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The quadrupolar Kondo ground state in $U_{1-x}Th_xBe_{13}$

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Abstract. The transport, calorimetric and magnetic properties of $U_{1-x}Th_xBe_{13}$ have been investigated. For $U_{0.9}Th_{0.1}Be_{13}$ we have observed all low-temperature asymptotics predicted to date for the quadrupolar Kondo effect (QKE). Namely, this compound demonstrates a logarithmic increase of C/T where C is the specific heat, square-root temperature dependences of the resistivity and susceptibility, absence of magnetoresistivity as well as deviating to positive values of the non-linear susceptibility when temperature decreases. We have found that the Hall effect for the QKE is quenched in low magnetic fields. The anomalous properties of $U_{0.9}Th_{0.1}Be_{13}$ are compared with corresponding characteristics of UBe_{13} and $U_{1-x}Th_xBe_{13}$ for $x > 0.1$.

Since the discovery of the non-Fermi-liquid (NFL) character of the normal state of superconducting cuprates, the NFL physics of metals has been a subject of growing theoretical and experimental interest. A few mechanisms can lead to the formation of the NFL ground state: (a) reduced dimensionality; (b) proximity to the quantum (magnetic) phase transition at zero temperature; (c) the presence of a strong disorder in a normal (one-channel) Kondo system; and (d) the two- (multi-) channel Kondo effect [1–7]. The last possibility, which involves qualitatively new aspects of the Kondo effect, was suggested to be realized in some U-atom-based heavy-fermion compounds [4] and for the electrons interacting with symmetric two-level atomic systems [8, 9]. From modelling the interaction of electrons with U atoms, characterized by a specific crystal-field scheme (the 3–7–8 model), Cox [4] proposed explaining the unusual normal-state properties of UBe_{13} in terms of the quadrupolar Kondo effect (QKE). In the QKE model the quadrupolar degrees of freedom of a non-magnetic U atom in the $5f^2$ ($J = 4$) Γ_3 ground-state doublet are screened 'antiferroquadrupolarly' by local orbital motion of the conduction electrons. The electron spin degeneracy automatically leads to the two-channel Kondo effect if the real spin of the electron is substituted for with a 'pseudo-spin' in the form of an electric quadrupolar moment.

From studying temperature dependences of the specific heat, magnetic susceptibility and resistivity, Seaman *et al* [5] concluded that $U_{0.2}Y_{0.8}Pd_3$ shows properties corresponding to the formation of the QKE ground state. Later, it was found that the situation is more complex because the ground state is strongly affected by magnetic fluctuations [7, 10] and currently the quantum magnetic phase transition (QMPT) model seems to describe experiment more adequately. As for UBe_{13}, it is well known that the ground state of this compound is not of Fermi-liquid type. But at the same time the main asymptotics of the thermodynamic and transport properties of UBe_{13}, especially magnetoresistance and non-linear susceptibility

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(see below), are clearly inconsistent with the behaviour predicted for the QKE. In this paper we give a short experimental review of the properties of $U_{1-x}Th_xBe_{13}$ solid solutions, concentrating on the $U_{0.9}Th_{0.1}Be_{13}$ compound where the ground state has recently been found to be reminiscent of those expected for a QKE [11–16]. Experimental details as well as details of the sample preparation have already been published elsewhere [11, 14, 15].

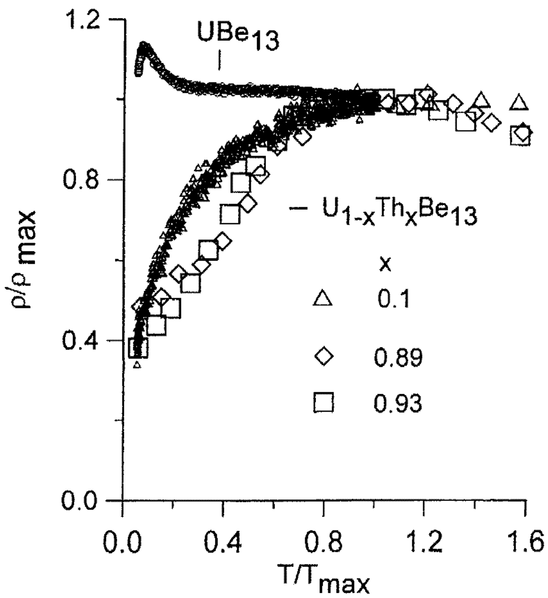

Figure 1. Normalized temperature dependences of the 'magnetic' part of the resistivity (see the text) for UBe_{13} and for $U_{1-x}Th_xBe_{13}$ ($x = 0.1$, 0.89 and 0.93).

It is well known that a small degree of substitution of Th for U results in unusual non-monotonic suppression of the superconducting transition temperature of $U_{1-x}Th_xBe_{13}$ [17] coexisting for $0.02 < x < 0.04$ with a second low-temperature phase transition of unknown origin. The first study of magnetic and transport properties of the $U_{1-x}Th_xBe_{13}$ system for Th concentration exceeding 6% (namely, over the whole range $0 \leqslant x \leqslant 1$) was reported [18, 19] practically simultaneously with the proposal of a QKE [4]. Those measurements showed that the ground state of $U_{1-x}Th_xBe_{13}$ for $x \geqslant 0.1$ is qualitatively different from that of UBe_{13}. Before giving further analysis of the ground-state properties of $U_{1-x}Th_xBe_{13}$ compounds it is worthwhile to stress one important conclusion which follows from the result of this early work [18, 19], namely the scaling character of the magnetic and transport (resistivity) properties for $x \geqslant 0.1$. In fact, it was found that temperature dependences of magnetic susceptibility normalized by the U concentration behave similarly over the whole $0.1 < x < 0.93$ concentration range, deviating only for UBe_{13} [19]. The scaling properties of $U_{1-x}Th_xBe_{13}$ are nicely demonstrated by plotting the temperature dependences of the resistivity [18] in normalized coordinates. Figure 1 presents in normalized coordinates $\rho/\rho_{max} = f(T/T_{max})$ temperature dependences of the 'magnetic' part of the resistivity $\rho_m = \rho(U_{1-x}Th_xBe_{13}) - \rho(ThBe_{13})$ for four different $U_{1-x}Th_xBe_{13}$ solid solutions from the concentrated ($x \approx 0, 0.1$) and diluted (0.89 and 0.93) limits. The characteristic temperature T_{max} corresponds to a maximum in resistivity, ρ_m, and varies between $T_{max} \sim 30$ K for the limit of high U concentration to about $T_{max} \sim 60$ K for $U_{0.07}Th_{0.93}Be_{13}$. It is clearly seen that the data for UBe_{13} strongly deviate from the scaling picture observed for $x \geqslant 0.1$. Therefore, the behaviour presented by figure 1 clearly indicates that *single-ion physics works for $U_{1-x}Th_xBe_{13}$ at least between the diluted limit* ($x \sim 0.9$) *and the concentrated regime,* $x \sim 0.1$. Similar results were obtained later by Kim *et al* [20].

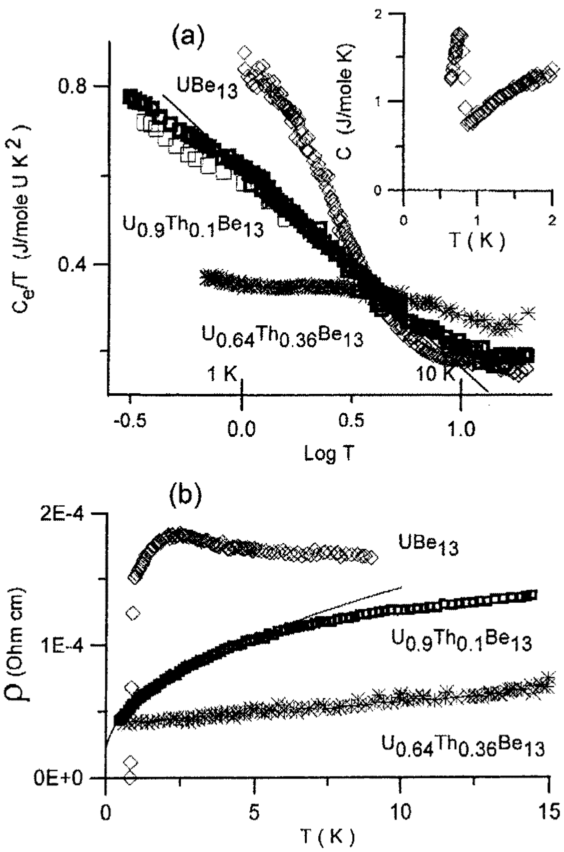

Figure 2. (a) The temperature dependence of the electronic heat capacity C_e/T versus $\log(T)$ of $U_xTh_{1-x}Be_{13}$ compounds. Open squares show data for $U_{0.9}Th_{0.1}Be_{13}$ measured in the magnetic field $H = 8$ T. The solid line refers to the logarithmic-in-T dependence discussed in the text. The inset shows the low-temperature range of the specific heat of UBe_{13}, presented as C versus T and showing the superconducting transition. (b) Temperature dependences of the electrical resistivity of UBe_{13}, $U_{0.9}Th_{0.1}Be_{13}$ and $U_{0.64}Th_{0.36}Be_{13}$ presented as ρ versus $T^{1/2}$. The solid line corresponds to a square-root-of-T dependence described in the text.

Let us now consider the low-temperature properties of $U_{0.9}Th_{0.1}Be_{13}$, which are comparable with those predicted for the QKE. The normalized electronic term in the heat capacity C_e/T is a linear function of $\lg T$ between 0.7 K and about 6 K (see figure 2(a)). A magnetic field of about 8 T practically does not affect the logarithmic behaviour, except at sufficiently low temperatures where a slight deviation from the asymptotic $\Delta C_e/T \sim \log T$ behaviour is observed. The magnetic susceptibility, measured in the various fields (0.1 T $< B <$ 4 T), saturates at low temperatures as a square-root function of temperature [13]: $\chi \sim \chi_0 - \alpha\sqrt{T}$. An important experimental fact is that between about 6 K and 0.7 K the resistivity also varies as the square root of temperature: $\rho(T) \sim \rho_0 + A\sqrt{T}$

(figure 2(b)). Between 0.7 K and 0.08 K the resistivity saturates approximately as a linear function of temperature $\Delta\rho \sim CT$ [21].

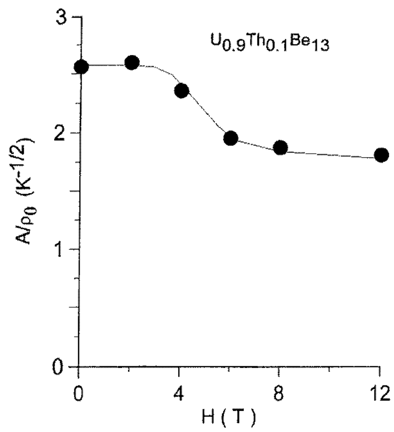

Figure 3. The magnetic field dependence of the coefficient A as a square-root-of-temperature dependence of the resistivity $\rho = \rho_0 + AT^{1/2}$ for $U_{0.9}Th_{0.1}Be_{13}$ between 1.7 K and 5 K, normalized by the extrapolated residual resistivity ρ_0. The line is a guide for the eye.

The large negative magnetoresistance, present in UBe_{13}, becomes negligible in $U_{0.9}Th_{0.1}Be_{13}$ [12]. Figure 3 shows the effect of the magnetic field on the normalized coefficient A/ρ_0 in the square-root slope of the resistivity between 1.7 and 5 K. It is clearly seen that the resistivity is affected only by a magnetic field exceeding 3 T.

By measuring the non-linear susceptibility at different fixed temperatures $\chi_3(T)$, we can perform an experimental test for magnetism of the $U_{0.9}Th_{0.1}Be_{13}$ ground state [14]. The non-linear susceptibility χ_3 measures the leading non-linear term in the magnetization M along the direction of the magnetic field B:

$$M = \chi_1 B + (1/3!)\chi_3 B^3 + \cdots. \tag{1}$$

In cubic symmetry χ_3 is given by [22]

$$\chi_3 = \chi_3^{111} + \Delta\chi_3 \frac{[3(b_x^4 + b_y^4 + b_z^4) - 1]}{2} \tag{2}$$

where b_i $(i = 1, 2, 3)$ are the directional cosines of the magnetic field.

In the frame of the Cox model for a single ion with a quadrupolar moment $Q, \Delta\chi_3$ should have the following asymptotic behaviour [24]:

$$\Delta\chi_3 = \frac{Q^2}{2T} f\left(\frac{T}{T_Q}\right) = \begin{cases} Q/2T & (T \gg T_Q) \\ (\alpha Q/2T_0)\ln(T_Q/T) & (T \ll T_Q) \end{cases} \tag{3}$$

(here $\alpha \sim 0.1$ and T_Q is the quadrupolar Kondo temperature). For a magnetic doublet ground state, χ_3 is negative and strongly temperature dependent [23]: $\chi_3 \sim -1/T^3$. On the other hand, if magnetic moments are screened through the one-channel Kondo interactions, then outside the temperature interval $T \ll T_K$ (where χ_3 should saturate to large negative values), a weaker $\chi_3(T)$-dependence should be observed, for example $\chi_3 \sim -1/T^\alpha$ with $0 < \alpha < 3$. For the low-lying quadrupolar doublet, the anisotropic factor $\Delta\chi_3(b_i)/\chi_3$ is large and strongly temperature dependent (see equation (3)); for the (111) direction χ_3 is small and negative, but it changes from negative to positive and is logarithmically divergent when $T \to 0$ for the (110) and (100) magnetic field directions [24]. If measurements of the non-linear susceptibility are carried out on the polycrystalline material (as in the case of $U_{0.9}Th_{0.1}Be_{13}$ samples), then we may expect for the QKE the $\chi_3(T)$-behaviour which is a consequence of the angle averaging over highly anisotropic χ_3, and, according to the estimations of Ramirez *et al* [24] a minimum of χ_3, followed by a positive logarithmically divergent behaviour at $T \to 0$, should be observed.

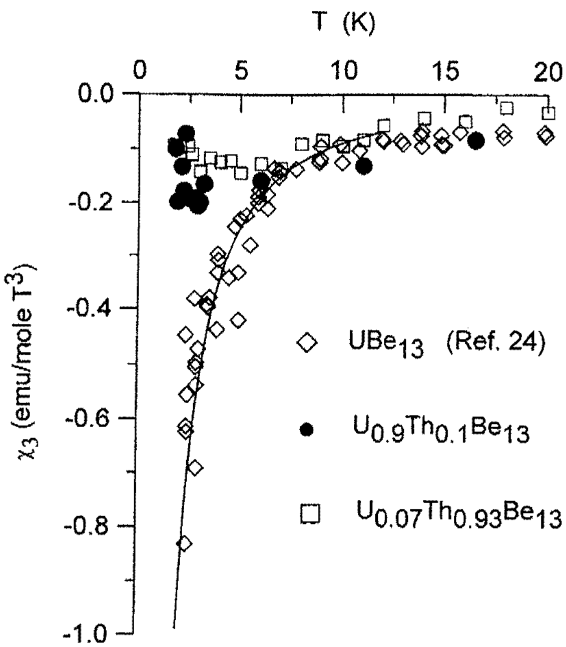

Figure 4. The temperature dependence of the non-linear susceptibility of UBe_{13} (taken from reference [23]; the line corresponds to the fit of the data and it is described in the text), of $U_{0.9}Th_{0.1}Be_{13}$ and of $U_{0.07}Th_{0.93}Be_{13}$.

Figure 4 shows the non-linear susceptibility as a function of temperature for UBe_{13} [24], $U_{0.9}Th_{0.1}Be_{13}$ and $U_{0.07}Th_{0.93}Be_{13}$. *Again, as for the resistivity (figure 1), one clearly sees the similarity of the ground state of $U_{1-x}Th_xBe_{13}$ ($0.1 < x < 0.93$) compounds and also the qualitatively different $\chi_3(T)$-behaviour for UBe_{13}.* We tried to fit the UBe_{13} data by using $\chi_3 \sim -1/T^{\alpha}$ and we obtained the result that over a wide temperature interval between 2 K and 12 K the dependence $\chi_3 \sim -1/T^{1.5}$ is seen [25], indicating the possible presence of Kondo screening of the magnetic ground-state doublet in UBe_{13}. On the other hand, the behaviour of $\chi_3(T)$ for the Th-doped samples for $x > 0.1$ clearly shows the presence of a non-magnetic ground-state doublet comparable with that predicted for a QKE model. If one extrapolates the $\chi_3(T)$-behaviour found for $U_{0.9}Th_{0.1}Be_{13}$ to the low-temperature interval $T < 1.7$ K, then from the intersection point T_i of the $\chi_3(T)$-curve with the $\chi_3 = 0$ axis ($T_i \sim 1.5$ K) one may estimate an upper limit for the quadrupolar ordering temperature Θ_Q. According to [23], $T_i = (1+\gamma)\Theta_Q$ where $\gamma = (2J-1)(2J+3)/(2J^2+2J+1)$. Such an estimation done for $U_{0.9}Th_{0.1}Be_{13}$ gives $\Theta_Q \sim 0.7$ K which is in good agreement with the characteristic temperature corresponding to the transition from a square-root to a linear temperature dependence of the resistivity [21].

In order to understand the unusual transformation of the ground state of $U_{1-x}Th_xBe_{13}$, we proposed that the $5f^2$ and $5f^3$ configurations of the U atom in UBe_{13} are degenerate [14], resulting in valence and corresponding spin ($0 \leftarrow\ \rightarrow 1$) fluctuations. The effect of spin fluctuations on the heat capacity was experimentally observed in $U_{1-x}Th_xBe_{13}$ ($0 \leqslant x \leqslant 0.06$) solid solutions by Knetsch [26]. A possible mechanism of such fluctuations is as follows: the Γ_6 magnetic ground-state doublet, corresponding to the $5f^3$ configuration of the U atom, overlaps with an excited state of the $5f^2(\Gamma_3)$ configuration (for example, with the Γ_4 triplet). In this case the quantum fluctuations between Γ_3 and Γ_4 levels will strongly enhance the width of the Γ_4 state resulting in its possible overlap with the non-magnetic ground-state doublet. Substitution for the U with Th may remove the $5f^3(\Gamma_6)$–$5f^2(\Gamma_4)$ degeneracy and substantially decrease the Γ_3–Γ_4 overlap in the $5f^2$ configuration, which may lead to the appearance of the non-disturbed non-magnetic Γ_3 ground-state doublet for $x \geqslant 0.1$.

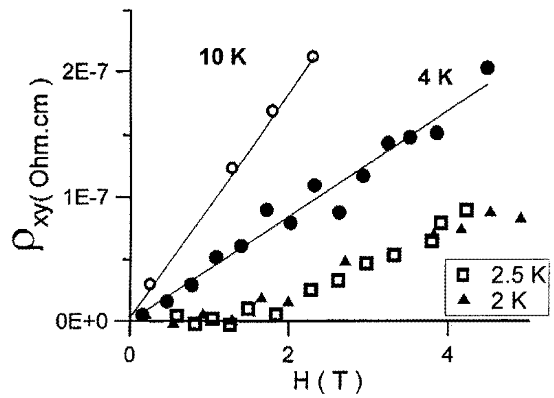

Figure 5. The magnetic field dependence of the Hall resistivity of $U_{0.9}Th_{0.1}Be_{13}$ at different fixed temperatures.

The transformation from the magnetic to the non-magnetic Kondo ground state in $U_{1-x}Th_xBe_{13}$ may be monitored by studying the Hall effect [15, 16]. It was found previously that the low-temperature maximum in the resistivity of UBe_{13} ($T_{max} \approx 2.5$ K) is accompanied by a maximum in the anomalous Hall effect, followed by a strong decrease of the Hall effect and a change of sign near the superconducting transition temperature. The field dependence of the Hall resistivity ρ_{xy} in UBe_{13} was found to be a linear function of the magnetic field lower than a few teslas [27]. Substitution for U of more than 5% of Th results in a dramatic effect on the behaviour of the Hall resistivity ρ_{xy}: for $x \sim 0.05$ an anomalous Hall effect is seen only in low fields $H < 1$ T [28]. A further increase of Th concentration qualitatively changes the behaviour of the Hall resistivity. For $U_{0.9}Th_{0.1}Be_{13}$ a linear term in the Hall resistivity ρ_{xy}/H vanishes asymptotically in a limit of small fields [16] and the non-zero Hall coefficient recovers only in higher magnetic fields between 2 T and 3 T and at temperatures $T > 3$ K (see figure 5). We showed that such unusual behaviour of the Hall effect may be a universal specific feature of the two-channel Kondo ground state [16]. In fact for $H \rightarrow 0$ the AHE contributions to each of the two scattering channels with phase shifts $\delta_3^{1,2} = \pm\pi/4$ completely compensate each other, because for these phase shifts $R_H^A = R_H^{A,1} + R_H^{A,2} = 0$ where $R_H^{A,i} \sim \sin\delta_2 \sin(2\delta_3 - \delta_2)$ [29] (δ_2 is a phase shift for the orbital quantum number $L = 2$ and is equal for the two channels). The Hall effect is a convenient tool for studying a scaling of the QKE with magnetic field [28].

To *summarize,* the substitution of Th for U in $U_{1-x}Th_xBe_{13}$ solid solutions results in the formation of an NFL ground state which may be described in terms of the quadrupolar Kondo model. Future studies should concentrate on possible transformations of the QKE ground state with a further dilution of U with Th. In that context, the further confirmation of the realization of the QKE in $U_{1-x}Th_xBe_{13}$ solid solutions will be a clear demonstration that the ground state seen in $U_{0.9}Th_{0.1}Be_{13}$ does not appear only due to its proximity to a certain quantum phase transition point but may be also seen in the limit of more diluted U atoms [30]. The scaling presented by figures 1 and 4 evidently contradicts a simple QMPT scenario and supports the explanation based on the QKE model. Moreover, the presence of the maxima in the temperature dependence of the resistivity (figure 1) for a diluted limit evidently contradicts a normal one-channel Kondo model, where a minimum in the resistivity $\rho(T)$ is normally observed. On the other hand, the presence of the maxima may be explained by the two-channel (QKE) scenario where both minima and maxima in the resistivity may be observed [31]. Some deviation from the scaling behaviour may be due to a possible local distortion of a cubic symmetry for the small U-atom concentrations.

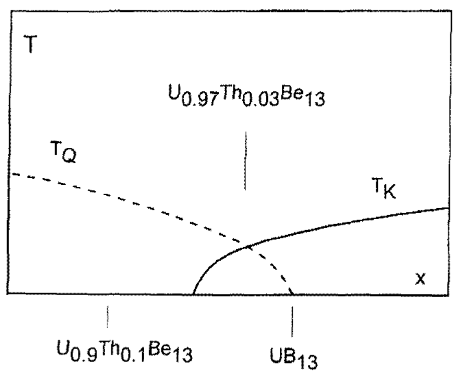

Figure 6. A schematic phase diagram for $U_{1-x}Th_xBe_{13}$ (T_Q—characteristic quadrupolar Kondo temperature; T_K—one-channel Kondo temperature).

A gradual suppression of the spin fluctuations and the appearance of the quadrupolar Kondo interactions imply the possibility of the phase diagram for the $U_{1-x}Th_xBe_{13}$ solid solutions shown schematically in figure 6. The stoichiometric UBe_{13} may be situated in a region very close to a critical point corresponding to the transition from the magnetic to the non-magnetic Kondo quadrupolar state. This idea is supported by recent experiments done by Steglich's group [32] where a field-independent temperature dependence of the resistivity $\Delta\rho \sim T^{3/2}$, characteristic for the proximity to the QMPT, was found in high magnetic fields suppressing the superconductivity. The critical concentration region ($0.02 < x < 0.04$), where heavy-fermion superconductivity coexists with another low-temperature phase transition, may be determined by the condition $T_K \approx T_Q$ when neither spin fluctuations nor the quadrupolar moment are effectively screened. This may explain a second phase transition seen in the superconducting state as a cooperative Jahn–Teller phase transition in the system of partially screened U-atom quadrupolar moments (earlier, this possibility was considered only for UBe_{13} [4]), which also induces a small ordering magnetic moment. Finally, for $x > 0.05$ the formation of the quadrupolar Kondo ground state with a gradually enhanced characteristic quadrupolar Kondo temperature may occur.

Acknowledgments

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