

Soft-x-ray $M_{2,3}$ absorption spectra of some transition-metal halides

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The soft-x-ray $M_{2,3}$ absorption spectra due to excitation of $3p$ electrons of transition metals, Cr, Mn, Fe, Co, and Ni, and the metal ions in the halides, CrCl_2 , CrBr_3 , MnF_2 , MnCl_2 , MnBr_2 , FeCl_2 , FeBr_2 , CoF_2 , CoCl_2 , CoBr_2 , NiCl_2 , and NiBr_2 , are obtained at room temperature. Synchrotron orbital radiation from a 1.3-GeV electron synchrotron at the Institute for Nuclear Study in Tokyo is used as a light source. The fine structures of the spectra are observed on the low-energy side of the absorption threshold of all the transition-metal halides except for nickel halides. These structures suggest the existence of the localized d levels which lie a few eV below a $4s$ band.

I. INTRODUCTION

Compounds of the first-row transition metals have many peculiar properties different from the other compounds and determination of their electronic band structure is essential to understand these properties. However, unfortunately, the electronic band structures of these compounds, especially transition-metal halides, have not been well studied yet. It is well known that the soft-x-ray spectroscopy gives an important information about the energy-band structures of solids. A common feature of these compounds is that these metal ions have unpaired electrons in the $3d$ shell. Therefore, it is expected that the absorption spectra show many detailed structures associated with the distribution of the empty $3d$ states. Though there are several investigations¹⁻³ on the optical-absorption spectra of some of these substances, only a few investigations^{4,5} have been made on the soft-x-ray absorption spectra. Brown, Gähwiller, and Kunz⁵ studied the $M_{2,3}$ absorption spectrum of NiO. They interpreted the obtained spectrum in terms of the ground state and important x-ray-excited states of Ni^{2+} and suggested that their results agree with the model of the NiO band structure discussed by Adler and Feinleib.⁶ However, the $M_{2,3}$ absorption spectra of the metal ions in transition-metal halides have not yet been reported.

The purpose of the present paper is to show the $M_{2,3}$ absorption spectra for transition metals, Cr, Mn, Fe, Co, and Ni, and the metal ions in the halides, CrCl_2 , CrBr_3 , MnF_2 , MnCl_2 , MnBr_2 , FeCl_2 , FeBr_2 , CoF_2 , CoCl_2 , CoBr_2 , NiCl_2 , and NiBr_2 , and to investigate the distribution of the empty $3d$ and $4s$ states which bear upon the electrical, optical, and magnetic properties of the transition-metal halides.

II. EXPERIMENTAL

The $M_{2,3}$ absorption spectra were obtained by the use of synchrotron radiation from a 1.3-GeV electron synchrotron at the Institute for Nuclear Study, University of Tokyo. A soft-x-ray monochromator newly designed by the INS-SOR group was used. This monochromator consists of a plane-glass grating with 1080 grooves per mm and a concave mirror coated with aluminum. The wavelength scanning is performed by simple rotation of the grating. The detailed descriptions of this monochromator appeared in the literature by Miyake *et al.*⁷ The electron synchrotron was operated at the energy of 1.15 GeV during the absorption measurements. An aluminum-coated pre-reflector was used at the incidence angle of 85° arc in front of the entrance slit to cut off the high-energy component in the synchrotron radiation and to avoid a radiation damage of the grating. The exit slit was used with the width of $30 \mu\text{m}$. The detector was a windowless Be-Cu photomultiplier with 20 stages (HTV-R425). The sample chamber, which has an evaporation system, was attached between the monochromator and a detector chamber and was evacuated to 4×10^{-6} Torr during measurements. Absorption films were prepared by the evaporation *in situ* onto thin collodion substrates supported by fine nickel meshes. As all the transition-metal halides contain water of crystallization, each material was heated in vacuum to remove the water. The thickness of the samples was 2000–4000 Å, which could be estimated from interference color of the films.

III. RESULTS AND DISCUSSION

The $M_{2,3}$ absorption spectra of Cr, CrCl_2 , and CrBr_3 are shown in Fig. 1. Although the general

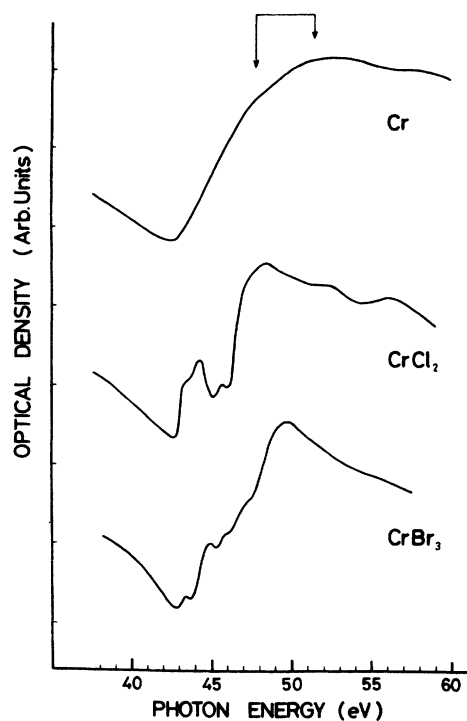


FIG. 1. $M_{2,3}$ absorption spectra of Cr, CrCl_2 , and CrBr_3 .

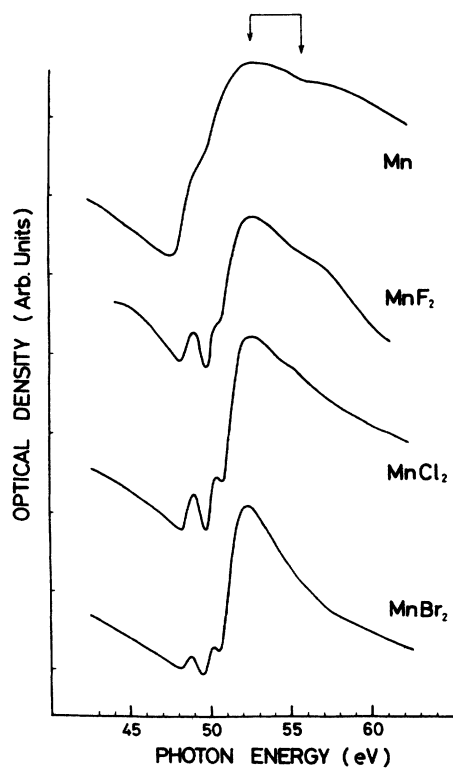


FIG. 2. $M_{2,3}$ absorption spectra of Mn, MnF_2 , MnCl_2 , and MnBr_2 .

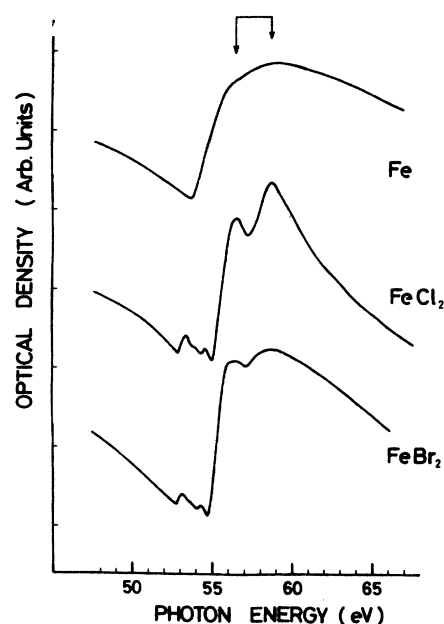


FIG. 3. $M_{2,3}$ absorption spectra of Fe, FeCl_2 , and FeBr_2 .

features of the spectra of the transition metals, Cr, Mn, Fe, Co, and Ni, agree with the earlier results obtained by Sonntag *et al.*⁸ in the present experiment the shoulder structures, which represent the $M_{2,3}$ spin-orbit splittings, are observed at the absorption thresholds of the spectra of all the transition metals. The splitting is estimated at about 3.7 eV for chromium and is shown by a linked arrow in Fig. 1. The absorption curve of CrCl_2 is somewhat different from that of CrBr_3 . Figure 2 shows the absorption curves of Mn and its halides. The $M_{2,3}$ spin-orbit splitting is clearly observed and estimated at about 3.2 eV in manganese. The absorption curves of MnF_2 , MnCl_2 , and MnBr_2 are very similar to one another, nevertheless these halides have different crystal structures. The absorption spectra of Fe, FeCl_2 , and FeBr_2 are shown in Fig. 3 and those of Co, CoF_2 , CoCl_2 , and CoBr_2 are shown in Fig. 4. The $M_{2,3}$ spin-orbit splitting is estimated at about 2.2 and 2.8 eV for iron and cobalt, respectively. The general features of the absorption spectra of CoF_2 , CoCl_2 , and CoBr_2 are alike, while the crystal structure is different among these three materials. The locations of the corresponding peaks in the structure of the absorption spectra shift to the lower energy from the fluoride to the bromide. This tendency is commonly observed for the spectra of all the transition-metal halides. Figure 5 shows the $M_{2,3}$ absorption spectra of Ni, NiCl_2 , and NiBr_2 . The $M_{2,3}$ spin-orbit splitting is estimated at about 2.3 eV. In the case of NiCl_2 and NiBr_2 , the struc-

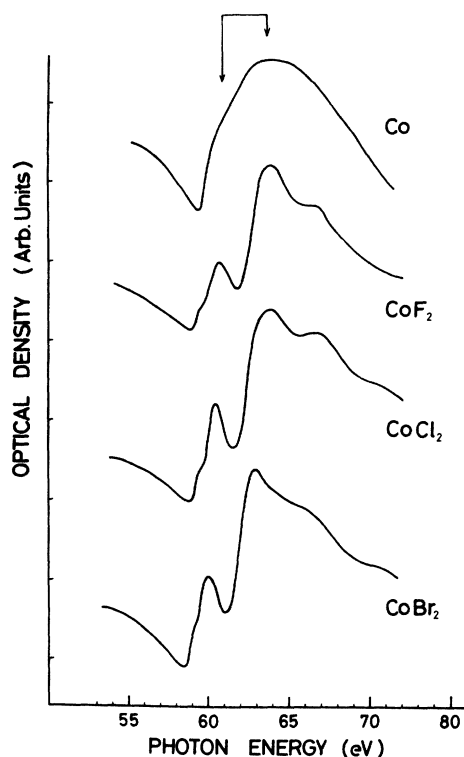


FIG. 4. $M_{2,3}$ absorption spectra of Co, CoF_2 , CoCl_2 , and CoBr_2 .

ture could not be clearly observed on the low-energy side of the absorption threshold.

Figure 6 shows the $M_{2,3}$ absorption spectra of CrCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , and NiCl_2 . These substances have the crystal structure of the CdCl_2 -type except for CrCl_2 and contain the metal ions which have the electronic configuration of $3d^n$, where n is 4, 5, 6, 7, and 8 for Cr, Mn, Fe, Co, and Ni, respectively. It should be noted that the structures of the spectra of the transition-metal halides, not only the chlorides but the other halides, are classified into two groups. The one consists of a rather weak and narrow band occurring on the low-energy side of the absorption threshold and the other consists of an intense and rather broad band appearing on the high-energy side of the threshold. The positions of the absorption thresholds are shown by T in Fig. 6. These features are common to all the spectra except for the low-energy structure for NiCl_2 . These metal ions have unpaired electrons in the $3d$ shell and the $M_{2,3}$ absorption is due to the transition from the $3p$ levels of these metal ions. Therefore, it should be expected that the spectrum shows the influence of the empty $3d$ states.

Adler and Feinleib⁶ proposed a model of the NiO band structure which consists of a filled band asso-

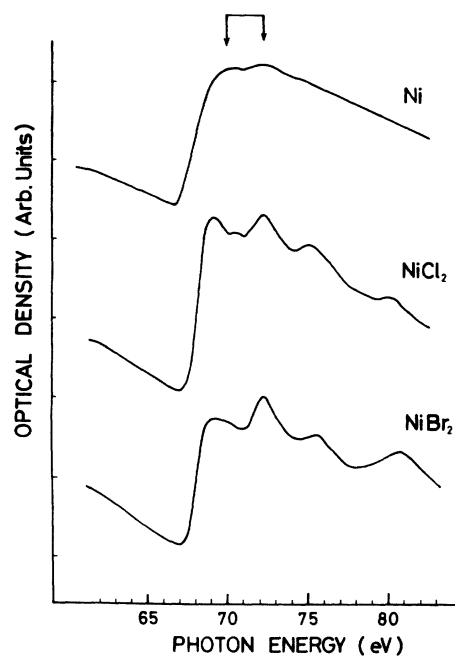


FIG. 5. $M_{2,3}$ absorption spectra of Ni, NiCl_2 , and NiBr_2 .

ciated with the O^{2-} $2p$ states situated well below the Fermi level, an empty Ni^{2+} $4s$ band above the Fermi level and very narrow nickel $3d$ levels between these two bands. These $3d$ levels are pri-

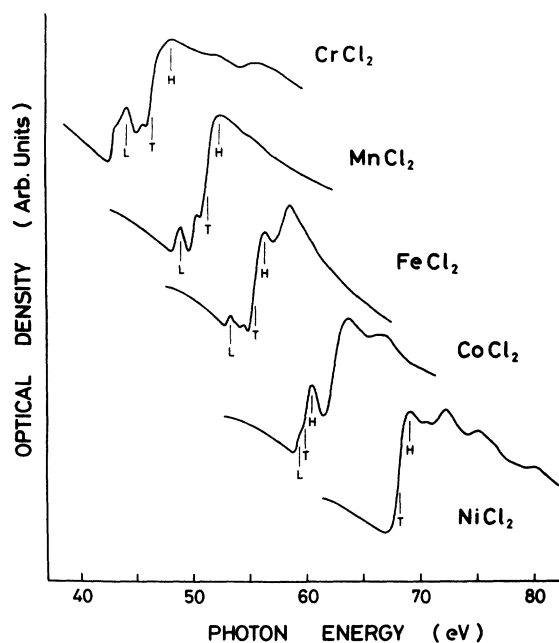


FIG. 6. $M_{2,3}$ absorption spectra of some transition-metal chlorides.

marily localized because of small wave-function overlap, and filled by eight electrons. Messick, Walker, and Glosser⁹ measured the optical reflectance spectra of MnO, CoO, and NiO, and supported the mixed-band-localized-states model proposed by Adler and Feinleib. Recently, the Ni $M_{2,3}$ absorption spectrum of NiO was obtained by Brown *et al.*⁵ The spectral profile on the high-energy side of the threshold is similar to that of NiCl₂ obtained by the present experiment. They also calculated the ground state and important x-ray-excited states of the Ni²⁺ ion in order to interpret the spectrum of NiO, and obtained the similar ordering of levels occurring in the soft-x-ray region as Adler and Feinleib suggested in the optical region of NiO. Then they interpreted the spectrum of NiO in terms of the configurations of the ground state and the excited states of the Ni²⁺ ion and assigned the weak structure on the low-energy side of the threshold to the $3p^5 3d^9$ configuration and the structure on the high-energy side to the $3p^5 3d^8 4s$ configuration.

Assuming that the band structures of the transition-metal halides are not so different from the band model of the transition-metal oxides proposed by Adler and Feinleib, the $3d$ bands of these substances may be primarily localized and lie a few eV below the $4s$ conduction band. These localized $3d$ states are partially filled, and the $4s$ band is empty. Then it may be considered that the absorption of the $3p$ electron to the $3d$ states may occur on the low-energy side of the threshold which corresponds to the beginning of the broad and intense absorption to the $4s$ band.

As the results the low-energy structures observed in the present experiment may be attributed to the intra-atomic transitions from the $3p$ states to the $3d$ states. The detailed structures in the low-energy structures may be due to the $3p^5 3d^{n+1}$

multiplet (including the crystalline-field splittings as considered in the case of the formation of the d^* levels by Adler and Feinleib). The origin of the high-energy structures may be attributed to the transition from the $3p$ states to the empty $4s$ band. Of course, the $4s$ band in the crystal forms the conduction band and hence may be expected to show the band structures. The energy separation between the first peak of the low-energy structures (shown by L in Fig. 6) and that of the high-energy structures (shown by H in Fig. 6) becomes smaller with the order of CrCl₂, MnCl₂, FeCl₂, and CoCl₂. It may suggest that the energy separation between the empty $3d$ states and the $4s$ band of these substances becomes smaller with this order. Moreover, the narrow absorption profile of each one of the low-energy structures may also suggest that the $3d$ states have the small wave function overlap with nearest-neighbor ions and thus the $3d$ states are well-localized states in the transition-metal halides. In the case of metals, these two groups are not clearly separated in the absorption spectra. It may be due to the fact that the large overlap between the d band and the s band in the metal leads to the single broad band. As a conclusion the spectra of all the transition-metal halides seem to represent the structures derived from both the localized and one-electron band states and to suggest the existence of the localized d levels which lie a few eV below the $4s$ band in these substances.

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