# Quadrupolar Kondo Effect in Uranium Heavy-Electron Materials?

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(Received 5 June 1987)

The possibility of an electric quadrupole Kondo effect for a non-Kramers doublet on a uranium (U) ion is a cubic metallic host is demonstrated by model calculations showing a Kondo upturn in the resistivity, universal quenching of the quadrupolar moment, and a heavy-electron anomaly in the electronic specific heat. With inclusion of excited crystal-field levels, some of the unusual magnetic-response data in the heavy-electron superconductor $UBe_{13}$ may be understood. Structural phase transitions at unprecedented low temperatures may occur in U-based heavy-electron materials.

PACS numbers: 71.28.+d, 71.70.Ej, 72.15.Qm, 75.20.Hr

Heavy-electron materials have received much attention because of their interesting many-body physics [e.g., giant electronic specific heats $c_{el}(T)$ ($T$ being the temperature) unaccounted for by simple one-electron theory] and exotic low-temperature magnetic and superconducting instabilities.[1,2] A central question of the field is, "How universal are the phenomena?" Specifically, consider $CeCu_2Si_2$ and $UBe_{13}$. Both compounds are superconductors with nearly identical $c_{el}$ curves from 1 to 10 K, and corresponding effective Fermi temperatures of about 10 K. The resistivities of the two materials [$\rho(T)$] are very similar, with negative $d\rho/dT$ above about 10 K.[1]

However, $UBe_{13}$ and $CeCu_2Si_2$ differ substantially in their magnetic response; e.g., $c_{el}(T)$ is nearly field independent for $UBe_{13}$ (up to $\simeq 10$ T), while $CeCu_2Si_2$ shows about a 20% drop in comparable fields.[1,3] In addition, the magnetic neutron-scattering cross section has a quasielastic peak at about 1 meV for $CeCu_2Si_2$ (corresponding to the Fermi temperature),[4] while the peak in $UBe_{13}$ is at 15 meV.[5]

In this paper, I propose that the above disparities may arise from differing underlying symmetries for U and Ce. In particular, I consider an Anderson model[6,7] for a single U site which leads to the novel possibility of an electric quadrupole Kondo effect. This is the central result of this paper: weak field dependence of measured properties and a missing quasielastic line immediately follow. Kondo anomalies appear in $\rho(T)$, $c_{el}(T)$, the quadrupolar susceptibility $\bar{\chi}_Q(T)$, and the magnetic (van Vleck) susceptibility. Moreover, $\bar{\chi}_Q(T)$ is a universal function of $T/T_h$ ($T_h$ is a characteristic Kondo scale) which logarithmically diverges for $T \rightarrow 0$. This non-Fermi-liquid behavior may yield structural instabilities at unprecedented low temperatures in U-based heavy-electron materials.

In the Anderson-model picture, Ce heavy-electron behavior is attributed to the Kondo effect (quenching of the magnetic moment of the lone Ce $4f$ electron by antiferromagnetic interaction with conduction electrons, with concomitant formation of a narrow heavy-electron resonance). The characteristic energy scale for quenching the spin is $k_B T_0$, and $T_0$ serves as a degeneracy temperature and a measure of the fluctuation rate of the local moment. Thus, the neutron-scattering quasielastic peak is near $k_B T_0$.

Gross heavy-electron properties for Ce compounds [enhanced $c_{el}(T)$ and magnetic susceptibility $\chi(T)$, negative $d\rho/dT$ at higher temperatures, quasielastic peak in the neutron-scattering cross section] are accounted for in a single-impurity Anderson model.[2,8] Alloying experiments on $(Ce_xLa_{1-x})Pb_3$ show the specific heat normalized to Ce content to be the same above 2 K for several $x$ between 0 and 1.0.[9] It is only at low temperatures for the full lattice that coherence (Bloch's theorem) is manifest with $\rho(T)$ going to zero, and that intersite correlations play a role (as evidenced by momentum dependence in the magnetic neutron-scattering cross section, magnetic order, and superconductivity).

For a U ion with a nominally stable $5f^2$ configuration at a cubic-symmetry site, it is possible to have a low-lying nonmagnetic quadrupolar doublet which is quenched. The heavy-electron behavior is then associated with local quadrupolar fluctuations at an energy scale $k_B T_h$, defined more precisely below.

The data for dilute U-based intermetallic alloys is far less substantial[10-12] than for Ce, but recent work offers hope for understanding the gross features of concentrated U systems from the dilute limit.[13]

The model U site has these essential features: (i) A stable $5f^2$, $J=4$ Hund's-rule ground state within the $LS$ coupling scheme is assumed at a site of cubic symmetry (as per $UBe_{13}$). Rigorously, an intermediate-coupling description is necessary for actinide ions; however, the ions lie close to the $LS$ limit.[14,15] (ii) The crystal-field–split $J=4$ multiplet has a ground-state $\Gamma_3$ nonmagnetic doublet (see Table I) at energy $\epsilon_f$. While excluded by the point-charge model,[16] stable $\Gamma_3$ levels have been observed in many cubic praseodymium intermetallics (with low-lying $4f^2$ rather than $5f^2$).[17] (iii) Only a $\Gamma_4$ triplet excited level is retained within the $J=4$ multiplet, at energy $\epsilon_f+\Delta$. (iv) A $5f^1$ configuration lies above the $\Gamma_3$ level by $|\epsilon_f|$; all other configurations are neglected. (v) Hybridization of the $f$ levels with the conduction band (of width $D$) is expressed in terms of the matrix element

$$\langle k\alpha;5f^1\phi\,|\,H_{hyb}\,|\,5f^2\gamma\rangle = VN_{sites}^{-1/2}\Lambda(\alpha;\gamma;\phi), \qquad (1)$$

TABLE I. Ionic cubic crystal-field split states for the model uranium impurity (after Ref. 16). The fifth column gives the projected electric-quadrupole moment. The $J=\frac{5}{2}$ results may also be used for conduction partial-wave states.

| $J$ | State | Form | $\langle J_z\rangle$ | $\langle J_z^2-J(J+1)\rangle$ |
|---|---|---|---|---|
| 4 | $\lvert\Gamma_3+\rangle$ | $0.54(\lvert 4\rangle+\lvert -4\rangle)-0.65\lvert 0\rangle$ | 0 | +8.0 |
| 4 | $\lvert\Gamma_3-\rangle$ | $0.71(\lvert 2\rangle+\lvert -2\rangle)$ | 0 | −8.0 |
| 4 | $\lvert\Gamma_4\pm\rangle$ | $0.35\lvert\mp 3\rangle+0.94\lvert\pm 1\rangle$ | ±0.5 | −14.0 |
| 4 | $\lvert\Gamma_4 0\rangle$ | $0.71(\lvert 4\rangle-\lvert -4\rangle)$ | 0 | +14.0 |
| $\frac{5}{2}$ | $\lvert\Gamma_7\pm\rangle$ | $0.41\lvert\mp\frac{5}{2}\rangle-0.91\lvert\pm\frac{3}{2}\rangle$ | ±0.83 | 0 |
| $\frac{5}{2}$ | $\lvert\Gamma_8\pm 2\rangle$ | $0.91\lvert\pm\frac{5}{2}\rangle+0.41\lvert\mp\frac{3}{2}\rangle$ | ±1.83 | +8.0 |
| $\frac{5}{2}$ | $\lvert\Gamma_8\pm 1\rangle$ | $\lvert\pm\frac{1}{2}\rangle$ | ±0.5 | −8.0 |

where $k$ indexes conduction wave number, and $\alpha$, $\gamma$, and $\phi$ are shorthand for the conduction, $f^1$, and $f^2$ angular-momentum states in the cubic field (see Table I for further explanation). $\lambda(\alpha;\gamma;\phi)$ is a group-theoretic factor containing a Clebsch-Gordon coefficient in the cubic basis, which has been calculated numerically. The one-electron hybridization matrix element $V$ is replaced in favor of $\Gamma=\pi N(0)V^2$, $N(0)$ the Fermi-level density of conduction states. I do not expect realistic extensions of assumptions (i)-(iv) to modify qualitatively any conclusions presented here.[18]

This model can explain the $UBe_{13}$ neutron-scattering data. Having no spin moment, the $\Gamma_3$ level for the U site will give no quasielastic neutron-scattering line. The peak in the magnetic neutron-scattering cross section could then arise from inelastic magnetic-dipole transitions between the $\Gamma_3$ and $\Gamma_4$ levels with $\Delta$ being roughly 15 meV (the splitting may be renormalized by hybridization). The observed Schottky anomaly at 70 K in $c_{el}(T)$ for $UBe_{13}$ is in accord with an inelastic origin for the 15-meV peak, as noted before.[19] Crystal fields have been previously reported in only one uranium intermetallic.[20]

For $\Gamma=0$, the model also yields the following: (1) $\chi(T)$ is dominated by the van Vleck contribution of the $\Gamma_3$-$\Gamma_4$ transitions. For $\Delta=15$ meV, $\chi(0)$ is estimated as 0.013 emu/mol, to be compared with the experimental values of 0.012–0.016 emu/mol for $UBe_{13}$.[1] Consistent with the explanation of $\chi(0)$ are the facts (a) that the observed neutron-scattering cross section integrates to give 80% of the measured static susceptibility[5] and (b) that data for $\chi(T\to 0)$ change little with pressure compared to the specific heat[21] (which suggest that they arise from different mechanisms). A model requiring quenching of a $5f^3$ magnetic Kramers doublet[19] would lead to a quasielastic line and similar pressure dependence in $\chi(T)$ and $c_{el}(T)/T$. (2) The model gives little magnetic-field dependence below $(0.2\text{–}0.3)\Delta/\mu_B$, which could be of order 30–50 T.

A limiting case (the 3-7-8 model) clarifies the origin of the quadrupolar Kondo effect: Take $\Delta$ to infinity, omit the ($5f^1$, $J=\frac{5}{2}$, $\Gamma_s$) levels, and omit the conduction $j=\frac{7}{2}$ partial-wave states. According to group theory, the remaining ($5f^1$, $J=\frac{5}{2}$, $\Gamma_7$) and ($5f^2$, $J=4$, $\Gamma_3$) levels mix only via the conduction $j=\frac{5}{2}$, $\Gamma_8$ partial waves.

Applying a canonical transformation[22] to the 3-7-8 model yields an effective exchange interaction between pseudospin-$\frac{1}{2}$ electric-quadrupole moments of the form

$$H_{ex}=-2J_{ex}\boldsymbol{\sigma}_3\cdot[\boldsymbol{\sigma}_8(0)+\boldsymbol{\sigma}_{\bar{8}}(0)], \tag{2}$$

where $\boldsymbol{\sigma}_3$ is a pseudospin-$\frac{1}{2}$ matrix for the $\Gamma_3$ quadrupole, $\boldsymbol{\sigma}_8$ ($\boldsymbol{\sigma}_{\bar{8}}$) are pseudospins formed from the $\Gamma_8+2$, $\Gamma_8+1$ ($\Gamma_8-2$, $\Gamma_8-1$) partial waves (see Table I), and $J_{ex}$ is proportional to $\Gamma/\pi\epsilon_f N(0)$, which is negative. Equation (2) has the form of a two-channel antiferromagnetic Kondo problem; to my knowledge, this is only the second possible realization of the multichannel model.[23]

The thermodynamics of this two-channel problem are obtainable through the Bethe-*Ansatz* approach,[24] but dynamics and the extension of the model to excited crystal-field levels are presently beyond this method. Consequently, I have adopted a numerical self-consistent perturbation-theory approach which has proven quite successful for calculations of thermodynamics, transport coefficients, and excitation spectra for the single-site Ce problem.[8] Extensive descriptions of that method appear elsewhere.[25,26] Some calculations may be performed analytically for low temperatures and frequencies.[27] In the presence of the excited $\Gamma_4$ level, the analytically obtained low-energy behavior maps onto the 3-7-8 model described above.

Figure 1 shows $\rho(T)$ calculated for the 3-7-8 model normalized to its analytically estimated zero-temperature value. The Kondo effect is clearly manifested in the negative slope.

Also shown in Fig. 1 is the temperature-dependent effective moment $\mu_Q^2(T)=T\tilde{\chi}_Q(T)$, where $\tilde{\chi}_Q(T)$ is the quadrupolar susceptibility of the $\Gamma_3$ doublet. $\mu_Q^2$ is normalized to unity for an isolated moment. This figure demonstrates (i) the quenching of the quadrupole moment (it vanishes for zero temperature), and (ii) the effective moment is a universal function of $T/T_h$, where $T_h$ is proportional to $D\exp[1/2N(0)J_{ex}]$ and defined operationally here from $\rho(T_h)/\rho(0)=\frac{1}{2}$. Such universality is well known for the usual spin Kondo effect.[28]

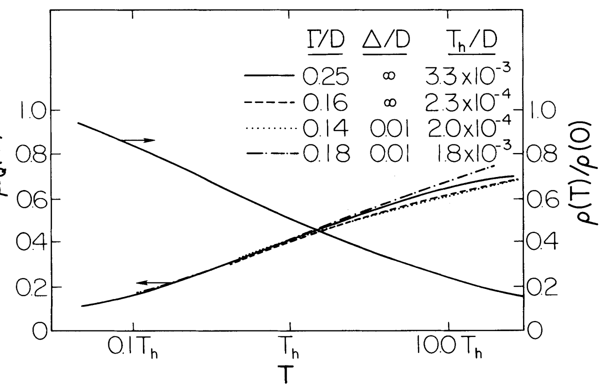


FIG. 1. Resistivity $[\rho(T)]$ and effective moment $[\mu_Q^2(T)]$ of the model U ion. The upper two table entries correspond to the 3-7-8 model. For the lower two table entries, the temperature-dependent occupancy of the $\Gamma_3$ level has been divided out of $\mu_Q^2(T)$.

Note that inclusion of the excited $\Gamma_4$ level yields $\mu_Q^2(T)$ curves indistinguishable from those of the 3-7-8 model at low temperatures. Variational methods have been used previously to demonstrate the stability of the singlet (quenched moment) ground state in the absence of a crystal field.[29]

Figure 2(a) shows the absorptive part of the dynamic van Vleck susceptibility $\chi_{vV}''(\omega,T)$ associated with $\Gamma_3 \rightarrow \Gamma_4$ transitions, which is directly related to the magnetic neutron-scattering cross section. The shape and temperature dependence for the larger $\Gamma$ value agree qualitatively with data for $UBe_{13}$.[30] Figure 2(b) displays the associated static susceptibility $\chi_{vV}(0)$, which shows temperature dependence well below $\Delta/k_B$. This is in rough agreement with experiment (filled squares and filled lozenges on the plot).[1] However, $\chi_{vV}(0)$ is reduced, in a parameter-dependent fashion, by typically 20%–40% over the zero-$\Gamma$ limit.

Figure 3 displays calculated $c_{el}(T)$ curves for various parameter values. The dominant feature is the Schottky anomaly of the $\Gamma_4$ level. The low-temperature shoulders visible in Fig. 3 for the higher two $\Gamma$ values are tentatively associated with the quadrupolar Kondo anomaly ($T_h$ being far too small to observe the anomaly for $\Gamma = 0.11$). Numerical limitations for $T \rightarrow 0$ render the peak height and position of these anomalies imprecise.

Quantitative agreement with data for $UBe_{13}$ might be possible with inclusion of an excited ($5f^2$, $J=4$, $\Gamma_5$) level. This adds to the entropy and van Vleck susceptibility.[31]

It is important to note that, for $\Gamma \rightarrow 0$, a stable $\Gamma_3$ level may lead to collective Jahn-Teller (JT) structural instabilities for arbitrary quadrupole-strain coupling strength.[32] The Kondo effect quenching of the quadrupole moment suppresses the JT instability in a manner analogous to the suppression of magnetic order in spin Kondo systems.[26] However, the low-energy two-channel

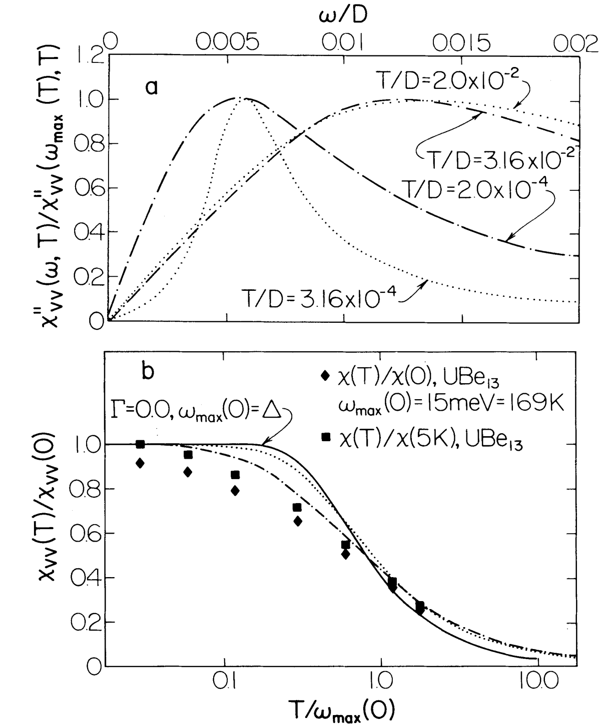


FIG. 2. van Vleck susceptibility (a) dynamic-$\chi_{vV}''(\omega,T)$; (b) static-$\chi_{vV}(T)$ for the model U ion. Line types are the same as Fig. 1. In (a) note that hybridization shifts the peak position from $\Delta$ and introduces strong temperature-dependent broadening of the $\Gamma_4$ level. In (b), $\omega_{max}(0)$ is the peak position of the zero-temperature dynamic susceptibility, equal to $\Delta$ for $\Gamma \rightarrow 0$.

character of this problem leads to non-Fermi-liquid behavior: $\chi_Q(T)$ and $c_{el}(T)/T$ diverge weakly as $\ln(T_h/T)/T_h$. (This divergence may be inferred from Bethe-

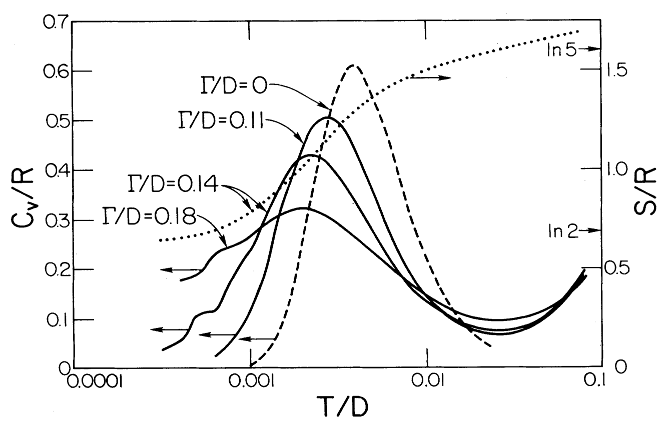


FIG. 3. Specific heat for the model U ion. Note that the Schottky anomaly broadens and shifts downwards as $\Gamma$ is raised from zero. The ratio of the peak temperature to $\omega_{max}(0)$ stays roughly constant. The right-hand axis refers to the entropy (dotted curve).

*Ansatz* treatments[24] and from the approach used in this work). As a result, the JT transition temperature may be reduced from the $\Gamma=0$ value of $T_{\rm JT0}$ to a temperature of order $T_h \exp(-T_h/T_{\rm JT0}) \ll T_h$.

Some data for $UBe^{13}$ are apparently and notably inconsistent with my model. The magnetoresistance has a field dependence reminiscent of the pure spin Kondo effect.[33] The muon Knight shift below the superconducting transition temperature $T_c$ for pure $UBe_{13}$ is strongly suppressed as might be expected from BCS theory.[34] In my model, the Knight shift arises from transferred coupling to $\chi_{\rm vV}(T)$, which should show little change below $T_c$. [Note: neutron form factor[35] and $^9$Be nuclear-magnetic-resonance measurements[36] of $\chi(T)$ do not show appreciable change below $T_c$.]

It is a pleasure to acknowledge useful conversations with G. Aeppli, N. E. Bickers, W. G. Clark, S. L. Cooper, P. Fulde, J. Herbst, J. Hirsch, M. Klein, M. B. Maple, D. E. MacLaughlin, L. J. Sham, S. Shapiro, F. Steglich, and J. W. Wilkins. This research (and computer time at the San Diego Supercomputer Center) was supported by National Science Foundation Grant No. DMR-85-14195, and by National Science Foundation Grant No. PHY-82-17853 (supplemented by funds from the U.S. National Aeronautics and Space Administration).

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