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Mixed valence of U determined using the de Haas–van Alphen effect: Application to $U_xTh_{1-x}Be_{13}$

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de Haas–van Alphen measurements made on $U_xTh_{1-x}Be_{13}$ for $x \leqslant 0.1$ reveal that U enters the $ThBe_{13}$ lattice as a mixed valent impurity of average valence ~ 4.7, evinced by topological changes in the Fermi surface with x. This implies that U exists in the tetravalent $5f^2$ configuration when diluted and that the strong correlations in UBe_{13} involve $5f^2 \rightarrow 5f^1$ transitions. Possible scenarios for the nature of the $U_xTh_{1-x}Be_{13}$ ground state are discussed.

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The renormalized quasiparticle band picture, comprised of hybridized conduction and f electron states, has been largely successful at accounting for the Fermi liquidlike properties of heavy-fermion metals.[1,2] Though simplifications regarding the many body effects need to be made, this model contains much of the essential physics for explaining the dual observation of the de Haas–van Alphen (dHvA) effect and field-induced metamagnetic transitions as a general feature of stoichiometric heavy-fermion alloys.[2–5] There are, however, a few exceptions for which the existence of a Fermi liquid state is highly questionable.[6] The stochiometric compound UBe_{13} could belong to this class.[7,8] Notably, it does not appear to undergo a metamagnetic transition,[9] nor have dHvA oscillations been observed that can be definitively linked to the heavy-fermion ground state.[10,11] Compelling evidence for heavy quasiparticles in this material, meanwhile, is provided by the large specific-heat jump that occurs on entry into the superconducting phase.[12]

Clearly, the absence of a Fermi-liquid state in UBe_{13} would prohibit a direct exploration of its quasiparticle properties by means of the dHvA effect. While we cannot probe the non-Fermi-liquid regime, should this exist, we can at least discern the effect of substituting U $5f$ electrons into a suitable MBe_{13} host lattice as provided, for example, by $ThBe_{13}$. Studies of the electronic specific heat throughout the $U_xTh_{1-x}Be_{13}$ series have shown that non-Fermi-liquid-like behavior appears to subside for concentrations $x \lesssim 0.9$.[13] While there are many reasons for expecting appreciable behavioral differences between U and Ce impurities,[1] dHvA studies on $Ce_xLa_{1-x}B_6$ have shown that the electronic structure changes in a continuous fashion with x, with both the quasiparticle effective masses increasing and the Fermi surface volume expanding gradually so as to accommodate the itinerant fraction of $4f$ electrons.[14] What was learned from this study is that dHvA measurements can be utilized to determine the valence of the impurity ion as well as the quasiparticle effective masses.[1,15]

dHvA measurements on $U_xTh_{1-x}Be_{13}$, in this paper, reveal that the Fermi surface changes significantly with x for $0 < x \lesssim 0.1$, while the effective masses do not. The changes in the Fermi surface topology, alone, indicate that U enters the $ThBe_{13}$ lattice as a mixed valent impurity of average valence $v_U \sim +4.7$ when diluted. We show that this result provides important clues as to the magnetic configuration of those $5f$ electrons that are localized, and ultimately to the nature of the transitions giving rise to mixed valence. Noting the close correlation between the dimensions of the MBe_{13} lattice and the degree of $5f$ electron itinerancy, we further address the question as to why the Kondo effect need not necessarily precede a heavy fermion ground state as x is increased from the dilute limit.

Because the MBe_{13} cage is structurally resilient to a large variety of substitutions M, including Th (Refs. 16,17) (the nonmagnetic analoque element most electronically similar to U in the periodic table), it provides an opportunity for the x dependence of the interactions to be studied over the entire concentration range. Single crystals of $U_xTh_{1-x}Be_{13}$ with $x = 0$, 0.005, 0.015, 0.05, 0.1, and 0.2 were grown in Al flux. The dHvA oscillations in the magnetic torque were measured using a phosphor bronze cantilever capacitance magnetometer, with the axis of the magnetic induction B rotated to within $\sim 3°$ of the $\langle 100 \rangle$ direction in the $\{100\}$ plane. The crystals were aligned using the visible $\{100\}$, $\{110\}$, and $\{111\}$ faces. Temperatures between 500 mK and 20 K were obtained by either evaporating or heating a closed container of ^{3}He liquid or gas, while magnetic fields extending to ~ 33 T were provided by the National High Magnetic Field Laboratory, Tallahassee.

An example of dHvA oscillations in the magnetic torque measured in $U_{0.1}Th_{0.9}Be_{13}$ at ~ 4 K is shown in Fig. 1(a), with the Fourier transform (for the same interval in reciprocal magnetic field) shown in Fig 1(b). The x dependence of the frequencies corresponding to orbits predicted by band-structure calculations and/or that have already been confirmed to exist experimentally in pure $ThBe_{13}$ (Refs. 11 and 18) are plotted in Fig. 2(a). The sign of the slope of the x dependence of the various frequencies identifies whether they are electron- or holelike. Of the two possible effects that

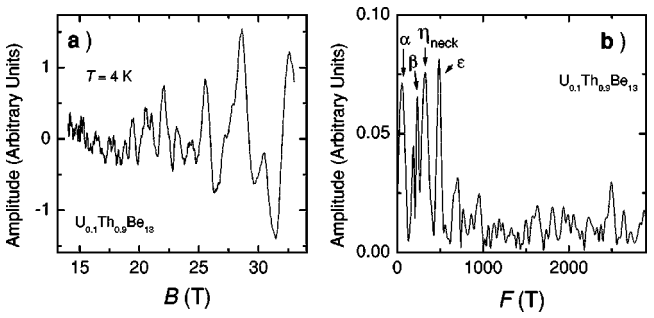

FIG. 1. (a) de Haas–van Alphen oscillations measured in the magnetic torque of $U_{0.1}Th_{0.9}Be_{13}$ at $T\sim 4$ K. (b) A Fourier transformation over the same interval in reciprocal magnetic field. The frequencies are labeled in accordance with Ref. 11.

could give rise to frequency changes as a function of x, we can rule out the contraction of the lattice on doping with U, since the lattice parameter ($\mathbf{a}\sim 10.3794$) of $U_{0.1}Th_{0.9}Be_{13}$ is only 0.17% less than that ($\mathbf{a}\sim 10.3970$) of pure $ThBe_{13}$.[17] This could only account for changes in the Fermi surface cross-sectional area of order $\sim 0.41\%$; i.e., much lower than those observed experimentally. The experimental observations can therefore only be attributed to a change in the density of itinerant electrons with x. According to Luttinger's theorem, a simple proportionality between itinerant electron density and Fermi surface volume always applies,[19] even in the most strongly correlated systems. Thus, when applied to heavy-fermion systems, dHvA experiments can determine the extent to which the f electrons contribute to the Fermi surface volume. In $Ce_xLa_{1-x}B_6$, for example, each Ce ion contributes ~ 0.1 $4f$ electrons to the Fermi surface volume at fields above the metamagnetic transition.[14,15]

Before extracting similar information on $U_xTh_{1-x}Be_{13}$ from Fig. 2(a), it is helpful to consider the possible ways in

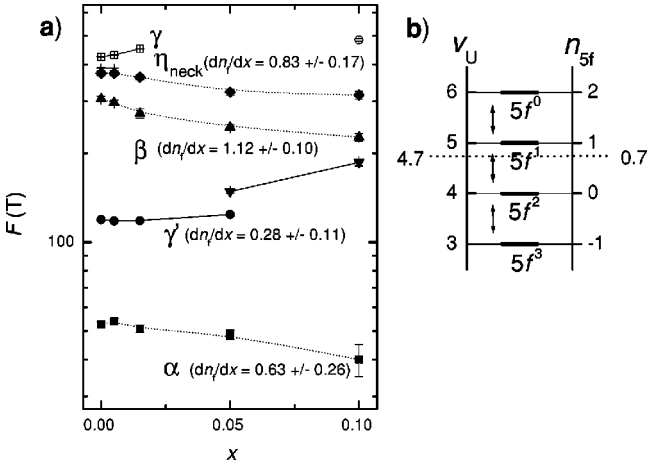

FIG. 2. (a) A plot of several of the key frequencies observed throughout $U_xTh_{1-x}Be_{13}$ versus concentration x. The frequencies have been labeled according to the schematics of Ref. 11, with the exception of γ' which has not yet been identified. Solid (dotted) lines depict electron (hole) orbits. (b) An illustration of the possible $5f$ electron configurations of U versus the itinerant fraction of $5f$ electrons n_{5f} and the U valence v. The arrows indicate the transitions between different localized f states that prevail.

which U ions could modify the Fermi surface on being substituted into $ThBe_{13}$. The Fermi surface of $ThBe_{13}$ is known to be mainly made up of Be^{II} p electrons,[11,16] with the extent to which each contributes to the Fermi surface volume being strictly integral and the net valence of Th being $v_{Th}=+4$. U, on the other hand, can exist in several possible valence states, $+3<v_U<+6$, with conventional band-structure calculations no longer being physically meaningful when v_U is nonintegral. This primarily concerns the failure of band-structure calculations to account for the effects of the effective Coulomb repulsion U_{ff} that becomes particularly important in narrow f band systems. Perhaps emphasizing this point, the present band-structure calculations, which do not include U_{ff}, predict a significant $5f$ electron spectral weight at the Fermi energy E_F.[16] Yet, these spectral features are both too shallow to account for the large electronic specific heat[17] and too narrow (~ 0.1 eV) to account for the broad photoemission spectra.[20]

To better understand the delicate balance between itinerant and localized f electron behavior, it is therefore instructive, first, to consider the simpler case of Ce impurities for which there is usually only one $4f$ electron of relevance to the problem. In Ce-based heavy-fermion systems, U_{ff} is often thought to be large enough (of order 1 eV or more) so that the $4f$-band splits into two narrow corelike levels; one singly occupied in the $4f^1$ configuration at an energy E_f deep below the Fermi energy E_F, and the other doubly occupied in the $4f^2$ configuration at an energy E_f+U_{ff} far enough above E_F that its existence can often be ignored.[1] The extent n_{4f} to which these $4f$ electrons contribute to the Fermi surface volume then depends on the balance between the hybridization potential V, the on-site Coulomb repulsion U_{ff}, and the depth of E_f below E_F. Note that $n_{4f}=v_{Ce}-v_{La}$ is equivalent to the valence difference between Ce and the nonmagnetic reference element La. In a few Ce-based materials, dHvA experiments below the metamagnetic transition have confirmed the existence of weak hybridization, for which $n_{4f}\lesssim 1$, where, in the hybridized many-body band picture, large effective masses result from the fact that $V\ll U_{ff}$.[1,2]

Because of the probable existence of more than one $5f$ electron per U ion, its f electron physics is somewhat more complicated. Provided transitions occur between only two different localized $5f$ electron configurations, however, particle number conservation continues to imply some rather simple constraints: while n_{5f} can assume any value in the range $-1\leqslant n_{5f}\leqslant 2$, it still remains equivalent to the valence difference $n_{5f}=v_U-v_{Th}$ between U and Th, with the localized fraction of $5f$ electrons being given by $2-n_{5f}$. The possible configurations of U are depicted in Fig. 2(b). Thus by application of Luttinger's theorem, we can infer n_{5f} from the x dependence of the Fermi surface cross sections $A(x)=2\pi eF(x)/\hbar$. The application of this idea to $Ce_xLa_{1-x}B_6$ at fields above the metamagnetic transition was particularly trivial in that case owing to the simple elliptical Fermi surface topologies of MB_6 compounds.[14] In $ThBe_{13}$, however, the Fermi-surface topology is considerably more complicated with many of the larger sections having still not been

observed.[11] An alternative method, therefore, is to determine n_{5f} from the partial derivative $\partial n_{5f}(x)/\partial x \approx \partial n/\partial E \times \partial E/\partial A \times \partial A/\partial x$, where Luttinger's theorem implies that $\partial n_{5f} \equiv \partial n$. Here, $\partial n/\partial E$ is the density of states, which has been both calculated and verified experimentally to be $g(E_F) \sim 1.2 \times 10^{47}$ states per m^3J,[16] $\partial A/\partial E = 2\pi m^*/\hbar^2$ is the cyclotron effective mass, which can be obtained from the temperature dependence of the dHvA oscillations, while $\partial A/\partial x \sim \Delta A/\Delta x$ can be extracted directly from Fig. 2(a). This method is accurate provided $\partial n_{5f}(x)/\partial x$ is constant for $0 \leqslant x \leqslant 0.1$. Given that $\partial n(x)/\partial x$ changes very little over this range,[16] and a far greater error originates from the effective mass measurement made at $x=0$, this is a fair assumption to make. Estimates for four of the orbits are, therefore, shown in Fig. 2(a), and an average made over these four orbits yields $\partial n_{5f}(x)/\partial x \sim 0.7 \pm 0.2$, implying that $v_U \sim 4.7 \pm 0.2$ in Fig. 2(b). Thus, as with $4f$ electrons in $Ce_xLa_{1-x}B_6$,[15] we find that the $5f$ electrons also contribute to the Fermi surface volume in a nonintegral manner. While this value of v_U appears to be inconsistent with the value that has been considered to explain magnetic data,[21,22] it does appear to be consistent with the estimate of v_U for U in MBe_{13} inferred on the basis of a chemical bonding topology analysis.[23] As can be seen in Fig. 2(b), it further implies that the U impurities exist in the $5f^2$ configuration prior to mixing (or hybridizing), with the mixing then giving rise to $5f^2 \rightarrow 5f^1$ transitions.

While dHvA experiments yield no direct information on the magnetic configuration of the localized $5f$ electrons, $5f^2 \rightarrow 5f^1$ transitions have been proposed as one of the possible routes to the quadrupolar Kondo effect,[7] and non-Fermi-liquid-like behavior.[1,7,24] The applicability of this model to UBe_{13}, or $U_xTh_{1-x}Be_{13}$, would require the lowest energy $J=4$, $5f^2$ multiplet to exist in the Γ_3 configuration rather than Γ_5 as a result of the cubic crystal symmetry environment. Since the Γ_3 multiplet is nonmagnetic (i.e., $J_z=0$), with only a finite electric quadrupole moment remaining, one could speculate that this Γ_3 state is consistent with the lack of a metamagnetic transition in UBe_{13},[9] which requires a Zeeman mechanism. It nevertheless remains unclear how the quadrupolar interactions, should these be relevant, manifest themselves on the quasiparticle properties in the mixed valent regime $0 < x \ll 1$, how this could give rise to a spin fluctuationlike effects at intermediate concentrations,[13] or why the quasiparticle effective mass in Fig. 3(a) does not increase as does the scattering rate in Fig. 3(b). What is clear, from the present study, is that $U_xTh_{1-x}Be_{13}$ behaves very much like a weakly interacting Fermi liquid for $x \leqslant 0.1$, within which the U ions function primarily as charged impurities. The charged nature of the impurities is evinced both by the valence difference and by the increase in the quasiparticle scattering rate τ^{-1} with x in Fig. 3(b).

Perhaps the most intriguing aspect of these results is that they show that it is not necessary for any type of Kondo effect to precede the development of a heavy fermion ground state in $U_xTh_{1-x}Be_{13}$ as x is increased from the dilute limit. Instead, the low effective masses in Fig. 3(a), together with the fractional U valence state, is more typical of a mixed valent system.[1] In such as system, the f electron self-energy $\Sigma(E,k) \sim E_F - E_f$, which is responsible both for the mass enhancement and for the formation of the Kondo resonance, is relatively small. Such a ground state is realized when the highest occupied corelike f electron level lies very close to E_F, enabling it to hybridize directly with the conduction electron bands. Specific-heat measurements, at $x=0.1$, further corroborate this picture, yielding an electronic specific-heat coefficient $\gamma = x \times \gamma_U \sim 9$ mJ mol^{-1} K^2 that is only marginally higher than that of pure $ThBe_{13}$.[17]

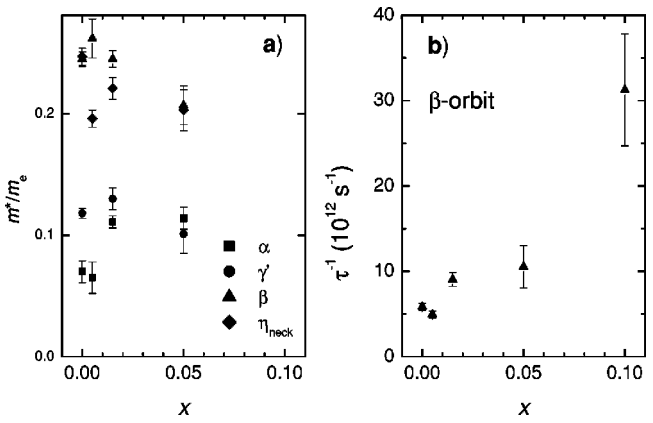

FIG. 3. (a) The effective masses measured as a function of x for four orbits. Reliable effective mass estimates were not obtained for $x=1$. (b) The quasiparticle scattering rate τ^{-1} obtained by fitting the field dependence of the amplitude to $A_0 \exp(-\pi/\omega_c\tau)$ where $\omega_c = eB/m^*$, having corrected for temperature.

While the effective masses within the $U_xTh_{1-x}Be_{13}$ series are relatively unenhanced at low concentrations, specific-heat studies have shown that γ_U (per U ion) undergoes a dramatic increase for $x \gtrsim 0.5$.[17] The pronounced increase in τ^{-1} with x implies that this region of the phase diagram is inaccessible to dHvA measurements. The inability to observe dHvA oscillations in pure UBe_{13}, in this work and in others,[11] is further suggestive of there being no recovery of Fermi liquidlike behavior as $x \rightarrow 1$. Although γ for UBe_{13} is some ~ 150 times greater than that of $ThBe_{13}$, because the effective masses in pure $ThBe_{13}$ are so low (in the 0.07 to 0.2 m_e range with m_e being the free electron mass), the effective masses in UBe_{13} should not be any higher than those in other heavy-fermions systems in which quantum oscillations have been observed.

The development of strong correlations only for $x \gtrsim 0.5$ is a likely consequence of the sensitivity of the interactions to the lattice dimensions. Evidence for a strong coupling of the itinerancy of the f electrons to the lattice is provided by the data of Kim *et al.*,[17] whereby Kondo-like behavior in $U_xM_{1-x}Be_{13}$ occurs only when the lattice parameter **a** is less than or equal to that $\mathbf{a}_U$ of pure UBe_{13}. Kim *et al.* attributed this to the increased hybridization V resulting from the reduced U-Be separation distance for $\mathbf{a} \leqslant \mathbf{a}_U$. However, an increase in hybridization usually results in lower effective masses,[1,2] and it is difficult to imagine how the existence of Kondo-like behavior only for $\mathbf{a} \leqslant \mathbf{a}_U$ could be a matter of mere coincidence. An explanation along the lines of ''Kondo collapse'' is more consistent with these observations. While

this mechanism manifests itself most strongly in elemental Ce and U, in the form of a structural phase transition,[1] a ''collapse'' of the size of the lattice of UBe_{13} (along with that of heavy fermion $NpBe_{13}$), relative to those of other actinide and rare-earth MBe_{13} compounds, is clearly apparent in Fig. 2 of Ref. 16. Kondo collapse results from the effective reduction in the size of the U (or Ce) ions when f electrons, formerly in localized states, are shed to the conduction sea, with the increased U-Be overlap subsequently resulting in a feedback process that encourages further f electron itinerancy. The increased kinetic energy of the compressed conduction electrons E_F eventually counteracts this collapse, but not until nearly all of the available f electrons are itinerant and the valence is nearly integral; it is therefore likely that $v_U \rightarrow 5$ as $x \rightarrow 1$. As a consequence, $\Sigma(E,k) \sim E_F - E_f$ also becomes larger, leading to heavier masses. Light masses for $x \leqslant 0.1$ can now be understood to result from the fact that too large a concentration $(1-x)$ of Th prevents the Kondo collapse from occurring, thereby mitigating heavy-fermion behavior. Conversely, if the size the host MBe_{13} lattice is already smaller than that of UBe_{13}, as is the case when $M=$ Y or Sc, the U impurities enter that lattice in-''precollapsed'' state whereby Kondo-like behavior ensues at all concentrations $0 < x \leqslant 1$.[17] To test this hypothesis, it would be necessary to perform experiments on $U_xTh_{1-x}Be_{13}$ under hydrostatic pressure.

In summary, we have shown that $U_xTh_{1-x}Be_{13}$ exhibits Fermi liquid behavior for $x \leqslant 0.1$, for which the presence of light quasiparticles, together with the strong dependence of the Fermi surface topology on x, evidences mixed valent behavior. It appears that Kondo-like behavior is activated only upon collapse of the lattice. The fact that each U ion adds ~ 0.7 extra electrons to the Fermi surface volume indicates that the $5f$ electrons are in the $5f^2$ configuration prior to mixing, which is one of the possible configurations that could give rise to the quadrupolar Kondo effect.[7]

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