Crystal Field Model of the Magnetic Properties of URu_2Si_2

P. Santini
Institut de Physique Théorique, Université de Lausanne, CH-1015 Lausanne, Switzerland

G. Amoretti
Dipartimento di Fisica, Universitá di Parma, I-43100 Parma, Italy
(Received 22 December 1993)

We propose a model based on quadrupolar ordering of localized f electrons to explain the 17.5 K phase transition of URu_2Si_2. The tiny staggered magnetic moment observed by neutron scattering is interpreted as a weak secondary effect associated to the symmetry-breaking perturbation. The model is able to account for the observed behavior of the linear and nonlinear susceptibilities throughout the transition. A connection with the quadrupolar Kondo theory is proposed.

PACS numbers: 75.10.Dg, 75.20.Hr, 75.30.Cr

In spite of an intense experimental effort, the rich magnetic properties of U intermetallics are far from being understood theoretically. Because of the complexity of the Hamiltonian of these systems, including intraion interactions, crystal electric field (CEF) terms, hybridization processes, and interion interactions of various types, it is usually difficult to individualize the minimal microscopic model containing the essential of the physics, even at a qualitative level. Although the compound URu_2Si_2 is usually regarded as a heavy-fermion system, many of its properties can also be explained in terms of local moments in a CEF. The electronic specific heat presents a maximum at ~30 K [1,2] which can be interpreted as a CEF Schottky anomaly. At a comparable temperature scale $T_M \sim 50$ K, maxima are observed in the susceptibility, in the resistivity, and in the thermal expansion [1–5]. Although these features could be attributed to the onset of a low temperature coherent Kondo-lattice regime below T_M, the connection with the conventional Kondo physics is not immediate. In fact, the absence of a transverse magnetic response indicates that the spin-flip processes necessary for the Kondo effect are pushed up to high energies. A simpler alternative explanation can be given in terms of CEF. For instance, the resistivity curve is very similar to the one observed in some rare-earth compounds, and explained in terms of scattering of conduction electrons by localized and dispersive spin fluctuations [6,7]. Actually, strongly dispersive excitations, polarized along the c axis, are observed in URu_2Si_2 by neutron scattering, and interpreted as transitions between two CEF singlets [8,9]. Also, the same mechanism of scattering by CEF excitons well accounts for the moderate mass enhancement ($\gamma \sim 50$ mJ/mol K^2) observed at low T in URu_2Si_2 [10]. A further indication of CEF-like physics is given by the sharp metamagnetic transitions at about 35–40 T [11,12].

The main problems with the CEF model arise in connection with the 17.5 K phase transition. This transition has been attributed to a type-I antiferromagnetic ordering along the c axis, with an ordered moment of $\sim 0.03\mu_B$ [1,4,8,9,13]. However, so small a value cannot be reconciled with the large anomalies observed at T_N in many quantities, such as specific heat [1,2], linnear [2,14] and nonlinear [14] susceptibilities, resistivity, and thermal expansion [5]. Moreover, the transition is associated with a big change in magnetic dynamics, since above T_N neutron peaks broaden considerably. Although a singlet-singlet CEF model describes quite well the spin excitations below T_N, it fails to explain the properties of URu_2Si_2 if an antiferromagnetic order parameter is assumed [9,15]. The most straightforward explanation of this inconsistency is that the fundamental order parameter producing the anomalies is not the tiny staggered moment, this latter being only a secondary effect associated to the symmetry-breaking perturbation. This picture, proposed already in Ref. [14], is supported by the unconventional temperature dependence of the staggered moment, $\mu \sim (T_N - T)^{1/2}$ over a very wide temperature range [16,17]. This dependence, which is not order-parameter-like, could not be reconciled with the strong and conventional temperature dependence of the gap [9], if the gap opening were controlled by the staggered magnetic molecular field (MF).

In this Letter, we propose an interpretation of the phase transition based on quadrupolar ordering of localized f electrons. Multipolar interactions in metallic $4f$ and $5f$ systems are not small, usually. They are mediated by conduction (k) electrons through direct or virtual-mixing k-f processes [18,19]. The various k-f multipole processes are the result of an algebraic expansion, and their amplitude is not small. As a starting point, we deduce the possible CEF level schemes compatible with the observed high-T ($T > T_N$) specific heat and susceptibility properties, interpreted as CEF effects. We stress that we are not claiming that URu_2Si_2 is merely a CEF system such as, for instance, UO_2. We are just assuming that the CEF Hamiltonian is a reasonable zeroth order approximation, and that k-f processes, are not so important to completely overwhelm the CEF behavior, in particular for the low-lying singlets. In any case, we do not expect to obtain more than a semiquantitative agreement. We assume U^{4+} ionization and a $^3H_4$ Hund's rule ground multiplet. The

0031-9007/94/73(7)/1027(4)$06.00

Hamiltonian includes the CEF contribution and the multipolar interaction decoupled in mean-field

$$H = \sum_{k,q} B_k^q O_k^q + \lambda Q \langle Q \rangle , \quad (1)$$

where $O_k^q [(k,q) = (2,0), (4,0), (4,4), (6,0), (6,4)]$ are Stevens operator equivalents for $J = 4$ and B_k^q are the corresponding CEF parameters. The eigenstates of the tetragonal CEF Hamiltonian are defined in Table I. The splittings between $\Gamma_{t1}^1, \Gamma_{t2}, \Gamma_{t1}^2$ and the value of ϵ are linked by a constraint [20]. Q is the symmetrized operator equivalent representing one of the possible multipolar order parameters, which have been deduced in Ref. [13]; $\langle Q \rangle$ is its self-consistent mean value; λ is the MF constant, representing the Fourier-transformed multipolar interaction at the (unknown) ordering wave vector. To calculate the nonlinear susceptibility χ_3, defined as in Ref. [14], we add an external magnetic field H along c, which gives a Zeeman term $-g\mu_B J_z H$, and a mean-field RKKY interaction term, $-N_A g^2 \mu_B^2 \lambda_0 J_z \langle J_z \rangle$. If the order is not dipolar, this latter is effective only in the presence of the external field, producing a finite $\langle J_z \rangle$. The constant λ_0 is the same which shifts the inverse susceptibility in the Curie-Weiss law, and is proportional to the Fourier transform at $q = 0$ of the RKKY couplings. χ_3 is derived by subtracting the moment induced by an external field $H = 2$ T, and the corresponding linear contribution $\mu_{\text{lin}} = \chi_H$. This calculation demands imposing two linked self-consistency conditions due to the two MF interaction terms (multipolar and RKKY). By using a parametrization acting directly on the CEF spectrum, we will first individualize three possible CEF spectral schemes, associated to three quite restricted classes of B_k^q sets. For any given set, λ_0 will be chosen as the optimal translation of the inverse susceptibility. The multipolar MF constant λ will be fixed by the neutron scattering data, as we will describe later.

A strong constraint on the possible spectral schemes is given by the weak transversal magnetic response. Single crystal neutron inelastic scattering measurements do not detect any transverse excitation up to 33 meV [8]. Although the two doublets, which supply the transversal matrix elements, could be so broadened not to be easily detected in an energy-resolved measurement, the weak and flat transversal susceptibility and magnetization curves support a bare CEF level scheme with the two doublets lying well above the singlets. Moreover, entropy considerations indicate that no more than three singlets can be settled in the low energy window. By properly inverting the CEF eigenproblem [21], we express the unintuitive B_k^q parameters in terms of four spectral splittings and of the value of ϵ. In this way we can individualize much more easily and effectively the possible CEF level schemes. We find that there are only three kinds of low-lying ($E \lesssim 12$ meV) singlet groups compatible with both doublets being high lying ($E \gtrsim 30$ meV). The first one (scheme A) is the group $\Gamma_{t1}^1 - \Gamma_{t2} - \Gamma_{t1}^2$. The second one (scheme B) is the group $\Gamma_{t4} - \Gamma_{t1}^1 - \Gamma_{t2}$; the third one (scheme C) is the group $\Gamma_{t3} - \Gamma_{t1}^1 - \Gamma_{t2}$. Notice that one can pass from a set of sates of type C to a corresponding set of type B by a rotation of 45° around the c axis. In schemes B and C the parameter ϵ is quite constrained, since one has to choose $|\epsilon| \gtrsim 0.65$ (and, of course, $|\epsilon| < 1/\sqrt{2}$ from normalization). A further characterization is possible by using the c axis susceptibility data. All the singlet groups are compatible with a susceptibility maximum at 50 K: with scheme A one must use $|\epsilon| \lesssim 0.3$ and a splitting $\Gamma_{t1}^1 - \Gamma_{t2}$ around 7.5 meV; with schemes B and C, by letting the levels in the sequence above, and with a certain freedom left for the positions of Γ_{t1}^1 and Γ_{t2}. In all cases, the value of λ_0 we derive is negative, indicating antiferromagnetic interactions. This is expected from the antiferromagneticlike dispersion of the excitations and the negative Curie-Weiss temperature.

By using scheme A in the configuration which gives a maximum in χ at ~50 K, one gets at the same time a maximum in the specific heat at ~30 K, but the peak value for this latter is too high ($\gtrsim 6$ J/mole K against an experimental value of ~4.6). Besides J_z, these three singlets can support order parameters of type $J_x J_y (J_x^2 - J_y^2)$, and $J_x J_y J_z (J_x^2 - J_y^2)$. However, with none of these order parameters did we succeed in reproducing the experimental features, no matter the value chosen for λ.

We pass now to analyzing schemes B and C. In scheme B the multipoles $J_x J_y$ and $J_z (J_x^2 - J_y^2)$, and in scheme C the multipoles $(J_x^2 - J_y^2)$ and $J_z J_x J_y$, are the best candidates as order parameters. In fact, all these operators have vanishing diagonal matrix elements, but they connect the two singlets of type $|M_J = \pm 2\rangle$ with the ones of type $|M_J = \pm 4\rangle$. One obtains then more naturally multipole rather than dipole ordering, since at low T multipole fluctuations are low energy processes, whereas dipole fluctuations are high energy ones. If we use the information obtained from the specific heat and susceptibility maxima we deduce that Γ_{t1}^1 and Γ_{t2} are located roughly between ~3.5 and 4.5 meV and between 7 and 11 meV, respectively. No further constraints on ϵ are needed. We have in this way individualized quite a restricted range of variability for the three spectral

TABLE I. Tetragonal CEF states for $J = 4$. The energies corresponding to the parameters given in the text are given.

State	Form	E (meV)
$\|\Gamma_{t3}\rangle$	$1/\sqrt{2}(\|2\rangle + \| -2\rangle)$	0
$\|\Gamma_{t1}^1\rangle$	$\epsilon(\|4\rangle + \| -4\rangle) + \gamma\|0\rangle$	3.8
$\|\Gamma_{t2}\rangle$	$1/\sqrt{2}(\|4\rangle - \| -4\rangle)$	9.6
$\|\Gamma_{t5}^1\rangle$	$\alpha\|\pm 3\rangle + \beta\|\mp 1\rangle$	41.8
$\|\Gamma_{t4}\rangle$	$1/\sqrt{2}(\|2\rangle - \| -2\rangle)$	46.0
$\|\Gamma_{t5}^2\rangle$	$\beta\|\pm 3\rangle - \alpha\|\mp 1\rangle$	71.2
$\|\Gamma_{t1}^2\rangle$	$\gamma/\sqrt{2}(\|4\rangle + \| -4\rangle) - \epsilon\sqrt{2}\|0\rangle$	75.4

parameters characterizing completely the three low-lying singlets, namely ϵ, $E(\Gamma_{t1}^1)$ and $E(\Gamma_{t2})$. Concerning the remaining levels, they do not play a very big role in the low-T properties. Anyway, the energy of Γ_{t1}^2 is automatically fixed by the mentioned constraint once the low energy scheme has been chosen. Γ_{t3} (Γ_{t4} in scheme C) is set at high energy, as well as the doublets. By using level schemes of this type, we have analyzed the phase transitions associated with the different order parameters. The multipolar MF constant λ could be derived in principle by imposing the value for the $T = 0$ ordered multipolar moment. Since this information is missing, we use as an alternative experimental information the value of the matrix element $T = g\mu_B |\langle 0|J_z|1\rangle|$ of the inelastic transition, which is directly connected to the value of the ordered moment. In fact, both depend on the degree of mixing of Γ_{t3} and Γ_{t4} with Γ_{t1}^1, Γ_{t2}, and Γ_{t1}^2. Neutron scattering gives $T \sim 1.2\mu_B$ [9].

Without going into details, by using the octupoles $J_zJ_xJ_y$ and $J_z(J_x^2 - J_y^2)$, we cannot obtain a satisfactory model for the phase transition. On the contrary, we find that the observed behavior can be reproduced with the quadrupole J_xJ_y in scheme B. The same behavior is obtained by a 45° rotation of the total Hamiltonian (including the CEF and the quadrupolar terms) around c, namely by using the quadrupole $J_x^2 - J_y^2$ in scheme C. By choosing λ to give a matrix element of exactly $1.2\mu_B$, the corresponding transition temperature tends to be too high, around 25–35 K. Transition temperatures in the range 20–25 K can be obtained with matrix elements of the order of $1\mu_B$, which seems to us a reasonable compromise. We present the results for an optimal level scheme, corresponding to CEF parameters (in MeV units) $B_2^0 = -0.657$, $B_4^0 = -8.323 \times 10^{-3}$, $B_6^0 = -1.004 \times 10^{-3}$, $B_4^4 = -4.307 \times 10^{-2}$, $B_6^4 = 6.051 \times 10^{-3}$. These parameters correspond to a scheme of type C. The corresponding scheme of type B is obtained by reverting the sign of B_4^4 and B_6^4. The value of the MF constants are $\lambda_0 = -68.9$ mole/emu and $\lambda = 1.85 \times 10^{-1}$ meV. The transition temperature is 22 K, and the matrix element of the inelastic transition is $\sim 1\mu_B$. We show in Fig. 1 the linear c-axis susceptibility, and in Fig. 2 the specific heat and the nonlinear c-axis susceptibility. The linear susceptibility is in reasonable agreement with experiment, making allowance for the shift of T_N. A good fit of the a-axis susceptibility can be obtained by using a transversal exchange constant about eight times the c-axis one. This is analogous to what is observed in $CeRu_2Si_2$ [22]. The specific heat above T_N, with a maximum value of 4.6 J/mole K, is also consistent with Ref. [2]. The form of the anomaly at T_N is not well reproduced, however, since the calculated specific heat is almost divergent. The mean field transition is too abrupt, and entropy is removed much more quickly than in the real system. However, we remark that the total entropy change between $T = 0$ and

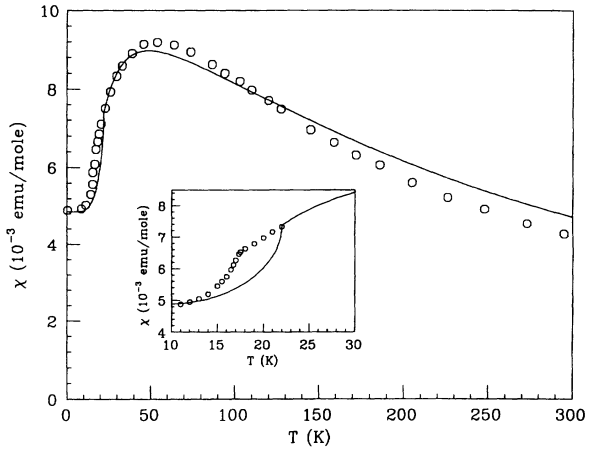

FIG. 1. Susceptibility along the c axis, χ, vs temperature from the CEF-MF model. Experimental points are taken from Ref. [1]. Inset: χ vs temperature in the vicinity of the phase transition. Experimental points from Ref. [14] have been rescaled by a constant to make them homogeneous to those of Ref. [1].

$T = 22$ K, namely the area under the C/T vs T curve, is about $0.40R$ in our model, which is comparable with the value of $\sim 0.35R$ which we estimate from the experimental curve of Ref. [2], so that the anomaly in C/T is distorted in the model, while roughly conserving the underlying area. This means that the ordering process is slower in the real system than in the bare CEF-MF model, but the total disorder removed is comparable. We will comment later about a possible reason for this discrepancy. At T_N, the linear susceptibility has a discontinuous first derivative, decreasing more quickly below T_N. The nonlinear susceptibility curve is flat above T_N, and has a λ-like anomaly at T_N. These behaviors agree

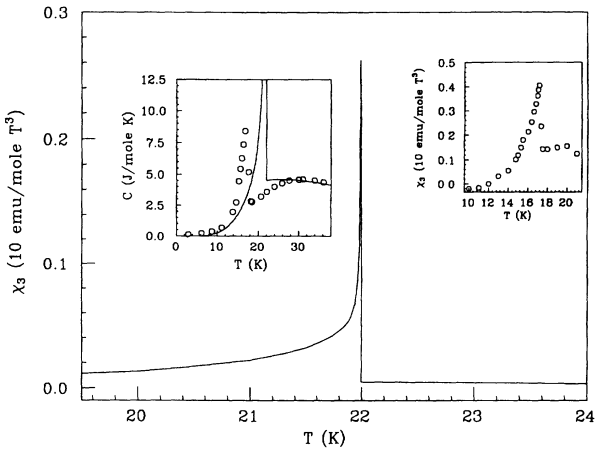

FIG. 2. Nonlinear susceptibility along the c axis, χ_3, vs temperature from the CEF-MF model. Right-hand inset: Experimental points from Ref. [14]. Left-hand inset: Specific heat C vs temperature. Experimental points from Ref. [2].

well with the measurements of Ref. [14]. The calculated nonlinear susceptibility is, however, too small above T_N, even if the jump is comparable, and the λ-like anomaly is too narrow. This latter defect is probably due again to the excessive abruptness of the transition in our model, reducing the size of the critical region. The former could either be due to conduction electron effects, which will be discussed later, or to the fact that the third-order susceptibility can contain additional contributions [23], for instance in the presence of cooperative O_2^0 terms. Since the characteristic λ anomaly in χ_3 is already present we prefer not to complicate the model by trying to include these extra contributions.

The dispersion of the magnetic excitations can be fitted to the neutron data by the usual random phase approximation formula, with a proper choice of the couplings $J_{\mathrm{RKKY}}(q)$, as is done in Ref. [9]. We remark, however, that $J_{\mathrm{RKKY}}(q = 0) \propto \lambda_0$ has been already fixed from the susceptibility data. If we use this value we obtain for the transition at $q = 0$ an energy of $\sim$13 meV, near the experimental value of $\sim$13.2 meV. Finally, the proposed CEF level scheme is compatible with a metamagnetic transition at a field of the order of 35 T [11,12].

The simple CEF-MF model seemingly contains already much the physics of the system. Its defects are very likely to be due to our neglect of conduction electron effects other than yielding effective f-f interactions. The low energy part of the CEF level structure we deduced is quite close to the one used by Cox in his quadrupolar Kondo theory of UBe_{13} [24], since the Γ_3 cubic doublet he uses splits in tetragonal symmetry just into the two singlets Γ_{t3} and Γ_{t1}^1. We propose the following picture: In the generalized k-f exchange Hamiltonian, containing either Coulomb and virtual-mixing contributions, the usual dipolar processes are ineffective at low T due to the CEF anisotropy, which raises them to several tens of meV. On the contrary, quadrupolar processes are not quenched. For a single U ion they can lead to a quadrupolar Kondo state, in which Γ_{t3} and Γ_{t1}^1 are mixed with k states. This state is analogous to the one-ion dipolar Kondo state in a weak magnetic field, the noncubic CEF terms playing the role of the magnetic field. In a lattice of U ions, this same k-f interaction induces the effective quadrupolar f-f coupling which we included in our Hamiltonian. We propose that above T_N a Kondo-like state is formed. This yields a broadening of the spectral weight of Γ_{t3} and Γ_{t1}^1 due to the dynamical mixing of these two states produced by the Kondo interaction. This would explain the broad peak observed in neutron scattering. Below T_N an ordering of the f quadrupoles develops, and a static mixing of Γ_{t3} and Γ_{t1}^1 occurs. In a MF picture including k electrons [25], the opening of the $\Gamma_{t3} - \Gamma_{t1}^1$ gap driven by the quadrupole MF tends then to decouple these two states, as it is observed experimentally (alternatively, or at the same time, a decoupling could be produced by a partial gapping of the Fermi surface induced by the symmetry breaking state). We think that either the broadening of the levels and the decoupling process near T_N, tend to make the transition less abrupt than in our model, the bare CEF behavior being recovered only as the order parameter grows.

In conclusion, a model based on ordering of localized f quadrupoles can reproduce semiquantitatively the magnetic properties of URu_2Si_2.

We are very grateful to G. H. Lander and L. C. Andreani for useful discussions. This research was supported in part by the Swiss National Science Foundation, Grant No. 2000-037642.93/1.

[1] T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).
[2] W. Schlabitz, J. Baumann, B. Pollit, U. Rauchschwalbe, H. M. Mayer, U. Ahlheim, and C. D. Bredl, Z. Phys. B **62**, 171 (1986).
[3] T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh, Phys. Rev. B **33**, 6527 (1986).
[4] M. B. Maple *et al.*, Phys. Rev. Lett. **56**, 185 (1986).
[5] A. de Visser *et al.*, Phys. Rev. B **34**, 8168 (1986).
[6] P. Bossard *et al.*, in *Crystalline Electric Field and Structural Effects in f-Electron Systems*, edited by J. E. Crow, R. P. Guertin, and T. Mihalisin (Plenum Press, New York, 1980), p. 407.
[7] A. I. Abou Aly *et al.*, Phys. Rev. Lett. **35**, 1387 (1975).
[8] C. Broholm, J. K. Kjems, W. J. L. Buyers, P. Matthews, T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh, Phys. Rev. Lett. **58**, 1467 (1987).
[9] C. Broholm, H. Lin, P. Matthews, T. E. Mason, W. J. L. Buyers, M. F. Collins, A. A. Menovsky, J. A. Mydosh, and J. K. Kjems, Phys. Rev. B **43**, 12 809 (1991).
[10] T. E. Mason and W. J. L. Buyers, Phys. Rev. B **43**, 11 471 (1991).
[11] F. R. de Boer *et al.*, Physica (Amsterdam) **138B**, 1 (1986).
[12] K. Sugiyama *et al.*, J. Phys. Soc. Jpn. **59**, 3331 (1990).
[13] M. B. Walker, W. J. L. Buyers, Z. Tun, W. Que, A. A. Menovsky, and J. D. Garrett, Phys. Rev. Lett. **71**, 2630 (1993).
[14] A. P. Ramirez, P. Coleman, P. Chandra, E. Brück, A. A. Menovsky, Z. Fisk, and E. Bucher, Phys. Rev. Lett. **68**, 2680 (1992).
[15] G. J. Nieuwenhuys, Phys. Rev. B **35**, 5260 (1987).
[16] E. D. Isaacs *et al.*, Phys. Rev. Lett. **65**, 3185 (1990).
[17] T. E. Mason *et al.*, Phys. Rev. Lett. **65**, 3189 (1990).
[18] L. L. Hirst, Adv. Phys. **27**, 231 (1978).
[19] P. Fulde and M. Loewenhaupt, Adv. Phys. **34**, 589 (1986).
[20] G. Amoretti, A. Blaise, and J. Mulak, J. Magn. Magn. Mater. **42**, 65 (1984).
[21] P. Santini and G. Amoretti (to be published).
[22] P. Haen *et al.*, J. Low. Temp. Phys. **67**, 391 (1987).
[23] P. Morin and L. Schmitt, Phys. Lett. **73A**, 67 (1979).
[24] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[25] T. Yamamoto and F. Ohkawa, J. Phys. Soc. Jpn. **57**, 3562 (1988).