Theory of Electric Quadrupole Transition in the XMCD Spectra at the Yb L_3 Edge of Mixed Valence Yb Compounds in High Magnetic Fields

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Abstract. The spectra of X-ray magnetic circular dichroism by the electric quadrupole transition (EQ-XMCD) are theoretically studied at the Yb L_3 edge of mixed valence compounds, YbInCu_4 and YbAgCu_4, around the field-induced valence transition in high magnetic fields. Using a new formulation with a single impurity Anderson model, which directly connects the EQ-XMCD spectra with the weights of the Yb 4f angular momentum j_z in the ground state, we show that the EQ-XMCD intensity of YbAgCu_4 is more than twice as large as that of YbInCu_4. This explains the reason for that the EQ-XMCD spectra was very recently measured successfully for YbAgCu_4, whereas no experimental evidence of EQ-XMCD has so far been obtained for YbInCu_4. Different EQ-XMCD intensities for the two materials and a peculiar field dependence of EQ-XMCD intensities are discussed on the basis of the weights of j_z in the ground state.

1. Introduction

X-ray magnetic circular dichroism (XMCD) gives us the bulk-sensitive, element-specific and site-selective information on electronic states in ferromagnetic and ferrimagnetic materials [1]. Most of mixed valence rare earth compounds are paramagnetic, but by applying high magnetic fields they are magnetized so that the measurements of XMCD become possible [2].

Recently experimental observations of X-ray absorption spectroscopy (XAS) and its XMCD were successfully made at the Yb L_3 edge of mixed valence Yb compounds, YbInCu_4 and YbAgCu_4, by utilizing pulsed high magnetic fields up to about 40T [3, 4, 5, 6]. By applying magnetic fields, the Yb valence number of YbInCu_4 and YbAgCu_4 changes rapidly around 30 T, which is denoted by the field-induced valence transition. Investigations of XMCD spectra for these materials have so far been made for the electric dipole (ED) transition measured around the field-induced valence transition, but another interesting subject is those due to the electric quadrupole (EQ) transition, which is stimulated by new experimental findings [6].

For YbInCu_4, the present author analyzed theoretically the experimental XMCD spectra [4] due to the ED transition with a single impurity Anderson model (SIAM) [7], but no clear signature of the XMCD due to the EQ transition (denoted by EQ-XMCD) was recognized in the experimental data. For YbAgCu_4, on the other hand, the EQ-XMCD spectra have been measured very recently by Nakamura et al., and the confirmation of the EQ-XMCD spectra
has also been made by theoretical calculations (by the present author) [6]. It is necessary to calculate the EQ-XMCD spectra for both YbInCu$_4$ and YbAgCu$_4$ and compare the results, in order to understand why the EQ-XMCD spectra could be measured for YbAgCu$_4$ but could not for YbInCu$_4$. For this purpose, we present in this paper a new formulation of the EQ-XMCD spectra with SIAM, where the EQ-XMCD spectra are directly connected with the weights of the Yb 4$f$ angular momentum $j_z$ in the ground state, by extending the theory of XMCD spectra due to the ED [2] and EQ [6] transitions. A different field dependence in the calculated EQ-XMCD spectra for YbInCu$_4$ and YbAgCu$_4$ will be explained on the basis of the difference in the field-induced valence transition of the two materials, which is clearly seen from the field dependence of the weights of $j_z$ in the ground state.

2. Model and Formulation

As a model to describe the XMCD spectra by the EQ transition at the Yb L$_3$ edge of YbInCu$_4$ and YbAgCu$_4$ in high magnetic fields, we use SIAM [8, 9]. The Hamiltonian of the system is written, in the hole picture, as [7]

$$H = \sum_{\nu} (\epsilon_{f,\nu} + g_J \mu_B j_z h) f^\dagger_{\nu} f_\nu - \sum_{\mu} \epsilon_{p,\mu} p^\dagger_{\mu} p_\mu + \sum_{k,\nu} \epsilon_k a^\dagger_{k,\nu} a_{k,\nu} + \sum_{k,\nu} (V_k a^\dagger_{k,\nu} f_\nu - V_k^* f^\dagger_{\nu} a_{k,\nu}) + U_{ff} \sum_{\nu > \nu'} f^\dagger_{\nu} f_{\nu'} f^\dagger_{\nu'} f_\nu;$$  

where the first, second and third terms represent, respectively, the single hole energies of the Yb 4$f$ states, the Yb 2$p$ states and the ligand band, the fourth term is the hybridization between Yb 4$f$ and ligand band states, and the last term represents the Coulomb interaction between Yb 4$f$ holes. Here, $g_J$ is the Landé g-factor, $\mu_B$ is the Bohr magneton, $h$ is the external magnetic field, and the indices $\nu$ and $\mu$ denote a set of quantum numbers $(j, j_z)$ and $(j', j_z')$ of the 4$f$ (and ligand band) and 2$p$ states, respectively, with the JJ coupling scheme $(j$ and $j'$ being fixed at 7/2 and 3/2). For more details on the model, see ref. [7].

The effect of the hybridization between the 4$f$ and ligand-band states is taken into account within the lowest order approximation of the $1/N_f$ expansion method [8], where $N_f$ ($=8$ for $j=7/2$) is the number of degeneracy of the 4$f$ state in zero magnetic field. We disregard the effect of the 4$f^2$ hole configuration by putting $U_{ff} = \infty$. The ground state $|g\rangle$ (with energy $E_g$) is obtained by diagonalizing the Hamiltonian $H$ in the form:

$$|g\rangle = c_0^{(g)}|0\rangle + \sum_{k,j_z} c_{k,j_z}^{(g)}|k, j, j_z\rangle.$$  

(2)

Here, $|0\rangle$ is the state where all the holes (except for 4$f$ holes) below the Fermi level $\epsilon_F$ ($=0$) are occupied, and $|k, j, j_z\rangle = f^\dagger_{k,j}(a_{k,j})|0\rangle$.

By the EQ transition, a 4$f$ hole with $\nu = (7/2, j_z)$ makes a transition to the 2$p_{3/2}$ state with $\mu = (3/2, j_z')$, so that the final state is expressed as

$$|f_{k,\nu,\mu}\rangle = p^\dagger_{\mu} a_{k,\nu}|0\rangle,$$  

(3)

where the hole with $(k, \nu)$ in the ligand band corresponds to a hole included in the state $|k, j, j_z\rangle$ in the ground state $|g\rangle$. The energy $E_{k,\nu,\mu}$ of this final state depends on $k$ but does not depend on $\nu$ and $\mu$ because of the degeneracy. The XAS spectrum by the EQ transition for $\pm$ helicity light is given by

$$F^\pm(\omega) = \sum_{k,\nu,\mu} |\langle f_{k,\nu,\mu}|M^\pm_{EQ}(\nu; \mu)|g\rangle|^2 \frac{\Gamma/\pi}{(\omega - E_{k,\nu,\mu} + E_g)^2 + \Gamma^2},$$  

(4)
where \( M_{\text{EQ}}^{\pm}(\nu, \mu) \) is the matrix element of the atomic EQ transition between \( \nu \) and \( \mu \) states. We take a geometry where the magnetic field is antiparallel to the direction of the X-ray propagation, then \( M_{\text{EQ}}^{\pm}(\nu, \mu) \) is expressed as

\[
M_{\text{EQ}}^{\pm}(\frac{7}{2}, j_z; \frac{3}{2}, j'_z) = \langle 4f \frac{7}{2} j_z | r^2 C^{(2)}_{\pm1} | 2p \frac{3}{2} j'_z \rangle = \sum_{m_p, m_f, s_f} (-1)^{3-m_f} \langle \frac{7}{2} j_z | 3m_f \frac{1}{2} s_f \rangle \\
\times \langle 1m_p \frac{1}{2} s_f | \frac{3}{2} j'_z \rangle \left( \begin{array}{ccc} 3 & 2 & 1 \\ -m_f & \pm 1 & m_p \end{array} \right) \langle 4f || r^2 C^{(2)} || 2p \rangle,
\]

by using the Clebsch-Gordan coefficients, the \( 3\cdot j \) symbol and the reduced matrix element.

Now we introduce a very convenient expression of the EQ-XMCD spectrum to study the difference in EQ-XMCD spectra for YbInCu \( 4 \) by using the Clebsch-Gordan coefficients, the \( 3\cdot j \) symbol and the reduced matrix element.

\[
E_{k_{\nu}, \nu', \mu} - E_g = E_0 \delta_{k, k_0},
\]

where \( \delta \) is the Kronecker \( \delta \)-function and \( k = k_0 \) corresponds to the Fermi level. Then the XMCD spectrum is expressed as

\[
F_{\text{XMCD}}(\omega) = F^+(\omega) - F^-(\omega) = \sum_{j_z} A_{j_z}^{(g)} B_{j_z}(\omega),
\]

where

\[
A_{j_z}^{(g)} = \sum_k |\epsilon_{k, -j_z}^{(g)}|^2,
\]

\[
B_{j_z}(\omega) = \sum_{j_z} \left( |M_{j_z, j'_z}^+|^2 - |M_{j_z, j'_z}^-|^2 \right) \frac{\Gamma/\pi}{(\omega - E_0)^2 + \Gamma^2}.
\]

We note that \( A_{j_z}^{(g)} \) is the weight of the Yb \( 4f \) angular momentum \( j_z \) in the ground state and \( B_{j_z}(\omega) \) is the contribution from each \( j_z \) to the EQ-XMCD spectrum. It is checked that \( E_{k_{\nu}, \nu', \mu} \) has a prominent peak for \( \epsilon_k \) just on the Fermi level for YbInCu \( 4 \) and YbAgCu \( 4 \), so that the approximate relation (6) is well acceptable.

3. Calculated results

For YbInCu \( 4 \), the value of \( A_{j_z}^{(g)} \) for each \( j_z \) was already calculated as a function of the magnetic field in ref. [7], and the result is reproduced in Fig. 1. For details on the calculation of \( A_{j_z}^{(g)} \), see ref. [7]. The function \( B_{j_z}(\omega) \), which is common for YbInCu \( 4 \) and YbAgCu \( 4 \), can easily be calculated, and the result is shown in Fig. 2, where the maximum amplitude of \( B_{j_z}(\omega) \) is normalized to be unity and we put \( E_0 = 0 \) and \( \Gamma = 2.5 \) eV. By using these results, the XMCD spectrum of YbInCu \( 4 \) is calculated for various magnetic field strengths, and the result is shown in Fig. 3. It is seen that the XMCD spectrum is negative and its amplitude first increases with the magnetic field, but it takes a maximum around 30 ~ 40 T and decreases with further increase in the magnetic field. The peak value of the XMCD spectrum is plotted as a function of the magnetic field in Fig. 4. In order to understand the field-dependence of the XMCD spectra, it is important to note from Fig. 2 that the states of \( j_z = 5/2 \) and 3/2 cause the negative XMCD, those of -5/2 and -3/2 cause the positive one with the same amplitudes, but those of 7/2 and -7/2 give no XMCD because of the selection rule. At zero magnetic field, all \( j_z \) states have the same weight, resulting in no XMCD signal, but by applying the magnetic field the weights of \( j_z = 5/2 \) and 3/2 become larger than -5/2 and -3/2, so that the amplitude of the negative XMCD increases. For magnetic fields higher than the field-induced valence transition around 30 T, the
weight of $j_z = 7/2$ increases rapidly, so that the XMCD amplitude decreases, and it vanishes in the limit of high magnetic field because the ground state tends to a pure $j_z = 7/2$ state.

Similar calculations are also performed for YbAgCu$_4$. The parameters of SIAM are determined so as to reproduce the experimental magnetization curve and valence numbers [6], as in the case of YbInCu$_4$. The results of $A^{(g)}_{j_z}$, $F_{\text{XMCD}}(\omega)$ and the XMCD peak intensity are shown in Figs. 5, 6, and 4, respectively. As seen from Figs. 1 and 5, the field-induced valence transition in YbAgCu$_4$ is much broader and more gradual than that in YbInCu$_4$, so that the induced magnetization below 30 T is larger and the weight of the $j_z = 7/2$ state above 30 T is smaller than those in YbInCu$_4$. This is the reason for that the intensity of the XMCD signal is larger for YbAgCu$_4$ than for YbInCu$_4$. Very recently the EQ-XMCD spectra for YbAgCu$_4$ were measured by Nakamura et al. [6] and the behavior of its peak intensity shown in Fig. 4 was confirmed for the magnetic field up to 35 T, but no clear evidence of EQ-XMCD was observed.
The weights $A_j^{(g)}$ of the states $j_z$ in the ground state of YbAgCu$_4$ as a function of the magnetic field.

The XMCD-EQ spectra of YbAgCu$_4$ for various values of magnetic field.

experimentally for YbInCu$_4$ because of its smaller intensity.

In conclusion, we can say that the EQ-XMCD intensity for YbInCu$_4$ is so small as to be comparable with or smaller than the experimental noise level, but that for YbAgCu$_4$ is larger than the noise level. Experimental observations of the EQ-XMCD spectra with higher resolution for YbInCu$_4$ and those for magnetic fields higher than 35 T for both YbInCu$_4$ and YbAgCu$_4$ are desirable in the future investigations.

Acknowledgments
The author would like to thank Prof. Y. H. Matsuda for providing experimental data and for useful discussions. He was partially supported by a Grant-in-Aid for Scientific Research C (No. 90029504) from the Japan Society for the Promotion of Science.

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