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Crystal-field effects in the first-order valence transition in $YbInCu_4$ induced by an external magnetic field

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Abstract

As was shown earlier (Dzero M O, Gor'kov L P and Zvezdin A K 2000 *J. Phys.: Condens. Matter* **12** L711), the properties of the first-order valence phase transition in $YbInCu_4$ over a wide range of magnetic fields and temperatures can be perfectly described on the basis 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.

As 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 γ–α transition in metallic Ce (for the phase diagram of Ce, see [1]). It turns out that $YbInCu_4$ is the only stoichiometric compound known in which an isostructural valence transition at ambient pressure has been observed [2]. However, as was pointed out in [2], the isostructural valence transition is just the extreme limit of the very common competition that occurs between local-moment and itinerant behaviour in many strongly correlated compounds.

The valence transition induced by an external magnetic field in $YbInCu_4$ and its alloys has been studied in [3]. The most interesting result of [3] is that the data extracted from the resistance measurements can be used to collapse all of the pressure-dependent data, as well as those from doped variants of $YbInCu_4$ at ambient pressure, onto a universal B–T phase diagram (here B is magnetic field, T is temperature).

The physics which may 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 proposal of the Falicov–Kimball–Ramirez (FKR) model [10]. Another approach in which the γ–α transition is ascribed to Mott's first-order transition in a subsystem of f electrons was first discussed in [11].

Very often the γ–α transition in Ce is interpreted on the basis of the Kondo volume-collapse (KVC) model [12, 13]. In the KVC model Ce atoms at the transition are treated as

Ce^{3+} ions in both the 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 T_K the expression

$$T_K \propto \exp\left\{-\frac{|\varepsilon_f^*|}{\Gamma}\right\} \tag{1}$$

where $|\varepsilon_f^*|$ is the effective position of the localized level below the chemical potential and the level 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 [12] connects the first-order transition with strong non-linear dependence of the Kondo scale (1) ($|\varepsilon_f^*| \ll \Gamma$) on the volume through the volume dependence of the hybridization matrix element (in Ce the change in the unit-cell volume is large: $\delta v/v \sim 20\%$!)

Nevertheless, the KVC model seems not to be applicable in the case of $YbInCu_4$, where the volume changes are extremely small [5, 6]. For that reason, the FKR model has recently been revisited in [14]. 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 [3] is preserved in the calculations [14]. This is probably due to the same mechanism as the above, i.e. due to large differences between the energy scales for the two phases (it seems however that the constant a in (2) strongly depends on the parameter choice).

As was discussed in [4], the universality of the first-order transition line for $YbInCu_4$ and its alloys in the B–T plane can be described on the basis of an entropy first-order transition between the local-f-moment phase and another phase with a compensated moment. It was also suggested in [4] that the mixed-valence transition is driven by the change in the electronic screening: the high-temperature phase can be described as a band-like semimetal with a small carrier concentration and accordingly screening is weak, which favours localization of the f electrons. At lower temperatures, after a phase transition occurred, even the f electrons formed a band state, so a small change in occupation numbers would not forbid the 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, the appearance of anisotropy in the phase diagram with respect to the direction of an applied field. We also would like to analyse the relation obtained experimentally in [5, 6]:

$$a\mu_B B_{c0} = T_{v0} \tag{2}$$

on the basis of the crystal-field Hamiltonian:

$$\hat{H} = \hat{H}_{\text{crystal}} + g_J\mu_B\hat{\boldsymbol{J}}\cdot\boldsymbol{B}. \tag{3}$$

When a magnetic ion is placed in a cubic environment, the spatial degeneracy of its angular momentum is removed by the electrostatic field due to the neighbouring charges. For example, the $J = 5/2$ multiplet for a Ce ion is split into a Γ_7 doublet and Γ_8 quartet while the $J = 7/2$ multiplet of an Yb ion is split into a Γ_6 doublet, Γ_7 doublet and Γ_8 quartet.

For $J = 7/2$ the wavefunctions for the representations Γ_6, Γ_7 and Γ_8 are given by [7]

$$\Gamma_6: \quad \begin{cases} \psi_1 = \sqrt{\frac{5}{12}}|+\frac{7}{2}\rangle + \sqrt{\frac{7}{12}}|-\frac{1}{2}\rangle \\ \psi_2 = \sqrt{\frac{5}{12}}|-\frac{7}{2}\rangle + \sqrt{\frac{7}{12}}|+\frac{1}{2}\rangle \end{cases} \tag{4}$$

$$\Gamma_7: \quad \begin{cases} \psi_3 = \frac{\sqrt{3}}{2}|+\frac{5}{2}\rangle - \frac{1}{2}|-\frac{3}{2}\rangle \\ \psi_4 = \frac{\sqrt{3}}{2}|-\frac{5}{2}\rangle - \frac{1}{2}|+\frac{3}{2}\rangle \end{cases} \tag{5}$$

$$\Gamma_8: \quad \begin{cases} \psi_5 = \sqrt{\frac{7}{12}}|+\frac{7}{2}\rangle - \sqrt{\frac{5}{12}}|-\frac{1}{2}\rangle \\ \psi_6 = \sqrt{\frac{5}{12}}|-\frac{7}{2}\rangle - \sqrt{\frac{7}{12}}|+\frac{1}{2}\rangle \\ \psi_7 = \frac{1}{2}|+\frac{5}{2}\rangle + \frac{\sqrt{3}}{2}|-\frac{3}{2}\rangle \\ \psi_8 = \frac{1}{2}|-\frac{5}{2}\rangle + \frac{\sqrt{3}}{2}|+\frac{3}{2}\rangle. \end{cases} \tag{6}$$

According to [4] the first-order transition line in the B–T plane is determined by the equation

$$TS(B,T) = \text{constant}. \tag{7}$$

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

$$TS(B,T) = -T \ln\left\{\sum_{n=1}^{8} \exp\left(-\frac{\lambda_n}{T}\right)\right\} \tag{8}$$

where λ_n are the eigenvalues, obtained by solution of the eigenvalue problem (3) for wavefunctions (4)–(6).

Now we have to find eigenvalues λ_n. Rewriting the last term in (3) as

$$g_J \mu_B \hat{\boldsymbol{J}} \cdot \boldsymbol{B} = \hat{J}_z \beta_z + \hat{J}_+ \beta_- + \hat{J}_- \beta_+ \tag{9}$$

where $\hat{J}_\pm = \hat{J}_x \pm \mathrm{i}\hat{J}_y$ and $\beta_\pm = (g_J \mu_B/2)(B_x \pm \mathrm{i}B_y)$, $\beta_z = g_J \mu_B B_z$, the matrix elements H_{ij} of (3) are given by

$$H_{ij} = \begin{vmatrix} E_6 + \frac{7}{6}\beta_z & \frac{7}{3}\beta_- & 0 & 0 & \frac{\sqrt{35}}{3}\beta_z & -\frac{7}{3}\beta_- & \sqrt{\frac{35}{3}}\beta_+ & 0 \\ \frac{7}{3}\beta_+ & E_6 - \frac{7}{6}\beta_z & 0 & 0 & -\frac{\sqrt{35}}{3}\beta_+ & -\frac{\sqrt{35}}{3}\beta_z & 0 & \sqrt{\frac{35}{3}}\beta_- \\ 0 & 0 & E_7 + \frac{3}{2}\beta_z & -3\beta_+ & 3\beta_- & 0 & \sqrt{3}\beta_z & \sqrt{3}\beta_+ \\ 0 & 0 & -3\beta_- & E_7 - \frac{3}{2}\beta_z & 0 & \frac{\sqrt{35}}{2}\beta_+ & \sqrt{3}\beta_- & -\sqrt{3}\beta_z \\ \frac{\sqrt{35}}{3}\beta_z & -\frac{\sqrt{35}}{3}\beta_- & 3\beta_+ & 0 & E_8 + \frac{11}{6}\beta_z & \frac{\sqrt{35}}{3}\beta_- & -\frac{2}{\sqrt{3}}\beta_+ & 0 \\ -\frac{7}{3}\beta_+ & -\frac{\sqrt{35}}{3}\beta_z & 0 & \frac{\sqrt{35}}{2}\beta_- & \frac{\sqrt{35}}{3}\beta_+ & E_8 - \frac{11}{6}\beta_z & 0 & -\sqrt{\frac{35}{12}}\beta_- \\ \sqrt{\frac{35}{3}}\beta_- & 0 & \sqrt{3}\beta_z & \sqrt{3}\beta_+ & -\frac{2}{\sqrt{3}}\beta_- & 0 & E_8 - \frac{1}{2}\beta_z & 3\beta_+ \\ 0 & \sqrt{\frac{35}{3}}\beta_+ & \sqrt{3}\beta_- & -\sqrt{3}\beta_z & 0 & -\sqrt{\frac{35}{12}}\beta_+ & 3\beta_- & E_8 + \frac{1}{2}\beta_z \end{vmatrix} \tag{10}$$

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

$$\langle\Gamma_6|\hat{H}_{\text{crystal}}|\Gamma_6\rangle = E_6 \qquad \langle\Gamma_7|\hat{H}_{\text{crystal}}|\Gamma_7\rangle = E_7 \qquad \langle\Gamma_8|\hat{H}_{\text{crystal}}|\Gamma_8\rangle = E_8. \tag{11}$$

As it turns out, the secular equation

$$\det\|H_{ij} - \lambda\delta_{ij}\| = 0$$

with the Hamiltonian matrix given by (10) cannot be solved exactly in its general form, but there exist exact solutions for particular cases, such as $\boldsymbol{B} = (0, 0, B_z)$. The eigenvalues in that case are

$$\lambda_{1,2}(\beta_z) = \tfrac{1}{2}\left\{E_6 + E_8 + \tfrac{24}{7}\beta_z \pm \sqrt{\left(E_6 - E_8 - \tfrac{16}{21}\beta_z\right)^2 + \tfrac{8960}{441}\beta_z^2}\right\} \tag{12}$$

$$\lambda_{3,4}(\beta_z) = \tfrac{1}{2}\left\{E_6 + E_8 - \tfrac{24}{7}\beta_z \pm \sqrt{\left(E_6 - E_8 + \tfrac{16}{21}\beta_z\right)^2 + \tfrac{8960}{441}\beta_z^2}\right\} \tag{13}$$

$$\lambda_{5,6}(\beta_z) = \tfrac{1}{2}\left\{E_7 + E_8 + \tfrac{8}{7}\beta_z \pm \sqrt{\left(E_7 - E_8 + \tfrac{16}{7}\beta_z\right)^2 + \tfrac{768}{49}\beta_z^2}\right\} \tag{14}$$

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

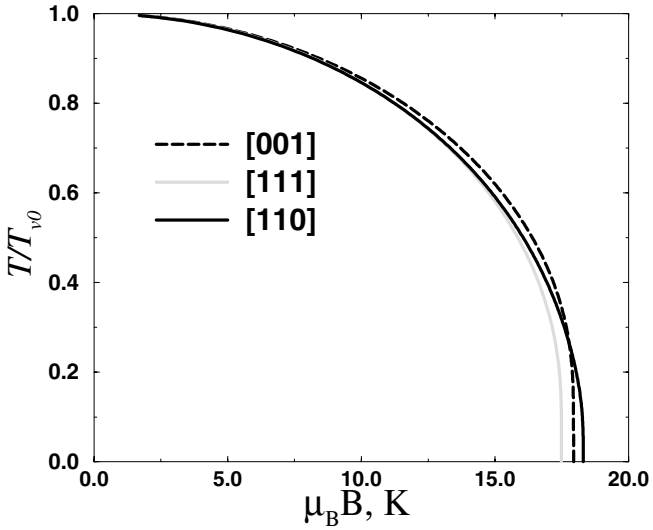

Figure 1. The phase diagram for $YbInCu_4$ shows some anisotropy with respect to the direction of the external magnetic field: $\boldsymbol{B}$ along one of the main cubic axes (dashed curve), $\boldsymbol{B}$ in the *easy plane* (solid black curve) and $\boldsymbol{B}$ along the one of the main cubic diagonals (solid grey curve).

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

Now, we can define the constant in equation (7) as follows:

$$\begin{aligned} &TS(B,T) = T_{v0}S_0(0,T_{v0}) \\ &S_0 = \ln\left[4 + 2\exp\left(-\frac{\delta E_{6,8}}{T_{v0}}\right) + 2\exp\left(-\frac{\delta E_{7,8}}{T_{v0}}\right)\right]. \end{aligned} \tag{16}$$

According to [8], $\delta E_{6,8} = E_6 - E_8 \simeq 3.2$ meV and $\delta E_{7,8} = E_7 - E_8 \simeq 3.8$ meV.

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

In the rest of the paper, we would like to produce an equation for the phase boundary, when $\boldsymbol{B} = (0, 0, B_z)$. Let us introduce the following notation:

$$b = B/B_{v0} \qquad \tau = T/T_{v0} \qquad \tan(\varphi) = b/\tau \qquad \left(0 < \varphi < \frac{\pi}{2}\right).$$

Then

$$\tau = \tilde{U}^{-1}(\varphi) \tag{17}$$

$$b = \tilde{U}^{-1}(\varphi)\tan(\varphi) \tag{18}$$

$$\tilde{U}^{-1}(\varphi) = \frac{1}{S(0,T_{v0})}\sum_{n=1}^{8}\exp[-\tilde{\lambda}_n(\varphi)] \tag{19}$$

with $\tilde{\lambda}_n(\varphi)$ being the eigenvalues (12)–(15). Thus, the equation for the phase transition line is given by

$$b^2 + \tau^2 = R(\varphi) \qquad R(\varphi) = [\cos(\varphi)\tilde{U}(\varphi)]^{-2}.$$

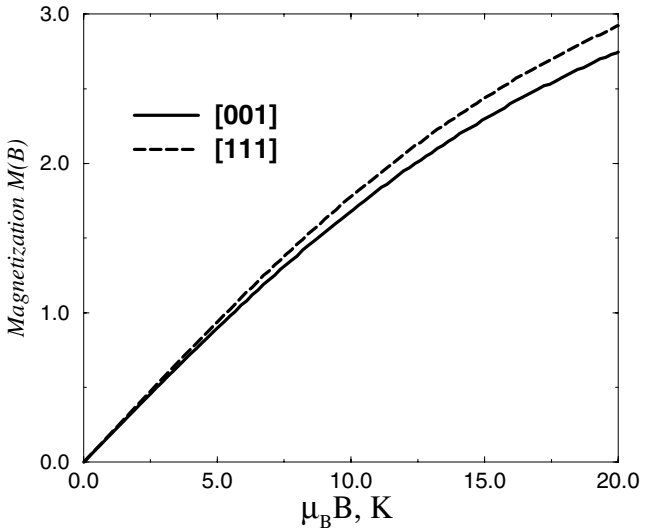

Figure 2. The magnetization curve shows some anisotropy with respect to the direction of the external magnetic field in agreement with our result for the phase diagram where the same type of anisotropy is found. The calculations were performed for $T = 0.75T_{v0}$.

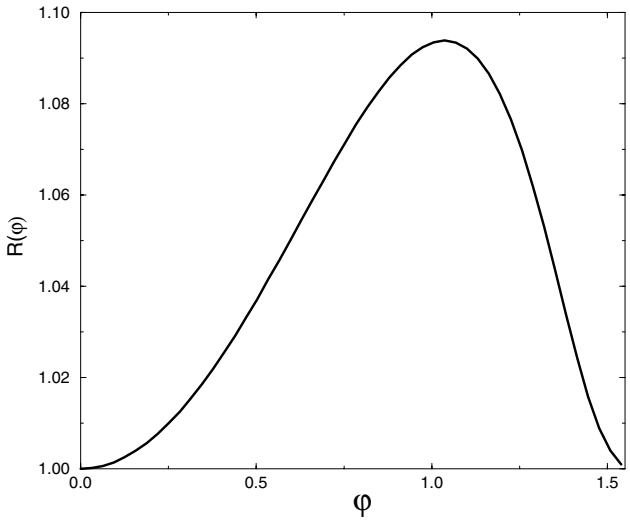

Figure 3. Deviations of $R(\varphi)$ from 1 do not exceed 10%.

As we see in figure 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 types of interaction (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 μ 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 a by reducing the change in the entropy at $T = T_{v0}$. As we see from the results of our calculations of B_{c0} (table 1), when only crystal-field effects are taken into account, the change in a is less than 10%.

Table 1. Values of B_{c0} and a obtained from the phase diagram (figure 1) for different magnetic field orientations.

Field orientation	B_{c0} (T)	a
[001]	30.9	2.29
[111]	30.1	2.34
[110]	31.95	2.24

We should mention that although the crystal-field effects do not change the value of the a-parameter in (2), this is not the case if one is trying to verify relation (2) on the basis of an exact solution for the Kondo model with $J = 7/2$ [9]. As it turns out, in that case, the value of a strongly depends on the energy scale, given by T_K. This result is in fact similar to the result obtained by [14] using the dynamical mean-field theory (DMFT) approach based on the FKR model. Thus, the experimentally verified existence of anisotropy in the phase diagram will serve as proof of our initial idea of a free-Yb-ion 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, the anisotropy of the critical field value B_{c0} is of the order of $\simeq 2$ T and in principle can be seen experimentally.

Preliminary experiments have been carried out in the National High Magnetic Field Laboratory (Tallahassee), and showed relatively good agreement with theoretical predictions based on of the present model [15].

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