On the possibility to detect multipolar order in URu$_2$Si$_2$ by the electric quadrupolar transition of resonant elastic x-ray scattering


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Resonant elastic x-ray scattering is a powerful technique for measuring multipolar order parameters. In this paper, we theoretically and experimentally study the possibility of using this technique to detect the proposed multipolar order parameters in URu$_2$Si$_2$ at the U-L$_3$ edge with the electric quadrupolar transition. Based on an atomic model, we calculate the azimuthal dependence of the quadrupolar transition at the U-L$_3$ edge. The results illustrate the potential of this technique for distinguishing different multipolar order parameters. We then perform experiments on ultraclean single crystals of URu$_2$Si$_2$ at the U-L$_3$ edge to search for the predicted signal, but do not detect any indications of multipolar moments within the experimental uncertainty. We theoretically estimate the orders of magnitude of the cross section and the expected count rate of the quadrupolar transition and compare them to the dipolar transitions at the U-M$_4$ and U-L$_3$ edges, clarifying the difficulty in detecting higher order multipolar order parameters in URu$_2$Si$_2$ in the current experimental setup.

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I. INTRODUCTION

The heavy-fermion compound URu$_2$Si$_2$ undergoes a phase transition at $T_{HO} = 17.5$ K to the so-called “hidden order” (HO) phase, in which the sharp discontinuous specific heat signals a clear second-order phase transition [1]. Earlier studies based on neutron scattering [2,3] and muon spin rotation [4] conclude that it is a phase transition to a type-I antiferromagnet with the ordered moment polarized along the tetragonal c axis. However, the observed ordered moment is anomalously very small ($\sim 0.04 \pm 0.01 \mu_B$) [2–4], which cannot account for the observed large entropy loss ($\sim 0.2 R \ln 2$), and the primary order parameter (OP) is unlikely to be a magnetic dipole. Further high-pressure experiments on URu$_2$Si$_2$ find a first-order phase transition from the HO phase to a large moment antiferromagnetic (LMAF) phase [5–7]. These findings further indicate that the HO phase is distinct from the LMAF and the primary OP should be some complex object which is different from a magnetic dipole.

Theoretically, many different schemes of OPs have been proposed, such as multipolar order [8–18], charge- or spin-density wave [19–22], chiral spin state [23], orbital antiferromagnetism [24], helicity order [25], dynamic symmetry breaking [26], nematic order [27], hybridization wave [28], and hystatic order [29,30]. However, through 30 years of efforts, there is still a lack of convincing evidence to uncover the HO mystery. For a more complete review of the theoretical and experimental progress, see Refs. [31,32].

Among the many proposals of OPs, the multipolar order is a promising candidate. Recently, Raman-scattering experiments [33–35] find a sharp low-energy excitation with $A_{2g}$ symmetry below $T_{HO}$. Further analysis [34,35] indicates that this $A_{2g}$ excitation is consistent with the hexadecapolar order proposed by Haule and Kotliar [14]. However, these Raman-scattering experiments provide indirect information about the ground state in the sense that they cannot measure modes at the ordering wave vector. Wave-vector-resolved techniques are desirable to make more definitive conclusions. Among the many options, resonant elastic x-ray scattering (REXS) is a powerful tool to directly detect the order of electrons including complex spin and charge multipoles [36,37]. There have been already a few REXS experiments [38–41] performed to identify the multipolar order in the HO phase of URu$_2$Si$_2$. Amitsuka et al. [40] and Walker et al. [41] performed REXS experiments at the U-M$_4$ (3d$_{3/2} \rightarrow 5 f$) edge below $T_{HO}$ and their results have excluded the possibility of any quadrupolar OPs. However, the M$_2$ edge involves electric dipolar transitions ($E1$) and has minimal sensitivity to multipoles with a rank larger than 2. The electric quadrupolar transition ($E2$) can be used to detect octupole and hexadecapole, but unfortunately, the intensity of $E2$ is usually much weaker than that of $E1$.

Recently, dos Reis et al. [42] discussed a sizable $E2$ contribution to the U-L$_{2,3}$ magnetic circular dichroism signal in their study of U compounds. The enhanced $E2$ signal may be due to the large wave vector $k$ (10.615 and 8.699 Å$^{-1}$) at L$_{2,3}$ edges which means that the term $ik \cdot r$ in the expansion of $e^{ik \cdot r}$ cannot be ignored. This unexpected finding provides a promising hope to use the E2 transition to directly detect multipolar OPs in URu$_2$Si$_2$.

In this paper, we theoretically and experimentally study the possibility to detect the proposed multipolar OPs in URu$_2$Si$_2$ via $E2$ transition of REXS. Based on an atomic model, we first calculate the azimuthal dependences to show that it can identify different multipolar OPs by symmetry. Then, we do REXS experiments on an ultraclean sample of URu$_2$Si$_2$ single
crystal to search for the possible signal of multipolar OPs. Finally, we justify the experimental results by theoretically estimating the relative strength of E2 transition at the L3 edge (L3–E2) compared with E1 transition at the M4 edge (M4–E1) and L3 edge (2p3/2 → 6d,L3–E1), and the expected flux of the scattered photons.

II. METHODS

A. Atomic calculations

Figure 1(a) is the crystal structure of URu2Si2, which has a body-centered tetragonal structure. In the present study, we assume a type-I antiferromultipolar order on U sites, where sublattice A, U(0,0,0), and sublattice B, U(0.5,0.5,0.5), have opposite signs of the expectation value of the multipolar moment. The ordering wave vector is QAB = (0,0,1). Figure 1(b) is a typical experimental setup of REXS. A beam of polarized x ray k is incident on the sample with an angle θ and then the scattered x rays k′ with outgoing angle θ and specific polarization is analyzed. φ is the azimuthal angle. For linear polarization, π (σ) polarization is parallel (normal) to the scattering plane.

absorption and emission processes,

$$\hat{D} = P^{(m) \cdot} \sum_R \hat{D}^{(m)}_R = P^{(m) \cdot} \left( \sum_R e^{iQ \cdot R} \sum_i \hat{P}^{(m)}_{R,i} \right),$$  (3)

$$\hat{D}^{(m)\dagger} = P^{(m)\dagger \cdot} \sum_R \hat{D}^{(m)\dagger}_R = P^{(m)\dagger \cdot} \left( \sum_R e^{-iQ \cdot R} \sum_i \hat{P}^{(m)\dagger}_{R,i} \right),$$  (4)

where $R$ is the site index, and $i$ is the index of electron that is bound to site $R$. $P^{(m)\dagger}$ is a rank-$m$ tensor for the geometry part including polarization and wave vector of photon, $\hat{P}^{(m)}_{R,i}$ is a single-particle rank-$m$ tensor operator of electron.

For the E1–E1 transition,

$$P^{(1)} \cdot \hat{P}^{(1)} = \varepsilon_x \hat{x} + \varepsilon_y \hat{y} + \varepsilon_z \hat{z},$$  (5)

$$P^{(1)\dagger \cdot} \hat{P}^{(1)\dagger} = \varepsilon_x^\ast \hat{x} + \varepsilon_y^\ast \hat{y} + \varepsilon_z^\ast \hat{z}.$$  (6)

For the E2–E2 transition [43],

$$(\hat{P}^{(2)}_1)_1 = \frac{\sqrt{3}}{2} (\hat{x}^2 - \hat{y}^2),$$  (7)

$$P^{(2)}_1 \cdot \hat{P}^{(2)}_1 = \frac{1}{2} (3\hat{\epsilon}_x^2 - \hat{\epsilon}_y^2),$$  (8)

$$P^{(2)}_1 \cdot \hat{P}^{(2)}_1 = \sqrt{3}\hat{\epsilon}_x,$$  (9)

$$P^{(2)}_1 \cdot \hat{P}^{(2)}_1 = \sqrt{3}\hat{\epsilon}_y,$$  (10)

and

$$P^{(2)}_1 \cdot \hat{P}^{(2)}_1 = \sqrt{3}\hat{\epsilon}_z.$$  (11)

where

$$P^{(2)}_1 = \frac{k}{3} (\varepsilon_x \hat{k}_x - \varepsilon_y \hat{k}_y),$$  (12)

$$P^{(2)}_2 = \frac{k}{3} (2\varepsilon_x \hat{k}_x - \varepsilon_y \hat{k}_y),$$  (13)

$$P^{(2)}_3 = \frac{k}{3} (\varepsilon_x \hat{k}_x + \varepsilon_y \hat{k}_y),$$  (14)

$$P^{(2)}_4 = \frac{k}{3} (\varepsilon_x \hat{k}_x + \varepsilon_y \hat{k}_y),$$  (15)

where $k$ and $\hat{k}$ are the length and direction of the wave vector, respectively. We assume the absorption and emission process take place at the same site, then the scattering amplitude can be written as

$$F_{gs} \propto \sum_R e^{-iQ \cdot R} F_{gs}^R,$$  (17)

with

$$F_{gs}^R = \sum_n \langle g | \hat{D}^{(m)}_R | n \rangle \langle n | \hat{D}^{(m)}_R | g \rangle$$  (18)

where $\hat{D}_R = P^{(m) \cdot} \hat{D}^{(m)}_R$ and $\hat{D}^{(m)}_R = P^{(m)\dagger \cdot} \hat{D}^{(m)\dagger}_R$.  

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We further make a single-atom approximation, i.e., approximating the states $|g⟩$ and $|n⟩$ as single atomic states. Then the total scattering amplitude can be written as the summation of the contributions from two sublattices $A$ and $B$ of $U$ atoms,

$$ \mathcal{F}_{gg} \propto \sum_{R_A} e^{-i\mathbf{q} \cdot \mathbf{R}_A} \mathcal{F}_{R_A}^{R_A} + \sum_{R_B} e^{-i\mathbf{q} \cdot \mathbf{R}_B} \mathcal{F}_{R_B}^{R_B}, \quad (19) $$

where

$$ \mathcal{F}_{R_A}^{R_A} = \sum_n \langle g^A | \hat{D}_{R_A}^{\dagger} | n^A \rangle \langle n^A | \hat{D}_{R_A} | g^A \rangle, \quad (20) $$

$$ \mathcal{F}_{R_B}^{R_B} = \sum_n \langle g^B | \hat{D}_{R_B}^{\dagger} | n^B \rangle \langle n^B | \hat{D}_{R_B} | g^B \rangle. \quad (21) $$

$|g^A⟩(|n^A⟩)$ and $|g^B⟩(|n^B⟩)$ are the ground (intermediate) states of $U$ atoms $A$ and $B$, respectively. In calculation, we choose the ground states to induce opposite signs of the expectation value of multipolar moment at the $A$ and $B$ sites.

We use the Cowan-Butler-Thole approach [44–47] to exactly diagonalize the atomic Hamiltonian for ground and excited configurations and then get the transition matrix. For URu$_2$Si$_2$, we assume a $5f^2$ ground configuration. For the $M_A-E1, L_2-E1$ and $L_3-E2$ transitions, the excited configurations are $3d^5f^3, 2p^5f^2d^6l^1$, and $2p^5f^3$, respectively. The Slater integrals $F^k, G^k$ and spin-orbit coupling (SOC) $\zeta$ of the valence and core electrons are calculated by the Hartree-Fock (HF) methods in Cowan's code [44]. Usually, HF will overestimate them, so we rescale $F^k, G^k$ by 80% and rescale SOC $\zeta$ by 92% for $2p$ core hole and 96% for $3d$ core hole, respectively. The parameters are listed in Tables I–IV in the Appendix.

According to Hund’s rule coupling, the $5f^2$ configuration has a ground state with total angular momentum $J = 4$ under $SO(3)$ symmetry. With $D_{6h}$ crystalline electric field symmetry, these nine ground states will split into five singlets and two doublets [17,48]:

$$ |A_1^3(\alpha)⟩ = \cos \alpha |0⟩ + \frac{\sin \alpha}{\sqrt{2}} (|4⟩ + |−4⟩), \quad (22) $$

$$ |A_2^3(\alpha)⟩ = \sin \alpha |0⟩ - \frac{\cos \alpha}{\sqrt{2}} (|4⟩ + |−4⟩), \quad (23) $$

$$ |A_2⟩ = \frac{i}{\sqrt{2}} (|4⟩ - |−4⟩), \quad (24) $$

$$ |B_1⟩ = \frac{1}{\sqrt{2}} (|2⟩ + |−2⟩), \quad (25) $$

$$ |B_2⟩ = \frac{i}{\sqrt{2}} (|2⟩ - |−2⟩). \quad (26) $$

$$ |E_1^{(1)}(\beta)⟩ = \cos \beta |∓1⟩ + \sin \beta |±1⟩ \pm 3), \quad (27) $$

$$ |E_2^{(2)}(\beta)⟩ = \sin \beta |∓1⟩ - \cos \beta |±1⟩. \quad (28) $$

In Ref. [17], the authors list the definition of the multipole up to rank 5. We will follow this definition in the present paper and only discuss multipole up to rank 4 that can, in principle, be detected via the $E2$ transition. We build different ground states which will induce dipole, quadropole, octupole, and hexadecapole orders.

The ground state that will induce $A_{2+}$ ($A_{2−}$) order can be constructed by a linear combination of $|A_{2g}⟩$ and $|A_{1g}^{(2)}⟩$,

$$ |g^{A(B)}⟩ = \frac{1}{\sqrt{2}} (|A_{2g}⟩ \pm e^{i\eta}|A_{1g}^{(2)}⟩), \quad (29) $$

where the plus sign is for $|g^A⟩$ and the minus sign for $|g^B⟩$. Note that the subscript $+$ ($−$) in $A_{2+}$ ($A_{2−}$) means time-reversal even (odd). When $\eta = 0$, it will induce a $A_{2+}$ hexadecapolar order $H_6 = \frac{\sqrt{5}}{2} J_z (J_z^2 - J_z^2)$, while $\eta = \pi/2$ will induce a $A_{2−}$ dipolar order $J_z$ and octupolar order $T_2^\zeta = \frac{1}{3} J_z (5 J_z^2 - 3 J_z^2)$. This scheme is proposed by Haule and Kotliar [14] by a LDA+DMFT calculation. In their LDA+DMFT calculation, they also figure out $a$ in $A_{2g}$ should be about 40. $H_6$ is proposed to be the primary OP in the HO phase. It can be also induced as a secondary OP in the hastatic order scheme [30].

The ground state that will induce $B_{1+}$ ($B_{1−}$) order can be written as

$$ |g^{A(B)}⟩ = \frac{1}{\sqrt{2}} (|B_{1g}⟩ \pm e^{i\eta}|A_{1g}^{(2)}⟩). \quad (30) $$

When $\eta = 0$, it will induce a $B_{1+}$ quadrupolar order [10] $O_{2y} = \frac{\sqrt{3}}{2} J_2^2 - J_2^2$ and hexadecapolar order $O_{42} = \frac{\sqrt{3}}{4} (J_2^2 - J_2^2)(7 J_2^2 - J_2^2)$, while $\eta = \pi/2$ will induce a $B_{1−}$ octupolar order [12] $T_2^\zeta = \frac{\sqrt{3}}{2} J_z (J_z^2 - J_z^2)$. The ground state that will induce $B_{2+}$ ($B_{2−}$) order can be written as

$$ |g^{A(B)}⟩ = \frac{1}{\sqrt{2}} (|B_{2g}⟩ \pm e^{i\eta}|A_{1g}^{(2)}⟩). \quad (31) $$

When $\eta = 0$ it will induce a $B_{2+}$ quadrupolar order [10] $O_{4y} = \sqrt{3} J_2 J_2$ and hexadecapolar order $H_6 = \frac{\sqrt{5}}{2} J_z (J_z^2 - J_z^2)$, while $\eta = \pi/2$ will induce a $B_{2−}$ octupolar order [12] $T_2^\zeta = \frac{\sqrt{3}}{2} J_z (J_z^2 - J_z^2)$.

### B. REXS experiment

URu$_2$Si$_2$ samples were grown using the Czochralski method [49]. The residual resistivity ratio (RRR) was measured in various pieces of sample; the REXS experiment was performed on the sample with the highest RRR ($= 361$). REXS measurements were performed across the U–L$_3$ edge ($\approx 17.21$ keV) at the 6-ID-B beamline of the Advanced Photon Source at Argonne National Laboratory. The sample was glued to a Cu holder using GE varnish. The holder was placed inside a Be dome filled with He gas, which in turn was mounted on the cold finger of a He closed cycle cryostat. A six circle diffractometer was used to move through reciprocal space. Measurements were performed using a scintillator point detector with $1 \times 1$ mm$^2$ slits. Tetragonal notation with $a = b = 4.108$ Å and $c = 9.514$ Å is used throughout the paper.
(a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k) (l)

FIG. 2. The calculated azimuthal dependence of a (0,0,3) reflection of the L_3-E transition in both σπ and σσ channels for different proposals of multipolar OPs. The incident photon energy is 17.167 keV and the azimuthal angle is defined with respect to the [100] direction.

For each proposal, the intensity is normalized by the maximum intensity of its σπ channel. (a),(b) A2+ hexadecapole $H_σ^α$; (c),(d) A2− dipole $J_σ$ and octupole $T_σ^α$; (e),(f) B1+ quadrupole $O_{σ22}$ and hexadecapole $O_{σ42}$; (g),(h) B1− octupole $T_{xyz}^α$; (i),(j) B2+ quadrupole $O_{σxy}$ and hexadecapole $H_β^σ$; (k),(l) B2− octupole $T_β^σ$.

III. RESULTS AND DISCUSSION

A. Azimuthal dependence for different multipolar order parameters

In REXS experiments, azimuthal measurements are used to identify the symmetry of the underlying OPs. Although Nagao et al. [43] have figured out the analytic formula of the azimuthal dependences for E2 transition, we still explicitly calculate and plot the azimuthal dependences to show the symmetry difference for different multipolar OPs. The results for a (0,0,3) reflection are plotted in Fig. 2. For each multipolar OP, both σπ and σσ channels are plotted, and their intensity is normalized by the maximum of the σπ channel. Figures 2(a) and 2(b) plot the results of the A2+ hexadecapole $H_σ^α$. It shows an eightfold symmetry with a π/8 phase shift between the σπ and σσ channels. The peak intensity of the σσ channel is about two orders of magnitude larger than that of the σπ channel. The eightfold symmetry is a characteristic of this $H_σ^α$ hexadecapolar OP. Figures 2(c) and 2(d) show the results of the A2− dipole $J_σ$ and octupole $T_σ^α$. It shows a nonzero constant in the σπ channel and no signal in the σσ channel. Figures 2(e) and 2(f) display the results of the B1+ quadrupole $O_{σ22}$ and hexadecapole $O_{σ42}$. It shows a $d_{xy}$ wave pattern in the σπ channel and no signal in the σσ channel. Figures 2(g) and 2(h) the results of the B1− octupole $T_{xyz}^α$ shows a $d_{xy}$ wave pattern in the σπ channel and no signal in the σσ channel. Figures 2(i) and 2(j) plot the results of the B2+ quadrupole $O_{σxy}$ and hexadecapole $H_β^σ$ exhibiting a $d_{z^2−r^2}$ wave pattern in the σπ channel and a $d_{x^2−y^2}$ pattern in the σσ channel. Finally, the results of the B2− octupole $T_β^σ$ are shown in Figs. 2(k) and 2(l) where a $d_{z^2−r^2}$ wave pattern is seen in the σπ channel and nothing is seen in the σσ channel.

In general, we find that there are no signals in the σσ channel for time-reversal broken OPs. The azimuthal dependence shows different symmetries for different multipoles, so it can be used to distinguish multipolar OPs.

B. REXS results

The body-centered tetragonal structure of URu2Si2 forbids Bragg peaks with $H + K + L = 2n + 1$. We infer that the HO state breaks the body-centered symmetry by creating inequivalent U sites, thus allowing Bragg peaks at these once forbidden positions. We performed an extensive search for HO Bragg peaks along the (0,0,L) and (1,0,L) directions; results for the former are displayed in Fig. 3. Broad peaks are observed at (0,0,2n + 1). However, these peaks persist through the phase transition at $T_{HO}$, strongly suggesting that these are not related to the HO phase. Additionally, no resonance enhancement is observed across the U-L_3 edge. This suggests...
et al. indeed observed a very strong quadrupolar peak in the absorption spectrum at the $L_1$, $L_2$, and $L_3$ edges of gadolinium in a $4f$ compound gadolinium gallium garnet. However, no results of $5f$ compounds have been reported, so it is worth to try in $5f$ compounds, such as URu$_2$Si$_2$. Borrmann spectroscopy requires samples that are much thicker than the nominal x-ray penetration depth and sufficiently perfect that at least some x rays can transmit through the sample without encountering defects, which may be a challenge for sample growth.

Polarization analysis of the outgoing x rays can also be advantageous (despite the strong reduction in x-ray throughput that it imposes) because, as we will demonstrate, the HO Bragg peak should be observed in the $\sigma\pi$ channel. Additionally, identifying the energy and cross section of the $L_3$-$E2$ transition will greatly facilitate the search for superlattice peaks.

### C. Intensity estimation of the $L_3$-$E2$ transition

We further justify the negative experimental results by estimating the intensity of the $L_3$-$E2$ transition. Usually, the intensity of the $E2$ transition will be much weaker than that of the $E1$ transition. This is mainly caused by the very small overlap integral of $r^2$ between the core hole and valence orbitals. Thus, it is critical to give an estimation of the relative intensity of the $L_3$-$E2$ transition compared with known experiments which have strong intensity, such as the $M_4$-$E1$ transition. Roughly, the relative intensity between $L_3$-$E2$ and $M_4$-$E1$ is

\[
\frac{I(L_3 - E2)}{I(M_4 - E1)} \propto \left(\frac{k \omega_{L_3} (2p | r^2 | 5f)}{3 \omega_{M_4} (3d | r | 5f)}\right)^4 \left(\frac{\Gamma_{M_4}}{\Gamma_{L_3}}\right)^2 ,
\]

and that between $L_3$-$E2$ and $L_3$-$E1$ is

\[
\frac{I(L_3 - E2)}{I(L_3 - E1)} \propto \left(\frac{k (2p | r^2 | 5f)}{3 (2p | r | 6d)}\right)^4 ,
\]

where $\omega_{L_3}$ and $\omega_{M_4}$ are the x-ray frequency of the $L_3$ and $M_4$ edges, and their ratio is about 4.6. Based on the HF calculations, the overlap integral ratios are $(2p | r^2 | 5f)/(3d | r | 5f) \approx 0.013$ and $(2p | r^2 | 5f)/(2p | r | 6d) \approx 0.2$, respectively. $\Gamma_{M_4}$ and $\Gamma_{L_3}$ are the core-hole lifetime widths for the $M_4$ and $L_3$ edges, respectively, and their ratio is $\Gamma_{M_4}/\Gamma_{L_3} \approx 0.4$. For the $L_3$ edge, $k/3 \approx 2.9$. Thus, the intensity of $L_3$-$E2$ is about $10^{-4}$ times smaller than that of $M_4$-$E1$ and $10^{-1}$ times smaller than that of $L_3$-$E1$. Here, we should note that $6d$ orbitals are much broader in URu$_2$Si$_2$, which will lead to larger overlap integrals than those based on the atomic $6d$ orbitals, so $L_3$-$E2$ is not just one order of magnitude smaller than that of $L_3$-$E1$. We may expect larger overlap integrals for the $M_3$-$E2$ ($3p_{3/2} \rightarrow 5f$) transition, so we also calculate the relative intensity between $M_3$-$E2$ and $M_4$-$E1$. The results show that the intensity of $M_3$-$E2$ is also about $10^{-4}$ times smaller than that of $M_4$-$E1$. The reason is that, although the calculated overlap integral $(3p | r^2 | 5f)$ is about 14 times larger than that of $(2p | r^2 | 5f)$, both the x-ray frequency and wave vector of the $M_3$ edge are about 0.25 times

![Figure 3](image-url)
FIG. 4. (0,0,3) REXS intensity as a function of incident photon energy and polarization. The incoming light is linearly polarized and the polarization of the outgoing light is not analyzed. We compare the results of the $M_{4}$-$E_{1}$ transition with the $L_{3}$-$E_{2}$ transition and the $L_{3}$-$\left(E_{1} + E_{2}\right)$ transition. We consider different ordering schemes: (a)–(c) Antiferrodipole $J_{z}$ and antiferro-octupole $T_{\alpha z}$ at $\phi = 0$. (d)–(f) Antiferroquadrupole $O_{xy}$ and antiferrohexadecapole $H_{\beta z}$ at $\phi = 0$. (g)–(i) Antiferroquadrupole $O_{xy}$ and antiferrohexadecapole $H_{\beta z}$ at $\phi = \pi/4$. (j) Antiferro-octupole $T_{\beta z}$ at $\phi = 0$. (k) Antiferrohexadecapole $H_{\alpha z}$ at $\phi = 0$. (l) Antiferrohexadecapole $H_{\alpha z}$ at $\phi = \pi/8$. Smaller than that of the $L_{3}$ edge; as a result, the enhancement effect from the larger overlap integral is canceled out. The intensity of $M_{3}$-$E_{2}$ is not stronger than that of $L_{3}$-$E_{2}$.

However, this rough estimation does not consider many details of the scattering process, such as the ground state and the intermediate excited states, the interference effects of intermediate states, the smearing effect of core-hole lifetime width, and the geometry of the experimental setup. To give a better estimation, we exactly diagonalize the atomic ground and excited Hamiltonians to get the eigenstates and the transition matrix, and then we choose different ground states and experimental geometries to calculate the cross section according to Eqs. (1) and (2). The calculated results of a (0,0,3) reflection are shown in Fig. 4. The azimuthal angle $\phi$ is defined with respect to the [100] direction and the polarization of outgoing light is not analyzed. We plot both the $\sigma$ and $\pi$ polarizations of the incident light. The difference of energy levels between 6$d$ and 5$f$ is...
set to be 10 eV. We assume a type-I antiferromultipolar order with \( Q_{AF} = (0,0,1) \) in the simulation. Figures 4(a)–4(c) are the results for the ground state [Eq. (29)] that induces \( A_{2g} \) orders: dipole \( J_{d} \) and octupole \( T_{d}^{3} \). The \( E \) transition can only detect \( J_{d} \), but \( E_{2} \) can detect both of them. The azimuthal angle is set to be \( \varphi = 0 \). For this ground state, the intensity of \( L_{3}-E_{2} \) is about \( 10^{-6} \) times smaller than that of \( M_{4}-E_{1} \). However, the intensity of \( L_{3}-E_{2} \) is almost the same order of magnitude as that of the \( L_{3}-E_{1} \) transition. In Fig. 4(c), the left peak is from the \( E_{2} \) transition and the right peak is from the \( E_{1} \) transition. Figures 4(d)–4(i) plot the results for the ground state [Eq. (31)] that induces \( B_{2g} \) order: quadrupole \( O_{xy} \) and hexadecapole \( H_{6}^{2} \). In Figs. 4(d)–4(f) the azimuthal angle is \( \varphi = 0 \). We find that the intensity of the \( L_{3}-E_{2} \) transition is \( 10^{-3} \) times smaller than that of the \( M_{4}-E_{1} \) transition and has the same order of magnitude as that of \( L_{3}-E_{1} \). In Figs. 4(g)–4(i), the azimuthal angle is set to be \( \varphi = \pi/4 \). For \( \sigma \) polarization, the intensity of \( L_{3}-E_{2} \) is about \( 10^{-4} \) times smaller than that of \( M_{4}-E_{1} \) and \( 10^{-5} \) smaller than that of \( L_{3}-E_{1} \). However, for \( \pi \) polarization, it is only \( 10^{-5} \) times smaller than that of \( M_{4}-E_{1} \) and much larger than that of \( L_{3}-E_{1} \) so that there is only an \( E_{2} \) peak. Figure 4(j) is the result for the ground state [Eq. (31)] that induces \( B_{2g} \) octupolar order \( T_{d}^{\beta} \). The intensity is at least eight orders of magnitude smaller than that of \( M_{4}-E_{1} \). Another \( B_{1g} \) octupolar \( T_{d37} \) has the same order of magnitude as that of \( T_{d}^{\beta} \). Figures 4(k) and 4(l) are the results for the ground state [Eq. (29)] that induces the \( A_{2g} \) hexadecapolar order \( H_{6}^{2} \). For \( \varphi = 0 \), both \( \sigma \) and \( \pi \) polarizations are at least seven orders of magnitude smaller than that of \( M_{4}-E_{1} \). For \( \varphi = \pi/8 \), \( \sigma \) polarization is about five orders of magnitude smaller than that of \( M_{4}-E_{1} \). We emphasize that the atomic calculation underestimates the intensity of the \( L_{3}-E_{1} \) transition due to the itinerant character of \( 6d \) orbitals, so the intensity of \( L_{3}-E_{1} \) should be much larger than that of \( L_{3}-E_{2} \) in reality.

Based on these atomic results, we find that there are many factors that will affect the REXS cross section, such as the interference of the intermediate states, the interference effect of core-hole lifetime width, the experimental geometry, and the details of the ground states. Overall, the intensity of the \( L_{3}-E_{2} \) transition is at least five or six orders of magnitude smaller than that of \( M_{4}-E_{1} \), so the signal of the \( L_{3}-E_{2} \) transition is indeed very weak. A more advanced approach for these effects, the combination of more advanced first-principle calculations, such as density functional theory plus dynamical mean-field theory (DFT+DMFT), with REXS cross-section calculations is needed. Despite this, the simple atomic simulations still give us preliminary estimations about the strength of the \( E_{2} \) transition.

To further confirm the weakness of the \( L_{3}-E_{2} \) signal, we estimate the flux of the scattered photons by calculating the absolute value of the cross section. For a typical flux of \( 10^{11} \) ph/s/100 meV/(100 \times 100 \) \( \mu m^{2} \), a rough upper bound of the flux of scattered photons is \( 10^{4} \) ph/s/eV/ rad for the \( M_{4}-E_{1} \) transition, while it is \( 10^{-1} \)–\( 10^{-2} \) ph/s/eV/ rad for the \( L_{3}-E_{2} \) transition. This makes it very difficult to detect experiments, which is consistent with the experimental results.

### IV. SUMMARY

In summary, we have studied the possibility to detect multipolar OPs in URu2Si2 by REXS in the \( U \) \( L_{3}-E_{2} \) transition channel. The REXS experiments do not find any clear signal indicating multipolar OPs. An estimation based on atomic calculations indicates that the intensity of the \( L_{3}-E_{2} \) transition is indeed much smaller than that of the \( M_{4}-E_{1} \) transition and the flux of the scattered photons is too small such that it is very difficult to detect the \( E_{2} \) signal. It seems that it still is not practical to use the \( E_{2} \) transition of currently available REXS experiments to detect the multipolar OPs. Developing experimental techniques to enhance the \( E_{2} \) signal is urgently needed to identify the multipolar OPs not only in URu2Si2 but also in other compounds, such as UO2, NpO2, and Ce1−xLaxB8 [52].

### ACKNOWLEDGMENTS

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### APPENDIX: SLATER INTEGRALS AND SPIN-ORBIT COUPLING PARAMETERS

We list the Slater integrals and spin-orbit coupling parameters used in our calculations in Tables I–IV.

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### APPENDIX: SLATER INTEGRALS AND SPIN-ORBIT COUPLING PARAMETERS

We list the Slater integrals and spin-orbit coupling parameters used in our calculations in Tables I–IV.
TABLE III. Slater integrals and spin-orbit coupling parameters for excited configuration $2p^5f^26d^1$ (in eV).

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<th>$F^0_{\sigma\tau}$</th>
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TABLE IV. Slater integrals and spin-orbit coupling parameters for excited configuration $3d^5f^3$ (in eV).

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