Nonlinear Susceptibility: A Direct Test of the Quadrupolar Kondo Effect in $UBe_{13}$

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We present the nonlinear susceptibility as a direct test of the quadrupolar Kondo scenario for heavy fermion behavior, and apply it to the case of cubic crystal-field symmetry. Within a single-ion model we compute the nonlinear susceptibility resulting from low-lying $\Gamma_3 (5f^2)$ and Kramers $5f^3$ doublets. We find that nonlinear susceptibility measurements on single-crystal $UBe_{13}$ are inconsistent with a quadrupolar $(5f^2)$ ground-state of the uranium ion; the experimental data indicate that the low-lying magnetic excitations of $UBe_{13}$ are predominantly dipolar in character.

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There exist several metallic systems whose novel thermodynamic, magnetic and transport properties are not adequately described by conventional Fermi liquid theory; specific examples include the quasi-one dimensional conductors, [1] certain actinide heavy fermion materials [2, 3] and the layered cuprate superconductors. [4, 8] The search and characterization of non-Fermi liquid (NFL) fixed points is thus a topic of active research. [4–8] In this Letter we present an unambiguous experimental test of the quadrupolar Kondo effect, a model proposed by Cox [5] to characterize the NFL behavior observed in the cubic three-dimensional heavy fermion material $UBe_{13}$. We use the nonlinear susceptibility ($\chi_3$) as a direct probe of low-lying quadrupolar fluctuations, and compute its behavior within a single-ion model for the case of cubic crystal-field symmetry; these predictions are then compared to $\chi_3$ measurements on single-crystal $UBe_{13}$.

Most heavy fermion metals display a dramatic reduction in resistivity at low temperatures associated with the development of coherent quasiparticle propagation. $UBe_{13}$ is atypical, undergoing a superconducting transition directly from a normal state with a large incoherent resistivity [9] of order 140$\mu\Omega$ cm. The low-temperature dependences of the magnetic susceptibility [9] and the specific heat [9] are logarithmic in the approach to the superconducting transition. Resistance, [10] specific heat, [11], susceptibility [12] and magnetoresistance [13] measurements indicate that Fermi liquid behavior is restored at low temperatures under an applied pressure. Thus $UBe_{13}$ is a metal with a tuneable Fermi temperature ($T_F^*$) such that $T_F^* < T_c$ at ambient pressure. The microscopic physics underlying this suppressed, pressure-dependent [10, 13] and field-dependent [14] $T_F^*$ is a crucial issue for the characterization of the complex many-body ground-state of $UBe_{13}$.

Cox [4] has proposed that novel single-ion physics is responsible for the observed NFL behavior in $UBe_{13}$. The observation of a well-defined Schottky anomaly [15] at $T \sim 180K$ indicates that the uranium ion is in a local-moment rather than an intermediate valence regime; [10] however, it can assume either the $U^{4+}$ ($5f^2$) or the $U^{3+}$ ($5f^3$) nominal valence state, [3, 15] and neither quasi-elastic neutron scattering [17] nor photoemission [18, 19] measurements can unambiguously resolve the crystal-field assignments. In a cubic environment
Cox has identified a non-magnetic quadrupolar ($\Gamma_3$) ground-state of the $U^{4+}$ ion. He suggests that fluctuations within this non-Kramers doublet are overscreened by the conduction electrons; this quadrupolar Kondo effect then leads naturally to a non-Fermi liquid ground-state. In an alternate scenario, supported by NMR measurements consistent with a $U^{4+}$ valence state, the low-lying spin excitations are dipolar; the NFL behavior is attributed to the system’s proximity to a $T = 0$ quantum phase transition, analogous to that recently observed in $MnSi$ by Lonzarich and coworkers.

The nonlinear susceptibility ($\chi_3$) is an ideal test of the quadrupolar Kondo effect in $UBe_{13}$; it can distinguish unambiguously between a low-lying quadrupolar and Kramers crystal-field doublet. In the paramagnetic state, $\chi_3$ measures the leading nonlinearity in the magnetization

$$M = \chi_1 B + \frac{1}{3!} \chi_3 B^3 + \ldots$$

in the direction of the applied field ($B$); it was originally proposed as a direct probe of order-parameter fluctuations in spin glasses. Morin and Schmitt extended this technique to non-random spin systems, where they used the nonlinear susceptibility to study quadrupolar interactions in rare-earth intermetallic compounds.

The most general form for $\chi_3$ in a cubic environment is

$$\chi_3 = \chi_{311} + \Delta \chi_3 \Phi(\hat{b})$$

where $\Phi(\hat{b})$ is the cubic harmonic

$$\Phi(\hat{b}) = \frac{1}{2} \left[ 3(b_x^4 + b_y^4 + b_z^4) - 1 \right]$$

and the $b_i$ ($i = 1, 2, 3$) are the direction cosines of the field. The numerical factors in $\Phi(\hat{b})$ are chosen so that $\Delta \chi_3 \equiv \chi_{310} - \chi_{311}$; the “powder-averaged” component of the nonlinear susceptibility is $\bar{\chi}_3 = \chi_{311} + \frac{7}{20} \Delta \chi_3$.

The ratio of the two contributions to $\chi_3$ in (2) is qualitatively different for a quadrupolar and a magnetic ground-state. An isolated Kramers doublet results in a nonlinear
susceptibility $\chi_3 = -\frac{n^4}{3^7}$ that is isotropic, reflecting the negative curvature of the Brillouin function. For an isolated doublet with a quadrupolar moment $Q$, the field-dependent part of the Hamiltonian is $\hat{H} = \frac{1}{2}B^2 \hat{Q}_{ab} b_a b_b$, where $\hat{Q}_{ab} \propto [\hat{J}_{a}\hat{J}_{b} - \frac{1}{3}\delta_{ab} J(J+1)]$ is the quadrupole operator; \[20\] more explicitly

$$\hat{H} = \frac{QB^2}{2} \begin{bmatrix} q_{zz} & q_{xx} - iq_{yy} \\ q_{xx} + iq_{yy} & -q_{zz} \end{bmatrix}$$

where $q_{aa} = b_a^2 - \frac{1}{3}$ ($a = x, y, z$). Diagonalizing $H$, we find that the splitting of the quadrupolar doublet is given by

$$E_{T^\pm} = E_T \pm QB^2 \sqrt{\frac{\Phi(b)}{4!}}$$

which yields an anisotropic nonlinear susceptibility $\chi_3(\hat{b}) = \frac{Q^2}{2T} \Phi(b)$. In Cox’s model \[3\] for $UBe_{13}$, there is partial quenching of $Q$ by the conduction sea and

$$\Delta \chi_3 = \frac{Q^2}{2T} f(T/T_0) = \begin{cases} \frac{Q}{2T} & T >> T_0 \\ \frac{\alpha}{2T_0} \ln(T_0/T) & T << T_0 \end{cases}$$

where $T_0$ is the “Bethe ansatz” Kondo temperature; \[27\] the exact solution of the two-channel Kondo model \[27–29\] yields an asymptotic form for $f(x)$ with an associated value \[27\] $\alpha = 1/\pi^2 \approx 0.10$. Thus the quadrupolar Kondo hypothesis predicts a $\Delta \chi_3(\hat{b})$ that increases logarithmically with decreasing temperature.

In this idealized discussion we have neglected the Van Vleck contributions to $\chi_3$. In practice, a uranium atom in a magnetic configuration ($U^{3+}$) with a moment $\mu(H) = \mu_0 + \frac{B^2 A(b)}{3!}$ will exhibit a small $\Delta \chi_3 = \frac{4\mu_0 A(b)}{T}$ due to the nonlinearity in $\mu(H)$. Conversely, $\chi_3$ for a $U$ ion with a low-lying quadrupolar doublet ($U^{4+}$) will have an isotropic Van Vleck component ($\chi_3^{VV}$) that has a weak temperature dependence. Despite these additional contributions, we expect the anisotropic component of the nonlinear susceptibility

$$\frac{\Delta \chi_3(\hat{b})}{\chi_3} \equiv \frac{(\chi_3(\hat{b}) - \chi_3^{111})}{\chi_3^{111}}$$

to be small and nearly temperature-independent for a uranium atom with a dipolar ground-state; by contrast, $\frac{\Delta \chi_3(\hat{b})}{\chi_3}$ should be large and strongly temperature-dependent if the low-lying fluctuations are quadrupolar in nature.
Single-ion crystal-field calculations allow us to quantify the preceding discussion, and they have been performed for \( J = 4 \) and \( J = \frac{9}{2} \) manifolds of \( f \) orbits in a cubic environment. \[20\] The overall energy scale \((W)\) and the level ordering \((x)\) have been adjusted to fit the total entropy in the observed Schottky anomaly, \([15]\) and the resulting energy schemes are displayed in Figure 1. The associated \( \chi_3(\hat{b}) \) and \( \frac{\Delta \chi_3(\hat{b})}{\chi_3} \) are shown in Figure 2 and 3 respectively, where the moment has been normalized by a fit to the measured high-temperature susceptibility; \([30]\) the numerical solution of the two-channel Kondo model \([27]\) has been used to determine the effects of screening in Figure 3.

In order to test the quadrupolar scenario in \( UBe_{13} \), we measured \( \chi_3 \) along the three principal crystal axes of an oriented single crystal grown from \( Al \) flux. The superconducting transition temperature, a rough measure of the sample quality, was found by specific heat to be \( T_c = 0.75K \) for this crystal. Measurements were also performed on a a polycrystalline sample with \( T_c = 0.96 \). Finally a third sample, an unoriented single crystal with \( T_c = 0.48K \), was studied. For the \( \chi_3 \) measurements on the oriented crystal, the orientation was achieved with a precision of \( \pm 3 \) degrees; the data were taken as \( M \) vs. \( B \) at fixed temperatures up to 4 Tesla in a Quantum Design SQUID magnetometer. The deviation from linearity was only \( \sim 2\% \) at the lowest temperature and the highest field; it was attributed to the leading nonlinear contribution of \( M \) to \( \chi_3 \). The magnetization data were fit to the expression \( M = \chi_0 + \chi_1 B + \frac{1}{3!} \chi_3 B^3 \), where \( \chi_0 \) was included to avoid systematic errors associated with both trapped flux in the superconducting solenoid and a small \( \sim 10 \) ppm), ubiquitous ferromagnetic signal which saturated at \( \sim 1 \) Tesla. The temperature dependence of \( \chi_3 \) is displayed in Figure 4. The data were typically fit over the region \( 2 < B < 4 \) Tesla; in this field range, \( M/B - \chi_0 \) was always linear with respect to \( B^2 \). The linear part, \( \chi_1 \) (not shown), agrees well with published values. \([9]\) Figure 4 shows the nonlinear susceptibility measured in the 111, the 110, and the 100 directions. We note that the observed \( \chi_3 \) is both negative and monotonically decreasing with decreasing temperature; its magnitude is significantly greater than that predicted for the quadrupolar scenario (Figure 2a), but comparable in size at \( T \sim 10K \) with that expected from a dense concentration of only partially quenched \( U \).
magnetic doublets.

The observed magnitude and temperature dependence of $\chi_3$ was similar for the other two samples studied. The measurements on the polycrystalline sample (Figure 4) provide a crucial control on our results; here we expect the impurity level to be low given the relatively high observed value of $T_c$. The polycrystalline sample displays behavior in $\chi_3(T)$ similar to that of the orientation-averaged single-crystal. This result, combined with the large magnitude of $\chi_3$, exclude the possibility that the observed $\chi_3$ is due a residual background of magnetic impurities.

The measured anisotropy in the nonlinear susceptibility (Figure 4 inset) is small ($\Delta\chi_3(b)/\chi_3 \sim 3 \times 10^{-1}$) with a very weak temperature dependence; moreover it appears, at the level of one standard deviation, to have the opposite sign to that expected for the quadrupolar scenario (see Figure 3). These results strongly favor a magnetic model for the uranium ions in $UBe_{13}$ with a low Kondo temperature. One can try to reconcile these results with the quadrupolar scenario by invoking a large Van Vleck contribution ($\chi_{VV}^3$); it would result from virtual spin or valence fluctuations into higher lying multiplets of the $U$ ion. Such a term would scale approximately with $1/\Delta_x$, where $\Delta_x$ is the gap to the higher multiplets. In order for $\chi_{VV}^3 \sim \frac{1}{\Delta_x}$ to be much larger than $\Delta\chi_3 \sim \frac{1}{T_0}$ we need $\Delta_x < T_0$, a condition inconsistent with the initial assumption of a well-defined quadrupolar ground-state.

We now return to the possible origins of NFL behavior in $UBe_{13}$. Though a single-ion mechanism cannot be ruled out,[31] a canonical Kondo model for the magnetic $U$ ion results in a Fermi liquid ground-state. Furthermore one expects a system with a low-lying Kramers doublet to display a reduction in $\gamma \equiv \frac{c}{T}$ when $g\mu_B B \sim T_F^*$, in contrast to that observed[32] for $UBe_{13}$. Thus we conclude that these results cannot be explained within a single-ion picture and require a more sophisticated approach, possibly one that has an intrinsic pressure- and field-dependent $T_F^*$. We are tempted to identify the observed NFL behavior as a lattice phenomenon, possibly attributed to the system’s proximity to a $T = 0$ quantum phase transition.[45] Two different types of experiments would clarify this situation. First, thermodynamic and transport studies on $U_xTh_{1-x}Be_{13}$ would probe the behavior of dilute
$U$ atoms in the cubic environments, thereby indicating the importance of lattice effects. Second the nonlinear susceptibility as a function of pressure could be measured; we expect a shoulder in $\chi_3 \sim \frac{1}{T_0}$ that coincides with the observed development of Fermi liquid behavior in the resistance, specific heat, and the magnetoresistance.

In conclusion we have performed a series of nonlinear susceptibility measurements on the cubic heavy fermion system $UBe_{13}$. We find a small weakly temperature-dependent anisotropy, $\frac{\Delta \chi_3(\hat{b})}{\chi_3}$, in the nonlinear susceptibility that is difficult to reconcile with the quadrupolar Kondo scenario. These results provide strong evidence for a Kramers doublet ground-state in the $U^{3+}$ ions of $UBe_{13}$ and suggest a lattice mechanism for the observed non-Fermi liquid behavior. Further experiments have been proposed to test this conjecture.

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Fig. 1. The $J = 4$ quadrupolar and the (b) $J = \frac{9}{2}$ dipolar single-ion energy schemes for $UBe_{13}$ where the overall energy scale and the level ordering are determined by a two-parameter fit to the specific heat measurements of Felten et al. [15]
Fig. 2. The nonlinear susceptibility in the [100], [111] and [110] directions for (a) the $J = 4$ and (b) the $J = \frac{9}{2}$ energy schemes displayed in Figure 1.
Fig. 3. The anisotropic part of the nonlinear susceptibility for the $J = 4$ level scheme of Fig. 1. The low-temperature $\frac{\Delta \chi_3}{\chi_3}$ (dotted line) was determined by normalizing the single-ion anisotropy with the screening function $f(T/T_0)$ from the solution of the two-channel Kondo problem; [27] here the value $T_0 = 1.5K$ was extracted from the observed specific heat [15]. For the $J = \frac{9}{2}$ scheme of Figure 1 $\frac{\Delta \chi_3(b)}{\chi_3} = 0$. 
Fig. 4. The measured nonlinear susceptibility ($\chi_3(\hat{b})$) and $\Delta \chi_3(\hat{b}) / \chi_3$ (inset) for single-crystal and polycrystalline $UBe_{13}$. 