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 Γ_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 predominately *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 [2–6], and the layered cuprate superconductors [7,8]. 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 a simple 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 (χ_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 χ_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 *tunable* 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 [5] 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 $T \sim 180$ K indicates that the uranium ion is in a local moment rather than an intermediate valence regime [16]; however, it can assume either the U^{4+} ($5f^2$) or the U^{3+} ($5f^3$) nominal valence state [5,15], and neither quasielastic neutron scattering [17] nor photoemission [18,19] measurements can unambiguously resolve the crystal-field assignments. In a cubic environment Cox identified a nonmagnetic *quadrupolar* (Γ_3) ground state [5,20] 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 [21]. In an alternate scenario supported by NMR measurements [22] 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 [4,6], analogous to that recently observed in MnSi by Lonzarich [23].

The nonlinear susceptibility (χ_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, χ_3 measures the leading nonlinearity in the magnetization

$$M = \chi_1 B + (1/3!)\chi_3 B^3 + \cdots \quad (1)$$

in the direction of the applied field (B); it was originally proposed as a direct probe of order-parameter fluctuations in spin glasses [24]. Morin and Schmitt [25] extended this technique to nonrandom spin systems, where they used the nonlinear susceptibility to study quadrupolar interactions in rare-earth intermetallic compounds.

The most general form for χ_3 in a cubic environment is [26]

$$\chi_3 = \chi_3^{111} + \Delta\chi_3 \Phi(\hat{b}), \quad (2)$$

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

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

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

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$\Delta\chi_3 \equiv \chi_3^{100} - \chi_3^{111}$; the "powder-averaged" component of the nonlinear susceptibility is $\overline{\chi_3} = \chi_3^{111} + \frac{7}{20}\Delta\chi_3$.

The ratio of the two contributions to χ_3 in (2) is qualitatively different for a quadrupolar and a magnetic ground state. An isolated Kramers doublet [25] results in a nonlinear susceptibility $\chi_3 = -\mu_0^4/3T^3$ 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

$$\hat{H} = \frac{QB^2}{2}\begin{bmatrix} q_{zz} & q_{xx} - iq_{yy} \\ q_{xx} + iq_{yy} & -q_{zz} \end{bmatrix}, \qquad (4)$$

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

$$E^q_{\Gamma_\pm} = E_\Gamma \pm QB^2\sqrt{\frac{\Phi(\hat{b})}{4!}}, \qquad (5)$$

which yields an *anisotropic* nonlinear susceptibility $\chi_3(\hat{b}) = (Q^2/2T)\Phi(\hat{b})$. In Cox's model [5] for UBe_{13}, there is partial quenching of Q by the conducting sea and

$$\Delta\chi_3 = \frac{Q^2}{2T}f(T/T_0) = \begin{cases} \dfrac{Q}{2T}, & T \gg T_0, \\ \dfrac{\alpha Q}{2T_0}\ln(T_0/T), & T \ll T_0, \end{cases} \qquad (6)$$

where T_0 is the "Bethe ansatz" Kondo temperature [27]; the exact solution of the two-channel Kondo model [28,29] 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 χ_3. In practice, a uranium atom in a magnetic configuration (U^{3+}) with a moment $\mu(H) = \mu_0 + B^2A(\hat{b})/3!$ will exhibit a small $\Delta\chi_3 = 4\mu_0A(\hat{b})/T$ due to the nonlinearity in $\mu(H)$. Conversely, χ_3 for a U ion with a low-lying quadrupolar doublet (U^{4+}) *will* have an *isotropic* Van Vleck component (χ_3^{VV}) that has a weak temperature dependence. Despite these additional contributions, we expect the anisotropic component of the nonlinear susceptibility

$$\frac{\Delta\chi_3(\hat{b})}{\chi_3} \equiv \frac{\chi_3(\hat{b}) - \chi_3^{111}}{\chi_3^{111}} \qquad (7)$$

to be *small* and nearly temperature independent for a uranium atom with a dipolar ground state; by contrast, $\Delta\chi_3(\hat{b})/\chi_3$ 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 Fig. 1. The associated $\chi_3(\hat{b})$ and $\Delta\chi_3(\hat{b})/\chi_3$ are shown in Figs. 2 and 3, respectively, where the moment has been normalized by a fit to the measured high-temperature susceptibility [30];

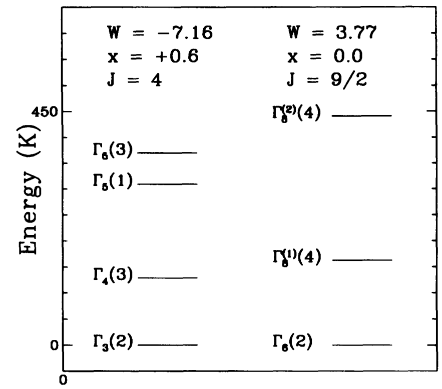

FIG. 1. The $J = 4$ quadrupolar and the $J = \frac{9}{2}$ dipolar single-ion energy schemes for UBe_{13} where the overall energy scale and the level ordering are determined by a two-parameter fit to the specific heat measurements of Felten *et al.* [15].

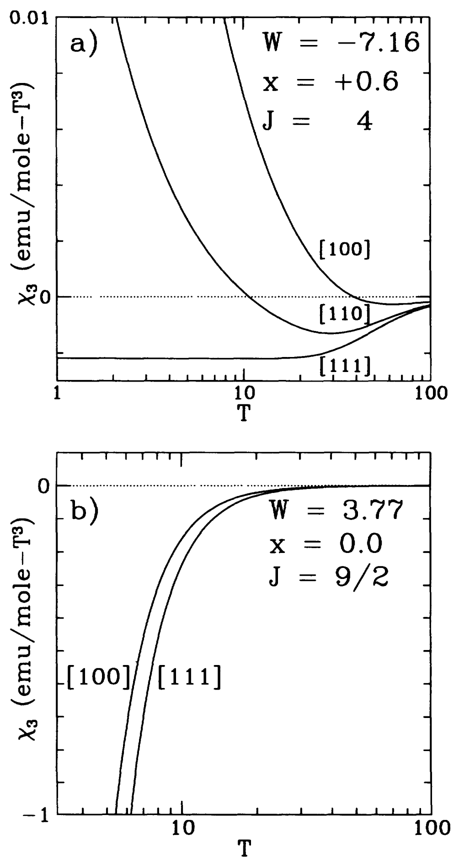

FIG. 2. The nonlinear susceptibility in the [100], [111], and [110] directions for (a) the $J = 4$ and (b) the $J = \frac{9}{2}$ energy schemes displayed in Fig. 1.

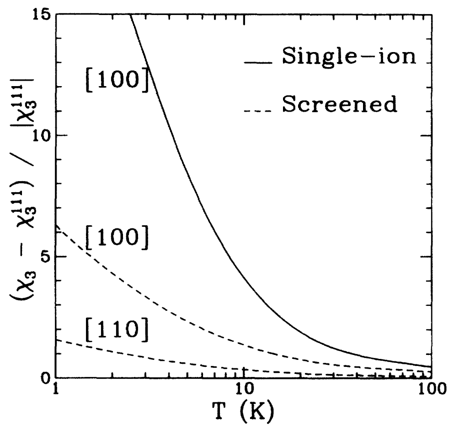

FIG. 3. The anisotropic part of the nonlinear susceptibility for the $J = 4$ level scheme of Fig. 1. The low-temperature $\Delta\chi_3/\chi_3$ (dotted line) was determined by normalizing the single-ion anisotropy with the screening function $f(T/T_0)$ from the solution of the two-channel Kondo problem [27]; here the value $T_0 = 1.5$ K was extracted from the observed specific heat [15]. For the $J = \frac{9}{2}$ scheme of Fig. 1 $\Delta\chi_3(\hat{b})/\chi_3 = 0$.

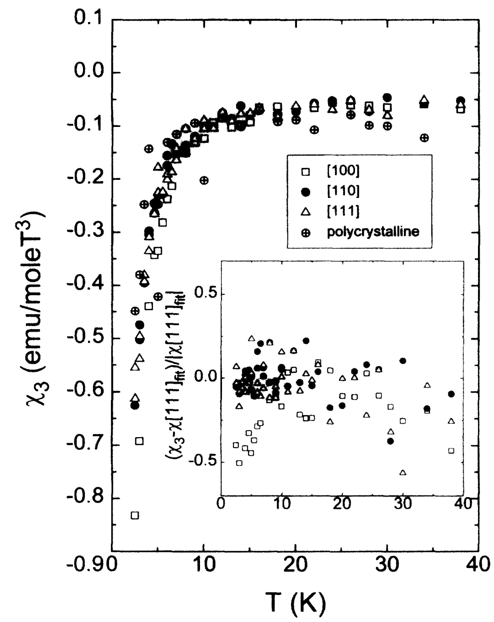

FIG. 4. The measured nonlinear susceptibility $[\chi_3(\hat{b})]$ and $\Delta\chi_3(\hat{b})/\chi_3$ (inset) for single-crystal and polycrystalline UBe_{13}.

the numerical solution of the two-channel Kondo model [27] has been used to determine the effects of screening in Fig. 3.

In order to test the quadrupolar scenario in UBe_{13}, we measured χ_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 $T_c = 0.75$ K for this crystal. Measurements were also performed on a polycrystalline sample with $T_c = 0.96$ K. Finally, a third sample, an unoriented single crystal with $T_c = 0.48$ K, was studied. For the χ_3 measurements on the oriented crystal, the orientation was achieved with a precision of $\pm 3°$; the data were taken as M vs B at fixed temperatures up to 4 T 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 χ_3. The magnetization data were fit to the expression $M = \chi_0 + \chi_1 B + (1/3!)\chi_3 B^3$, where χ_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 T. The temperature dependence of χ_3 is displayed in Fig. 4. The data were typically fit over the region $2 < B < 4$ T; in this field range, $M/B - \chi_0$ was always linear with respect to B^2. The linear part χ_1 (not shown) agrees well with published values [9]. Figure 4 shows the nonlinear susceptibility measured in the 111, 110, and 100 directions. We note that the observed χ_3 is both *negative* and monotonically *decreasing* with decreasing temperature; its magnitude is significantly greater than that predicted for the quadrupolar scenario [Fig. 2(a)], but comparable in size at $T \sim 10$ K with that expected from a dense concentration of only partially quenched U magnetic doublets.

The observed magnitude and temperature dependence of χ_3 was similar for the other two samples studied. The measurements on the polycrystalline sample (Fig. 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 χ_3, exclude the possibility that the observed χ_3 is due a residual background of magnetic impurities.

The measured anisotropy in the nonlinear susceptibility (Fig. 4, inset) is small $[\Delta\chi_3(\hat{b})/\chi_3 \sim 3 \times 10^{-1}]$ 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 Fig. 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 (χ_3^{VV}); 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 Δ_x is the gap to the higher multiplets. In order for $\chi_3^{VV} \sim 1/\Delta_x$ to be much larger than $\Delta\chi_3 \sim 1/T_0$ 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 $\gamma \equiv c_v/T$ 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 [4,6]. 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 [33], thereby indicating the importance of lattice effects. Second, the nonlinear susceptibility as a function of pressure could be measured; we expect a shoulder in $\chi_3 \sim 1/T_0^3$ that coincides with the observed development of Fermi liquid behavior in the resistance [10], the specific heat [11], and the magnetoresistance [13].

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, $\Delta\chi_3(\hat{b})/\chi_3$, 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}. Since coherence effects cannot change the dipolar character of the low-energy excitations of UBe_{13}, these results suggest a lattice mechanism for the observed non-Fermi-liquid behavior. Further experiments have been proposed to test this conjecture.

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