Resonant x-ray scattering study of the URu_2Si_2 hidden-order phase

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Resonant x-ray scattering experiments have been performed on a high-quality single crystal of URu_2Si_2, cut with a [101] direction specular. Data have been collected at the uranium M_4 absorption edge below the hidden-order transition temperature, $T_H = 17.5$ K, exploring the region of the reciprocal space plane $[H0L]$ with $1 \leqslant H \leqslant 1.85$ and $1.8 \leqslant L \leqslant 2.1$. Within the sensitivity of our measurements, the results obtained exclude electric quadrupoles of any symmetry as a hidden-order parameter with a propagation vector in the explored region.

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The mystery of the order parameter (OP) in URu_2Si_2 remains unsolved after two decades of intense study. The large specific-heat anomaly[1] at $T_0 = 17.5$ K signals a release of considerable entropy, which is usually associated with a conventional OP breaking the overall symmetry of the solid. As is well known, in URu_2Si_2, the only significant microscopic change in the static properties at 17.5 K is the appearance of a small dipole moment corresponding to antiferromagnetic (AF) order of the uranium moments. The AF order has the moment directions along the [001] c axis of the tetragonal unit cell ($a = 4.12$ Å; $c = 9.58$ Å) with an ordering wave vector of $Q_0 = [100]$.[2] However, the magnitude of this dipole moment $\mu_0 \sim 0.02\mu_B$ is far too small to account for the large change in entropy. The dipole moment is now considered to be parasitic and not an intrinsic property of URu_2Si_2.[3–5] The OP is thus still considered a mystery, and has been called the "hidden order" (HO).

Many theories have been proposed for the HO. Relevant to the resonant x-ray scattering (RXS) experiments discussed in this paper, are those proposing the ordering of higher-order multipoles. Quadrupolar ordering (rank 2) was first proposed in 1994 (Refs. 6–8) and further quadrupoles[9,10] and (rank 3) octupoles[11,12] have been proposed since 1994. More recently, even more exotic types of HOs have been proposed including (rank 4) hexadecapole[13] and a magnetic (i.e., breaking time-reversal symmetry, rank 5) triakontadipole.[14] Either neutron scattering or RXS can, in principle, observe all these types of orderings.[15] However, such observations may be far from trivial, and may extend these techniques beyond what is conventionally undertaken. Neutron scattering, which we shall discuss later, is insensitive to charge multipoles, whereas RXS is the technique of choice for such studies and can, under certain conditions, also observe the magnetic octupole.

Since the original investigation of Broholm *et al.*,[2] a considerable amount of work has been reported. In particular, Wiebe *et al.*[16,17] and Bourdarot and collaborators[4,18–21] address a number of models that have been proposed for the HO. These experimental neutron studies have not established directly an OP in the conventional sense, but they have shown that in the HO phase the excitation spectrum is different from that in the normal phase, either above T_N or above the critical pressure that induces a large dipole magnetic moment of $\sim 0.4\mu_B$. This raises the interesting question as to whether the OP may be related to fluctuations, a question already raised by Bernhoeft *et al.*,[22] and further elaborated on in much detail by Oppeneer and collaborators.[23,24] In such theories, and others as well,[25–27] no additional elastic diffraction peak is predicted to appear below T_N. However, triakontadipole magnetic multipole ordering[14] could, in principle, be seen with neutron scattering. Such a multipole would only have a finite cross section at high momentum transfer, $Q = 4\pi \sin\theta/\lambda$, where θ is the Bragg angle and λ is the wavelength of the radiation, of ~ 7.5 Å^{-1}. Although no measurements have been performed to this high value of Q of the neutron magnetic form factor, all studies to date[2,16,28] have shown that the form factor decreases as a function of momentum transfer, as expected for a normal dipole moment. Thus, at least at Q_0, the ordering proposed in Ref. 14 seems highly improbable.

Perhaps the most striking example of finding such a HO is the study reported on NpO_2, where for half a century the nature of the ordering at 25 K remained a mystery.[29,30] RXS experiments, however, found a clear signature of quadrupolar ordering.[31] Later, neutron experiments showed that the primary OP was a magnetic (rank 5) triakontadipole.[32,33] The experience obtained in these studies led us to reexamine URu_2Si_2 in an effort to find the HO.

Three such RXS experiments have been reported on URu_2Si_2.[22,34,35] These have all focused on the magnetic dipole signal at Q_0 and, significantly, have all used crystals with the specular direction [001], which is also the cleavage plane for the crystals. Reflections of the form $[00L]$ were examined along the specular c^* direction. As expected, these experiments were performed at the U M_4 energy ($E = 3.728$ keV, wavelength $\lambda = 3.32$ Å). With this photon energy and the lattice parameters, it is essentially impossible (because of geometrical considerations) to obtain any reflections of the form $[H0L]$, with $H > 0$. However, searching only along the high-symmetry direction $[00L]$ is potentially limiting. Indeed, superlattice reflections arising from quadrupolar order in URu_2Si_2 would coincide with those associated with the (parasitic) magnetic dipole moment. The two signals can be separated by polarization analysis, as for σ-polarized incident x rays (polarization perpendicular to the scattering plane), all scattering from the magnetic dipoles has π polarization (parallel to the scattering plane), while the signal from the electric quadrupoles would be scattered both in the π and in the σ channels.[36] The observation of a superlattice reflection in the σ-σ channel would provide conclusive evidence for a quadrupolar OP. However, structure-factor effects may make the σ-σ scattering amplitude zero along specular reflections, and quadrupolar scattering would occur only in the σ-π channel, where it would be masked by the strong magnetic dipole scattering. For example, in UO_2, where magnetic-dipole ordering can be found along an analogous [001] direction, the quadrupolar ordering does not appear along these directions,[37] because the σ-σ cross section vanishes. On the other hand, by using an off-specular reflection, such as the [112], the signal from the electric-quadrupolar scattering is partially σ-σ and therefore observable. Without *a priori* knowledge of either the symmetry of the possible multipolar ordering or the relationship between the two uranium ions in the unit cell, searching only along [001] could be restrictive. Note that in Ref. 35 searches at other Q vectors slightly away from [001], such that $H \leqslant 0.4$, are reported, but no new peaks were found.

The experiments reported here were performed on the ID20 7-circle diffractometer at the European Synchrotron Radiation Facility in Grenoble, France.[38] The energy of the incident photons was tuned to the M_4 edge of uranium and the temperature throughout the experiment was 12 K (the minimum of the closed-cycle refrigerator available). All experiments were performed in the vertical plane with an incident photon polarization of σ. A Au(111) analyzer was used to measure both the σ-σ and σ-π scattered intensities. In this configuration all dipole magnetic scattering will appear only in the σ-π channel. Higher multipole scattering will appear in both channels.

The crystal used for the studies was cut with a [101] direction specular in order to give access to a more general part of reciprocal space. Single crystals were grown by the Czochralski method using a tetra-arc furnace. The samples were cut by a spark cutter and were subsequently annealed at 1075 °C for 5 days under ultrahigh vacuum. The surface was polished with diamond paste of 0.1-μm grain. The residual resistivity ratio (RRR) of the sample taken from nearly the same position was more than 100. From the same ingot, we could clearly observe Shubnikov-de Haas oscillations, indicating the high quality of the present sample.[39] In contrast to the superconducting properties, the normal phase intrinsic properties such as the spin dynamics or the specific heat anomaly are robust and weakly sensitive to disorder (RRR). However, the suspected extrinsic value of μ_0 seems to vary with the crystal's origin.

On cooling below 17 K scattering from the weak magnetic dipole signal reported previously[22,34,35] was observed at the (201) and (102) reflections. Their energy dependence and width in **Q** space were identical to those reported earlier.[22,34,35] The width in **Q** space suggests the correlations giving rise to this signal are short range in nature.[22,34]

Figure 1 shows the intensity for the (201) reflection as a function of the azimuthal angle Ψ (rotation about the scattering vector). The theoretical angular dependence was calculated following the procedure described in Ref. 40. The data observed in the σ-π and σ-σ channels agree well with that expected for antiferromagnetic order of magnetic dipoles

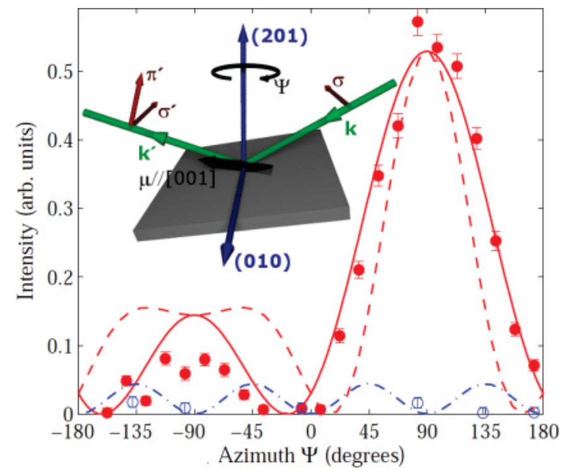

FIG. 1. (Color online) Azimuthal dependence of the (201) reflection with $\Psi = 0$ corresponding to the [010] axis being parallel to the incident beam. Solid (red) circles correspond to the intensities in the σ-π channel, and the full (red) line to the theoretical intensity variation for magnetic dipoles ordered along [001], normalized at the maximum intensity. The dashed red line is the σ-π intensity dependence expected for Q_{xy} quadrupole order. Open (blue) circles correspond to the intensities measured in the σ-σ channel, and the dashed-dotted blue line is the σ-σ intensity dependence expected for Q_{xy} quadrupole ordering. There would be zero intensity in σ-σ for the magnetic dipole ordering. The inset shows schematically the scattering geometry, with symbols defined in the text.

directed along [001]. (For a [00L] reflection the magnetic intensity for such an azimuthal scan is independent of Ψ.) On the contrary, the observed intensity oscillation does not reproduce that expected for Q_{xy} electric quadrupole order, being broader in the angular range between 0° and 180°, and narrower in the range between 0° and −180°. This eliminates the Q_{xy} quadrupoles as OPs, as already reported in Refs. 22 and 35.

Figure 2 shows the calculated Ψ dependence for the four remaining quadrupoles. The experimental data, Fig. 1, completely exclude that the ordering at $Q_0 = [100]$ has any quadrupolar component. Data in the σ-σ channel were collected with high statistics at $\Psi \approx 0°$, 90°, and 135°, but no signal above the background has been observed. The absence of σ-σ intensity at $\Psi = 90°$, excludes $Q_{x^2-y^2}$ and $Q_{3z^2-r^2}$ as OPs [Figs. 2(a) and 2(d)], whereas Q_{zx} and Q_{yz} are excluded by the results obtained for $\Psi = 0°$ and 135°, respectively. This conclusion is consistent with previous findings.[22,35]

Following Amitsuka *et al.*,[35] we have searched for any signal away from Q_0 that could indicate an additional OP. Reference[35] covered the region [$H0L$], with $0.25 \leqslant H \leqslant 0.42$ and $2 \leqslant L \leqslant 3$. As shown in Fig. 3, we covered a range $1 \leqslant H \leqslant 1.85$, $1.88 \leqslant L \leqslant 2.08$, and also in considerable detail the area $1.35 \leqslant H \leqslant 1.45$, $1.8 \leqslant L \leqslant 2.1$, which includes the so-called $Q_1 = [1.4\,0\,2]$ wave vector that is associated with nesting in the Fermi surface and also is the wave vector at which an inelastic signal is found in neutron scattering.[2] No additional intensity was found, and no differences observed between intensity maps collected at 12 and 20 K, below and above the phase transition.

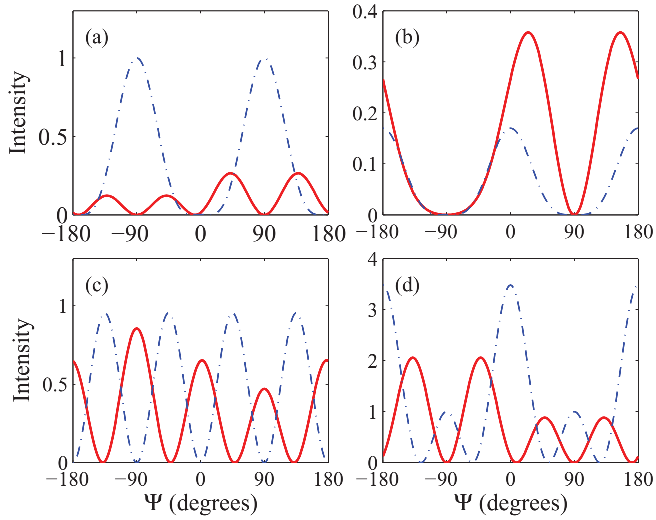

FIG. 2. (Color online) Azimuthal dependence for the (201) reflection of the (a) $Q_{x^2-y^2} = J_x^2 - J_y^2$, (b) $Q_{zx} = J_z J_x + J_x J_z$, (c) $Q_{yz} = J_y J_z + J_z J_y$, and (d) $Q_{3z^2-r^2} = 3J_z^2 - J(J+1)$ quadrupole orderings. The full red line is the σ-π channel, and the dashed blue line is the σ-σ channel. The dependence of the Q_{xy} is already shown in Fig. 1. Panels (b) and (c) are in strong contrast to the azimuthal dependences for (003) for which there is zero intensity in σ-σ.

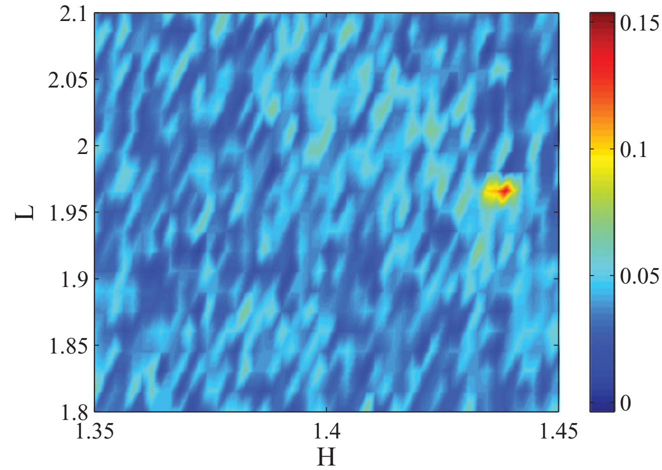

FIG. 3. (Color online) σ-σ intensity map measured in the $[H0L]$ plane with the sample kept at 12 K and $\Psi = 98^\circ$. The covered region of reciprocal space includes the $Q_1 = [1.4\,0\,2]$ wave vector. The intensity maximum of 0.15 corresponds to ~5% of the maximum (201) intensity in the σ-π channel in Fig. 1. The small intensity at [~1.44 0 ~1.97] is spurious, as shown by its independence of temperature.

Our experiments eliminate any possibility that quadrupolar ordering occurs at $Q_0 = [100]$. No signal has been found either at Q_1 nor at incommensurate positions close to this wave vector. Quadrupolar ordering can also be a secondary consequence of the ordering of high-order multipoles, as is the case in NpO_2,[33] so our experiments indirectly test other potential ordered multipoles. However, this is not the case in the proposed model of Ref. 13, because no quadrupole is automatically induced to order in the case of a Γ_2 hexadecapole. The present experiment has focused on quadrupolar ordering, since this can be measured at the uranium M_4 energy and, if present, the matrix elements should give rise to observable signals.

Finally, we note that to observe high-order multipoles *directly*, more difficult experiments must be attempted. The RXS scattering amplitude is due to resonant processes in electric dipole (E_1) and electric quadrupole (E_2) transitions. In localized electron systems, the ground state and the intermediate state at the core-hole site are described in terms of the wave functions of the angular momentum operator J. The selection rule for the E_1 transition implies $\Delta J = 0$, ±1, that for the E_2 transition limits ΔJ to 0, ±1, ±2. RXS intensities at the $M_{4,5}$ edges in actinides are dominated by E_1 ($3d \to 5f$) transitions, and probe multipoles up to rank $p = 2$ (electric charge, magnetic dipole, and electric quadrupoles). E_2 transitions, on the other hand, probe parity-even multipoles up to rank $p = 4$, in particular, magnetic octupole ($p = 3$) and electric hexadecapole ($p = 4$) OPs. However, E_2 contributions at the $M_{4,5}$ edges can only appear indirectly, through $3d \to 6g$ or intermultiplet processes. A search for octupolar or hexadecapolar OPs should rather be performed at the $M_{2,3}$ ($3p \to 5f$) or at the L edges ($2p \to 5f$), where a E_2 signal would appear in the pre-edge energy region, although with intensities that are usually much smaller than those in the E_1 transition.[41] Electric quadrupoles being excluded as OPs by measurements at the $M_{4,5}$ edges, any measurable E_2 signal would be associated with either magnetic octupole or electric hexadecapole order. The energy dependence of the resonant signal, in principle, allows distinguishing between the two cases.[41] These experiments, certainly more difficult than those reported in the present paper, could be the basis for a future effort.

Our set of data now gives a sound basis for experimental and instrumental development. A remaining striking point is the continuous detection of the μ_0 diffraction signal at $Q_0 = [100]$, which is now viewed as a residual contribution originating from the high-pressure antiferromagnetic ground state above $P_x \sim 0.5$ GPa.[42] Symmetrically above P_x, there is a persistence of superconductivity in resistivity while it is well proved that bulk superconductivity exists only in the HO phase ($P < P_x$). Obviously, systematic real-space imaging is required to clarify the robustness of the parasitic effect.

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