Itinerant Magnetic Multipole Moments of Rank Five as the Hidden Order in URu_2Si_2

Francesco Cricchio, Fredrik Bultmark, Oscar Grånäs, and Lars Nordström

Department of Physics and Materials Science, Uppsala University, Box 530, SE-75121 Uppsala, Sweden

(Received 4 May 2009; revised manuscript received 20 July 2009; published 1 September 2009)

A broken symmetry ground state without any magnetic moments has been calculated by means of the local-density approximation to density functional theory plus a local exchange term, the so-called LDA + U approach, for URu_2Si_2. The solution is analyzed in terms of a multipole tensor expansion of the itinerant density matrix and is found to be a nontrivial magnetic multipole. Analysis and further calculations show that this type of multipole enters naturally in time reversal breaking in the presence of large effective spin-orbit coupling and coexists with magnetic moments for most magnetic actinides.

DOI: 10.1103/PhysRevLett.103.107202 PACS numbers: 75.10.Lp, 71.70.Ej, 71.70.Gm, 75.20.Hr

The magnetism involving the $5f$ states of the actinides shows many exotic behaviors. One of the most enigmatic is the tiny magnetic moment [1,2] observed in tetragonal URu_2Si_2 below a transition temperature of 17 K. It is established that the true ordering parameter driving the second order transition is hidden, i.e., not observable by standard techniques. A huge experimental effort has been made to uncover the true nature of this hidden order (HO). This has led to a lot of progress in determining the relevant phase diagram of URu_2Si_2, but the order has remained concealed. Under pressure the ordering temperature increases slightly, but more significantly, for pressures above 0.5 GPa there is a phase transition to an antiferromagnetic (AFM) state with magnetic moments of $0.3\mu_B$ [3]. The critical pressure increases with temperature and seems to reach a bicritical point around 1.3 GPa. The two phases HO and AFM have some properties in common. They both show large anomalies in thermodynamical [4] and transport quantities [5] at the critical temperature, signaling a large Fermi surface nesting. In fact, these quantities [4], as well as the Fermi surface geometry determined by the de Haas–van Alphen effect [6], show only smooth variations across the phase transition. Since there is a sharp transition between the two phases, and since the tiny moments observed in the HO phase are argued to be caused by sample dependent extrinsic effects, the order parameter in the HO can in principle be of completely different symmetry than in the AFM phase. In particular, the HO might be time reversal (TR) symmetric although the AFM clearly is not. On the other hand, the inflection point observed in the induced moment of an external magnetic field indicates that there is an ''adiabatic continuity'' between the two phases and hence that HO is TR odd [7]. Many explanations, more or less exotic, have been suggested for this HO, some of localized nature, e.g., quadrupoles [8] or octupoles [9], and some of itinerant nature as, e.g., multiple spin correlators [10], unconventional density waves [11], orbital currents [12], helicity order [13], or fluctuating moments [14]. Hitherto, none of these have been confirmed by experiments. In summary several crucial aspects of the HO are still under debate: whether the HO is of even or odd TR symmetry, whether it is of localized or itinerant character, and whether the HO and AFM phases are related or of different origin.

In this Letter we find that nontrivial magnetic dotriacontapole [15] (rank five) moments constitute the HO parameter in URu_2Si_2. In this material the Fermi surface nesting is found to be important for the stabilization of the calculated staggered multipole moments, and they can be viewed as an unconventional density wave (UDW) [11,16]. With decreased in-plane lattice constant the dipoles increase, giving rise to ordinary magnetic moments in accordance with pressure experiments [3] while the magnitude of the magnetic multipole decrease slightly.

The driving mechanism for magnetic ordering in conventional magnets is known to be the Stoner-like exchange, which is, for instance, included in local-density approximation (LDA) to the spin density functional theory (SDFT) approach [17]. When relativistic effects, especially the spin-orbit coupling (SOC), start to play an important role as in the actinides, the Stoner-like spin polarization is not sufficient anymore. It tends to overestimate the spin contribution to the magnetic moments while simultaneously it drastically underestimates the orbital contribution. This is known to be remedied by adding a more general exchange terms, that includes, for instance, an orbital polarization term [18,19]. A general form of exchange interactions within an atomic open shell is the screened Hartree-Fock term. This term is fused with the conventional SDFT formalism in the so-called LDA + U method [20,21]. Recently we have shown that, with this type of exchange, the SOC can be strongly enhanced. In the case of δ-Pu this was shown to quench the spin polarization leading to a TR even state [22] in accordance with experiments. The analysis of the ground state was achieved by a general expansion of the exchange energy, $E_X = \sum_{kpr} K_{kpr} \mathbf{w}^{kpr} \cdot \mathbf{w}^{kpr}$ in terms of the multipole tensor moments $\mathbf{w}^{kpr}$, where K_{kpr} are the corresponding exchange parameters, whose detailed derivation is given in Ref. [23]. These $\mathbf{w}^{kpr}$ tensors contain full information of the occupancy of the open shell

and correspond to density (current) multipoles for even (odd) k, while the index $p = 0$ ($p = 1$) describes the charge (spin) density and current [24]. The orbital (k) and spin (p) multipole moments are coupled to a total multipole, given by the index r. Hence $\mathbf{w}^{110}$ corresponds to a scalar product of spin and orbital current $s \cdot \ell$, while, e.g., $\mathbf{w}^{011}$ and $\mathbf{w}^{101}$ are proportional to spin and orbital moments. For descriptions of higher multipoles, see, e.g., Ref. [24].

In this study we apply the LDA + U approach and its multipole decomposition to a few different magnetic uranium systems, three supposedly normal systems: UAs, US, and USb in the NaCl structure, and URu_2Si_2 with its enigmatic HO in the tetragonal $ThCr_2Si_2$ structure. The calculations are set up according to the observed magnetic structure [1,25]: a single $q = (00\frac{1}{2})$, $q = (000)$, and a triple $q = (00\frac{1}{2})$, respectively, for the three "normal" compounds. The calculations were done [26] in the augmented plane waves and local orbitals method (APW + lo) [27] together with the LDA + U scheme as implemented [22,23] in the code ELK [28].

First, we notice that we achieve a good agreement with the experimental moments for the "normal" uranium systems [25] for U in the range of 0.6–1.0 eV, which is established as a reasonable range for the $5f$ states of U. These moments are also of the same magnitude as in other "beyond-LDA" calculations [29,30], with an enhanced orbital and slightly decreased spin moment compared to LDA calculations. In Fig. 1 we display the corresponding most significant tensor contributions to the exchange energy [22,23] as a function of the screened U parameter. Here we should note that we have adopted a strategy where the different Slater parameters are screened equivalently [23,31]. This has the advantage that the limit of vanishing U corresponds to an ordinary LDA calculation. The SOC-like multipole $\mathbf{w}^{110}$ has a large contribution to the total exchange energy. This leads in turn to the fact that the spin polarization decreases in importance compared to the LDA limit, $U = 0$. Although the finite U gives rise to an orbital polarization, the most striking effect is that a nontrivial high order multipole dominates, the $\mathbf{w}^{615}$ tensor, and that it plays a large role for all the uranium compounds. As given by its kpr indices, this contribution arises from a multipole of the spin magnetization density.

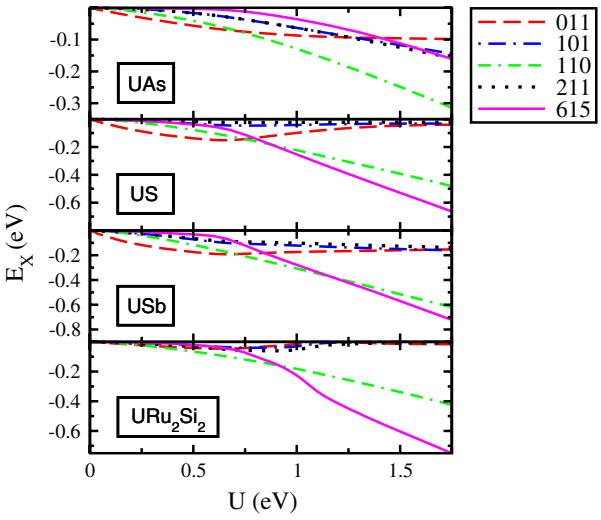

FIG. 1 (color online). The contributions to the exchange energy from the relevant polarization channels kpr as a function of U.

This observation of large higher order multipoles naturally leads to the question: How relevant are they for URu_2Si_2 with its tiny magnetic moments and hidden order parameter? In Fig. 1 we have also shown the decomposed exchange energies for URu_2Si_2. Here we see that, while the overall tendency is in accordance with what we found for the other uranium compounds above, the polarization of the 615 channels is even more prominent. These properties signal some anomaly, and we proceed to study this system under pressure.

From careful analysis of the results of experiments under uniaxial stress, one has concluded that the main variation in the pressure experiments arises from the contraction of the tetragonal a axis [32]. Therefore we have performed calculations with varying lattice constant a, to mimic the effect of pressure. The results for $U = 0.9$ eV are shown in Fig. 2, where we see a dramatic effect on the magnetic moments from small variations in lattice constant a away

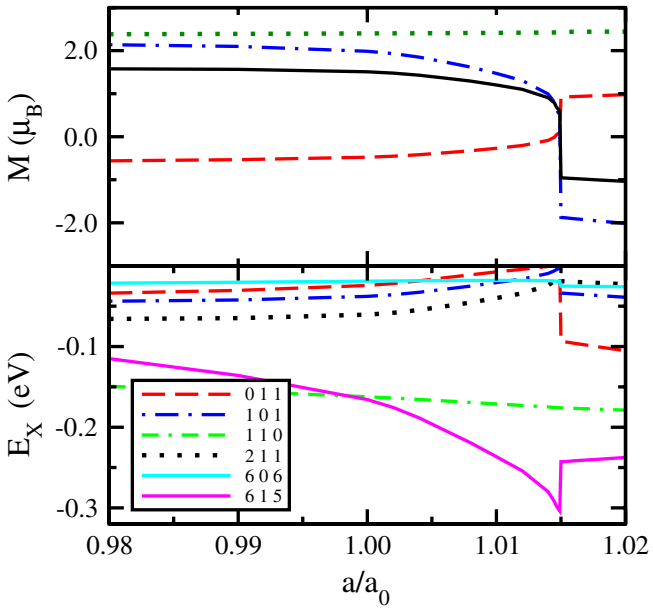

FIG. 2 (color online). In the upper part, the spin (red dashed line), orbital (blue dash-dotted line), and total (full black line) magnetic moments are shown as a function of variation in the in-plane lattice constant a with respect to the experimental one a_0, calculated with $U = 0.9$ eV. The $5f$ occupation is represented by a green dotted line. In the lower panel, the nonvanishing contributions to the exchange energy are displayed.

from a critical value, slightly (1.5%) larger than the experimental value a_0. At this critical value both the spin (SM) and orbital (OM) moments vanish, while simultaneously the 615 contribution to the exchange energy almost diverges. In fact all the vector contributions, 011, 101 and 211, go to zero at this point. In this work, where only the in-plane lattice constant is allowed to vary, the moments disappear only for a narrow range of this parameter. Future studies have to clarify whether this range increases when proper total energy optimizations, including proper Si site relaxation as well as variation of the c axis, are taken into account.

By Fourier transforming the real space dependence of the staggered 615 multipoles of Fig. 3, one can view them as forming a nonspherical or unconventional spin density wave [11,16] with angular momentum $k = 6$. Because of the strong SOC, this angular momentum couples with the spin $p = 1$ of the UDW to a total angular momentum $r = 5$. However, in tetragonal symmetry this UDW belongs to the same representation as the ordinary spherical spin density wave, the AFM order, so in general they mix. The formation of this UDW can be understood as that the large Fermi surface nesting [14] leads to a large degeneracy that is favorably split by TR breaking polarizations. Since in the present case the effective SOC is very large, this TR breaking cannot be a pure spin splitting. Instead, it is more convenient to study such TR breaking in the $j = 5/2$ subset of the f shell. Then it is possible to see that the order parameters that occur after the symmetry breaking are of the tensor type $\mathbf{w}^{k1(k-1)}$, with the larger contribution the larger k. This is how the 615 tensors moments naturally enter. Further analysis gives that there are three components of the 615 tensor that are allowed by symmetry. Two of them are large in the ordered state: the $w^{615}_{\pm 4} = (w^{615}_{4} + w^{615}_{-4})/\sqrt{2}$ component that drives the rapid variation in exchange energy as a function of the in-plane lattice constant and the w^{615}_{0} that is almost constant. From the plot of the spatial variation of the magnetization density arising from these dotriacontapole components in Fig. 3, we can note that it is closely related to the intra-atomic noncollinear spin density that always arises in the presence of SOC [33]. Since the exchange coupling enhances substantially the effective SOC, the resulting 615 polarization becomes more important than the ordinary spin polarization 011. For all cases, except UAs, the 615 exchange energy contribution bypasses the one of spin polarization for values of U around 1 eV. This finding, together with studies on other magnetic actinides [23], casts new light on the magnetism of uranium systems and actinides in general.

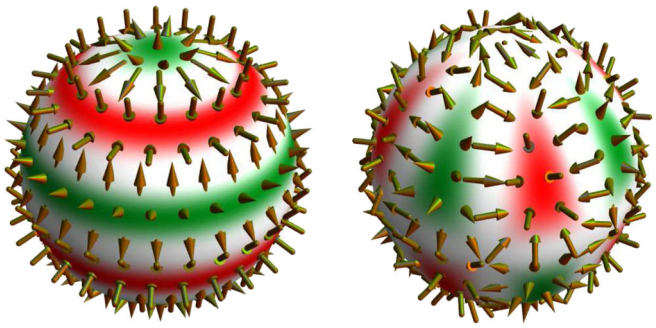

FIG. 3 (color online). The angular variation of the direction of the spin density for the two nonvanishing components of the dotriacontapole, w^{615}_{0} and $w^{615}_{\pm 4}$. The darker regions indicate where the spin axis is normal to the sphere, either outward (green) or inward (red).

From Fig. 2 we see that for smaller lattice constant, a, antiferromagnetic moments rapidly occur. For low pressures the SM takes a value of about $0.5\mu_B$, while the OM is larger and of opposite sign. This state is in a sense anomalous too since the SM is now antiparallel to the w^{615}_{0} moment, while they are parallel in the limit of weak SOC. However, as it is clear from our calculations, this AFM order is of minor importance since it is still the HO, the 615 multipole, that dominates the exchange energy. Although there is a connection between the AFM state, stabilized under pressure, and the HO phase, in line with the concept of adiabatic continuity [7], there are two different solutions in the calculation, and the transition from one to the other depends sensitively on the value of U. For values of U above 1.2 eV the transition is clearly of second order, while for values below 0.8 eV it is of first order. In between these values the numerical accuracy is not enough to safely determine the order. However, in order to properly describe this phase transition, accompanying lattice relaxations again have to be fully taken into account, which is out of the scope of this study.

Can the 615-tensor order parameter be observed at this critical lattice point where dipole tensors vanish? Because of its high rank, it is indeed a well-hidden order parameter, but since there is a magnetization density associated with it, as in Fig. 3, it will give rise to magnetic scattering in, e.g., neutron diffraction (ND) experiments although the integrated moment is zero. One problem, though, is that it belongs to the point group representation A_2, the same as any nonvanishing dipole order [34], so very careful analysis on high accuracy experiments is needed to distinguish this pure HO case from a tiny dipole moment case. However, if it is such dotriacontapole state which constitutes the HO, it can resolve a puzzling discrepancy between the tiny moments observed in ND [34,35] with the lack of local spin splitting detected by, e.g., NMR experiments [36]. It is not tiny dipole moments that give rise to the spin flip observed in the ND experiments, but the noncollinear 615 multipoles, which by nature have an extremely short-range stray field and hence lead to no hyperfine fields at the probing sites. Hence, there would be no need to invoke the idea of inhomogeneous ordering [36], i.e., that AFM order exists in part of the sample while HO exists in the rest.

In the calculations of the magnetic uranium compounds we generally find a coexistence of polarizations of the 615 channel and the 011 channel. An analysis of the properties of the density matrix gives that a 011 polarization is always permitted, and usually favorable, whenever full saturation of the other channels has not been reached. However, when both the w_0^{110} and w_0^{615} tensor components are saturated, an additional saturation of $w_{\pm 4}^{615}$ would cause the density matrix to acquire negative eigenvalues by any spin polarization w_0^{011}. Hence, these two latter types of polarization are competing, in accordance with our calculated results for URu_2Si_2 in Fig. 2. In this respect, the observation of a HO of URu_2Si_2 is the effect of the fact that the polarization of $w_{\pm 4}^{615}$ is nearly optimal and hence forbids the usual spin polarization.

In conclusion, we find that the dotriacontapoles $\mathbf{w}^{615}$ play a major role in all magnetic light actinides. What is unique in the case of URu_2Si_2 is that its polarization is so large that the usual dipole polarizations, e.g., spin polarization, are forced to vanish. Under pressure the 615 polarization decreases and dipole polarizations are again allowed. In experiments this fact manifests as an apparent dipole AFM order, although we find in our calculations that the HO candidate $\mathbf{w}^{615}$ still dominates the physics of the $5f$ shell. Our results imply that there is always a hidden order in the magnetic actinides, but it becomes perceptible only when it forces the dipoles to vanish as in URu_2Si_2.

The support from the Swedish Research Council (V. R.) is thankfully acknowledged. The computer calculations have been performed at the Swedish high performance center HPC2N under a grant provided by the Swedish National Infrastructure for Computing (SNIC).

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