Resonant X-Ray Scattering from CeB$_6$

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We calculate the resonant x-ray scattering (RXS) spectra near the Ce L$_{III}$ absorption edge in CeB$_6$, on the basis of a microscopic model that the 4$f$ states of Ce are atomic while the 5$d$ states form an energy band with a reasonable density of states. In the initial state, we employ an effective Hamiltonian of Shiina et al. in the antiferro-quadrupole (AFQ) ordering phase, while we construct the wave function consistent with the neutron scattering experiment in the magnetic ground state. In the intermediate state, we take full account of the intra-atomic Coulomb interaction. Without assuming any lattice distortion, we obtain sufficient RXS intensities on the AFQ superlattice spot. We obtain the spectral shape, the temperature and magnetic field dependences in good agreement with the experiment, thus demonstrating the mechanism that the intensity is brought about by the modulation of 5$d$ states through the anisotropic term of the 5$d$-4$f$ Coulomb interaction. In the magnetic ground state, a small pre-edge peak is found by the $E_2$ process. On the magnetic superlattice spot, we get a finite but considerably small intensity. The magnetic form factor is briefly discussed.

KEYWORDS: resonant X-ray scattering, CeB$_6$, orbital ordering, Ce L$_{III}$ absorption edge, magnetic form factor

§1. Introduction

Resonant x-ray scattering (RXS) has recently attracted much interest as a useful tool to investigate the orbital order, which neutron scattering experiments are usually difficult to probe. The resonant enhancement for the prohibited Bragg reflection corresponding to the orbital order has been observed in several transition-metal compounds by using synchrotron radiation with photon energy around the $K$ absorption edge.

For such $K$-edge resonances, 4$p$ states of transition metals are involved in the intermediate state in the electric dipolar ($E_1$) process, and they have to be modulated in accordance with the orbital order for observing signals. At the early stage, for LaMnO$_3$, such a modulation was considered to come from the anisotropic term of the 4$p$-3$d$ intra-atomic Coulomb interaction, but subsequent studies based on the band structure calculation have revealed that the modulation comes mainly from the lattice distortion via the oxygen potential on the neighboring sites. Similar conclusions have been obtained for $t_{2g}$-electron systems, such as YTiO$_3$ and YVO$_3$. This is because 4$p$ states are so extending in space that they are very sensitive to the electronic structure at neighboring sites.

Not only transition-metal compounds but also rare-earth-metal compounds show the orbital order (usually an ordering of quadrupole moments). Recently, RXS experiments were carried out around the Ce L$_{III}$ absorption edge in CeB$_6$, in which resonant enhancements have been found on the quadrupolar ordering superlattice spots. In particular, Nakao et al. have found a one-peak structure as a function of photon energy on the spot $G = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which was assigned to the $E_1$ process. Here $G$ is the scattering vector in units of $2\pi/a$ with $a$ being the lattice constant. They have also measured the temperature and the magnetic field dependences of the intensities. The purpose of this paper is to analyze their experimental result on the basis of a microscopic model and thereby to elucidate the mechanism for RXS in CeB$_6$. Some of the results reported here were briefly presented in a recent letter. In this paper, making a slight revision on the 5$d$ density of states, we describe explicitly the model as well as the calculational procedure. We also add the calculation of the RXS spectra on the magnetic ground state.

Each Ce atom is considered to be in the $f^1$-configuration, $^2F_{5/2}$. The $\Gamma_8$ quartet states have a lower energy than the $\Gamma_7$ doublet under the cubic crystal field. The 4$f$ states are assumed to be atomic as a first approximation. With decreasing temperatures the antiferro-quadrupole (AFQ) order appears at $T_Q = 3.2$ K with an ordering wave vector $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, as shown in Fig. 1(a). This phase transition originates from the intersite interaction between the atomic $\Gamma_8$ states by lifting the degeneracy of the $\Gamma_8$ states. Ohkawa derived an effective intersite interaction on the basis of a RKKY interaction. Recently, Shiina et al. extended his model by taking full account of the symmetry of the interaction as well as the order parameters. Thereby, they solved a longstanding controversy between the neutron diffraction and NMR in the context of the induced order parameters under the external magnetic field. We use the model Hamiltonian of Shiina et al. within the mean field approximation (MFA) for describing the initial state of the RXS process in the AFQ phase.
For $T < T_N (= 2.4 \text{ K})$, there appears a magnetic long-range order. According to the neutron scattering experiment, the ordering pattern of the magnetic moment is shown as in Fig. 1(b). We construct the wave function in the magnetic ground state to be consistent with the ordering pattern, and use it as the initial state of the RXS process. Our calculation is limited to $T = 0$, since an intersite interaction correctly reproducing the magnetic phase has not been derived yet.

In the intermediate state of the $E_1$ process, the 5$d$ states of Ce are involved so that they have to be modulated in accordance with the superlattice spots. Since the 4$f$ states are so localized in space that their coupling to lattice is very small. Actually the lattice distortion associated with the AFQ order has not been observed. Therefore, it is highly possible that the modulation is brought about by the Coulomb interaction between the 5$d$ states and the orbital ordering 4$f$ states. Introducing a reasonable density of states (DOS) for the 5$d$ states, we solve a scattering problem of the photo-excited 5$d$ electron; the scatterer is a complex of a 2$p$ hole and a 4$f$ electron.

Using the solution in the intermediate state, and combining it to the result in the initial state, we calculate the RXS spectra on an AFQ superlattice spot $G = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and on a magnetic superlattice spot $G = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the magnetic ground state. In the AFQ phase, we obtain sufficient intensities on the AFQ spot without assum-

Fig. 1. (a) Antiferro-quadrupolar structure of phase II. Open circles are cerium atoms with A and B representing sublattices. Solid small circles are boron atoms. (b) Magnetic structure of phase III predicted by the neutron scattering experiment. Only Ce atoms are shown. The arrows indicate the direction of the magnetic moment. The attached numbers represent sites of typical directions.

Fig. 2. Scattering geometry of x-ray scattering. Incident photon with wave vector $k_i$ and polarization $\sigma$ or $\pi$ is scattered into the state with wave vector $k_f$ and polarization $\sigma'$ or $\pi'$. The scattering vector is defined by $G = k_f - k_i$. The cross section for the scattering vector $G$ consists of three terms:

\[
\frac{d\sigma}{d\Omega}_{\mu \rightarrow \mu'} \propto |J_{\mu \rightarrow \mu'}(G, \omega)|^2 + \sum_{\alpha \alpha'} P_{\alpha}^{\mu \mu'} M_{\alpha \alpha'}(G, \omega) P_{\alpha'}^{\mu \mu'},
\]

\[
+ \sum_{\gamma \gamma'} Q_{\gamma}^{\mu \mu'} N_{\gamma \gamma'}(G, \omega) Q_{\gamma'}^{\mu \mu'}|, \quad (2.1)
\]
\[ J_{\mu \rightarrow \mu'}(\mathbf{G}, \omega) = -\frac{i\hbar\omega}{mc^2} \frac{1}{\sqrt{N}} \sum_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \times \left( \frac{1}{2} \mathbf{L}(\mathbf{G}, j) \cdot \Delta' + \mathbf{S}(\mathbf{G}, j) \cdot \mathbf{B} \right), \quad (2.2) \]

\[ M_{\alpha \alpha'}(\mathbf{G}, \omega) = \frac{1}{\sqrt{N}} \sum_j \sum_{n, \Lambda} p_n(j) \exp(-i\mathbf{G} \cdot \mathbf{r}_j) m \omega_n^2 \langle \Lambda | \Delta' | \psi_n(j) \rangle \times \frac{\langle \psi_n(j) | x_{\alpha}(j) | \Lambda \rangle \langle \Lambda | x_{\alpha'}(j) | \psi_n(j) \rangle}{\hbar \omega - (E_{\Lambda'} - E_{\Lambda} + i\Gamma)} \quad (2.3) \]

\[ N_{\gamma \gamma'}(\mathbf{G}, \omega) = \frac{1}{\sqrt{N}} \sum_j \sum_{n, \Lambda} k^2 \sum_{n', \Lambda'} p_n(j) \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \times \hbar \omega - (E_{\Lambda'} - E_{\Lambda} + i\Gamma) \langle \Lambda' | \Delta' | \psi_n(j) \rangle \times \frac{\langle \psi_n(j) | z_{\gamma}(j) | \Lambda' \rangle \langle \Lambda' | z_{\gamma'}(j) | \psi_n(j) \rangle}{m \omega_n^2}, \quad (2.4) \]

Here \( c \) is the velocity of photon and \( m \) is the electron mass. Note that the cross section is an order of the number of Ce sites.

The first term (eq. (2.2)) represents a non-resonant term for the magnetic superlattice spots. Since the magnetic moment comes mainly from 4f states which are well localized, it may be a good approximation to assign the moment to each site. The \( \mathbf{L}(\mathbf{G}, j) \) and \( \mathbf{S}(\mathbf{G}, j) \) are the form factors of the orbital and spin angular momenta at site \( j \), which are given by \[ \mathbf{L}(\mathbf{G}, j) = \frac{1}{2} \sum_n p_n(j) \times \langle \psi_n(j) | f(-\mathbf{G} \cdot \mathbf{r}) \mathbf{\ell} + \ell f(-\mathbf{G} \cdot \mathbf{r}) | \psi_n(j) \rangle, \]

\[ \mathbf{S}(\mathbf{G}, j) = \sum_n p_n(j) \langle \psi_n(j) | e^{-i\mathbf{G} \cdot \mathbf{r}} | \psi_n(j) \rangle, \]

with \[ f(x) = 2 \sum_{m=0}^{\infty} \frac{(ix)^m}{(m+2)m!}, \quad (2.7) \]

Here \( | \psi_n(j) \rangle \) represents the initial state at site \( j \), which will be evaluated within the MFA discussed in the next section. We take the thermal average with probability \( p_n(j) \). Operators \( \mathbf{\ell} \) and \( \mathbf{s} \) represent the orbital and spin angular momenta with the center of site \( j \). The \( \mathbf{L}(\mathbf{G}, j) \) and \( \mathbf{S}(\mathbf{G}, j) \) converge to the local orbital momentum and the spin angular momentum with \( \mathbf{G} \rightarrow 0 \). The scattering geometry is contained in quantities \( \Delta' \) and \( \mathbf{B} \), which are defined by

\[ \Delta' = \Delta' - (\Delta' \cdot \hat{\mathbf{G}}) \hat{\mathbf{G}}, \quad \Delta' = -4 \sin^2 \theta (\mathbf{e}' \times \hat{\mathbf{e}}), \quad (2.8) \]

\[ \mathbf{B} = \mathbf{e}' \times \hat{\mathbf{e}} + (\hat{\mathbf{k}_f} \times \mathbf{e}') (\hat{\mathbf{k}_f} \cdot \mathbf{e}) - (\hat{\mathbf{k}_f} \times \hat{\mathbf{e}}) \times (\hat{\mathbf{k}_i} \times \mathbf{e}), \quad (2.9) \]

where \( \mathbf{e} \) and \( \mathbf{e}' \) are the initial and scattered polarizations, and \( \hat{\mathbf{k}_i} \), \( \hat{\mathbf{k}_f} \), and \( \hat{\mathbf{G}} \) are normalized vectors of \( \mathbf{k}_i \), \( \mathbf{k}_f \), and \( \mathbf{G} \).

The second term in eq. (2.1) describes a resonant term by the \( E_1 \) process, where an electron in 2p states is virtually excited to 5d states and subsequently is recombined with the core hole. Since the 2p states are well localized around Ce sites, it is a good approximation to describe the scattering tensor as a sum of the contribution from each site of the core hole. The initial state \( | \psi_n(j) \rangle \) at site \( j \) has an energy \( E_n(j) \). The intermediate state \( | \Lambda \rangle \) consists of an excited electron on 5d states and a hole on 2p states with energy \( E_{\Lambda'} - E_n \) and the lifetime broadening width \( \Gamma \) of the core hole is assumed to be 2 eV. The dipole operators \( x_{\alpha}(j) \)’s are defined as \( x_1(j) = x, x_2(j) = y, \) and \( x_3(j) = z \) in the coordinate frame fixed to the crystal axes with the origin located at the center of site \( j \). The dipole matrix element \( A_{dp} = \int 0^\infty R_{3d}(r) R_{2p}(r) r^2 dr \) is implicitly included as a square in the expression (\( R_{3d}(r) \) and \( R_{2p}(r) \) are the radial wave functions for the 5d and 2p states, respectively). It is estimated as \( A_{dp} = 3.67 \times 10^{-11} \) cm for a Ce\(^{3+} \) atom within the Hartree-Fork (HF) approximation. The \( P^\mu \) and \( P'^\mu \) are geometrical factors for the incident and scattered photons, respectively, which are explicitly written in the Appendix of ref. 31.

The third term in eq. (2.1) describes a resonant term by the \( E_2 \) process, where an electron in 2p states is virtually excited to 4f states and subsequently is recombined with the core hole. In eq. (2.4), \( k \) is the wavenumber of the incident (and scattered) photon, which is \( \approx 2.91 \times 10^8 \) cm\(^{-1} \) around the \( L_{\text{II}} \) edge. The intermediate states \( | \Lambda \rangle \) consist of an excited electron on 4f states and a hole in 2p states with energy \( E_{\Lambda'} \). Quadrupole operators are defined as \( z_1 \equiv \sqrt{3}/2 (x^2 - y^2), z_2 \equiv (1/2) (3z^2 - r^2), z_3 \equiv \sqrt{3}z, z_4 \equiv \sqrt{3}x, \) and \( z_5 \equiv \sqrt{3}y \) in the coordinate frame fixed to the crystal axes. The quadrupole matrix element \( A_{fq} = \int \int R_{4f}(r)^2 R_{2p}(r)^2 r^2 dr \) is included as a square in the expression (\( R_{4f}(r) \) is the 4f radial wave function). It is estimated as \( A_{fq} = 5.69 \times 10^{-20} \) cm\(^2 \) for a Ce\(^{3+} \) atom within the HF approximation. The \( Q^\mu \) and \( Q'^\mu \) are geometrical factors for the incident and scattered photons, respectively, which are explicitly written in the Appendix of ref. 31.

§3. Initial State

Each Ce atom is approximately in the 4f\(^1 \)-configuration, \( ^2F_{5/2} \), in Ce\(_6\). The 4f states are so localized that their wave functions are well described to be atomic in the HF approximation. The cubic crystal field lifts the degeneracy; quadruply degenerate \( \Gamma_8 \) states have a lower energy than the doubly degenerate \( \Gamma_7 \) states. Since the \( \Gamma_8-\Gamma_7 \) separation energy is estimated as large as \( \approx 540 \) K, it is sufficient to consider only the \( \Gamma_8 \) states in the description of the initial state, which are explicitly written as

\[ | \pm \uparrow \rangle = \sqrt{5/6} \pm \frac{5/2}{2} \pm \sqrt{1/6} \pm \frac{3/2}{2}, \]

\[ | \pm \downarrow \rangle = \sqrt{5/6} \pm \frac{5/2}{2} + \sqrt{1/6} + \frac{3/2}{2}, \]

\[ | + \downarrow \rangle = \frac{1}{2}, \]

\[ | - \downarrow \rangle = -\frac{1}{2}. \quad (3.1) \]
to work well:

\[ H = D \sum_{\langle ij \rangle} \left[ (1 + \delta) \mu_i \cdot \mu_j + \tau_i^x \tau_j^y + \epsilon \sigma_i \cdot \sigma_j \right. \\
\left. + \frac{1}{2} \left( \tau_i^x \cdot \tau_j^x + \eta_i \cdot \eta_j + \zeta_i \cdot \zeta_j \right) \right] + g \mu_B \sum_i J_i \cdot H, \]

with

\[ J = \frac{7}{3} (\sigma + \frac{4}{7} \eta), \]

\[ \mu = (2 \tau^x \sigma^x, 2 \tau^y \sigma^y, 2 \tau^z \sigma^z), \]

\[ \tau' = (\tau^x, \tau^y), \]

\[ \eta = ((\sqrt{3} \tau^x - \tau^z) \sigma^x, (-\sqrt{3} \tau^x + \tau^z) \sigma^y, 2 \tau^z \sigma^z), \]

\[ \zeta = ((-\sqrt{3} \tau^x - \tau^z) \sigma^x, (\sqrt{3} \tau^x + \tau^z) \sigma^y, 2 \tau^z \sigma^z), \]

where \( \langle i, j \rangle \) represents the sum over nearest neighboring Ce pairs. Operators \( \tau \) and \( \sigma \) represent the spin matrix acting on the variables \( \tau \) and \( \sigma \) of the state \( |\sigma\rangle \), respectively. This system has been extensively studied within the MFA by Shiina et al.; \( \delta \sim 0.2 \) and \( \epsilon \sim 1 \) are known to be suitable for CeB\(_6\). In the following, we simply summarize the result of the MFA in connection to the RXS spectra.

In the absence of the magnetic field, an AFQ order is set in, as shown in Fig. 1(a). We have three types of possible ordered phase, in which one of the staggered quadrupole moments, \( \langle O_{xy} \rangle = 4 \langle r_0 \sigma_z \rangle \), \( \langle O_{yz} \rangle = 4 \langle r_0 \sigma_x \rangle \), and \( \langle O_{zx} \rangle = 4 \langle r_0 \sigma_y \rangle \), is finite. Here \( \langle X \rangle \) indicates the thermal average of operator \( X \). We simply call them as the \( O_{xy}, O_{yz}, \) and \( O_{zx} \) phases. For example, in the \( O_{xy} \) phase, applying the MFA to eq. (3.2), we obtain the eigenstates of the Hamiltonian at site \( j \):

\[ |\psi_1(j)\rangle = \frac{1}{\sqrt{2}} \left( |+ \uparrow \rangle + i | - \downarrow \rangle \right), \]

\[ |\psi_2(j)\rangle = \frac{1}{\sqrt{2}} \left( |+ \downarrow \rangle - i | - \uparrow \rangle \right), \]

\[ |\psi_3(j)\rangle = \frac{1}{\sqrt{2}} \left( |+ \uparrow \rangle - i | - \downarrow \rangle \right), \]

\[ |\psi_4(j)\rangle = \frac{1}{\sqrt{2}} \left( |+ \downarrow \rangle + i | - \uparrow \rangle \right), \]

with the eigenvalues,

\[ E_1(j) = E_2(j) = \mp z D (1 + \delta) |4 \langle r_0 \sigma_z \rangle|, \]

\[ E_3(j) = E_4(j) = \pm z D (1 + \delta) |4 \langle r_0 \sigma_z \rangle|, \]

where the upper(lower) sign in eqs. (3.12) and (3.13) is for A(B) sublattice. The \( 4 \langle r_0 \sigma_z \rangle \) is the staggered order parameter self-consistently determined, and \( z (=6) \) is the number of nearest neighboring pairs. Note that Kramers’ pairs, \( |\psi_1 \rangle \) and \( |\psi_2 \rangle \), as well as \( |\psi_3 \rangle \) and \( |\psi_4 \rangle \), are still degenerate in Phase II. The probability \( p_n(j) \) appeared in the preceding section is given by \( \propto \exp(-E_n(j)/T) \). Note that \( p_1(j) (= p_2(j)) > p_3(j) (= p_4(j)) \) at A sublattice, and vice versa at B sublattice.

The angular dependences of the charge density for those states are defined by

\[ C^{1,2}(\theta, \phi) = \frac{1}{2 |R_{1f}(r)|^2} \sum_{n=1,2} |\langle r, \theta, \phi | \psi_n \rangle|^2, \]

\[ C^{3,4}(\theta, \phi) = \frac{1}{2 |R_{4f}(r)|^2} \sum_{n=3,4} |\langle r, \theta, \phi | \psi_n \rangle|^2. \]

We calculate these quantities using the atomic function in the HF approximation. As shown in Fig. 3, \( C^{1,2}(\theta, \phi) \) is along the \( [1, 1, 0] \) direction, while \( C^{3,4}(\theta, \phi) \) is along the \( [1, 1, 0] \) direction. The charge distribution after thermal average is along the \( [1, 1, 0] \) direction at A sublattice, since \( p_1(j) (= p_2(j)) > p_3(j) (= p_4(j)) \) there. Such anisotropy leads to a modulation in the 5d states through the Coulomb interaction in the RXS process.

The magnetic field induces the staggered octupole moment in addition to the staggered quadrupole moments, as shown in the upper panel of Fig. 10. As shown in the same figure, the octupole moment has little influence on the RXS spectra. The magnetic field also induces the uniform dipole moment. Recently Saitoh et al. have carried out a neutral-diffraction experiment under magnetic field, and have reported the magnetic form factors. They have argued that a considerable amount of the magnetic moment is distributed around B atoms. In this context, it may be instructive to evaluate the magnetic form factors on Ce atoms, although they are not directly related to the present RXS study. We use the atomic wave function within the HF approximation in eqs. (2.5) and (2.6). Figure 4(a) shows the form factors on Ce atoms for various values of \( G \). The orbital moment is much larger than the spin moment, and the form factors decrease monotonically with increasing values of \( |G| \). These values do not fit the experimental data.
3.2 Magnetic Phase \((T < T_N)\)

With further decreasing temperature \((T < T_N)\), a magnetic long-range order appears (Phase III). The ordering pattern predicted by the neutron scattering experiment is shown in Fig. 1(b). The magnetic moment \(\mathbf{m}(r_j)\) is direct on the \(ab\) plane; it is given by

\[
\mathbf{m}(r_j) \propto \left\{ \begin{array}{c}
\cos \left( k_1 \cdot r_j + \frac{\pi}{4} \right) + \cos \left( k'_1 \cdot r_j - \frac{\pi}{4} \right) \mathbf{u}_{k_1} \\
\cos \left( k_2 \cdot r_j + \frac{3\pi}{4} \right) + \cos \left( k'_2 \cdot r_j + \frac{\pi}{4} \right) \mathbf{u}_{k_2}
\end{array} \right. ,
\]

(3.16)

where \(\mathbf{u}_{k_1}\) and \(\mathbf{u}_{k_2}\) are unit vectors along the \([-1, 1, 0]\) direction and along the \([1, 1, 0]\) direction, respectively, and \(k_1 = (1 + \frac{\pi}{4}), k_2 = (1 + \frac{3\pi}{4}), k'_1 = (\frac{\pi}{4}), k'_2 = (\frac{\pi}{4})\). Of course, there must exist other magnetic domains in which the moments are directing on the \(bc\) and \(ca\) planes.

The magnetic domain described by eq. (3.16) is expected to come from the \(O_{xy}\) phase with splitting the degeneracy of Kramers' doublet. We have no reliable effective inter-site interaction between Kramers' doublets; the inter-site interaction given by eq. (3.2) cannot describe the magnetic state. Therefore we are satisfied to derive the ground state wave function consistent with the distribution of the magnetic moment experimentally determined. First we note that the angular momentum operator \(\mathbf{J}\) along \(\mathbf{n} = (\cos \phi, \sin \phi, 0)\) is represented within the space of \(|\psi_1\rangle\) and \(|\psi_2\rangle\) as

\[
\mathbf{n} \cdot \mathbf{J} = A|\psi_1\rangle\langle \psi_2| + A^*|\psi_2\rangle\langle \psi_1|,
\]

(3.17)

with \(A = -(1/3) \exp(-i\phi) - (i/\sqrt{3}) \exp(i\phi)\), while it is represented within the space of \(|\psi_3\rangle\) and \(|\psi_4\rangle\) as

\[
\mathbf{n} \cdot \mathbf{J} = B|\psi_3\rangle\langle \psi_4| + B^*|\psi_4\rangle\langle \psi_3|,
\]

(3.18)

with \(B = -(1/3) \exp(-i\phi) + (i/\sqrt{3}) \exp(i\phi)\). Considering the magnetic ordering pattern in Fig. 1(b), and noting that \(\mathbf{J}\) is pointing to the direction opposite to the local magnetic moment vector, we seek the eigenstate with the negative eigenvalue for eq. (3.17) with \(\phi = 3\pi/4\) for site 1, eq. (3.18) with \(\phi = -3\pi/4\) for site 2, eq. (3.17) with \(\phi = -\pi/4\) for site 3, and eq. (3.18) with \(\phi = \pi/4\) for site 4.

Thus we have the wave function in the ground state as

\[
|\psi_g\rangle = \left\{ \begin{array}{c}
\frac{1}{\sqrt{2}} \left( e^{-3\pi/4}|\psi_1\rangle + |\psi_2\rangle \right), \quad \text{for site 1}, \\
\frac{1}{\sqrt{2}} \left( e^{3\pi/4}|\psi_3\rangle + |\psi_4\rangle \right), \quad \text{for site 2}, \\
\frac{1}{\sqrt{2}} \left( e^{\pi/4}|\psi_1\rangle + |\psi_2\rangle \right), \quad \text{for site 3}, \\
\frac{1}{\sqrt{2}} \left( e^{-\pi/4}|\psi_3\rangle + |\psi_4\rangle \right), \quad \text{for site 4},
\end{array} \right.
\]

(3.19)

with the eigenvalue \(-0.91\). Considering the \(g\)-factor \(6/7\), we have the local magnetic moment \(0.78\mu_B\), which is close to the value \(0.85\mu_B\) from the analysis of the \(^{111}\)B-NMR measurement.\[4\]

The orbital and spin form factors are evaluated by using the above wave functions. Figure 4(b) shows the calculated result as a function of \(|\mathbf{G}|\). The form factors decreases monotonically with increasing values of \(|\mathbf{G}|\), which behavior is similar to that in Phase II under the magnetic field. We need these quantities to evaluate the non-resonant term, eq. (2.2), in the RXS spectra. However, as shown later, the non-resonant term gives much smaller contribution than the resonant terms in the ground state.

§4. Intermediate State

In the \(E_1\) process, an electron is excited from \(2p\) states to \(5d\) states at a Ce site. The \(2p\)-core hole states are split into the states with \(j_p = 3/2\) and \(j_p = 1/2\) (\(j_p\) is the total angular momentum) due to the strong spin-orbit interaction. In the following, we consider only the \(j_p = 3/2\) states (\(L_{III}\) edge).

Different from the \(4f\) states, the \(5d\) states are rather extended in space, so that they form an energy band with width \(~15\) eV through the hybridization with boron \(p\) states. We use a shape shown in Fig. 5 as a model of the \(5d\) density of states (DOS).\[3\]

We disregard the dependence on the symmetries \(xy, yz, zx, x^2-y^2,\) and \(3z^2-r^2\). It is assumed to be occupied by one electron per Ce site in the initial state. Such a rather arbitrary choice of the \(5d\)-DOS may be justified in a semi-quantitative study, since the RXS spectra is not sensitive to the shape and the filling of the \(5d\)-DOS. The retarded Green’s function for the excited \(5d\) electron is defined by

\[
G^{5d}(\hbar \omega) = \int_{\epsilon_F}^{\infty} \frac{\rho^{5d}(\epsilon)}{\hbar \omega - \epsilon + i\delta} d\epsilon,
\]

(4.1)

where \(\rho^{5d}(\epsilon)\) is the \(5d\)-DOS, and \(\epsilon_F\) is the Fermi en-
energy. Note that the energy of 5d states included implicitly an average interaction with electrons in 4f states.

Now we consider the resonant $1/(\hbar \omega - H_{\text{int}})$ with $H_{\text{int}}$ being the Hamiltonian in the configuration that there are one excited electron in the 5d band, one electron per Ce site in the 4f states, and one hole in 2p states at the central site (Fig. 5(a)). We neglect the screening effect by the already occupying electrons in the 5d band. When the excited “5d electron” is away from the central site, it can freely move; the Green’s function, eq. (2.3), describes this motion. At the same time, the “4f electron” is interacting with the “2p hole” on the central site (Fig. 5(b)). First, considering the Coulomb interaction between the 4f electron and the 2p hole and also the spin-orbit interaction at the central site, we solve the eigenvalue problem for the complex of the 4f electron and the 2p hole. In this calculation, we use the Slater integrals evaluated by the HF approximation in a Ce$^{3+}$ atom, which are listed in Table I. Let $|\lambda\rangle$ be the eigenstate with energy $E_{\lambda}$. On the other hand, when the 5d electron comes onto the central site, it interacts with the 2p hole as well as the 4f electron. We treat this system as a scattering problem of the 5d electron, in which the scatterer has 56 (4 × 14) internal degrees of freedom specified by $\lambda$ on the central site. 

Table 1. Slater integrals and the spin-orbit interaction for Ce$^{3+}$ atoms in the Hartree-Fock approximation (in units of eV).

| $G_{\text{f}}(2p, 5d)$ | $G_{\text{f}}(2p, 4f)$ | $G_{\text{f}}(4f, 5d)$ |
|---------------------|---------------------|---------------------|
| $F^0$ | 26.08 | 15.58 | 37.68 |
| $F^1$ | 12.43 | 0.568 | 1.540 |
| $F^2$ | 7.807 | 0.286 | 0.144 |
| $F^3$ | 5.618 | 0.093 | 0.128 |

$\zeta_{4f} = 0.132$ $\zeta_{5d} = 0.138$

In the RXS calculation, the above values of the anisotropic terms were reduced by multiplying a factor 0.8, while the values for $F^0(\alpha, \alpha')$ are replaced by much smaller values, $F^0(4f, 5d) = 0.0$, $F^0(4f, 4f) = 7.0$, $F^0(2p, 5d) = 4.0$ and $F^0(2p, 4f) = 12.0$.

Once we obtain the resonant, we can calculate the scattering amplitude, eq. (2.3), by using the relation,

$$
\sum_{\lambda} \frac{|\Lambda\rangle \langle \Lambda|}{\hbar \omega - (E_{\lambda} - E_{\alpha}(j)) + i\delta} = \sum_{m^d s^d \lambda} \sum_{m^d s^d \lambda'} |m^d s^d \lambda\rangle \left(\frac{1}{\hbar \omega - H_{\text{int}} + i\delta}\right)_{m^d s^d \lambda,m'^d s'^d \lambda'} \langle m'^d s'^d \lambda'|,
$$

for $j$ at the central site. It should be noted here that this resonant is the same at all sites of core hole. The scattering amplitudes become different at different sublattices after multiplying the matrix elements of the dipole operators between the initial and the intermediate states. Using the resonant, we can also calculate the absorption coefficient $A(\omega)$ in the $E_1$ process,

$$
A(\omega) \propto \sum_{j} \sum_{n, \alpha} p_n(j) \langle \psi_n(j)|x^n|m^d s^d \lambda\rangle \times \left(-\frac{1}{\pi}\right) \text{Im} \left(\frac{1}{\hbar \omega - H_{\text{int}} + i\delta}\right)_{m^d s^d \lambda,m'^d s'^d \lambda'} \langle m'^d s'^d \lambda'|x^n|\psi_n(j)\rangle,
$$

where $\text{Im}X$ indicates the imaginary part of the quantity $X$.

In the $E_2$ process, an electron is excited from 2p states to 4f states at Ce sites. Two electrons occupy the 4f states on the Ce site. Since the 4f states are well localized, it may be sufficient to consider only the core-hole site for the intermediate state $|\Lambda\rangle$ in eq. (2.4). We obtain $|\Lambda\rangle$ by numerically diagonalizing the Hamiltonian matrix within the space of two 4f electrons and one 2p hole. We fully take account of the multiplets, where the necessary Slater integrals as well as the spin-orbit interaction parameter are listed in Table I.
§5. RXS Spectra

5.1 Quadrupolar Ordering Phase ($T_N < T < T_Q$)

Before going to the discussion of the RXS spectra, we first calculate the absorption coefficient $A(\omega)$ with the help of eq. (4.4). The contribution from the $E_2$ process is safely neglected, since it is too small by the estimate of the HF transition matrix elements. Figure 6 shows the calculated result at $T = 2.7$ K, $H = 0$, in comparison with the experiment. The core-hole energy is adjusted such that the peak is located at $h\omega = 5722$ eV. Note that the temperature dependence is negligible. The spectrum is a reflection of the $5d$ DOS; the attractive interaction between the $5d$ electron and the core hole makes the peak move to the low-energy region. The calculated spectrum corresponds well to the experimental shape around the $L_{\text{III}}$ edge, indicating the appropriateness of the assumed $5d$ DOS. Considering the influence of the high energy region in the experimental spectra may come from the mixing of $5d$ states to other states such as $6s$ states of Ce and $3s$ states of B. Now we calculate the RXS spectra for $G = (1 1 1)$, following the procedure in the preceding section. Figure 7 shows the calculated spectra as a function of photon energy, in comparison with the experiment. The azimuthal angle $\psi$ is set to be zero such that the scattering plane contains the $[1, -1, 0]$ crystal axis. The relative volumes of three domains, the $O_{xy}$, $O_{yz}$ and $O_{zx}$ phases, are not known in the experiment, so that we have tentatively averaged the contributions from three phases with equal weight. Since the dependence on the photon energy is the same in three domains, the spectral shape is not influenced by the change of the relative volume of domains. Only changeable are the relative intensities between the $\sigma \rightarrow \sigma'$ channel and the $\sigma \rightarrow \pi'$ channel; in the $O_{xy}$ phase, the intensity of the $\sigma \rightarrow \pi'$ channel is larger than that of the $\sigma \rightarrow \sigma'$ channel. Such polarization analysis has not been done in the experiment. We obtain an one-peak structure from the $E_2$ process, in good agreement with the experiment. The contribution of the $E_2$ process is two order of magnitude less than that of the $E_1$ process, so that we have no pre-edge peak visible.

As mentioned before, the intensity arises from the $5d$ states modulated by the anisotropy in the $4f$ Coulomb interaction in the intermediate state. Figure 8 shows the intensity of the peak at $h\omega = 5722$ eV in the $O_{xy}$ phase, as a function of temperature. The curves are extended to $T < T_N$ by assuming the $O_{xy}$ phase. Its temperature...
dependence seems similar to that of $\langle \tilde{O}_{xy} \rangle^2$, indicating a direct reflection of the AFQ order.

Another important quantity is the dependence on the azimuthal angle. Figure 9 shows the RXS intensity of the peak at $h\omega = 5722$ eV. The contributions from three domains are separately shown. The dependence of the $\sigma \to \sigma'$ channel is quite different from that of the $\sigma \to \pi'$ channel. The curves in the $O_{xy}$, $O_{yz}$, and $O_{zz}$ phases can be transformed into those for the $O_{yz}$, $O_{zx}$, and $O_{xy}$ phases, respectively, by shifting $\psi$ with $2\pi/3$. This threefold symmetry around $\mathbf{G} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ perfectly matches the relation between the order parameters of three domains. Thus the azimuthal-angle dependence is closely related to the geometry of scattering as well as the symmetry of the AFQ order, not related to the details of the model. Therefore, the examination of the azimuthal angle dependence may be useful to determine the symmetry of the AFQ phase.

The initial state is rather sensitive to the magnetic field. For example, as shown in the upper panel of Fig. 10, a sizable staggered octupole moment $\langle \tilde{T}_{xyz} \rangle$ ($\equiv 2\langle \gamma' \rangle$) is induced by applying the magnetic field along the [0, 0, 1] direction. The lower panel of Fig. 10 shows the intensity of the peak at $h\omega = 5722$ eV as a function of magnetic field. The intensity increases only gradually with increasing $H$, which behavior is close to the variation of the staggered quadrupole moment. This indicates that the induced staggered octupole moment has little influence on the RXS spectra. Finally in this subsection, we demonstrate in Fig. 11 that the calculated temperature dependence reproduces well the experiment for $\mathbf{H} \parallel [1, 1, -2]$.\[14\]

5.2 Magnetic Ground State

Using the wave functions given in the preceding section for the magnetic ground state, we calculate the RXS intensities for the AFQ superlattice spot $\mathbf{G} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and for the magnetic superlattice spot $\mathbf{G} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. Figure 12 shows the calculated spectra as a function of photon energy for $H = 0$.

For $\mathbf{G} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the spectral shape is close to the one in the AFQ phase. The intensity of the main peak is a smooth extension from the $O_{xy}$ phase, as shown in Fig. 8.

This indicates that the primary origin is the anisotropic charge distribution associated with the AFQ order in the 4f states, and that the magnetic order, which lifts the degeneracy of Kramers' doublet, has little influence on this spot. On the other hand, a pre-edge peak around $h\omega = 5710$ eV is enhanced to become visible in the $E_2$ process.

For $\mathbf{G} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$, we have the intensity two order of
We have obtained relatively large RXS intensities on the AFQ superlattice spot without assuming the lattice distortion, thereby demonstrating the mechanism of the Coulomb interaction. This situation is different from that of transition-metal compounds. The temperature and magnetic field dependences of the RXS spectra reproduce well the experiment. We have found that the azimuthal-angle dependence is closely related to the symmetry of the AFQ order. Therefore this quantity may be useful to determine the order parameter. We hope this study prompts experimentalists to measure this quantity.

In the magnetic ground state, we have constructed the wave function to be consistent with the ordering pattern of the magnetic moment determined by the neutron scattering experiment. Using this as the initial state, we have calculated the RXS spectra on an AFQ superlattice spot and on a magnetic superlattice spot. The intensity on the AFQ spot is a smooth extension from the AFQ phase. In addition, we have found a small pre-edge peak in the \( E_2 \) process. Since the main peak intensity will be reduced by the absorption correction, the pre-edge peak might be observed in future experiment. On the magnetic superlattice spot, we have a finite but much smaller intensity than that on the AFQ spot. It may be hard to confirm experimentally the spectra on this spot.

We have assumed the shape of the 5d-DOS rather arbitrarily. This is partly justified by the fact that the characteristics of the RXS spectra discussed in this paper do not sensitively depend on the details of the 5d DOS. Nevertheless, a band structure calculation for the 5d states may be necessary for more quantitative study.

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[35] Explicitly, the 5d-DOS, $\rho^{5d}(x)$, for each symmetry is given by

$$
\rho^{5d}(x) = \begin{cases} 
0.008x + 0.04, & -5 < x < 0, \\
0.01x + 0.04, & 0 < x < 8, \\
-0.0277x + 0.342, & 8 < x < 12.33,
\end{cases}
$$

where $x$ is measured in units of eV with $x = 0$ corresponding to the Fermi level.

[36] It is known that the anisotropic terms of the Coulomb interaction are slightly reduced in solids; we use the atomic values in Tables I by reducing them with multiplying a factor 0.8. On the other hand, the values of $F^0(2p, 4f)$, $F^0(2p, 5d)$, $F^0(4f, 4f)$, and $F^0(4f, 5d)$ are considerably screened in solids, so that we use rather smaller values for them.

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