Theory of XAS and XMCD for the field-controlled valence mixed state in RE compounds

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Abstract. A valence fluctuating phenomenon, which is one of the most interesting subjects in strongly correlated electron systems, has been studied theoretically in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$, in which the field-induced valence transition from a nonmagnetic Eu$^{3+}$ state ($4f^6$) to a magnetic Eu$^{2+}$ state ($4f^7c^1$) was observed at around 40 Tesla by means of X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at Eu L-edges. Here, $c$ denotes a hole in a conduction band. Both XAS and XMCD in fields exhibit two peaks corresponding to the two valence states, although one of them is nonmagnetic. In this paper, we propose a model to explain the field-induced valence transition, in which the hybridization between the $4f^6$ state and the $4f^7c^1$ state plays an essential role. Comparing XAS and XMCD calculated with experimental data, we find that XAS and XMCD provide us with detailed microscopic information on the mixed valence state through the polarized 5$d$ electrons. Finally, we demonstrate how effective XAS and XMCD are for studying such mixed valence phenomena.

1. Introduction
In recent years, a pulsed magnetic field of a hundred Tesla (T) is produced and in fact used for studying magnetic materials in combination with synchrotron X-ray as well as neutron scattering experiments. A magnetic field of 100 T corresponds to 11.6 meV (134.5 K), which approaches an energy gap of an electronic phase. This implies that new electronic phases are able to be controlled by such an external magnetic field, if we choose an appropriate material. This is a quite interesting subject when we want to design new materials having interesting functions.

X-ray absorption spectroscopy (XAS) is a unique technology to reveal electronic and magnetic properties of materials since it provides us with such information of element selective as well as shell selective one. If we combine XAS with X-ray magnetic circular dichroism (XMCD), we can obtain quite detailed information not only of the electronic but of the magnetic properties of a targeted element in a compound. To this end, we need a sophisticated theory for XAS and XMCD, which is able to connect spectra observed to physical parameters of the model explaining the physical phenomena in materials.

In this paper, we focus our attention on the valence fluctuating phenomena observed in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ by means of XAS and XMCD. This compound is known to exhibit a valence transition at 65 K [1] between Eu$^{3+}$ and Eu$^{2+}$. The transition was monitored by the susceptibility, the magnetization and XAS at Eu L-edges and was analyzed by the interconfigurational fluctuation model [1], in which they introduced a phenomenological effective temperature to take into account the hybridization of the different 4$f$ electron configurations at zero temperature. On the same material, Matsuda et al. recently investigated a magnetic field
dependence of the valence states at low temperatures, killing thermal fluctuations, by means of XAS [2]. In their paper, they analyzed the results based on a model, in which the quantum mechanical hybridization between a nonmagnetic \( 4f^6 \) state \( (J_{4f} = 0) \) and magnetic \( 4f^7 \xi \) states \( (J_{4f} = 7/2) \) was taken into account, where \( J_{4f} \) is the total angular momentum of \( 4f \) electrons. The model reproduces nicely the field dependent XAS observed.

It is a purpose of this paper to extend the model proposed in the previous paper [2] in such a way that the model can be applicable to XMCD calculations, where more detailed information for magnetic states is necessary. In this sense, it is important to remember that the magnetization curve could not be well reproduced in low fields in the previous model, suggesting a necessary improvement. Considering this, we treat \( 4f \) electron states in more microscopic way in the present model and discuss XMCD using such \( 4f \) electron states.

In the next section, we present our model for the valence mixed state and discuss how the valence transition takes place. In Sec. 3, we give briefly the formulation for XAS and XMCD to make this paper self-contained. The last Sec. 4 is devoted to the results and discussions.

2. Model for a field-induced valence transition

In order to obtain deep insights into the magnetic-field-induced valence transition in EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\) observed, we propose here a model for a \( 4f \)-electron part of Eu states, in which the two valence states, \( \text{Eu}^{2+} \ (4f^6) \) and \( \text{Eu}^{2+} \ (4f^7 \xi) \), are considered with the hybridization matrix elements \( V \) between them. The \( LS \) state of the \( 4f^7 \xi \) configuration \( |(L_{4f}L_z)L_z, (S_{4f}S_z)S_z\rangle \) is specified with the spin and the orbital angular momentum of the \( 4f \) electron state \( |S_{4f}, L_{4f}\rangle \) and with those of \( \zeta \ (S_{\zeta}, L_{\zeta}) \). The spin-orbit interaction, \( \lambda \), and the Zeeman energy are also taken into account. Here, we restrict \( 4f^6 \) states to 49 states denoted by the total spin \( S_{4f} = 3 \) and the total orbital moment \( L_{4f} = 3 \), \(|4f^6 : L_z, S_z\rangle \), where \( L_z \) and \( S_z \) are \( L_{4f,z} \) and \( S_{4f,z} \), respectively. We also restrict the \( 4f^7 \xi \) states to 8 states where \( 4f^7 \) has \( S_{4f}'' = 7/2 \) and \( L_{4f}'' = 0 \), considering the Hund energy. Hereafter the \( 4f^7 \xi \) \( LS \) states are denoted as \(|4f^7 \xi : S_z''\rangle\). Thus, the Hamiltonian for the ground state is described as

\[
\mathcal{H}_g = \sum_{L_z,S_z=-3}^{3} \lambda M(L_z,S_z) |4f^6 : L_z + 1, S_z - 1\rangle \langle 4f^6 : L_z, S_z| + \text{h.c.}
\]

\[
+ \sum_{S_z''=-7/2}^{7/2} \left( E_{f7} - 2\mu_B H S_{z''} \right) |4f^7 \xi : S_z''\rangle \langle 4f^7 \xi : S_z''| + \sum_{S_z''=-7/2}^{7/2} \sum_{L_z,S_z=-3}^{3} F(L_z,S_z,S_z'') \left( |4f^6 : L_z, S_z\rangle \langle 4f^7 \xi : S_z''| + \text{h.c.} \right),
\]

where

\[
M(L_z,S_z) = \frac{1}{2} \langle 4f^6 : L_z + 1, S_z - 1 \mid L^+ S^- \mid 4f^6 : L_z, S_z \rangle,
\]

\[
F(L_z,S_z,S_z'') = \langle 4f^6 : L_z, S_z \mid \sum_{\mu=1}^{14} c^{\dagger}_{\mu} f_{\mu} \mid 4f^7 \xi : S_z'' \rangle = \sqrt{(4 + S_z)/7} \delta_{S_z', S_{z'} + 1/2} + \sqrt{(4 - S_z)/7} \delta_{S_z', S_{z'} - 1/2}.
\]

Here \( M(L_z,S_z) \) denotes a matrix element of the off-diagonal part of the spin-orbit interaction, \( L^+ S^- \), within the \( 4f^6 \) states while \( F(L_z,S_z,S_z'') \) is a matrix element connecting the \( 4f^6 \) states.
to the $4f^7\ell^1$ states: $f_\mu$ and $c_\mu^\dagger$ represent, respectively, a 4f-electron annihilation operator for 14 one-electron states with the quantum number $\mu$ and a creation operator for the corresponding conduction band state with $\mu$.

We set, in the case of zero field and zero hybridization, the ground state energy of Eu$^{3+}$ ($4f^6\ell$), $E_{g}$, to be 0 with $\lambda = 480$ K [3]. On the other hand, the energy of the Eu$^{2+}$ ($4f^7\ell^1$) state, $E_{f\ell} - E_{g}$, is assumed to be 190 K and the hybridization matrix element $V$ to be 120 K. These parameter values are chosen so that the calculated results of the magnetization curve and of the effective valence follow the experimental results.

Since the ground state has a nonmagnetic character while the next-lowest energy state has a magnetic one, it is not difficult to suppose that strong magnetic fields lower the energy of the latter and eventually result in the field-induced valence transition. In addition, the van Vleck term supports this magnetization process, which can be recognized in the magnetization curve. Such details of the ground state wave function sensitively affect XMCD spectra. Thus, we show in the next section such a field-induced valence transition is nicely traced by XAS and XMCD spectra, although the core 2p states as well as the empty 5d conduction band states are the main states for the XAS and XMCD process.

The ground state is now written symbolically as

$$|\psi_g\rangle = \sum_{L_z,S_z=-3}^{3} c_6(L_z,S_z) |4f^6 : L_z,S_z\rangle + \sum_{S''_z=-7/2}^{7/2} c_7(S''_z) |4f^7 \ell : S''_z\rangle,$$

(4)

where $c_6(L_z,S_z)$ and $c_7(S''_z)$ satisfy the normalization condition. Key quantities denoting the degree of the valence mixing are the symbols $|c_6|^2$ and $|c_7|^2$, with which the effective valence in the ground state, $v^\ast$, is defined,

$$v^\ast = 3.0 \times \sum_{L_z,S_z=-3}^{3} |c_6(L_z,S_z)|^2 + 2.0 \times \sum_{S''_z=-7/2}^{7/2} |c_7(S''_z)|^2.$$

(5)

The effective valence thus obtained is presented as a function of the field in Fig. 1, in which the valence transition can be seen at around 35 T. On the other hand, the magnetization is expressed by

$$m = \sum_{L_z,S_z=-3}^{3} |c_6(L_z,S_z)|^2 (L_z + 2S_z) + \sum_{S''_z=-7/2}^{7/2} |c_7(S''_z)|^2 2S''_z.$$

(6)

We note here that, in the present model, the magnetization process of the ground state consists of two parts, one is the degree of the hybridization between different valence states, Eu$^{3+}$ and Eu$^{2+}$ states, and the other is the magnetization process in each valence state. The two contributions collaborate and enhance each other at low fields, which is seen in Fig. 2. It is, however, noted that the magnetization curve observed increases more rapidly than that calculated in fields above 30 T, and tends to saturate above 40 T while the calculated one gradually increases in high fields. The reason for this quantitative discrepancy is not known at present.

It is conceivable that the final states, $|\psi_f\rangle$, of the two valence states are seriously affected and are separated by about 8 eV by the large core hole potential. Hence both states are hardly mixed. In addition, each valence state has a short life time of the core hole, resulting in a wide absorption width (about 5 eV for FWHM). Then, it is reasonable to determine parameters of the final state so as to fit the two peaks of the spectrum calculated to those observed: we assume $E_{\ell(4\ell)} = 6974$ eV for the 8 Hund states with the $4f^7$ configuration and $E_{\ell(4\ell)} = 6982$ eV for the 49 Hund states with the $4f^6$ configuration, neglecting the spin-orbit interaction.
Figure 1. The effective valence of the ground state, $v^*$, as a function of the magnetic field. The solid curve represents the result calculated by Eq.(5) while the open circles are estimated by fitting XAS calculated to the experimental spectra.

Figure 2. The magnetization curve as a function of the field. The solid curve represents the result calculated by Eq.(6) while the open squares are the experimental result [4].

3. X-ray absorption spectroscopy and X-ray magnetic circular dichroism

In this section, we summarize XAS and XMCD at the Eu $L$-edges [5], being concerned with the electric dipole (ED) transition from the initial configuration $2p^65d^n$ to the final configuration $2p^55d^{n+1}$, apart from the $4f$-electron part described in the previous section. Note that the XAS process involves only $2p$ core electrons and $5d$ conduction band electrons but the energies of the initial and the final states are dominated by the $4f$ electron state, discussed in the previous section: the fine structure of XAS reflects that of the density of states of the empty $5d$ band while the energy position of XAS is determined by the configuration of the $4f$ electrons in the final states with the strong core-hole potential and correlation energies.

In the calculation of the XAS and XMCD process, we make the following simplifications: (i) the Eu $5d$ states are treated by the cluster approximation including 17 Eu elements, in which the Coulomb and exchange interactions are ignored; (ii) there is no hybridization between the Eu $5d$ state and the Ni $3d$ state; (iii) there is no $5d$ electron in the initial state ($n = 0$); (iv) the intra-atomic exchange interaction of the $4f$ electrons with the $5d$ electrons is taken into account in a mean-field approximation, in which appropriate origin and scale are adopted; (v) the enhancement of the ED transition matrix element for XMCD [5], which depends on the mean-field of the exchange interaction, is taken into account in the effective ED operator given in eq.(9). This enhancement effect plays an important role in our case; (vi) the background of the $L$ absorption edges is represented by the arctangent function, as was used in the previous paper [2]; (vii) the electric quadrupole (EQ) transition is neglected.

In order to calculate the spectra, we define the initial and the final states for X-ray absorption process,

$$|\Psi_i\rangle = |\psi_i\rangle |2p^6 5d^0\rangle$$  \hspace{1cm} (7)

$$|\Psi_f\rangle = |\psi_f\rangle |2p^5 5d^1\rangle$$  \hspace{1cm} (8)

where $|2p^6 5d^0\rangle$ denotes the initial state with the fully occupied $2p$ core states and with the completely empty $5d$ conducting states. $|2p^5 5d^1\rangle$ is the final state with a core hole. Thus the
absorption spectrum with positive and negative helicities are defined as

\[ I(\omega)^\pm = \sum_l |\langle \Psi_l | T^\pm | \Psi_g \rangle|^2 L(\omega - E_l + E_g, \Gamma), \]  

where \( T^\pm \) denote the effective ED operator with positive and negative helicities for a transition from a core 2p state to a conducting 5d state including the enhancement effect, \( L \) is a Lorentzian function with the lifetime width of \( \Gamma (= 2.5 \text{ eV}) \), \( E_f \) and \( E_g \) are the energies of the final and ground states, respectively. With these, XAS and XMCD are, respectively, defined by

\[ I(\omega) = I(\omega)^+ + I(\omega)^-, \]  
\[ \Delta I(\omega) = I(\omega)^+ - I(\omega)^-. \]

Furthermore, we add an arctangent function to \( I(\omega) \) to simulate the background of the spectra. Thus, in Fig. 3 the XAS spectra and in Fig. 4 the XMCD spectra, which are obtained by a superposition of the two spectra for the 4f\(^7\) states and the 4f\(^6\) states shifted by 8 eV, are shown. These spectra are favorably compared with those experimentally observed in EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\) [6] and are in good qualitative agreement at each field.

**Figure 3.** XAS spectra calculated at the \( L_3 \)-edge for representative values of the magnetic field. The spectra show two peaks corresponding to different valence states, Eu\(^{2+} \) (4f\(^7\)) in the lower energy side and Eu\(^{3+} \) (4f\(^6\)) in the higher energy side. As the field is increased, the intensity for the former peak gets strong while the one for the latter gets weak.

**Figure 4.** XMCD spectra calculated at the \( L_3 \)-edge for representative values of the magnetic field. The spectra show two peaks corresponding to the magnetic Eu\(^{2+} \) (4f\(^7\)) state in the lower energy side and to the nonmagnetic Eu\(^{3+} \) (4f\(^6\)) state in the higher energy side.

4. Results and discussions

In this paper, we study theoretically XAS and XMCD spectra in the case of the field-induced valence transition in EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\). At a first glance, it is curious that the peak in the higher energy side has non-zero XMCD intensity since the peak corresponds to the nonmagnetic 4f\(^6\) state. However, the present model reproduces considerable XMCD intensity even for that peak. To understand this, we remind that in the ground state at finite fields the 4f\(^6\) state has magnetic character due to the hybridization with the magnetic 4f\(^7\) state. In addition, the 4f\(^6\) states in the final states may be magnetic because of a serious disturbance by the core hole.
and degenerate within the lifetime width. Then, the 5d states is polarized by the magnetic 4f⁶ states, which is the origin of XMCD at the higher energy peak. We emphasize that XMCD follows these situations accurately and hence provides us with very detailed information on the ground state. Thus, we have demonstrated that the hybridization between the 4f⁶ states and the 4f⁷ states in the present model is a key ingredient for XAS and XMCD. We can say XAS and XMCD are vital means for studying such a mixed valence problem, because not only of their selectivity of an atom and even of a shell but of their sensitivity to the wave functions.

Now, we give some comments on our simplifying assumptions made in our calculations. We have assumed no 5d electron in the initial state in the assumption (iii) and neglected the EQ transition in (vii). Although both effects of the 5d electron in the initial state and of the EQ transition are expected to modify spectral shapes in the low energy tail of the spectra, no such a fine structure in the low energy tail has been observed. Thus, we believe that the enhancement effect in (v) dominates these effects in the present case.

Next, we discuss the assumption (ii). In the case of the mixed valence state in CeFe₂, spontaneously magnetized Fe 3d electrons make the 5d states magnetically polarized and this effect dominates XMCD spectra at the nonmagnetic peak [7], since there is little possibility for the nonmagnetic 4f⁰ state to be magnetized. In the case of EuNi₂(Si₀.₁₈Ge₀.₈₂)₂, however, since the ground state of Eu³⁺ (4f⁶) can be polarized in fields, the weak effect of the polarized Ni 3d electrons by the 4f electrons on the 5d states [6] will be masked. It is still desirable to study a role of the Ni 3d electrons in XMCD in this compound. Also, in this context, it is interesting to make clear the different situations in cases of Eu [6] and Sm [8] compounds and in cases of Ce and Yb compounds.

In conclusion, we have succeeded in explaining the novel experimental results of XAS and XMCD for the valence mixed system of Eu and have revealed detailed electronic and magnetic properties of the system based on the microscopic model. We hope that the present work stimulates further experiments as well as sophisticated theories for the field-induced valence transition.

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