PHYSICAL REVIEW B VOLUME 37, NUMBER 18 15 JUNE 1988-II

Core-exciton absorption in the F K absorption spectra of $3d$ transition-metal fluorides

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(Received 28 December 1987)

Near-edge structure in the F K absorption spectra of $3d$ transition-metal fluorides, MnF_2, FeF_2, CoF_2, NiF_2, CuF_2, and ZnF_2, are measured. The shoulder structures or weak peaks located at the absorption threshold are observed. The origin of these peaks is attributed to the core-exciton absorption. This core-exciton absorption is accompanied by the transition from the $1s$ orbitals of fluorides to the $3d$ orbitals of the metal ion which hybridized with the anion $2p$ orbitals. Chemical shifts of the first peak are clearly observed and discussed in terms of the ionization potentials of the metal ions. It is found that the F K absorption spectra of the $3d$ transition-metal fluorides are quite similar to the Cl K absorption spectra of the $3d$ transition-metal chlorides.

The $3d$ transition-metal compounds display interesting magnetic and electrical properties arising from the electrons in the incomplete $3d$ shells. These $3d$ electrons are localized in the metal atoms, thus the electron-electron interaction seems to be large and the one-electron band scheme is not a good approximation in these compounds. The transition-metal halides are good insulators and take the form of ionic compounds. In order to investigate these electronic states, optical-absorption spectra,[1,2] valence-band photoelectron spectra,[3,4] and core-level x-ray photoelectron spectra[5-8] have been measured. Sakisaka *et al.*[2] measured the fundamental absorption spectra of the $3d$ transition-metal chlorides and bromides. They observed the weak peaks, which are located at the absorption threshold, and which shift systematically toward low energy on going from manganese halides to nickel halides. They interpreted these peaks with the charge transfer transition from the outermost p orbitals of halogen to the $3d$ orbitals of the transition metal. A similar phenomenon can be expected to be observed in the core-level absorption spectra from the ligand site. Therefore, in this study, we have measured the anion K absorption spectra of the $3d$ transition-metal fluorides to get the information about the $3d$ states of these compounds.

Experiments were carried out with a 10-m grazing incidence monochromator[9] at the BL12-C line at the 2.5-GeV electron storage ring of Photon Factory of National Laboratory for High-Energy Physics (KEK-PF). The angle of incidence was fixed at 89° and 1200-lines/mm concave grating was used. Both the entrance and exit slits were 10 μm in width. The energy resolution of this monochromator at the F K absorption region was about 0.3 eV. Spectra were measured by means of the absorption method with thin film. The absorption films were prepared by vacuum evaporation. The thickness was monitored by a quartz oscillator and was 1500–2000 Å in thickness. The sample chamber was evacuated to the vacuum of 2.6×10^{-7} Pa by an ion pump. The transmitted x rays were detected by a windowless photoelectron multiplier (HTV R595). The accumulation of the data and the control of the stepping motor for scanning the monochromator were done by a microcomputer system (AIDACS-3000). The K edges of N_2, O_2, and Ne gas were used as a wavelength standard.

Figure 1 shows the F K absorption spectra of Mn, Fe, Co, Ni, Cu, and Zn fluorides. In the case of FeF_2, the spectrum region is limited to below 705 eV because of the overlapping in the Fe $L_{2,3}$ absorption spectrum. The photon-energy values of the characteristic points in these spectra are given in Table I. The prominent features obtained in these absorption profiles are as follows. (1) Overall profiles above the main peak B are alike among the different transition-metal fluorides. (2) The first peak A shifts systematically to the low-energy side from MnF_2 to CuF_2. On the other hand, the peak A of ZnF_2 shifts to the higher-energy side compared to CuF_2. (3) In the spectra of MnF_2 and FeF_2, the peak A is split into two peaks A and A' although the peak A' of FeF_2 is somewhat fainter than MnF_2. These spectral features are much different from the metal $L_{2,3}$ absorption spectra of these same compounds.[10] As a reference, we show the metal $L_{2,3}$ absorption spectra of CrF_3, MnF_2, FeF_2, CoF_2, NiF_2, and ZnF_2 in Fig. 2. As seen from Fig. 2, metal $2p$ absorption spectra show multiplet splittings which are caused by strong p-d exchange interaction. Similar interaction between a core hole and the unpaired valence electrons has been observed in the spectra of $3p$-$3d$ excitation of the $3d$ transition-metal halides,[11,12] $2p$-$3d$ excitation of the $3d$ transition metals,[13,14] alloys,[15] and also observed in the spectra of $3d$-$4f$ excitation of the $4f$ rare-earth elements.[16-19] Comparing the spectra of Fig. 1 and Fig. 2, in the case of the interatomic transition, the core-hole effect is not so large, therefore, we can analyze the F K edge spectra in terms of the molecular-orbital scheme.

Now, we will consider the origin of the prominent peaks B and D in Fig. 1. We can see from Table I that

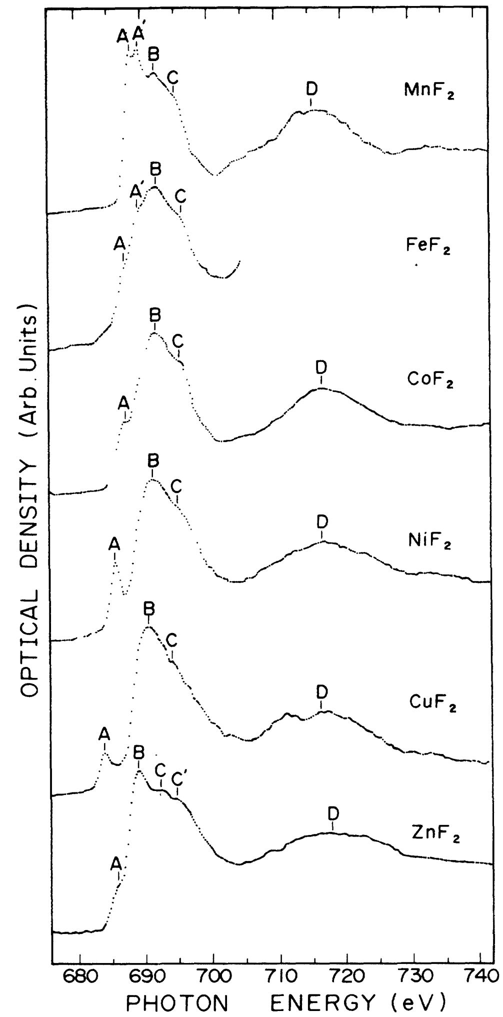

FIG. 1. Fluorine *K* absorption spectra of 3*d* transition-metal fluorides, MnF_2, FeF_2, CoF_2, NiF_2, CuF_2, and ZnF_2.

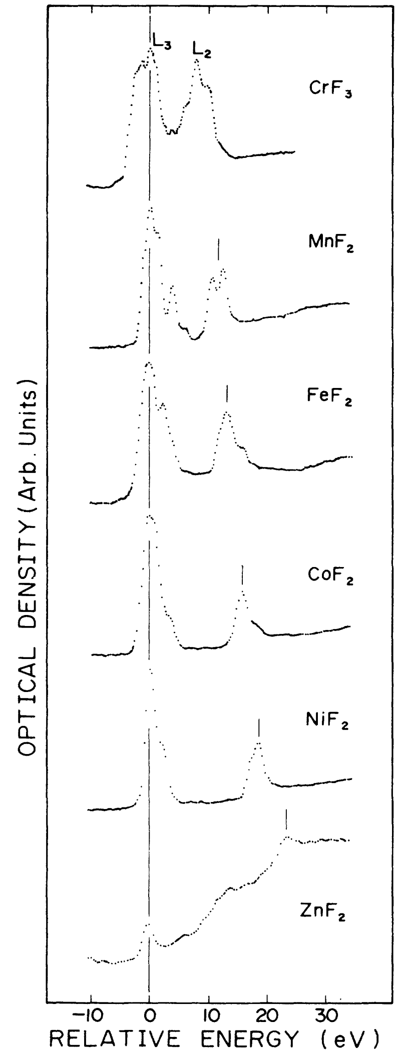

FIG. 2. Metal $L_{2,3}$ absorption spectra of 3*d* transition-metal fluorides, CrF_3, MnF_2 FeF_2, CoF_2, NiF_2, and ZnF_2. (Taken from Ref. 10.)

the photon energies of the peaks *B* and *D* are not as changed among these compounds as the peak *A*. These compounds crystallize in the same rutile structure except for CuF_2. Therefore, the spectral similarity is well understood by the same crystal and similar electronic structures if we neglect the behavior of 3*d* electrons. From the reason mentioned above, these main structures *B* and *D* may be reproduced as the x-ray-absorption near-edge structure (XANES) calculation by the multiple-scattering theory.[20] We have demonstrated this interpretation in the case of anion *K* XANES of alkali-metal fluorides,[21] alkaline-earth-metal fluorides,[22] alkaline-earth-metal ox-

TABLE I. Photon energies (eV) of the characteristic points in the fluorine *K* absorption spectra of MnF_2, FeF_2, CoF_2, NiF_2, CuF_2, and ZnF_2. The ionization energy values of the monovalent metal ions are also shown. (Taken from Ref. 24.)

	A	*A'*	*B*	*C*	*C'*	*D*	Ionization energy (eV)	
MnF_2	688.3	689.5	692.2	695.1		715.6	Mn^+	15.64
FeF_2	687.8	689.5	692.1	696.0			Fe^+	16.18
CoF_2	687.0		691.8	695.4		716.0	Co^+	17.05
NiF_2	685.9		691.3	695.4		716.0	Ni^+	18.15
CuF_2	684.0		690.7	694.6		716.6	Cu^+	20.29
ZnF_2	686.0		689.2	692.2	695.0	716.0	Zn^+	17.96

ides, and $3d$ transition-metal oxides.[23]

Next we consider the origin of the peaks A and A' which show large energy peak shifts as seen in Table I. These peak shifts are closely related to the change of the ionization energies of these $3d$ transition-metal monoions.[24] Therefore, it is obvious that the peak A represents the $3d$ character. However, the F K absorption is a transition from an anion $1s$ core level so that the direct transition to the $3d$ level is dipole forbidden. Therefore, we suppose that it may appear as a result of p-d hybridization in the valence orbitals. Similar energy shifts of the first peak which relate to the metal ion ionization energy have been observed in the fundamental absorption spectra[2] and also in the Cl K absorption spectra of the $3d$ transition-metal chlorides.[25] However, the recent XANES calculation for the F K edge of MnF_2 cannot represent the first peak.[26] We have obtained a similar result in the O K edge spectrum of CaO.[23] In the case of CaO, the first peak in an experimental curve was missed in the XANES calculation, and so we assigned the first peak to the core-exciton absorption, the same as in the case of the O K edge spectrum of MgO.[27] Therefore, we attribute the peak A in Fig. 1 to the core-exciton absorption. The core exciton is strongly localized in an atom, so it does not appear in a multiple-scattering calculation. In addition, the orbitals of these metal ions hybridize with those of the fluorine ions and form the molecular orbitals. The $3d$ orbitals mix with the p and s orbitals of fluorine and form the e_g and t_{2g} orbitals. In the fluorides of nickel, copper, and zinc, the t_{2g} orbital is completely filled, thus the only transition possible is to the e_g orbital (peak A). On the other hand, manganese and iron fluorides have both the unoccupied e_g and t_{2g} orbitals, therefore we can say the e_g and t_{2g} orbitals cause the peaks A and A', respectively. This assignment is based on the fact that the shifts of the peaks A and A' among different transition-metal fluorides are parallel to the ionization energies of the transition-metal ions, respectively. For these two reasons mentioned above, we conclude that the peaks A and A' are caused by core excitons which closely relate to the $3d$ electron states. However, in the present spectra, the presence of the peak A' in FeF_2 is rather faint and also we could not observe the peak A' in the spectrum of CoF_2. The resolution of the spectrometer is enough to detect these peaks. Therefore, it may be necessary to measure the spectra at liquid N_2 temperature to confirm the existence of the peak A' and also to check the temperature dependence of the peaks A and A'.

Finally, concerning the spectral feature, we can see a similarity between the F K edge spectra and the Cl K edge spectra[25] of the $3d$ transition-metal halides. The overall absorption structure and the observed chemical shift of the first peak are alike in both spectra. This resemblance may be understood naturally from the same electronic transition process in both cases. However, in the case of the Cl K edge spectra of $MnCl_2$ and $FeCl_2$, the first peak has not been split into two peaks. It may be due to the lower resolution of the spectrometer.

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