Low-field octupoles and high-field quadrupoles in URu$_2$Si$_2$

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The recent experimental finding of large-amplitude antiferromagnetism induced by uniaxial strain shows that the “hidden” low-field order of URu$_2$Si$_2$ breaks time reversal invariance. We propose a new crystal field model which supports $T^z_2$ octupolar order in the low-field phase, and quadrupolar order in a disjoint high-field phase. The temperature dependence of the linear and third order magnetic susceptibility is in good agreement with the observed behavior.

The nature of the $T_O = 17.5K$ phase transition of URu$_2$Si$_2$ is a long-standing puzzle. Though URu$_2$Si$_2$ was long considered as a “light” heavy fermion system, implying that the $f$-states should be included in the Fermi volume, many aspects of the normal state behavior are well described in terms of a localized $f$-electron model. Specific heat measurements show that an electronic entropy of $O(\ln 2)$ is released by the time the temperature reaches 30K, and a sizeable fraction of it is associated with the $\lambda$-anomaly at 17.5K. Thus the phase transition should be associated with the full-scale ordering of a localized degree of freedom per site, but the nature of the order parameter remains hidden. It is obviously not the tiny ($M_z \sim 0.03\mu_B$, $z$ being the tetragonal fourfold axis [001]) antiferromagnetic moment observed by neutron scattering. In fact, the association of micromagnetism with the 17.5K transition is dubious, since it depends on sample quality, while the thermodynamic transition itself is a robust sharp feature.

If one assumes that the observations are made on single-phase specimens, then the weak antiferromagnetism should be described as a secondary phenomenon driven by the primary ordering of the hidden order parameter. The staggered dipole moment and the hidden order parameter would possess the same spatial and time reversal symmetry. The finding of a first order transition to a high-pressure phase with large moments was argued to favour this scenario. A general symmetry analysis listed local octupoles as well as triple-spin correlators. We note, however, that an extensive mean field study by Santini et al considered the possibility of octupolar order, and discarded it in favor of the alternative of quadrupolar order. Most recently, unconventional density waves with alternating plaquette currents were advocated.

The plaquette current can give rise to weak orbital antiferromagnetism, and is thus in principle well suited to describe URu$_2$Si$_2$. However, these works are based on the extended $s$-band Hubbard model; we prefer a description emphasizing the orbital character of $f$-electrons.

We propose an alternative scenario in which hidden order and antiferromagnetism are of different symmetries. There is experimental evidence that the apparently tiny moments belong to a minority phase, and the hidden order of the majority phase is non-magnetic.

Assuming that hidden order is not of the same symmetry as $J^z$ dipoles, there are still two basic options: hidden order may, or may not, break time reversal invariance. Earlier, both possibilities seemed open, and Santini’s quadrupolar model gives an example of time reversal invariant hidden order. However, we are going to argue that recent observations necessitate to postulate time reversal invariance breaking hidden order.

According to a crucial recent experiment, uniaxial pressure applied in [100] or [110] directions induces a relatively large magnetic moment in direction [001]. In contrast, stress in the [001] direction does not induce any sizeable moment. Since stress is a time reversal invariant perturbation, it can induce magnetism only from an underlying (hidden) order which itself breaks time reversal invariance. The directionality of the effect indicates time reversal invariance breaking orbital order, most straightforwardly octupolar order.

Octupolar order as primary order parameter was suggested for Phase IV of Ce$_{1-x}$La$_x$B$_6$ and for NpO$_2$. Knowing such precedents, it is a plausible idea to check whether a difficult-to-identify order of an $f$-electron system is octupolar.

The tetragonal symmetry classification of the local order parameters in the absence of a magnetic field is given in Table I. $g$ and $u$ refer to "even" and “odd” under time reversal. Here we neglected wave vector dependence; it will be specified when we mean staggered rather than uniform moments.

| sym ($g$) | operator | sym ($u$) | operator |
|----------|----------|----------|----------|
| $A_{1g}$ | $E$      | $A_{1u}$ | $J_x J_y J_z (J^2_z - J^2_y)$ |
| $A_{2g}$ | $J_x J_y (J^2_x - J^2_y)$ | $A_{2u}$ | $J_x$ |
| $B_{1g}$ | $O_{3g}^2$ | $B_{1u}$ | $T_{xy} = J_x J_y$ |
| $B_{2g}$ | $O_{xy} = J_x J_y$ | $B_{2u}$ | $T^2_z = J_x (J^2_z - J^2_y)$ |
| $E_g$    | $\{O_{2z}, O_{2x}\}$ | $E_u$    | $\{J_x, J_y\}$ |

We argued that the $H = 0$ order parameter must be one of the $u$ operators; it cannot be $A_{2u}$ or $E_u$ because that would mean magnetic order; later we mention why...
it cannot be $A_{1u}$; so it must be one of the octupoles $T_{2}^{\beta}$ ($B_{2u}$), or $T_{2y}z$ ($B_{1u}$). Lacking a microscopic analysis of the multipolar interactions in URu$_2$Si$_2$, we cannot decide between the two, and arbitrarily choose the $T_{2}^{\beta}$ octupole as the zero-field order parameter.

Switching on a field $\mathbf{H} \parallel \hat{z}$, geometrical symmetry is lowered to $C_{4h}$. However, the relevant symmetry is not purely geometrical. Though taken in itself, reflection in the $xz$ plane corresponds to a mirror plane, and no symmetry operation (it changes the sign of the field), combining it with time reversal $\hat{T}$ gives the symmetry operation $\hat{T}\sigma_{v,x}$. The same holds for all vertical mirror planes, and $C_{2v}$ perpendicular to $\hat{z}$ axes, thus the full symmetry group consists of eight unitary and eight non-unitary symmetry operations.

$$\mathcal{G} = C_{4h} + \hat{T}\sigma_{v,x}C_{4h}. \quad (1)$$

We may resort to a simpler description observing that

$$\hat{\mathcal{G}} = C_{4} + \hat{T}\sigma_{v,x}C_{4} \quad (2)$$

is an important subgroup of $\mathcal{G}$, and we can base a symmetry classification on it. The multiplication table of $\hat{\mathcal{G}}$ is the same as that of $C_{4v}$, and therefore the irreps can be given similar labels. It is in this sense that the symmetry in the presence of a field $\mathbf{H} \parallel \hat{z}$ can be regarded as $C_{4v}$ (a convention used in [14]). The symmetry classification of the local order parameters valid in $\mathbf{H} \parallel \hat{z}$ is given in Table II. The results make it explicit that the magnetic field mixes dipoles with quadrupoles, quadrupoles with certain octupoles, etc.

**TABLE II: Symmetry classification of the lowest rank local order parameters for $\mathbf{H} \parallel \hat{z}$ (notations as for $C_{4v}$)**

| Symmetry | Basis operators |
|----------|-----------------|
| $A_{1}$  | $1, J_{z}$      |
| $A_{2}$  | $J_{x}J_{y}\{J_{x}^{2} - J_{y}^{2}\}, J_{x}J_{y}J_{z}\{J_{x}^{2} - J_{y}^{2}\}$ |
| $B_{1}$  | $O_{2}^{z}, T_{2}^{\beta}$ |
| $B_{2}$  | $O_{2y}^{z}, T_{2y}z$ |
| $E$      | $\{J_{x}, J_{y}\}, \{O_{xx}, O_{yy}\}$ |

In a field $\mathbf{H} \parallel \hat{z}$, there can exist ordered phases with four different local symmetries: $A_{2}$, $B_{1}$, $B_{2}$, and $E$. The zero-field $B_{2u}$-type $T_{2}^{\beta}$ octupolar order evolves into the $B_{1}$-type $T_{2}^{\beta}$-$O_{2}^{z}$ mixed octupolar–quadrupolar order (Figure 1). Experiments tell us that $B_{1u}$ (and also $B_{1}$) order is alternating ($Q = (111)$). The gradual suppression of octupolar order under field applied in a high-symmetry direction is well-known, e.g., from [17]. In our calculation, the octupole phase is suppressed at $H_{cr,1} \approx 34.7T$ (Figure 1).

There can be other kinds of order, but they cannot coexist with $B_{1}$ because they carry different symmetry labels. The phases can be disjoint, separated by non-ordered regimes, or when they press against each other, the transition must be first order. It is a question of detail whether isolated phases are bounded by critical lines or first order boundaries.

Seeking agreement with high-$T$ and large-field data we postulate a crystal-field model in which two levels tend to cross at $H > H_{cr,1}$, and they are connected by matrix elements of $E$ operators. Consequently, we find a high-field $E$ phase where $\{J_{x}, J_{y}\}$-type transverse dipolar order is mixed with $\{O_{xx}, O_{yy}\}$-type quadrupolar order (see Figure 1 and Table II). The overall appearance of our phase diagram closely resembles the results of high-field measurements. Some experiments identified additional domains in the $H$–$T$ plane, but we think that the two phases shown in Figure 1 are the most robust part of the phase diagram.

We assume stable $5f^{2}$ valence, and Hund’s rule $J = 4$ ground state. Let us seek a plausible level scheme to support the postulated ordering phenomena. It is accepted that the ground state is a singlet, and it is connected to another singlet across a gap of $\sim 100$K by a matrix element of $J^{z} \parallel \hat{z}$. In our scheme, $|t_{1}\rangle$ is the ground state, and $|t_{2}\rangle$ the $\Delta_{2} = 100$K excitation. We need the low-lying ($\Delta_{1} = 45$K) singlet $|t_{4}\rangle$ to allow induced octupole order. Finally, as in previous schemes [2], at least two more states are needed to fit magnetization data up to 300K. We found it useful to insert one of the doublets ($|d_{\pm}\rangle$). Level positions were adjusted to get good overall agreement with observations but we did not attempt to fine-tune the model. The list of the relevant crystal field states is given in Table II (we use $a = 0.98$, $b = 0.22$). The field dependence of the levels is shown in Figure 4.

Our crystal field scheme differs in essential details from previous ones [6], but the quality of fits to the suscepti-
The discontinuity of $\langle 0 | O_0 | 0 \rangle$ constant $\lambda$ decreases in magnetic field like $T_{\text{c}} \propto \lambda$. This has two effects. First, since $O_2^z \otimes O_2^\perp$ coupling, nevertheless $\langle O_2^z \rangle \neq 0$ in the $B_1$ phase, and $\langle J_z \rangle \neq 0$ in the $E$ phase.

At $H = 0$, the only non-vanishing octupolar matrix element is $C = \langle t_4 | T_2^z \rangle = 3.8$. Octupolar order is driven by the large $C$: assuming $\lambda_{\text{oct}} = 0.336$K we get the critical temperature $T_{\text{c}}(H = 0) = 17.2$K for $T_2^z$-type antiferro-octupolar order. Using a similar estimate, we find $\lambda_{\text{oct}} \approx 0.2K$ for NpO$_2$ which orders at 25K [18], thus the assumed octupolar coupling strength is not unreasonable [22].

The octupolar transition shows up as a break in the temperature derivative ($\partial \chi / \partial T$) of the linear susceptibility (Fig. 3 right). The sign of the discontinuity of slope is related to the fact that the critical temperature decreases in magnetic field like $T_{\text{c}}(H) \approx T_{\text{c}}(H = 0) - a_H H^2$ [17, 21]. An Ehrenfest relation [14, 17] connects the discontinuity of ($\partial \chi / \partial T$) to that of the non-linear susceptibility $\chi_3$ (Fig. 4 left).

Up to the vicinity of the $t_1-d_-$ level crossing shown in Fig. 2, field effects can be understood within the $|t_1\rangle - |t_4\rangle - |t_2\rangle$ subspace. Applying $H \parallel \hat{z}$ mixes $|t_2\rangle$ to $|t_1\rangle$. This has two effects. First, since $O_2^z$ connects $|t_2\rangle$ to $|t_4\rangle$, the order parameter acquires a mixed $T_2^z - O_2^z$ character (cf. Table III). Second, it reduces the octupolar matrix element, and thereby also $T_{\text{c}}$. With the parameters given before, the octupolar transition is fully suppressed at $H_{\text{c,1}} = 34.7T$ (see Fig. 1). There is an accompanying change in the slope of the magnetization curve which, however, is not noticeable on the scale of Fig. 4 (right).

A basis-independent description of field effects relies on the Landau expansion of the Helmlich potential $\mathcal{A}$ which yields the magnetic field as a derived quantity $H = (\partial \mathcal{A} / \partial J) [17]$. $\mathcal{A}$ is a sum of invariants. Two terms which are important for the present purpose, are contained in

$$I(A_{2n} \otimes B_{1g} \otimes B_{2u}) = c_1 J_z(-Q) T_2^z(Q) O_2^z(-Q) + c_2 J_z(0) T_2^z(-Q) O_2^z(0).$$ (4)

c_1$ and $c_2$ are non-zero even if we consider the lowest two levels only. The existence of this invariant can be exploited in several ways. In a uniform magnetic field, alternating octupolar order $T_2^z$ induces similarly alternating quadrupolar order $O_2^z$. Alternatively, it follows that in the presence of uniform quadrupolar polarization $O_2^z$, alternating octupolar order gives rise to a magnetic

| state | form | symmetry | energy [K] |
|-------|------|----------|------------|
| $|t_2\rangle$ | $1/\sqrt{2}(|4\rangle - |\mp\rangle)$ | $A_2$ | 100 |
| $|d_{\pm}\rangle$ | $a|\pm\rangle + \sqrt{1 - a^2}|1\rangle$ | $E$ | 51 |
| $|t_4\rangle$ | $1/\sqrt{2}(|2\rangle - |\mp\rangle)$ | $B_2$ | 45 |
| $|t_1\rangle$ | $b|4\rangle + |\mp\rangle + \sqrt{1 - 2b^2}|0\rangle$ | $A_1$ | 0 |

TABLE III: Tetragonal crystal field states used in the model.
moment $J_2$ with the same periodicity. Such a quadrupolar polarization is created by uniaxial stress applied in the [100] direction, which is observed to give rise to alternating magnetic moments of $O(0.1\mu_B)$, clearly different from micromagnetism [11]. Fig. 3 shows the stress-induced staggered magnetization for the same set of parameters as in previous plots. Sufficiently large stress suppresses octupolar order, like a sufficiently strong field does. The maximum induced moment is $\sim 0.5\mu_B$; the measured $\sim 0.2\mu_B$ [11] may belong to the rising part of the curve.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{stressMoment.png}
\caption{Stress-induced magnetic moment in the octupolar phase. Thick line: ($M_z$) staggered magnetization, thin line: $\langle T^z \rangle$ octupolar moment, as a function of the uniaxial pressure $\sigma || [100]$ ($\sigma$ in arbitrary units).}
\end{figure}

Stress applied along the $z$-axis induces $O_9^0$ which transforms according to the identity representation $A_{1g}$, thus it does not appear in the invariants, and it is not predicted to induce magnetism.

We note that the $A_{1g}$ triakontadipole $J_x J_y J_z (J_x^2 - J_y^2)$ (see Table I) would not give rise to stress-induced magnetism and is therefore not a suitable choice as order parameter in the limit $H \to 0$.

We now discuss the high-field behavior at $H > H_{cr,1}$. The single-ion levels $t_1$ and $d_-$ would cross at $H_{cross} = 37.3T$. Since $|t_1\rangle$ and $|d_-\rangle$ are connected by $E$ operators including $O_{xx}$, a range of fields centered on $H_{cross}$ is certain to favour $\{O_{xx}, O_{yz}\}$ quadrupolar order, and simultaneous $\{J_x, J_y\}$ dipolar order. We chose a weak quadrupolar interaction $\lambda_{quad} = 0.054K$ in Eqn. 3: this gives quadrupolar order between the critical fields $H_{cr,2} = 35.8T$ and $H_{cr,3} = 38.8T$. The amplitude of quadrupolar order is not small (Fig. 1) but the ordering temperature is low ($\sim 1K$) because the coupling is weak. The $E$ phase shows up as the steep part of the magnetization curve in Fig. 2 (right). For $\lambda_{quad} = 0$ we would have a jump-like metamagnetic transition at $H = H_{cross}$.

In summary, our crystal field scheme gives an $H-T$ phase diagram in overall agreement with experiments. Time reversal invariance breaking by the $T^z$ octupolar order in the low-field phase is essential to allow the prediction of large-amplitude antiferromagnetism induced by transverse uniaxial stress. The disjoint high-field phase has mixed quadrupolar–dipolar character.

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[1] N. Harrison, K.H. Kim, M. Jaime, and J.A. Mydosh, cond-mat/0307084 (2003), and references therein.
[2] W. Schlubitz et al, Z. Phys. B - Condensed Matter 62, 171 (1986).
[3] C. Broholm et al., Phys. Rev. Lett. 38, 1467 (1977).
[4] F. Bourdarot et al, cond-mat/0312206 (2003).
[5] D.F. Agterberg and M.B. Walker, Phys. Rev. B 50, 563 (1994). Three-spin correlator as order parameter was suggested by L.P. Gor’kov: Europhys. Lett. 16, 301 (1991).
[6] P. Santini and G. Amoretti, Phys. Rev. Lett. 73 1027 (1994); P. Santini, Phys. Rev. B 57 5191 (1998); P. Santini, Thesis (Lausanne, 1994).
[7] P. Chandra, P. Coleman, J.A. Mydosh and V. Tripathi, Nature (London) 417, 831 (2002); A. Virosztek, K. Maki, and B. Döra, Int. J. Mod. Phys. 16, 1667 (2002).
[8] K. Matsuda et al, Phys. Rev. Lett. 87, 087203 (2001).
[9] N. Shah, P. Chandra, P. Coleman, and J. A. Mydosh, Phys. Rev. B 61, 564 (2000).
[10] See, however, NMR evidence suggesting TRI breaking in: O.O. Bernal et al, Phys. Rev. Lett. 87, 196402 (2001).
[11] M. Yokoyama et al., cond-mat/0311199 (2003).
[12] H. Kusunose and Y. Kuramoto: J. Phys. Soc. Japan 70, 1751 (2001); K. Kubo and Y. Kuramoto: J. Phys. Soc. Japan 73, 216 (2004).
[13] P. Santini and G. Amoretti, Phys. Rev. Lett. 85, 2188 (2000), and references therein.
[14] We follow closely the method developed by R. Shih, H. Shiba, and P. Thalmeier: J. Phys. Soc. Japan 66, 1741 (1997). See also [15].
[15] T. Inui, Y. Tanabe, and Y. Onodera: Group Theory and Its Applications in Physics, Springer Series in Solid-State Sciences 78, Springer-Verlag, Berlin (1990).
[16] A model based on $T_{xy}$ ordering would give rather similar results.
[17] A. Kiss and P. Fazekas: Phys. Rev. B 68, 174425 (2003).
[18] M. Jaime et al, Phys. Rev. Lett. 89, 287201 (2002).
[19] K.H. Kim et al, Phys. Rev. Lett. 91, 256401 (2003); A. Suslov et al., Phys. Rev. B 68 020406 (2003); N. Harrison et al., Phys. Rev. Lett. 90, 096402 (2003).
[20] Since our scheme works with five states, it may seem to overestimate the entropy [2]. However, magnetic field and intersite interactions split off the lowermost two or three states, thus we have effectively a three-state model.
[21] T. Sakakibara et al, J. Phys. Soc. Japan 69, Suppl. A, 25 (2000).
[22] Dipole order cannot compete: Santini estimates a dipole coupling $\lambda_{dip} \lessapprox 2K$ from the high-$T$ susceptibility. $\langle t_2 \rangle \approx C/4$ and $\Delta_2 \approx 2\Delta_1$ lead to a Néel temperature much lower than $T_D$.
[23] The symmetry happens to coincide with that of the micromagnetic order which we ascribe to a minority phase. Our choice of alternating order corresponds to that of stress-induced strong antiferromagnetism [11].