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Multielectron satellites and spin polarization in photoemission from Ni compounds

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Valence-band photoemission and its spin polarization of insulating Ni ($Ni^{2+}:d^8$) compounds are studied by considering configuration interactions within the Ni-ligand cluster. It is found that the main lines, which have been assigned to d-hole (d^7) final states, are due to final states where the d hole is screened by a ligand-to-d charge transfer and that the satellite contains significant d^7 character. Effects of these final-state interactions on the multiplet structure and the spin polarization are discussed.

Valence-band photoemission from Ni shows a satellite[1] at ~ 6 eV below the Fermi level E_F, and the width,[1,2] and the exchange splitting[3] of the main d band is smaller by ~ 30% and ~ 50%, respectively, than the values calculated by the energy-band calculation.[4] According to theoretical studies using the Hubbard model,[5] the satellite has been identified as a two-hole bound state. The reduced bandwidth and exchange splitting have also been interpreted as due to electron correlation effects within the Ni $3d$ band. However, intratomic Coulomb energy between two d electrons U could not be adjusted to give at the same time correct satellite position and d bandwidth in the Hubbard model, and other interaction terms have been proposed to resolve this discrepancy.[6] On the other hand, in the case of oxides and halides of Ni, where electrons in the incomplete d^8 shell are localized in the ground state due to strong electron correlations (Mott insulators), photoemission spectra have been interpreted in terms of the final-state multiplets of the d^7 ion.[7] However, in spite of the different electronic structures, quite similar spectra have been obtained for insulating and metallic Ni compounds: the so-called multielectron satellites have also been observed in NiO, $NiCl_2$, $KNiF_3$, etc.,[8] (Fig. 1) and their $3p \rightarrow 3d$ resonance behavior[9,10] is quite similar to that of Ni metal,[11] although another mechanism, L (ligand) → d shake-up transitions,[7-9] has been attributed to the satellites.

In this paper, the satellite structures of the insulating Ni compounds are studied theoretically. A Ni atom and neighboring ligand atoms are considered. Hybridization between $3d$ and non-$3d$ (ligand) orbitals is explicitly taken into account together with strong $3d$-$3d$ correlations using a configuration-interaction (CI) formalism.[12] A remarkable result of the present study is that the main d band is predominantly due to final states with a d hole (d^7) screened by a $L \rightarrow d$ charge transfer, namely, $d^8\underline{L}$ final states, where $\underline{L}$ denotes a ligand hole (see the bottom panel of Fig. 1). This invalidates the previous interpretation that the main lines show the d^7 multiplet structure and that the satellite is due to the $L \rightarrow d$ shake-up transition. Instead, the multiplet structures of the mixed d^7, $d^8\underline{L}$, etc., configurations should be considered. We also note the significant d^7 character in the satellite region, which, according to the theory of Davis,[13] explains the resonant enhancement of the satellites rather than the main lines[9,10] in NiO and $NiCl_2$. In order to obtain further information, a spin-polarized photoemission experiment is proposed.

We consider a Ni^{2+} ion octahedrally coordinated by closed-shell O^{2-}, Cl^-, or F^- ions. The ground state is a mixture of the purely ionic d^8 configuration and the charge-transfer configuration $d^9\underline{L}$:

$$\Psi_g = a|d^8\rangle + b|d^9\underline{L}\rangle \quad . \tag{1}$$

The energy of (1) is lowered by the d-L hybridization relative to that of d^8. The state (1) with total symmetry ${}^3A_{2g}$ having a configuration $t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\uparrow}^2$ was found to be the lowest in energy as in the ligand-field (LF) theory.[14] The crystal-field splitting ($100q$) of the $3d$ level into t_{2g} and e_{2g} sublevels are not assumed *a priori* but results from different energies of different configurations.[12] The final state of d-electron emission is given by

$$\Psi_f(S\Gamma) = c|d^7\rangle + d|d^8\underline{L}\rangle + e|d^9\underline{L}^2\rangle \quad , \tag{2}$$

where S and Γ denote the total spin and symmetry, and

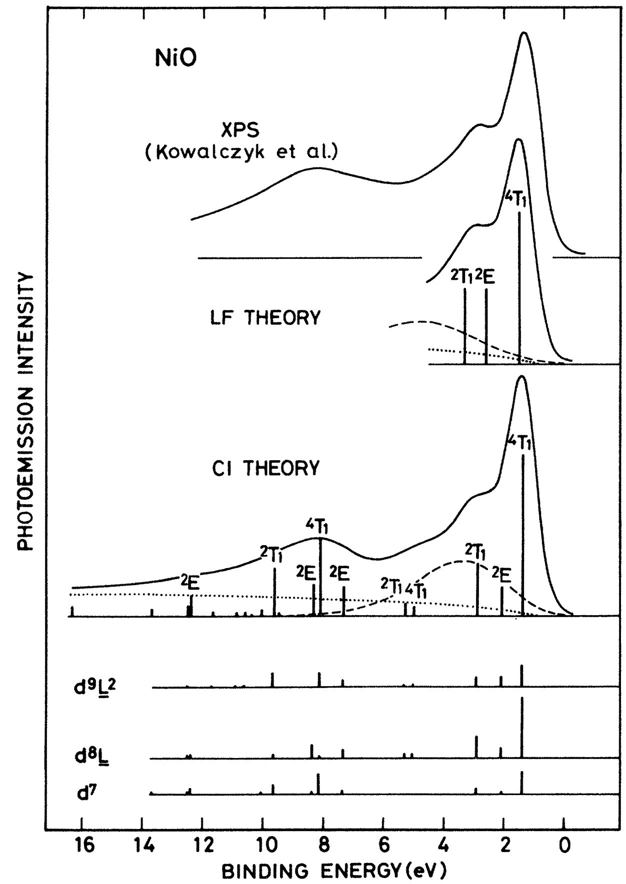

FIG. 1. Valence-band photoemission spectra of NiO calculated by the configuration-interaction (CI) and ligand-field (LF) theories, compared with the XPS spectrum (Kowalczyk *et al.*, in Ref. 16). The LF spectrum was calculated with $B=0.09$ eV, $C=0.42$ eV, and $10Dq=0.93$ eV. The multiplet lines have been lifetime broadened by widths which increase with increasing binding energy and have been convoluted by a Gaussian resolution function [full width at half maximum (FWHM) $=0.9$ eV]. Dotted lines represent the O $2p$ emission, and dashed lines integral backgrounds. On the bottom, final states are decomposed into the d^7, $d^8\underline{L}$, and $d^9\underline{L}$ components.

$S\Gamma={}^2E_g$, ${}^2T_{1g}$, and ${}^4T_{1g}$ are allowed by selection rules. d^7 in the ${}^2E_g$, ${}^2T_{1g}$, and ${}^4T_{1g}$ final states have, respectively, $t_{2g}^6e_g$, $t_{2g}^5e_g^2$, and $t_{2g}^5e_g^2$ configurations, and corresponding $d^8\underline{L}$ and $d^9\underline{L}^2$ are obtained by transferring electrons in the ligand molecular orbitals to the $3d$ orbitals conserving spin and orbital symmetry. In the calculation of the energies and eigenstates of (1) or (2), multiplet splitting of the free Ni ion[14] and d-L hybridization are considered. As a result of the hybridization, the multiplet structure is considerably modified. The transfer and overlap integrals were taken from the band calculation of NiO (Ref. 15). Energies involved in charge transfers, $E(d^8\rightarrow d^9\underline{L})$, $E(d^7\rightarrow d^8\underline{L})$, and $E(d^8\underline{L}\rightarrow d^9\underline{L}^2)$, were treated as adjustable parameters which are to be determined by a fit to experimental spectra.

The x-ray photoemission (XPS) spectrum of NiO was reproduced using $E(d^8\rightarrow d^9\underline{L})=4$ eV, $E(d^7\rightarrow d^8\underline{L})=-3.5$ eV, and $E(d^8\underline{L}\rightarrow d^9\underline{L}^2)=1$ eV as in Fig. 1. There one can see that all spectral features including the satellite are well reproduced. As these parameters are related to $-\epsilon_d$, $-\epsilon_L$ (ionization energies of the $3d$ and ligand orbitals), and $U-u$ (u: $3d$ electron-ligand hole attractive Coulomb energy, whose bare value 6.8 eV would be considerably reduced by interionic and intraionic polarization[16]) through $E(d^8\rightarrow d^9\underline{L})\sim\epsilon_d-\epsilon_L+U-u$ and $E(d^7\rightarrow d^8\underline{L})\sim\epsilon_d-\epsilon_L$, U is estimated to be 8–10 eV. $\epsilon_d-\epsilon_L\simeq-3.5$ eV may conflict with one-electron energies given by band calculations: $\epsilon_d>\epsilon_L$ (non-self-consistent, local-density approximation)[15] or $\epsilon_d\sim\epsilon_L$ (self-consistent Hartree-Fock),[17] but is consistent with many-electron energy levels obtained by an analysis of core-level satellites.[18] The above parameters give the d-electron number of 7.8 in the ground state, in good agreement with neutron diffraction experiment.[19]

The $d^8\underline{L}$ character of the main lines would explain the fact that the main lines appear to show widths only of experimental and lifetime broadening and not of bandwidth (~ 1 eV):[20] in the $d^8\underline{L}$-like final state, a d hole is accompanied by a $L\rightarrow d$ charge transfer and therefore three particles, the d hole, ligand hole, and the d electron transferred from the ligands have to hop simultaneously, which effectively reduces the transfer integrals by orders of magnitude as in the case of d-d excitons.[16] The appearance of the satellite and the narrowing of the main lines are thus attributed to electron correlations within the Ni $3d$ and ligand p orbitals. In the case of Ni metal, neighboring Ni $3d$ orbitals have been considered in the Hubbard model studies,[5,6] but Ni $4sp$ orbitals may also play a role as pointed out by Kanamori.[21] The d^7-like final states in the insulating Ni

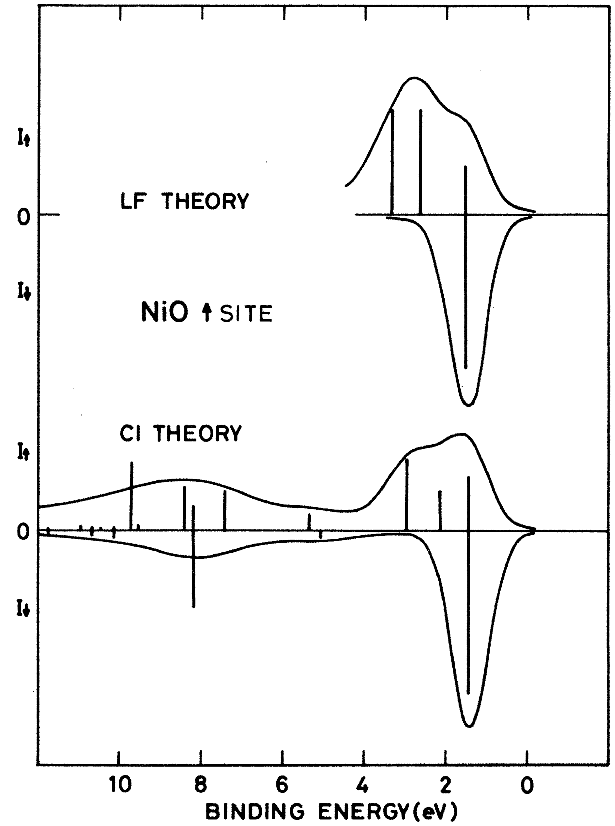

FIG. 2. Spin-resolved photoemission spectra from the ↑-spin Ni^{2+} ion in NiO. Only d-electron emission is shown, neglecting the O $2p$ emission, which has the same ↑ and ↓ intensities, and the background. Exchange splitting of the ${}^4T_{1g}$ final state is assumed too small to be resolved. The same broadening as in Fig. 1 has been used.

compounds may be viewed as two-hole bound states: the presence of a d hole results in a lowering of another d level on the same site, which is filled in the $d^8\underline{L}$ final states, and the d^7 state consists of the first d hole and the empty lowered d level.

Figure 2 shows the spin-resolved spectra of NiO. Simple calculations show that the ^2E_g and $2T_{1g}$ lines are 100% polarized in the positive ($\uparrow$) direction while $P=50\%$ for the $^4T_{1g}$ lines $[P=(I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)]$. In the figure is also shown spin-resolved spectra calculated based on the LF theory. The both results show negative polarization just below E_F followed by positive polarization at 2–4 eV, which is similar to that expected from the band theory.[20] In the LF theory, the spin-resolved intensity ratios of the three lines, $^4T_{1g}$, $^2T_{1g}$, and ^2E_g, are fixed, while the relative positions of the two T_{1g} lines and the ^2E_g line are dependent upon the assumed values of $10Dq$ and Racah parameters. In the CI theory, transfer of the spectral weight from the main lines to the satellite is related to the multiplet and crystal-field splittings of the main lines. More spectral weight is lost from the $^2T_{1g}$ and ^2E_g main lines than from $^4T_{1g}$, resulting in the reduction of the positive polarization at 2–4 eV and the increase of that in the satellite region. In the LF theory, if the spin is conserved in the $L \rightarrow d$ transition, $P \sim 25\%$ on the average would be expected in the satellite region, while the CI result shows that $P=30\%$–50% in this region. It is expected that as in Ni metal the polarization is enhanced near the $3p \rightarrow 3d$ resonance.[22] The enhancement is expected to occur mainly in the satellite region where there is predominantly d^7 character. The exchange splitting should be larger tha $\Delta_{\mathrm{CF}} \sim 1$ eV in the energy-band theory in order to make the $e_{g\downarrow}$ band empty. Exchange splitting observed in photoemission from the insulating Ni compounds may be defined as the binding-energy difference between $t_{2g\downarrow}$ emission ($^4T_{1g}$) and $t_{2g\uparrow}$ emission (an $I_\uparrow$-weighted average of the $^4T_{1g}$ and $^2T_{1g}$ energies). This is calculated to be ~ 0.9 eV in the CI calculation and ~ 1.2 eV in the LF calculation. In the CI theory, the exchange splitting is reduced by the transfer of the spectral weight which is more significant for $^2T_{1g}$ than for $^4T_{1g}$. Although NiO itself is an antiferromagnet with a high Néel temperature and its spin polarization cannot be studied experimentally, most of Ni compounds have common spectral features and spin polarization would be detectable in paramagnetic compounds at low temperatures and in high magnetic fields or in ferrimagnetic $\mathrm{RbNiF_3}$.[23]

In conclusion, the similar satellite structures and resonance behaviors in the systems with quite different electronic ground states, namely, itinerent Ni metal and Mott insulators, Ni oxides and chlorides were found to be due to similar physical process in the photoemission final state. The too narrow d bandwidth in Ni metal when U is adjusted to give the correct satellite position might therefore be attributed to the $sp \rightarrow d$ screening effects in the main d band. Kanamori noted that[21] in Ni unlike other $3d$ transition metals the $4sp$-like density of states (DOS) has a dip near E_F and that when a d hole is screened this leads to a deficiency of ~ 0.4 sp electron on the nearest-neighbor atoms. This situation is somewhat similar to the insulating Ni compounds in that the non-d DOS is small at E_F and that the d hole is not screened within the nearest-neighbor atoms: ~ 1 electron is missing on the ligands in the screened $d^8\underline{L}$ final states in NiO.

When going from Ni to Co to Fe to Mn compounds, $\epsilon_d - \epsilon_L$ becomes higher. This results in more d^{n-1} character in the main lines, and the LF theory becomes more relevant. This is consistent with the resonant photoemission results on a series of $3d$ transition-metal dichlorides that the main lines are more significantly enhanced in $\mathrm{FeCl_2}$ and $\mathrm{MnCl_2}$. Details of the CI theory and its application to resonant photoemission, optical absorption, and isochromat spectroscopy will be published elsewhere.

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