Ground state of ferromagnetic nickel and magnetic circular dichroism in Ni $2p$ core x-ray-absorption spectroscopy

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The electronic state of ferromagnetic Ni and the expected magnetic circular dichroism (MCD) in Ni $2p \rightarrow 3d$ x-ray-absorption spectroscopy [$2p$ (XAS)] are discussed from a viewpoint of $3d$ configuration interaction on the basis of the Anderson impurity model. The model includes multiplet effects arising from $3d$-$3d$ and $3d$-$2p$ electron interactions and a $3d$ interatomic exchange approximated by a molecular field acting on the $3d$ spin. By using commonly accepted values of the interaction strengths, it is shown that the ground state of a Ni atom in ferromagnetic Ni is expressed by a superposition of $3d^{10}$, $3d^9$, and $3d^8$ configurations with relative weights of 15%–20%, 60%–70%, and 15%–20%, respectively, and with an orbital-magnetic-moment contribution of $\sim 0.07\mu_B$ to the total moment of $0.6\mu_B$. With these results, we can explain the recently observed MCD in Ni $2p$ XAS.

The electronic state of ferromagnetic Ni has been a subject of continuous debate. The band theory on the basis of local-density-functional formalism explains various static properties such as bulk modulus and magnetization.[1] A theory beyond the band picture is, however, known to be needed to interpret experiments of various high-energy spectroscopies, such as valence-band photoemission with a satellite structure 6 eV below the Fermi level.[2-4] In addition to valence-band photoemission, the Ni $2p$ core x-ray photoemission spectroscopy ($2p$ XPS) spectrum is also known to exhibit a satellite above the main peak for both the core spin-orbit multiplets $2p_{1/2}$ and $2p_{3/2}$. It has been suggested that the satellite in $2p$ XPS must be explained not by the band model but by a many-body configuration-interaction (CI) viewpoint, where the electronic state of a Ni atom is described as a superposition of more than one $3d$ configurations[5] with weights quite different from the statistical ones resulting from band theory.

For $4f$ rare-earth and $3d$ transition-metal compounds, the CI viewpoint for metallic ions has successfully been applied to an interpretation of various high-energy spectroscopies on the basis of an Anderson impurity model or a ligand-field model.[6,7] These models assume that the hybridization between a given metal $3d$ or $4f$ orbital and surrounding delocalized orbitals, having amplitudes mainly in partner atoms and the state of the metal ion, is described by a superposition of more than one d or f configuration. Although the correlation between metallic ions is neglected in a discussion of electronic states, a description of them in terms of d or f atomic orbitals for a given ion seems to have a meaning as far as the local properties are concerned. The fact that multiplet structures peculiar to specific atomic configurations are observed in various spectroscopies gives an experimental support to the approach. It is also worth mentioning that, even in

pure Ni, the atomic multiplet structure is observed in Auger spectra and an analysis based on the Anderson model has successfully been carried out.[8] We may say that the CI approach for $3d$ and $4f$ electron systems picks out one metal ion, distinguishes it from others as a reservoir, and then describes the ground state of our system by a superposition of bases specified by the electron configuration of the metal ion and that of the reservoir.

The purpose of this paper is to discuss the ground state of ferromagnetic Ni from the CI viewpoint and to present expected differences in Ni $2p \rightarrow 3d$ x-ray-absorption spectroscopy [$2p$ (XAS)] between the right- and left-circularly polarized [(RCP) and (LCP), respectively] incident beams, i.e., magnetic circular dichroism (MCD) on the basis of a simplified Anderson model. Recently, much attention has been paid to magnetic x-ray dichroism, especially MCD in core photoabsorption[9] and photoemission spectra.[10] Very recently Chen et al. observed MCD in $2p$ XAS for Ni.[11] Recalling that in the 1970s the spin-resolved photoemission had great impact on a study of electronic structure itself, as well as magnetism of magnetic substances,[2] we can expect that MCD will also contribute strongly to the study and will resolve many ambiguities not solved by studies related to unpolarized x rays. The present work has, we think, a significance as an example of such studies. Our model includes the interaction between electrons producing multiplets of a Ni atom and a molecular field acting on the $3d$ spin. We will show that the ground state of a Ni atom in ferromagnetic Ni metal is to be described by a superposition of $3d^{10}$, $3d^9$, and $3d^8$ configurations with the weights of 15%–20%, 60%–70%, and 15%–20%, respectively, and a Ni atom has a spin moment of $\sim 0.53\mu_B$ and an orbital moment of $\sim 0.07\mu_B$ (if the total moment is assumed to be $\sim 0.60\mu_B$). We will furthermore show that these ground-state properties are well reflected in MCD of $2p$ XAS both for L_3 ($2p_{3/2}$) and

L_2 ($2p_{1/2}$), and are consistent with the MCD spectrum by Chen *et al.*

In ferromagnetic Ni, the number of $3d$ electrons of a Ni atom of interest is supposed to fluctuate through the hybridization between the $3d$ atomic orbital of the Ni atom and the orbitals of reservoir (hereafter denoted by v) which are mainly composed of neighboring Ni $3d$ orbitals and to some extent arising from plane-wave-like states. Starting from the state where the Ni atom of interest is in the $3d^{10}$ configuration and the reservoir states below the Fermi level ε_F are occupied, we assume the coupling of it with $3d^9v$, which in turn couples with $3d^8v^2$, through the hybridization and neglecting the states having electron-hole pair(s) in the reservoir;[6] the ground state of our system $|g\rangle$ is symbolically expressed as

$$|g\rangle = A|3d^{10}\rangle + B|3d^9v\rangle + C|3d^8v^2\rangle . \tag{1}$$

The unoccupied $3d$ state obtained by inverse photoemis-

sion[12] with an effective width of < 0.5 eV could be a rough estimate of the unoccupied reservoir, to which $3d$ electrons of the Ni atom are transferred. We hereafter tentatively neglect the bandwidth of the unoccupied reservoir. We suppose the energy of $|3d^9v\rangle$ measured from $|3d^{10}\rangle$ ε_d of -0.5- -1.0 eV, the effective $3d$-$3d$ interaction $U_{d\text{-}d}$ of 4–5 eV, the hybridization matrix element V of 0.6–0.7 eV, and the effective $2p$-$3d$ interaction in the final state of $2p$ XAS $U_{p\text{-}d}$ of 5–6 eV. These parameter values seem to be compatible with the commonly accepted ones.[8]

The Anderson impurity model used to describe the initial (ground) state and the final state of $2p$ XAS for our system may be, with the use of the hole picture, expressed as

$$H = H_1 + H_2 , \tag{2}$$

where

$$H_1 = \sum_\mu \left[\varepsilon_d a_{d\mu}^\dagger a_{d\mu} + V(a_{d\mu}^\dagger a_{v\mu} + \text{H.c.}) + \tfrac{1}{2} U_{d\text{-}d} n_{d\mu} \sum_{\mu'(\neq\mu)} n_{d\mu'} + U_{p\text{-}d} n_{d\mu} \sum_\xi n_{p\xi} - \Delta_M s_z(\mu) n_{d\mu} \right] \tag{3}$$

and

$$H_2 = H_{d\text{-}d}(F^2,F^4) + H_{p\text{-}d}(F^2,G^1,G^3) + H_d(\zeta_d) + H_p(\zeta_p) . \tag{4}$$

In Eq. (3), the origin of energy is taken at the reservoir level and the first, second, third, fourth, and fifth terms represent the energy of the $3d$ hole with μ symmetry, the hybridization between the $3d$ and reservoir states, $3d$-$3d$ and $2p$-$3d$ repulsive Coulomb interactions, and the Zeeman energy due to the molecular-field multiplied by μ_B, respectively; μ denotes the combined index specifying the $3d$ azimuthal quantum number and spin state; $s_z(\mu)$ denotes the z component of the $3d$ spin of the μth state. Equation (4) denotes all the interactions producing multiplets (given by Slater integrals F^k's and G^k's) between $3d$ holes ($H_{d\text{-}d}$) and between $2p$ and $3d$ holes ($H_{p\text{-}d}$) and the spin-orbit interaction in the $3d$ ($2p$) state H_d (H_p) with the coupling constant ζ_d (ζ_p); without Slater integrals with $k \neq 0$, both $H_{d\text{-}d}$ and $H_{p\text{-}d}$ vanish. We adopt the parameter values in units of eV given by de Groot *et al.* for $3d^9$ and their $2p^5 3d^9$ extrapolations;[13] $F^2 = 9.79$ and $F^4 = 6.08$ in $H_{d\text{-}d}$; $F^2 = 6.17$, $G^1 = 4.62$, and $G^3 = 2.63$ in $H_{p\text{-}d}$; $\zeta_p = -11.5$ and $\zeta_d = 0.08$.

For the parameter values of $\varepsilon_d = -1.0$ eV and $U_{d\text{-}d} = 5.0$ eV, we have the average energy differences among configurations (aside from the multiplet splitting due to H_2 [see Eq. (4)]) $E(3d^9v) - E(3d^{10}) = \varepsilon_d = -1.0$ eV and $E(3d^8v^2) - E(3d^9v) = \varepsilon_d + U_{d\text{-}d} = 4.0$ eV. By switching on the hybridization $V = 0.65$ eV and the molecular field $\Delta_M = 0.5$ eV (Ref. 14) together with H_2 [see Eq. (4)], we have the weight for each $3d$ configuration of the Ni atom in the ground state [see Eq. (1)] given by

$$|A|^2 = 0.18, \quad |B|^2 = 0.65, \quad \text{and} \quad |C|^2 = 0.17 , \tag{5}$$

and the $3d$ orbital and spin moments per Ni atom given by

$$M_{\text{orb}} = 0.07\mu_B \quad \text{and} \quad M_{\text{spin}} = 0.53\mu_B , \tag{6}$$

respectively; we chose Δ_M so as to obtain M_{orb}

$+ M_{\text{spin}} = 0.60\mu_B$. In the discussion of $2p$ XAS, we adopt $U_{p\text{-}d} = 6.0$ eV.

Next we briefly summarize the MCD experiment by Chen *et al.*[11] and make some comments. We define the integrated intensities of the $2p \rightarrow 3d$ absorption in the L_2 and L_3 region for the RCP (LCP) beam by $I_+(L_2)$ and $I_+(L_3)$ [$I_-(L_2)$ and $I_-(L_3)$], respectively; we note that the increase of the z component of orbital angular momentum for our system, accompanied by the photoabsorption ΔL_z, is equal to $+1$ (-1) for the RCP (LCP) beam. Their data then show that (i) $R_{\text{XAS}} \equiv [I_-(L_3) + I_+(L_3)]:[I_-(L_2) + I_+(L_2)] \sim 2.6:1$, (ii) $R_{\text{MCD}} \equiv [I_-(L_3) - I_+(L_3)]:[I_-(L_2) - I_+(L_2)] \sim -1.6:1$, and (iii) both for L_2 and L_3, $2p$ XAS has a satellite ~ 6 eV above the main peak, while the satellite of the MCD spectrum (difference spectrum between RCP and LCP) is ~ 4 eV above the main one, i.e., there is no MCD in the higher-energy region of each satellite peak.

If we adopt an atomic model where only one up-spin hole exists in the $3d$ orbitals and the $3d$ spin-orbit interaction is absent, we obtain, by taking into account the $2p \rightarrow 3d$ dipole transition, $R_{\text{XAS}} = 2:1$ and $R_{\text{MCD}} = -1:1$, regardless of crystalline symmetry, in disagreement with the experiment, and the result (iii) is an open question. A band-structure calculation also gives $R_{\text{MCD}} = -1:1$.[15] We note that any model with no orbital moment in the $3d$ system leads to the same result for R_{MCD}. If we improve the atomic model by introducing an orbital moment of $\sim 0.1\mu_B$, we obtain $R_{\text{MCD}} \sim -2:1$ and R_{XAS} larger than $2:1$, but result (iii) is still not explained.

We will show that our ground state given by Eqs. (5) and (6) explains the above-mentioned experiment. In our CI model, the initial $3d^9v$ ($3d^8v^2$) configuration is transferred to the $2p^5 3d^{10}v$ ($2p^5 3d^9v^2$) one in the final state of the photoabsorption; the initial $3d^{10}$ configuration

does not contribute to $2p$ XAS. We obtain the eigenvalue E_f and eigenstate $|f\rangle$ with the index f in the final state, which is a superposition of $|2p^5 3d^{10}v\rangle$ and $|2p^5 3d^9 v^2\rangle$, by diagonalizing Eq. (2) with Eqs. (3) and (4). Then we obtain the $2p$ XAS spectrum $F_\sigma(\omega)$ given by $F_\sigma(\omega) = \Sigma_f |\langle g|T_\sigma|f\rangle|^2 \delta(\omega + E_g - E_f)$ with ω, E_g, and T_σ being the incident photon energy, the energy of $|g\rangle$, and the operator of the dipole transition, respectively ($\sigma = +$ and $-$ for RCP and LCP, respectively). The MCD spectrum is hereafter defined by $F_-(\omega) - F_+(\omega)$. In order to demonstrate the importance of $3d^8$ being included in the initial state, we first present in Fig. 1 $F_\sigma(\omega)$ and the MCD spectrum calculated for the ground state [see Eq. (1)] with $|A|^2 = 0.26$, $|B|^2 = 0.74$, $|C|^2 = 0.0$, $M_{orb} = 0.08\mu_B$, and $M_{spin} = 0.52\mu_B$, which is obtained by modifying the initial-state parameters with the exception of the Slater integrals; the final-state ones are the same as above. The result shows that $R_{XAS} \sim 2.5{:}1$, $R_{MCD} \sim -1.8{:}1$, and we have the satellite in agreement with the experiment. The satellite peaks in $2p$ XAS and MCD spectra, however, extend over the common energy region, which is in disagreement with the experiment. In Fig. 2, we show the same quantities as in Fig. 1 for the ground-state described by Eqs. (5) and (6), where $R_{XAS} \sim 2.5{:}1$ and $R_{MCD} \sim -1.9{:}1$. We again have the satellite in $2p$ XAS similar to that given in Fig. 1 but the satellite intensity in MCD spectrum, in the higher-energy side, disappears in L_3 and is weakened in L_2, which is consistent with the experiment.

The main L_3 and L_2 peaks both for $2p$ XAS and MCD in Figs. 1 and 2 arise from the MCD active $3d^9$
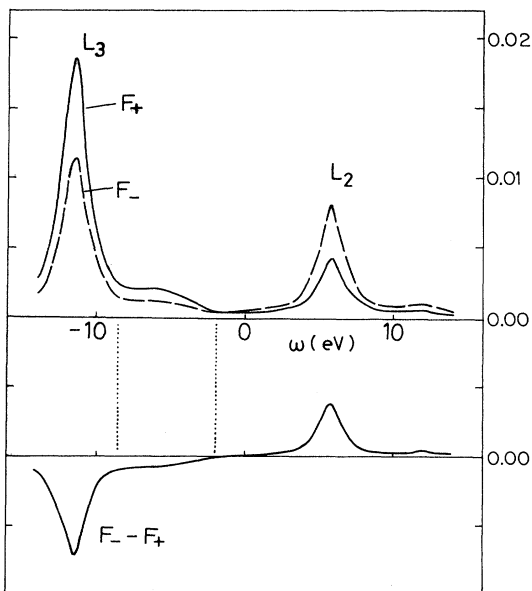

FIG. 2. Same as Fig. 1 except for the initial state including $3d^8$ given by Eqs. (5) and (6).

FIG. 1. The calculated $2p$ XAS for RCP (F_+) and LCP (F_-) beams and MCD ($F_- - F_+$) as a function of the photon energy ω; a Lorentzian broadening of 2.0 eV (full width at half maximum) is introduced. The initial state is assumed to be a superposition of $3d^{10}$ and $3d^9$ with the weights 26% and 74%, respectively, and $M_{orb} = 0.08\mu_B$ and $M_{spin} = 0.52\mu_B$.

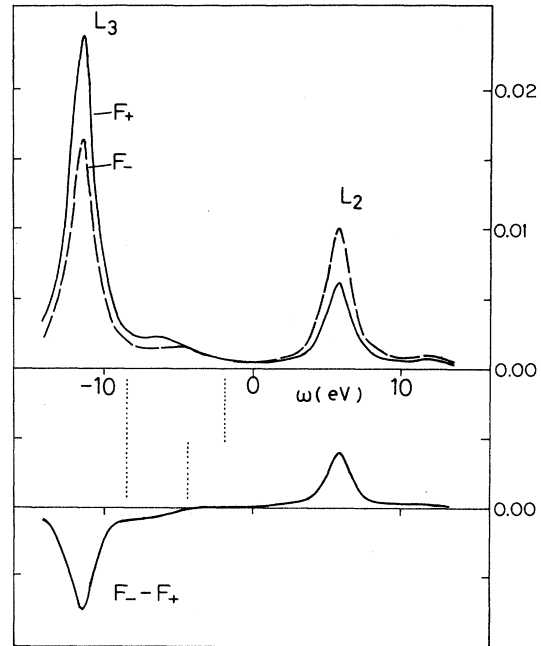$\rightarrow 2p^5 3d^{10}$ transition. In the absence of $3d^8$ in the ground state (see Fig. 1), the satellite of both $2p$ XAS and MCD spectra arises from the configuration mixing between the $2p^5 3d^{10}$ and $2p^5 3d^9$ in the final state and the MCD in the satellite is transferred from that of the main peak; the satellite structures of both $2p$ XAS and MCD spectra are similar to each other. When the $3d^8$ is, on the other hand, included in the ground state (see Fig. 2), the satellite also arises from the direct $3d^8 \rightarrow 2p^5 3d^9$ transition in addition to the above-mentioned configuration mixing in the final state. The initial state in this case contains many $3d^8$ multiplets and among them ^3F with the lowest energy is the main component. We have two types of direct $3d^8 \rightarrow 2p^5 3d^9$ transitions: (1) The initial state have a pair of up- and down-spin $3d$ holes, which is MCD inactive, and then the final state has a pair of up- and down-spin $2p$-$3d$ holes which mainly contributes to the higher-energy region of each satellite because of the $2p$-$3d$ exchange interaction. (2) The initial state has a pair of up-spin $3d$ holes, which is MCD active, and then the final state has a pair of up-spin $2p$-$3d$ holes which mainly contributes to the lower-energy region of each satellite because of the $2p$-$3d$ exchange interaction. The latter contribution to MCD is the same as that of each main peak in the lower-energy region of the satellite, while it is found to be reversed in the higher-energy region of the L_3 satellite. The feature of the MCD active $3d^8 \rightarrow 2p^5 3d^9$ transition causes the suppression of MCD on the higher-energy side especially of L_3 satellite shown in Fig. 2. We note that the effect of interference between the $3d^9 \rightarrow 2p^5 3d^{10}$ and $3d^8 \rightarrow 2p^5 3d^9$ is minor as far as MCD is concerned.

In conclusion, we discussed the ground state of ferromagnetic Ni from a CI viewpoint on the basis of the

Anderson impurity model taking into account atomic multiplets. We stressed the $3d^8$ configuration of a Ni atom, which is mainly composed of the ^3F multiplet, with the weight of 15%–20% being included in the ground state and an orbital contribution to the magnetic moment of $\sim 0.07\mu_B$. The former has been qualitatively suggested by Fuggle et al.[16] and the latter is consistent with the recent calculation by Eriksson et al.[17] We furthermore showed that with these values the recent MCD results are well explained. There may be various alternatives or improved methods to discuss our problem even within the Anderson model, details of which, and discussions on other spectroscopies expected from our picture, will be given elsewhere.

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