Nature of the Order Parameter in the Heavy-Fermion System URu_2Si_2

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The weak order parameter observed below the 17.5 K transition in URu_2Si_2 has been variously attributed to magnetic dipoles, quadrupoles, or octupoles. By polarized neutron scattering we show that the order parameter breaks time reversal invariance and so can not be quadrupolar or a spin nematic. Of the five dipolar and octupolar order parameters that are then allowed by symmetry, polarization analysis reveals that only the spin dipole, M_z, orders at the transition.

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Several superconductors with giant specific heats condense into an ordered phase at temperatures much higher than the transition to superconductivity. Thus URu_2Si_2 orders first [1] at $T_N = 17.5$ K and superconducts at $T_c = 1.2$ K. Little has been proved about the nature of the precursor ordered phase except that it breaks the translational symmetry of the lattice as shown by the appearance of additional weak Bragg peaks in neutron [2–4] and resonant x-ray [5] scattering. Whether the precursor phase increases the tendency for electron pairing is unknown, but the phase microscopically coexists [3,6] with the superconducting order below T_c.

For body-centered tetragonal URu_2Si_2 there is a large specific heat jump [1] at T_N whose magnitude suggests formation of a gap of order 130 K. This gap energy closely corresponds to the energy of the sharp longitudinal spin excitations that appear in neutron scattering [3] below the ordering temperature. The appearance below T_N of long-lived and intense spin waves (transition matrix element $\delta M_z \sim 1.2\mu_B$ along c) was used to suggest that the ordered state is magnetic. Yet when the weak Bragg peaks are interpreted as arising from an ordered array of magnetic dipoles along c, the $0.04\mu_B$ magnitude of the ordered moment is 100 times smaller than the full moment of a uranium ion. Moreover, the specific heat jump is an order of magnitude greater than can be accounted for by the mean field ordering of such weak moments, when the coupling to conduction electrons is ignored. (See Ref. [7] for the effect of coupling.)

The observations with unpolarized neutrons of weak Bragg peaks in URu_2Si_2 with an ordering wave vector $\mathbf{Q}_0 = (111)$ exhibited a structure factor [2,3] as a function of momentum transfer, $\mathbf{Q}$, that was consistent with simple antiferromagnetic dipole order along the long c axis of the tetragonal unit cell. However, there was no proof that other forms of order could not also explain the data. The lack of any theory that would stabilize a heavy-fermion system so close to the boundary of the magnetic instability has led to a number of speculations that the ordered state is more exotic.

If the broken symmetry were to be magnetic dipolar then it follows [3] that the intense spin waves, polarized along the same direction as the apparent ordered moment, must be longitudinal. Broholm *et al.* suggested that the system condensed into a singlet ground state with a singlet excited state. Such a model gives a good description of the spin excitations with a singlet-to-singlet transition energy of $\Delta = 115$ K, but gives too large an ordered moment. An extremely small ordered moment can occur, but only for a ratio of f electron exchange coupling, $J_f(Q_0)$, to splitting Δ, that lies extremely close [3] to the critical ratio for ordering of an induced moment system. To require the couplings to be nearly critical for the weak-moment heavy-fermion systems is unsatisfactory unless such systems lie naturally at the borderline of instability. It was later suggested [7] that the spin gap as it develops might reduce the electronic susceptibility that carries the indirect exchange, $J_f(Q_0)$, and thus stabilize the moment at a low value.

There are anomalous properties that might suggest that the ordering is unusual. The linear magnetic susceptibility [1,8] has a maximum well above the transition temperature, T_N, and the nonlinear susceptibility [9] is positive above T_N. It has been suggested that [10] it would be "prudent to consider quadrupolar (and octupolar) ordering possibilities," that [9] "an itinerant quadrupolar order parameter drives this mysterious transition," and that [11,12] there are strong arguments "in favor of a nontrivial phase." (Reference [11] introduces a method of classifying the types of exotic order in the exchange approximation.)

If spin nematic [12] or quadrupolar [10] order occurs, neutron scattering would detect this to the extent that the spatial deformation of the electronic cloud around a uranium atom would produce a characteristic pattern of displacement of the atoms in the unit cell. Such an order parameter, quadratic in the spin operators, would not break time reversal invariance and would not flip the neutron spin in a polarized neutron experiment.

It has recently been proposed theoretically [12] that a combination of three spins can order, not necessarily on the same site. Such a triple-spin correlator is not observable in the neutron scattering in the absence of a magnetic field H. However, the scattering intensity would grow rapidly as $(H/H_0)^4$ as the field increased up to a characteristic value of H_0 of order 10 T for URu_2Si_2. This suggestion leaves unexplained the zero-field peaks for which experiment provides definite evidence. Moreover the (100) Bragg satellite, rather than increasing, instead decreases [3] by 20% as the field along the easy c axis is increased to 3 T.

In this Letter we enumerate the order parameters allowed by symmetry in URu_2Si_2, and present polarized neutron data that determine which type of order occurs in practice. The ordering in URu_2Si_2 below 17.5 K is detected by the appearance of new Bragg peaks halfway between those of the parent body-centered tetragonal unit (bct) cell. The intensity of these antiferro peaks, for which $h+k+l=$odd, measures the square of the difference in order parameter amplitude between regions of the unit cell that are separated by $(\mathbf{a}+\mathbf{b}+\mathbf{c})/2$ such as the bct cell corner and the cell center. Thus the translational symmetry is broken, but no information is obtained about the multipolar character of the order. Unpolarized neutron measurements [3] have shown that broken-symmetry peaks are observed at (100), (102), (104), and (111), while the equivalent peak at (001) is absent.

We first present polarized neutron scattering measurements of the (100) and (111) broken-symmetry Bragg peaks. The DUALSPEC polarized beam spectrometer at NRU, Chalk River, was operated with two vertically polarized Heusler (111) crystals that selected the energy and spin of the incident and scattered beam. A Mezei flipper turned to rotate the neutron spin by π was placed between the URu_2Si_2 crystal and the analyzer so that both the spin-flip (SF) and non-spin-flip (NSF) scattering from the sample could be measured. For the (100) measurement a neutron beam collimated to 0.7° was filtered through 15 cm of cold beryllium and reflected by the Heusler monochromator set for a wavelength $\lambda=4.06$ Å. Additional removal of higher order neutrons was necessary because the (200) reflection seen in $\lambda/2$ is 10^4 times stronger than the (100) satellite and occurs at the same angle. Moreover the $\lambda/2$ unpolarized (222) reflectivity of the Heusler crystals is stronger than the desired polarized λ reflectivity of (111). Adequate attenuation of the residual $\lambda/2$ neutrons was obtained by installing two 2 mm pyrolytic graphite plates, one in the incident and one in the scattered beam. When the plates were rotated to the 17.6° angle that reflected out the $\lambda/2$ neutrons, the residual $\lambda/2$ flux at the detector decreased by a further factor of 15 while the reduction in the λ flux was only by a factor of 2.

The (100) Bragg peak was observed at 11 K with the URu_2Si_2 crystal oriented in its $(h0l)$ horizontal scattering plane in a ≈ 30 G guide field along the vertical b^* direction. The result depicted in Fig. 1 shows that the (100) intensity is predominantly in the spin-flip channel; that is, the order parameter of URu_2Si_2 has flipped the spin of the neutron. The intensity that remains in the wings in the non-spin-flip channel arises because the removal of $\lambda/2$ by the graphite reflectors is more effective at the center of the NSF scan because their mosaic spread is less than the beam divergence. With allowance for this effect we conclude that the (100) Bragg peak occurs entirely in the spin-flip channel.

Thus we have clearly shown that time reversal symmetry is broken by the weak order parameter, a result that may also be inferred from resonant x-ray measurements [5]. This result alone eliminates quadrupoles and spin nematics from further consideration, since these cannot flip the neutron spin. Moreover, for the (100) peak of URu_2Si_2 only M_y and M_z, the components of the order parameter perpendicular to $\mathbf{Q}$, contribute to the magnetic cross section. Since the guide field at the sample was

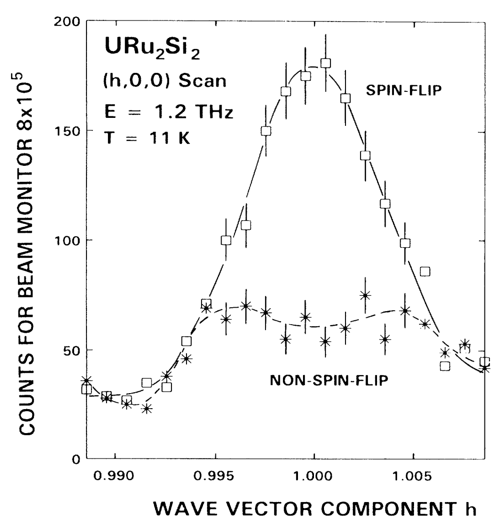

FIG. 1. The (100) Bragg peak corresponding to the broken symmetry below 17.5 K in URu_2Si_2 and showing a reversal or flip of the neutron spin by the order parameter.

along y or b^*, M_y would have appeared in the non-spin-flip channel. The observation that the scattering is in the spin-flip channel therefore shows that at $\mathbf{Q}=(100)$ the order parameter is seen through a nonzero value of $M_z(\mathbf{Q})$. Here $\mathbf{M}(\mathbf{Q})=\int d\mathbf{r}\langle g|\mathbf{M}(\mathbf{r})\exp(i\mathbf{Q}\cdot\mathbf{r})|g\rangle$ where $|g\rangle$ is the ground state, $\mathbf{Q}$ is the momentum transfer, and the magnetization density is $\mathbf{M}(\mathbf{r})$. Note that this still does not identify the order parameter because an octupole or three-spin correlator may give rise to an M_z component of scattering.

In a second polarized beam experiment neutrons of wavelength $\lambda=2.37$ Å were scattered from a sample at 4.3 K oriented in the (hhl) plane mounted in the horizontal field magnet cryostat [13]. The intensity of the (111) broken-symmetry peak was recorded in each spin channel as the 0.25 T guide field was rotated relative to $\mathbf{Q}=(111)$. A reduction of 40000 in the $\lambda/2$ contamination at (111) was obtained by filtration through two pyrolytic graphite crystals, one of which was a particularly effective filter made for DUALSPEC by the Matsushita Corporation. Since the (222) bct reflection is much weaker than (200), the requirement for a clean beam is less stringent at (111) than in the above experiment at (100). The flipping ratio of 23:1 observed for the nearby (112) bct reflection gives a measure of the polarizer, flipper, and beam path efficiencies.

As shown in Fig. 2 the (111) intensity is found to occur in the spin-flip channel when the guide field, and therefore neutron spin, are parallel to $\mathbf{Q}$. When the guide field is perpendicular to $\mathbf{Q}$, at an angle $\alpha=\arctan(a/c\sqrt{2})=17°$ to the c^* axis, the order parameter is seen only in the non-spin-flip channel. The summed intensities are not quite constant because of flux gradients in the neutron beam. The ratio of spin-flip and non-spin-flip intensity is seen in Fig. 2 to vary smoothly with the angle between $\mathbf{Q}$ and the neutron spin. The lines, which are the square of the cosine and of the sine of this angle, are what is expected for an $M_z(\mathbf{Q})$ component of the magnetic amplitude. This angular dependence arises if the neutron spin flips about the vector $\mathbf{Q}\wedge[M_z(\mathbf{Q})\hat{\mathbf{z}}\wedge\mathbf{Q}]$, which points in the α direction 17° from c^*, and at 90° from $\mathbf{Q}=(111)$. Thus our results, which show no spin flip at that angle, are consistent with $\mathbf{M}(\mathbf{Q})$ being in the z direction. If $\mathbf{M}(\mathbf{Q})$ were in the $\hat{\eta}=(\bar{1}10)$ direction, perpendicular to $\mathbf{Q}$ and to $\hat{\mathbf{z}}$, the scattering would occur in the spin-flip channel for all angles of the field in the (hhl) scattering plane. Our results therefore show that $M_\eta(\mathbf{Q})=0$. We shall show that the order parameter $M_z(M_x^2-M_y^2)$ would have been observable at (111) through the $M_\eta(\mathbf{Q})$ magnetic amplitude, and therefore cannot be present.

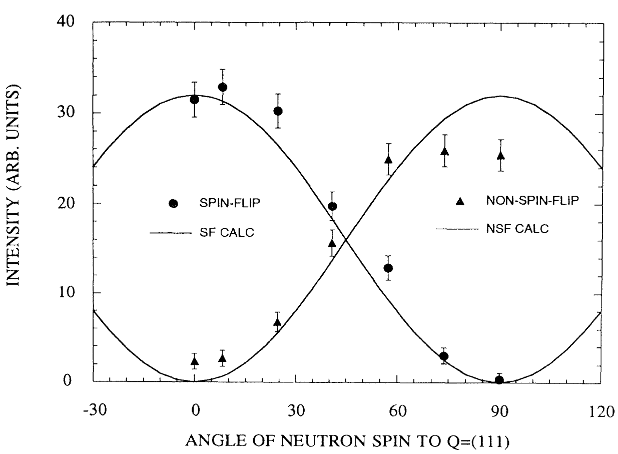

FIG. 2. Polarization of $\mathbf{Q}=(111)$ Bragg reflection in URu_2Si_2 against angle of neutron spin in the (hhl) plane. Only the antiferromagnetic dipole along the c axis is consistent with the data (lines).

We now enumerate the antiferro order parameters allowed by the particular symmetry of URu_2Si_2, and determine which are consistent with the polarized and unpolarized neutron diffraction results. Each uranium ion contains a partially filled $5f$ shell that may possess electric and magnetic multipole moments. The multipole moments of the uranium ion can be classified according to the irreducible representations of the D_4 rotational symmetry of the uranium site, together with an indication of whether these operators change sign under time reversal. We denote time reversal invariance (or not) by a superscript plus (or minus). The distinct symmetries of multipole moments that are possible at a given uranium site are $A_1^+=(3M_z^2-M^2)$, $A_2^+=M_xM_y(M_x^2-M_y^2)$, $B_1^+=M_x^2-M_y^2$, $B_2^+=M_xM_y$, $E^+=(-M_zM_y,M_zM_x)$, $A_1^-=M_xM_yM_z(M_x^2-M_y^2)$, $A_2^-=M_z$, $B_1^-=M_xM_yM_z$, $B_2^-=M_z(M_x^2-M_y^2)$, and $E^-=(M_x,M_y)$. Each multipole moment has been given one label (e.g., B_1^-) that refers to a particular irreducible representation of D_4 listed in Table I, and a second label (e.g., $M_xM_yM_z$) that allows the symmetry properties of the multipole moment to be deduced by inspection. This symmetry-based classification scheme is valid for ions having either an even or odd number of electrons and includes all possibilities corresponding to irreducible representations of D_4.

Since the neutron spin is flipped by the order parameter it follows that time reversal invariance is broken and that the Bragg peaks below T_N are seen through the magnetic cross section. This observation eliminates all even-order spin combinations such as quadrupoles and spin nematics. It therefore restricts attention to the five sym-

TABLE I. Character table for the point group D_4.

D_4	E	C_4^2	$2C_4$	$2C_{2x}$	$2C_{2\xi}$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	1	−1	1	−1
B_2	1	1	−1	−1	1
E	2	−2	0	0	0

metries above that break time reversal invariance.

For $\mathbf{Q}=(1,0,0)$ we have observed that $M_z(\mathbf{Q})\neq 0$ and $M_y(\mathbf{Q})=0$. This rules out the ordering with symmetry $E^-=(M_x,M_y)$, as was already clear from the absence of a peak at (0,0,1) in previous unpolarized experiments. Now consider an antiferro ordering of the multipole $M_xM_yM_z$. Because the ground state would be invariant, as is $\mathbf{Q}$, with respect to reflection in a plane perpendicular to the b axis and passing through a uranium ion, it follows that $M_z(\mathbf{Q})=0$ for $\mathbf{Q}=(h,0,l)$ in general, and for (1,0,0) in particular. Since this contradicts experiment the ordering cannot arise from $M_xM_yM_z$ octupoles. By a similar argument antiferro ordering of $M_xM_yM_z(M_x^2-M_y^2)$ multipoles is excluded.

There remain two possibilities, the octupole, $M_z(M_x^2-M_y^2)$, and the dipole, M_z. Write the octupole as $M_zM_\xi M_\eta$, where ξ is in the (1,1,0) spatial direction, and η is in the $(-1,1,0)$ direction, perpendicular to the (hhl) plane of the reciprocal lattice. Because the ground state of the octupole would be invariant under reflection in a plane perpendicular to the η direction, it follows that $M_z(hhl)=M_\xi(hhl)=0$. The octupole can only be seen in the (hhl) plane through the $M_\eta(hhl)$ amplitude. Our polarized experiment at $\mathbf{Q}=(1,1,1)$, however, shows that $M_\eta(hhl)=0$. Thus the octupole $M_z(M_x^2-M_y^2)$ may be excluded. The only order consistent with experimental facts is the magnetic dipole, M_z. The experiments rule out all orderings that are invariant under time reversal such as nuclear displacements, quadrupoles, or spin nematics.

There are weaker scattering amplitudes [14] that result from the spin-orbit (or Schwinger) and Foldy interactions. They depend on the Fourier transform of the total electronic plus nuclear charge density. Although the amplitudes may be appreciable for high-Z actinide ions [15], they always contain a contribution to spin-flip scattering about an axis perpendicular to the scattering plane. Since $M_y(1,0,0)$ and $M_\eta(1,1,1)$ have been observed to be zero, our results also rule out these weaker cross sections.

Polarized neutron experiments combined with symmetry arguments therefore show that the order parameter describing the ground state of URu_2Si_2 below T_N is an antiferromagnetic condensation of magnetic dipoles along the crystallographic c direction. In this direction the susceptibility is an order of magnitude larger than in the basal plane of the strongly tetragonal structure ($c/a\sim 2$). The reason that the magnetic order is unusually weak remains an enigma. Some mechanism needs to be sought that favors positioning of heavy-fermion systems like URu_2Si_2 near the boundary of the magnetic instability.

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