HEAVY FERMIONS

Chirality density wave of the “hidden order” phase in URu$_2$Si$_2$

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A second-order phase transition in a physical system is associated with the emergence of an “order parameter” and a spontaneous symmetry breaking. The heavy fermion superconductor URu$_2$Si$_2$ has a “hidden order” (HO) phase below the temperature of 17.5 kelvin; the symmetry of the associated order parameter has remained ambiguous. Here we use polarization-resolved Raman spectroscopy to specify the symmetry of the low-energy excitations above and below the HO transition. We determine that the HO parameter breaks local vertical and diagonal reflection symmetries at the uranium sites, resulting in crystal field states with distinct chiral properties, which order to a commensurate chirality density wave ground state.

In solids, electrons occupying 5f orbitals often have a partly itinerant and partly localized character, which leads to a rich variety of low-temperature phases, such as magnetism and superconductivity (7). Generally, these ordered states are characterized by the symmetry they break, and an order parameter may be constructed to describe the state with reduced symmetry. In a solid, the order parameter reflects the microscopic interactions among electrons that lead to the phase transition. In materials containing f-electrons, exchange interactions of the lanthanide or actinide magnetic moments typically generate long-range antiferromagnetic or ferromagnetic order at low temperatures, but multipolar ordering such as quadrupolar, octupolar, and hexadecapolar is also possible (2).

One particularly interesting example is the uranium-based intermetallic compound URu$_2$Si$_2$. It displays a nonmagnetic second-order phase transition into an electronically ordered state at $T_{HO} = 17.5$ K, and then becomes superconducting below 1.5 K (3, 4). Despite numerous theoretical proposals to explain the properties below $T_{HO}$ in the past 30 years (5–10), the symmetry and microscopic mechanism for the order parameter remain ambiguous, hence the term “hidden order” (HO) (11). In this ordered state, an energy gap in both the spin and charge response has been reported (12–18). In addition, an in-gap collective excitation at a commensurate wave vector has been observed in neutron scattering experiments (13, 14, 16). Recently, fourfold rotational symmetry breaking under an in-plane magnetic field (19) and a lattice distortion along the crystallographic a axis (20) have been reported in high-quality small crystals. However, the available experimental works cannot yet conclusively determine the symmetry of the order parameter in the HO phase.

URu$_2$Si$_2$ crystallizes in a body-centered tetragonal structure belonging to the $I4_1$ point group (space group no. 139 $I4_1/mmm$, Fig. 1A). The uniqueness of URu$_2$Si$_2$ is rooted in the coexistence of the broad conduction bands, composed mostly of Si-p and Ru-d electronic states, and more localized U-5f orbitals, which are in a mixed-valent configuration between tetravalent $4f^2$ and trivalent $4f^3$ (21). When the temperature is lowered below ~70 K, the hybridization with the conduction band allows a small fraction of each U-5f electron to participate in formation of a narrow quasiparticle band at the Fermi level, whereas the rest of the electron remains better described as localized on the uranium site.
Fig. 1. Schematics of the local symmetry of the quasi-localized states. (A) The crystal structure of URu$_2$Si$_2$ above $T_{HO}$, belonging to the $D_{4h}$ point group. Presented in three dimensions and $xy$-plane cut are illustrations showing the symmetry of the $A_{2g}$ state $|0\rangle$ and $A_{1g}$ state $|1\rangle$, where the positive (negative) amplitude is denoted by red (blue) color. The $A_{1g}$ state is symmetric with respect to the vertical ($\sigma_v$) and diagonal ($\sigma_d$) reflections, whereas the $A_{2g}$ state is antisymmetric with respect to these reflections. (B) Schematic of the band structure of a low-energy minimal model. The green dashed line denotes the conduction band $|CB\rangle$; the red and black dashed lines denote crystal field states of the U-5f electrons: the ground state $|0\rangle$ and the first excited state $|1\rangle$. Blue and red arrows denote the incident and scattered light in a Raman process, respectively. $W=\frac{1}{65}$ eV is the incoming photon energy (energy levels not to scale), $W$ is the hybridization strength between $|1\rangle$ and $|CB\rangle$; $w_0$ and $e_k$ are the resonance energies for $|0\rangle\rightarrow|1\rangle$ and $|0\rangle\rightarrow|CB\rangle$ excitations, respectively. (C) The crystal structure of URu$_2$Si$_2$ in the $HO$ phase, and illustrations showing the symmetry of the chiral states $|\sigma^+\rangle$ and $|\sigma^-\rangle$, and the excited state $|\sigma^0\rangle$. The left- and right-handed states, denoted by red and blue atoms, respectively, are staggered in the lattice. UL and UR denotes the two nonequivalent uranium sites in the $HO$ phase. (D) Schematics of the chirality density wave in the $HO$ phase. The uranium sites $U^L$ and $U^R$ are occupied by $|\sigma^+\rangle$ and $|\sigma^-\rangle$ states, respectively.

Fig. 2. Temperature dependence of the $A_{2g}$ Raman susceptibility. (A) The $A_{2g}$ Raman response function decomposed from the spectra measured in the $XY$, $X'Y'$, and RL scattering geometries (22). The solid lines are a guide to the eye, illustrating the narrowing of the Drude function (25): $\chi_{A_{2g}}^\omega(\omega,T)=\text{Im}[\Gamma(T)/\omega]^\alpha$, where $\Gamma(T)$ is the Drude scattering rate (indicated by the arrows), which decreases on cooling. Below 70 K, the Raman response deviates from the Drude function. Below $T_{HO}$, the Raman response shows spectral weight suppression below 6 meV and the appearance of an in-gap mode at 1.6 meV (7 and 13 K). (B) Temperature dependence of the static Raman susceptibility in $A_{2g}$ channel $\chi_{A_{2g}}^\omega(0,T)$ (red dots), and the static magnetic susceptibility along $c$ and $a$ axis from (3) are plotted as blue squares and black circles, respectively. $T_{HO}$ is marked by the dashed line. (C) Temperature dependence of the low-frequency Raman response in the $XY$ scattering geometry, dominantly composed of $A_{2g}$ excitations. A gaplike suppression develops on cooling, and an in-gap mode at 1.6 meV (black dashed line) emerges below $T_{HO}$. The full width at half-maximum of the mode decreases on cooling from ~0.75 meV at 13 K to ~0.3 meV at 7 K. The white line shows the temperature dependence of the BCS gap function.
from 5 meV at room temperature to 1 meV just above $T_{\text{HO}}$ (Fig. 2A). Below 70 K, the line shape deviates slightly from the Drude function, tracking the formation of the heavy fermion states by the hybridization of the itinerant conduction band and the $U$-5f states. Below 17.5 K, the $A_{2g}$ Raman response function shows suppression of low-energy spectral weight resembling the temperature dependence of the Bardeen-Cooper-Schrieffer (BCS) gap function, and the emergence of a sharp in-gap mode at 1.6 meV (Fig. 2B and C).

Figure 2B displays a comparison between the $\chi''(\omega)$ (right axis), showing that the responses are proportional to each other at temperatures above $T_{\text{HO}}$. This proportionality can be understood by noting that both susceptibilities probe $A_{2g}$-like excitations, as given by the minimal model of Fig. 1B. The extreme anisotropy of the magnetic susceptibility (Fig. 2B) also follows from this minimal model (22).

Having established the Raman response of $A_{2g}$ symmetry and its correspondence with the magnetic susceptibility, we now present our main results describing the symmetry breaking in the HO state. Figure 3 shows the Raman response in six scattering geometries at 7 K. The intense in-gap mode is observed in all scattering geometries containing $A_{2g}$ symmetry. The mode can be interpreted as a quasi-localized state, which can only appear in the $A_{2g}$ channel of the $\mathbb{D}_{4h}$ group. The $A_{2g}$ channel implies that the irreducible representation $A_{2g}$ of the $\mathbb{D}_{4h}$ point group merge into the $A_{g}$ representation of the lower group $\mathbb{C}_{4h}$. This signifies the removal of the local vertical and diagonal reflection symmetry operators at the uranium sites in the HO phase. Similarly, the intensity leakage into the RL scattering geometry measures the strength of orthorhombic distortion caused by broken fourfold rotational symmetry.

When the reflection symmetries are broken, an $A_{2g}$-like interaction operator $\Psi_{\text{HO}} = \mathbb{V}^\dagger |0\rangle |0\rangle$ mixes the $|0\rangle$ and $|1\rangle$ states, leading to two new local states $
abla = (1 - \frac{\mathbb{F}_2}{2\mathbb{G}_0}) |0\rangle + \frac{\mathbb{G}_0}{\mathbb{V}_1} |1\rangle$ with $V$ being the interaction strength (6). A pair of such states cannot be transformed into one another by any remaining $\mathbb{C}_{4h}$ group operators: a property known as chirality (or handedness). The choice of either the right-handed or the left-handed state on a given uranium site, $\nabla^+$ or $\nabla^-$, defines the local chirality in the HO phase (Fig. 1C). Notice that these two degenerate states both preserve the time-reversal symmetry, carry no spin, and contain the same charge, but differ only in handedness.

The same 1.6-meV sharp resonance has also been observed by inelastic neutron scattering at momentum commensurate with the reciprocal lattice vector, but only in the HO state (14, 16, 29). The Raman measurement proves that this resonance is a long-wavelength excitation of $A_{2g}$ character. The appearance of the same resonance in neutron scattering at a different wavelength, corresponding to the $c$-axis lattice constant, requires HO to be a staggered alternating electronic order along the $c$ direction. Such order with alternating left- and right-handed states at the uranium sites for neighboring basal planes has no modulation of charge or spin and does not couple to the tetragonal lattice; hence, it is hidden to all probes but the scattering of $A_{2g}$ symmetry. We reveal this hidden order to be a chirality density wave depicted in Fig. 1D.

The chirality density wave doubles the translational periodicity of the phase above $T_{\text{HO}}$; hence, it folds the electronic Brillouin zone, as recently observed by angle-resolved photoemission spectroscopy (30). It also gives rise to an energy gap, as previously observed in optics (12, 17, 18) and tunneling experiments (15, 31) and shown in Fig. 2C to originate in expelling the continuum of $A_{2g}$ excitations. The sharp resonance is explained by excitation from the ground state, in which a chirality density wave staggered $\nabla^+$ and $\nabla^-$, to the excited collective state (22).

A local order parameter of primary $A_{2g}$ symmetry, breaking vertical and diagonal reflections, with a subdominant $B_{3g}$ component, breaking fourfold rotational symmetry, can be expressed in terms of the composite hexadecapole local order parameter of the form (6, 22)

$$\pm \mathbb{V}[J_x - J_y/J_x + J_y](J_x + J_y + J_y + J_x)$$

where $J_x$, $J_y$ are in-plane angular momentum operators and the overline stands for symmetrization. A spatial order alternating the sign of this hexadecapole for neighboring basal planes is the chirality density wave (Fig. 1D) that consistently explains the HO phenomena as it is observed by Raman and neutron scattering (13, 14, 16, 29), magnetic torque (19), x-ray diffraction (20), and other data (11, 12, 17, 18, 30). Our finding is an example of exotic electronic ordering emerging from strong interaction among f electrons, which

**Fig. 3.** The Raman response function in six scattering geometries at 7 K. The arrows in each panel show the linear or circular polarizations for incident (blue) and scattered (red) light. The six scattering geometries are denoted as $\text{scat} = XX, XY, X'Y', YX, RR$, and RL, with $\text{inc}$ being the direction vector for incident light polarization and $\text{scat}$ being the scattered light polarization. $X = [100], Y = [010]$ are aligned along crystallographic axes; $X' = [110], Y' = [\bar{1}10]$ are at 45° to the $a$ axes; $R = (X + Y)/\sqrt{2}$ and $L = (X - Y)/\sqrt{2}$ are right and left circularly polarized light, respectively (22). The irreducible representations for each scattering geometry are shown within the $\mathbb{D}_{4h}$ point group. The data are shown in black circles, where the error bars show 1 SD. The red solid lines are fits of the in-gap mode to a Lorentzian, and the fitted intensity using the method of maximum likelihood is noted in each panel. By decomposition, the in-gap mode intensity in each symmetry channels are $I_{XX} = 2.6 \pm 0.1$, $I_{XY} = 0.7 \pm 0.1$, $I_{X'Y'} = 0.3 \pm 0.1$, and $I_{RR} = 0.1 \pm 0.1$. The full width at half-maximum of the in-gap mode is about 0.3 meV at 7 K (instrumental resolution of 0.17 meV is shown in the XY panel).
should be a more generic phenomenon relevant to other intermetallic compounds.

**Note added in proof:** While this paper was being reviewed, J. Buhot et al. (32) reproduced the $A_{2g}$ symmetry in-gap mode in a Raman experiment with 561-nm laser excitation and showed that the mode does not split in up to 10 T magnetic field.

**REFERENCES AND NOTES**

22. See supplementary materials on Science Online.

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**SUPPLEMENTARY MATERIALS**

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Material and Methods

Figs. S1 to S4

References (33–46)

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**APPLIED OPTICS**

Multiwavelength achromatic metasurfaces by dispersive phase compensation

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The replacement of bulk refractive optical elements with diffractive planar components enables the miniaturization of optical systems. However, diffractive optics suffers from large chromatic aberrations due to the dispersion of the phase accumulated by light during propagation. We show that this limitation can be overcome with an engineered wavelength-dependent phase shift imparted by a metasurface, and we demonstrate a design that deflects three wavelengths by the same angle. A planar lens without chromatic aberrations at three wavelengths is also presented. Our designs are based on low-loss dielectric resonators, which introduce a dense spectral window of optical modes to enable dispersive phase compensation. The suppression of chromatic aberrations in metasurface-based planar photonics will find applications in lightweight collimators for displays, as well as chromatically corrected imaging systems.

Refractive and diffractive optical components have fundamentally different responses to broadband light. For a material with normal dispersion, refractive lenses have larger focal distances for red light than for blue and prisms deflect longer wavelengths by a smaller angle; the contrary occurs for diffractive lenses and gratings (1, 2). This contrasting behavior arises because two different principles are used to shape the light: Refractive optics relies on the phase gradually accumulated through propagation, whereas diffractive optics operates by means of interference of light transmitted through an amplitude or phase mask. In most transparent materials in the visible, the refractive index $n$ decreases with increasing wavelength ($\lambda$) (normal dispersion). Because the deflection angle $\theta$ of a prism increases with $n$ and a lens focal length $f$ is inversely proportional to $n - 1$, the resulting effect is the one shown in Fig. 1, A and B. In a diffractive optical element (DOE), the beam deflection angle and the focal length instead increase and decrease with $\lambda$, respectively (Fig. 1, C and D), generating an opposite dispersion compared with standard refractive devices. Although for many applications a spatial separation of different wavelengths is desirable, in many others this represents a problem. For example, the dependence of the focal distance on $\lambda$ produces chromatic aberrations and is responsible for the degradation of the quality of an imaging system. Another difference between these technologies is the efficiency that is generally lower for diffractive optics due to the presence of higher diffraction orders. The wavelength dependence is typically much more pronounced in diffractive optics than in refractive optics, when low-dispersion materials are used in the latter (2). In refractive lenses, complete elimination of chromatic aberrations at two and three wavelengths is accomplished using, respectively, two and three elements (achromatic doublet and apochromatic triplet) arranged to achieve the same focal length at the wavelengths of interest (3). Supercromatic lenses are practically achromatic for all colors by correcting aberrations at four suitable wavelengths (4). Although successful, these strategies add weight, complexity, and cost to optical systems. On the other hand, DOEs have the advantage of being relatively flat, light, and often low cost. Blazed gratings and Fresnel lenses are diffractive optical devices with an analog phase profile and integrate some benefits of both technologies (e.g., small footprint and high efficiency), but they still suffer from strong chromatic aberrations. Multiorder diffractive lenses overcome this limitation by using thicker phase profiles to achieve chromatic correction for a discrete set of wavelengths (5). However, the realization of thick, analog phase profiles is challenging for conventional fabrication technologies. Metasurfaces are thin optical components that rely on a different approach for light control: A dense arrangement of subwavelength resonators is designed to modify the optical response of the interface. The resonant nature of the scatterers introduces an abrupt phase shift in the incident wavefront, making it possible to mold the scattered wavefront at will and enabling a new class of planar photonics components (flat optics) (5–8). Different types of resonators (metallic or dielectric antennas, apertures, etc.) have been used to demonstrate various flat optical devices, including blazed gratings (9–11), lenses (12–14), holographic plates (15), polarizers, and wave plates.
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Editor's Summary

Uncovering the symmetry of a hidden order

Cooling matter generally makes it more ordered and may induce dramatic transitions: Think of water becoming ice. With increased order comes loss of symmetry; water in its liquid form will look the same however you rotate it, whereas ice will not. Kung et al. studied the symmetry properties of a mysteriously ordered phase of the material URu$_2$Si$_2$ that appears at 17.5 K. They shone laser light on the crystal and studied the shifts in the frequency of the light. The electron orbitals of the uranium had a handedness to them that alternated between the atomic layers.

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