = \frac{1}{2} \left\{ E_{6} + E_{8} + \frac{24}{7} \beta_{z} \pm \sqrt{\left( E_{6} - E_{8} - \frac{16}{21} \beta_{z} \right)^{2} + \frac{8960}{441} \beta_{z}^{2}} \right\}, \]  

(12)

\[ \lambda_{3,4}(\beta_{z}) = \frac{1}{2} \left\{ E_{6} + E_{8} - \frac{24}{7} \beta_{z} \pm \sqrt{\left( E_{6} - E_{8} + \frac{16}{21} \beta_{z} \right)^{2} + \frac{8960}{441} \beta_{z}^{2}} \right\}, \]  

(13)

\[ \lambda_{5,6}(\beta_{z}) = \frac{1}{2} \left\{ E_{7} + E_{8} + \frac{8}{7} \beta_{z} \pm \sqrt{\left( E_{7} - E_{8} + \frac{16}{7} \beta_{z} \right)^{2} + \frac{768}{49} \beta_{z}^{2}} \right\}, \]  

(14)
\[ \lambda_{7,8}(\beta_z) = \frac{1}{2} \left\{ E_7 + E_8 - \frac{8}{7} \beta_z \pm \sqrt{\left( E_7 - E_8 - \frac{16}{7} \beta_z \right)^2 + \frac{768}{49} \beta_z^2} \right\}. \tag{15} \]

In what follows we present the numerical result, when external field is in the plane \( B = (B_x, B_y, 0) \) and analytical solution for the case mentioned above.

Now, we can define a constant in Eq. \( \text{(5)} \) as follows:

\[ T \cdot S(B, T) = T_{c0} \cdot S_0(0, T_{c0}), \tag{16} \]

\[ S_0 = \ln \left[ 4 + 2 \exp \left( -\frac{\delta E_{6,8}}{T_{c0}} \right) + 2 \exp \left( -\frac{\delta E_{7,8}}{T_{c0}} \right) \right], \]

According to \( \delta E_{6,8} = E_6 - E_8 \simeq 3.2\text{meV} \) and \( \delta E_{7,8} = E_7 - E_8 \simeq 3.8\text{meV} \).

As we already mentioned, the equation \( \text{(16)} \) defines a phase diagram in the \( B - T \) plane. The results of our calculation are plotted on Fig. 1. As we can see, there is a strong anisotropy in a phase diagram with respect to the direction of an external magnetic field. We also have calculated magnetization as a function of an external magnetic field for a given temperature, Fig. 2. As it turns out, magnetization also depends on the direction of an applied field.

In the rest of the paper, we would like to write down an equation for the phase boundary, when \( B = (0, 0, B_z) \).

Let us introduce the following notations:

\[ b = B/B_{c0}, \ \tau = T/T_{c0}, \ \tan(\varphi) = b/\tau \ (0 < \varphi < \frac{\pi}{2}). \]

Then

\[ \tau = \bar{U}^{-1}(\varphi), \tag{17} \]

\[ b = \bar{U}^{-1}(\varphi) \tan(\varphi), \tag{18} \]

\[ \bar{U}^{-1}(\varphi) = \frac{1}{S(0, T_{c0})} \sum_{n=1}^{8} \exp \left[ -\tilde{\lambda}_n(\varphi) \right], \tag{19} \]

with \( \tilde{\lambda}_n(\varphi) \) being the eigenvalues \( \{\tilde{\lambda}_1, \tilde{\lambda}_2, \tilde{\lambda}_3, \tilde{\lambda}_4, \tilde{\lambda}_5, \tilde{\lambda}_6, \tilde{\lambda}_7, \tilde{\lambda}_8\} \). Thus, the equation for the phase transition line is given by:

\[ b^2 + \tau^2 = R(\varphi), \ R(\varphi) = \left[ \cos(\varphi)\bar{U}(\varphi) \right]^{-2}. \]

As we see on Fig. 3, deviations of \( R(\varphi) \) from 1 do not exceed 10%. Generally speaking, as one may see from Table 1, the \( a \) value is relatively robust with respect to including new type of interactions (or anisotropy) in our model. For example, if one takes the susceptibility of a lower phase into account, it decreases \( a \) by reducing the value for the net moment \( \mu \) which in our case is less then \( 4\mu_B \) and the latter corresponds to the free ion model, but on the other hand it increases one by reducing a change in the entropy at \( T = T_{c0} \). As we see from results of our calculations of \( B_{c0} \) (Table 1), when only crystal fields effect are taken, the change in \( a \) is less then 10%.
anisotropy in the phase diagram will serve as a proof of our initial idea of free Yb ions model.

To summarize, we have shown that the phase diagram for the first order valence transition in YbInCu$_4$ in the $B - T$ plane acquires some anisotropy with respect to the direction of an external magnetic field if crystal-field split multiplets are taken into consideration. We have also found that within the present framework, that the anisotropy of the critical field value $B_{c0}$ is of the order of $\approx 2$ Tesla and in principle can be seen experimentally.

TABLE I. Values of $B_{c0}$ and $a$ obtained from the phase diagram Fig. 1 for different magnetic field orientations.

| Field Orientation | $B_{c0}$, Tesla | $a$ |
|-------------------|-----------------|-----|
| [001]             | 30.9            | 2.29|
| [111]             | 30.1            | 2.34|
| [110]             | 31.95           | 2.24|

Preliminary experiments have been carried out in the National High Magnetic Field Laboratory (Tallahassee) and showed relatively good agreement with theoretical prediction in terms of the present model.

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