

X-ray Mn $K\beta$ emission spectra of manganese oxides and manganates

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X-ray Mn $K\beta$ emission spectra of metallic manganese, MnO, MnO₂, K₂MnO₄, and KMnO₄ are accurately measured by the fluorescent excitation method using a two-crystal spectrometer. The results show that molecular-orbital theory provides a suitable interpretation for x-ray $K\beta$ emission spectra of the manganese oxides and manganates. The valence bands of the manganates are mainly composed of the $4p(\pi, \sigma)$ characters of the molecular orbitals for tetrahedrally coordinated MnO₄⁻, while the valence bands of the manganese oxides are composed of mainly the $4p(\pi)$ and $4p(\sigma)$ characters, and also the $3d(\pi, \sigma)$ characters of the molecular orbitals for octahedrally coordinated oxides. These characters give rise to the structures in the valence band of the manganese oxides. The peak *A*, which is observed in the spectra of the manganese compounds, is ascribed to the transition of mainly $1t_2$ or $t_{1u}(\sigma_g) \rightarrow 1s$. The manganates exhibit a simple $K\beta_{1,3}$ peak, while the manganese oxides show a pronounced $K\beta'$ line. It is understood according to Tsutsumi's proposal on the origin of the $K\beta'$ line.

I. INTRODUCTION

Recently attempts have been made to determine the structure of the density of states in the valence band of the solids by means of not only band theory but also molecular-orbital theory. Compounds of elements in the first transition series, which have unpaired electrons in the $3d$ shell, may be considered to have complicated valence-band structures. In the present investigation, the x-ray Mn $K\beta$ emission spectra of the manganese compounds are accurately observed by using a high-resolution spectrometer to study the correlation between the valence-band structure and the $K\beta$ x-ray emission spectra, because manganese has many chemical compounds with different oxidation numbers.

The Mn $K\beta$ emission spectrum consists of a diagram line $K\beta_{1,3}$, an emission band $K\beta_5$, a non-diagram line $K\beta'$, etc. According to Tsutsumi,^{1,2} the origin of the $K\beta'$ line is derived from the exchange interaction between the electrons in the incomplete $3d$ shell of elements in the first transition series and the hole in the incomplete $3p$ shell owing to the emission of the $K\beta_{1,3}$ line, and thus the energy separation between the $K\beta'$ and $K\beta_{1,3}$ lines and the intensity ratio of the $K\beta'$ to $K\beta_{1,3}$ lines depend on the number of the unpaired $3d$ electrons. Consequently, some correlation would be expected between the features of the $K\beta'$ line and the valence- and/or conduction-band structures of transition metals and their compounds, because the number of the unpaired $3d$ electrons is related to these band structures. Also the $K\beta_5$ band has a relation to these band structures. Although the $K\beta$ emission spectra of manganese compounds have been investigated by several authors,^{3,4} in the present investigation these spectra are precisely measured for various manganese compounds with a wide range of the oxidation states and discussed in terms of molecular-orbital theory.

II. EXPERIMENTAL

The manganese $K\beta$ emission spectra of metallic manganese, manganese monoxide, manganese dioxide, potassium manganate, and potassium permanganate were excited by the fluorescent excitation method to avoid undesirable chemical change induced by electron bombardment. The spectra were obtained with a two-crystal spectrometer, which was used in the (1, 1) position with (101) planes of quartz crystals. The full width at half-maximum of the (1, -1) position is 0.52 eV for the manganese $K\beta_{1,3}$ wavelength. The tungsten-target x-ray tube was operated at 48 kV and 50 mA. The metallic manganese was in the form of a solid block and the other compounds were pressed polycrystalline slabs. The temperature of the apparatus was stabilized within $\pm 1.5^\circ\text{C}$ during measurements. Counts for a preset time were taken automatically at regular intervals of 9 or 18 sec of arc in Bragg angle, by means of a step scanning method. The preset times were 100–200 sec for the $K\beta_1$ line. Because the intensity of the $K\beta_5$ band is very weak, each observed point of the $K\beta_5$ band was measured for a time interval 20 times longer than for the case of the $K\beta_{1,3}$ line. The reagent-grade specimens (purity > 99%) were checked by the x-ray diffraction patterns before and after the experiments. The results showed that no chemical change occurred during the experiments.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the Mn $K\beta$ spectra of metallic manganese, MnO, MnO₂, K₂MnO₄, and KMnO₄. The $K\beta'$ line is observed for metallic manganese and clearly observed for MnO and MnO₂ which appear to have five and three unpaired electrons, respectively, but is not detectable for K₂MnO₄ and KMnO₄.

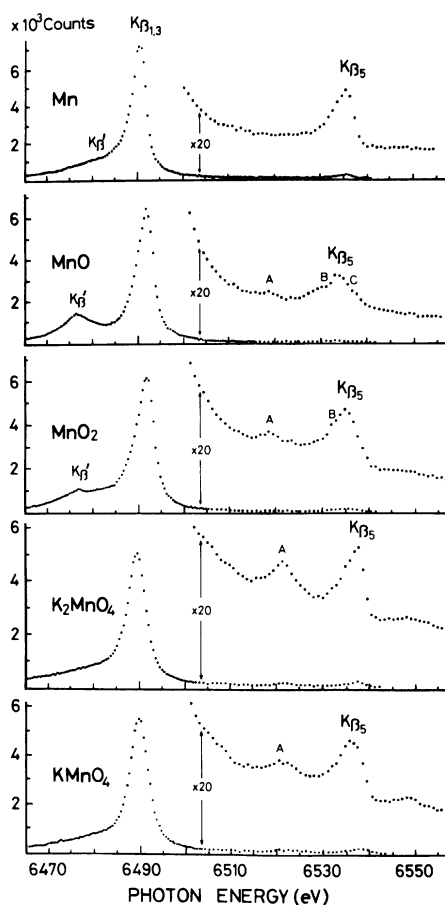


FIG. 1. Mn $K\beta$ spectra of metallic Mn, MnO, MnO₂, K₂MnO₄, and KMnO₄.

which appear to have one and no unpaired electron, respectively. These results are consistent with the prediction mentioned above. Table I shows the photon energies of the $K\beta_{1,3}$ and $K\beta'$ lines and the peak of the $K\beta_5$ band, and the peak intensity ratios of the $K\beta'$ line and the $K\beta_5$ band to the $K\beta_{1,3}$ line. According to Tsutsumi's proposal the energy separation between the $K\beta'$ and $K\beta_{1,3}$ lines is given by^{1,2}

Substance	Photon energy (eV)			Intensity ratio	
	$K\beta_5$	$K\beta_{1,3}$	$K\beta'$	$K\beta_5/K\beta_{1,3}$	$K\beta'/K\beta_{1,3}$
Mn	6535.2	6490.45 ^a	6481.43	0.020	0.11
MnO	6532.3	6491.88	6476.7	0.011	0.19
MnO ₂	6534.2	6491.88	6477.16	0.019	0.14
K ₂ MnO ₄	6537.1	6489.98		0.023	
KMnO ₄	6535.2	6489.98		0.021	

^aValue taken from J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967), and is used as the standard line.

TABLE II. Comparison between the observed and the calculated values.

Substance	$K\beta'$			
	Calc. (eV)	Obs. (eV)	Calc. I'/I	Obs. I'/I
Mn	3.55	9.02	0.34	0.11
MnO	10.44	15.18	0.71	0.19
MnO ₂	7.36	14.72	0.60	0.14

$$\Delta E = J(2S + 1), \quad (1)$$

and the intensity ratio of the $K\beta'$ to $K\beta_{1,3}$ lines is

$$I'/I = 2S/(2S + 2), \quad (2)$$

where J is the exchange integral⁵ between the electrons in the $3p$ and $3d$ shells and $2S$ is the number of the unpaired electrons in the incomplete $3d$ shell. Although these equations neglect effects due to the angular momentum of the orbitals and the crystalline field, their prediction may be useful as a rough comparison with the experimental values. The comparison between the experimental and the calculated values is shown in Table II. In this calculation the hydrogenlike wave functions of the $3d$ and the $3p$ electrons were used,⁵ and the effective nuclear charges ($Z - \sigma$) were determined by Slater's rule.⁶ The $2S$ value, the effective nuclear charge, the J value, and the calculated result are shown in Table III.

Figure 2 shows the $K\beta_5$ bands of the substances mentioned above. The tails of the $K\beta_{1,3}$ lines were subtracted assuming that they are smooth, and the intensity of each $K\beta_5$ band is normalized at its peak. The feature of the $K\beta_5$ band of metallic manganese shows an abrupt rise on the high-energy side and typically metallic character. The $K\beta_5$ bands of compounds show some structures. They are tentatively designated as A , B , and C as shown in Fig. 2.

The small peak A , which appears on the low-energy side of the $K\beta_5$ band, becomes more intense with increasing oxidation number of the substance. The energy separation of this peak from the high-energy edge of the $K\beta_5$ band, which is considered

TABLE III. The number of unpaired electrons in the $3d$ shell, the effective nuclear charge, the J value, and the result calculated from them.

Substance	Number of unpaired $3d$ electrons	$K\beta_1$ and $K\beta'$				I'/I
		$Z - \sigma_{3d}$	$Z - \sigma_{3p}$	J (eV)	ΔE (eV)	
Mn	1.1	6.6	14.1	1.69	3.55	0.34
Mn ²⁺	5	6.6	14.1	1.69	10.44	0.71
Mn ⁴⁺	3	7.3	14.1	1.84	7.36	0.60

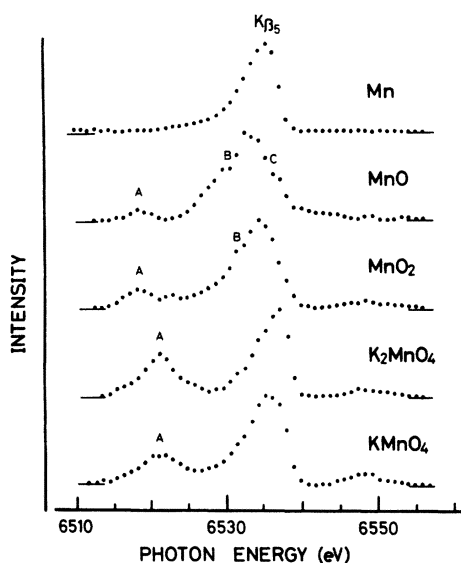


FIG. 2. Mn $K\beta_5$ spectra of metallic Mn, MnO, MnO₂, K₂MnO₄, and KMnO₄.

to correspond to the top of the valence band, is about 19 eV for KMnO₄. Because the binding energy of the 2s level of the oxygen atom is about 23 eV,⁷ the peak A is considered to be due to the crossover transition from the 2s state of oxygen to the 1s state of manganese. We shall discuss again this peak A later.

The valence band of metallic manganese is composed of mainly the 3d band with a contribution from the 4s band. However, the interpretation of valence-band x-ray spectra of nonmetallic substances, especially of transition-metal compounds, appears to be less clearcut. Band theory is appropriate for analysis of the spectra of metals,⁸⁻¹⁰ whereas molecular-orbital (MO) theory appears to be more appropriate for application to compounds.¹¹⁻¹³ The results of the energy-band calculations¹⁴ which have been carried out for transition-metal monoxides clearly predict that the transition-metal monoxides should be conductors, while the oxides such as MnO and NiO are insulators. Thus the MO interpretation of the $K\beta$ band of the manganese compounds will be discussed below in detail.

Let us consider first the measured $K\beta$ bands of tetrahedrally coordinated crystalline manganates, KMnO₄ and K₂MnO₄. Figure 3 shows an MO energy-level diagram for tetrahedrally coordinated MnO₄²⁻, which is shown by Balhausen and Gray.¹⁵ We assume that the peak A may be ascribed to the crossover transition of 2s(oxygen) → 1s following to the discussion mentioned above. This assumption appears to be justified because the 1*t*₂ and 1*a*₁ orbitals lie at about 20–22 eV below the *t*₁ orbital which is the highest occupied orbital. These 1*t*₂

and 1*a*₁ orbitals consist primarily of the σ_s orbitals of oxygen, and moreover the 1*t*₂ orbital has some 4*p* character of manganese. Then the $K\beta_5$ band is ascribed to (*t*₁, 3*t*₂, 2*a*₁, 2*t*₂, 1*e*) – 1*s* transitions. The measured $K\beta_5$ bandwidth is about 10 eV. However, before the comparison of this measured width with the theoretical one, the measured width must first be corrected for the widths of the spectral window and the *K* level.

The spectral window is estimated to be 0.52 eV from the full width at half-maximum of the (1, -1) position for Mn $K\beta_{1,3}$ wavelength, and the *K* level width is estimated to be 2.5 eV from the full width at half-maximum of the $K\alpha_1$ line of metallic manganese which was measured with the spectrometer having sufficient resolution.¹⁶ The width of the $K\alpha_1$ line is mainly determined by the *K*-level width, because the *L*_{III}-level width may be much smaller than the *K*-level width though the $K\alpha_1$ line is related to the *K* and *L*_{III} levels. Then the corrected bandwidth is estimated to be about 7 eV, whereas the energy difference between the *t*₁ and 1*e* orbitals is 5 eV. The difference between the corrected and predicted values is considered to be caused by the orbital broadening due to the crystalline field. This method of correction for the measured $K\beta_5$ bandwidth is also supported by the fact that the measured $K\beta_5$ bandwidth of metallic manganese is about 9 eV and the corrected width of 6 eV is well agree with the width of 6 eV obtained from an *L*_{III} soft x-ray spectrum.¹⁷

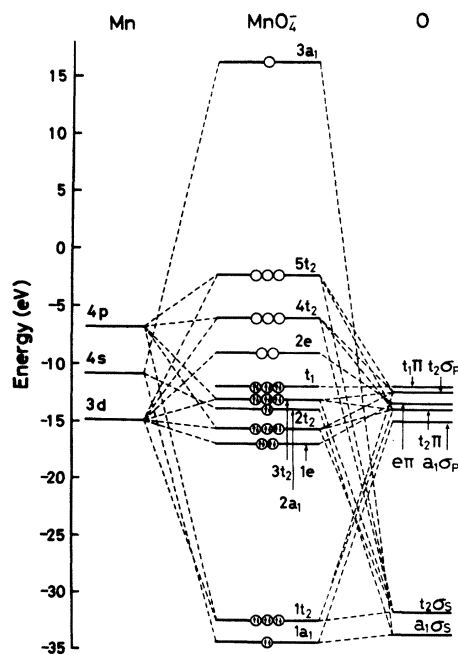


FIG. 3. Molecular-orbital energy-level diagram for tetrahedrally coordinated MnO₄²⁻.

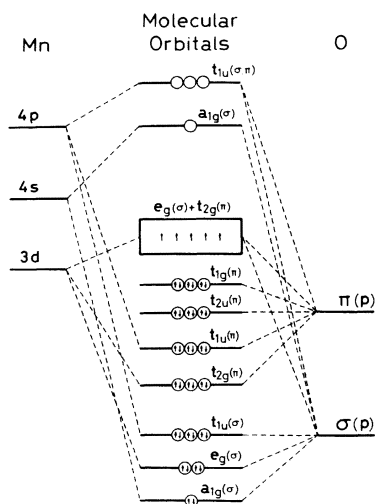


FIG. 4. Tentative molecular-orbital energy scheme for octahedrally coordinated oxides of manganese.

Although quantitative information concerning transition probabilities is not available, the intense part of the $K\beta_5$ band may be ascribed to $4p(\pi, \sigma) \rightarrow 1s$ transitions which obey selection rules for electric dipole radiation. Also we may expect forbidden transitions such as the electric quadrupole transition. The relative probabilities of electric quadrupole transition $3d \rightarrow 1s$ to dipole transition $4p \rightarrow 1s$ in transition elements are in the ratio of 1:100.¹³ However, because the contribution of the $4p$ character to the $4p(\pi, \sigma)$ bonding orbitals is small,¹⁵ we may expect the considerable intensity due to the quadrupole transition relative to the intensity due to the dipole transitions $4p(\pi, \sigma) \rightarrow 1s$. For MnO_4^{2-} an electron should be added in the $2e$ orbital^{19,20} in Fig. 3. It might be considered that this gives rise to the broadening into the $K\beta_5$ bandwidth of MnO_4^{2-} , however the $K\beta_5$ bandwidth of MnO_4^{2-} is measured as almost same as that of MnO_4^- . It might be due to the small contribution of an electron in the $2e$ orbital to the principal transition associated with many electrons in the $4p(\pi, \sigma)$ orbitals.

Now let us consider the $K\beta$ bands of octahedrally coordinated crystalline oxides, MnO and MnO_2 . MnO has a sodium-chloride-type crystal structure,²¹ and each Mn^{2+} ion is octahedrally coordinated by six oxygen atoms. MnO_2 has a rutile-type crystal structure,²¹ but each Mn^{4+} ion is considered to be octahedrally coordinated by oxygen, although the octahedra surrounding manganese cations are slightly distorted. Figure 4 shows a tentative MO energy-level scheme for octahedrally coordinated oxides. It is derived from that shown by Balhausen and Gray¹⁵ for complexes, and modified to represent for ionic crystals. Follow-

ing our consideration on the origin of the $K\beta$ line, MnO and MnO_2 must be high-spin complexes. Then the exchange energy associated with spin-orbit coupling may amount to more than the energy splitting between the $t_{2g}(\pi)$ and $e_g(\sigma)$ orbitals, which is caused by the ligand field and estimated to be about 1 eV.^{22,23}

The electron population in Fig. 4 represents the case of MnO . The $e_g(\sigma)$ and $t_{2g}(\pi)$ orbitals are populated with electrons having spins parallel to one another. As the case of manganate, the peaks A of the oxides may be ascribed to the crossover transition of $2s$ (oxygen) $\rightarrow 1s$ or $[t_{1u}(\sigma_s), e_g(\sigma_s), a_{1g}(\sigma_s)] \rightarrow 1s$ (these orbitals are not shown in Fig. 4). Also similarly the $K\beta_5$ band is ascribed to $[t_{1g}(\pi), t_{2u}(\pi), t_{1u}(\pi), t_{2g}(\pi), t_{1u}(\sigma), e_g(\sigma), a_{1g}(\sigma)] \rightarrow 1s$ transitions. As seen from Fig. 4, these $t_{1g}(\pi)$, $t_{2u}(\pi)$, $t_{1u}(\pi)$, $t_{2g}(\pi)$, $t_{1u}(\sigma)$, $e_g(\sigma)$, and $a_{1g}(\sigma)$ orbitals are separated into two groups which are derived from the π and σ orbitals of oxygen, respectively. These two groups may correspond to the main peak of the $K\beta_5$ band and the shoulder B, respectively. Also the shoulder C may be assigned to $[e_g(\sigma), t_{2g}(\pi)] \rightarrow 1s$ transitions. Messick, Walker, and Glosser²³ investigated the optical reflectance spectra of MnO and obtained the energy separation of 2.3 eV between the $3d^5$ level and the most dense part of the valence band which is mainly composed of the $2p$ character of oxygen. This energy separation nearly coincides with the energy separation of about 3 eV between C and the main peak of the $K\beta_5$ band.

In the case of MnO_2 two electrons should be removed from the $e_g(\sigma)$ orbital. This may cause the obscuring of the shoulder C in comparison with the case of MnO . It is observed in Fig. 2. Moreover, the experimental result shows that the $K\beta_5$ bandwidth of MnO_2 is narrower than that of MnO . Of course, the intense part of the $K\beta_5$ bands of the oxides may be ascribed to $4p(\pi, \sigma) \rightarrow 1s$ transitions, however we may also expect the other transitions such as the electric quadrupole transition as mentioned before.

The weak peaks are observed above 6540 eV in the $K\beta$ spectra of the oxides and manganates. This peak was not observed for metallic manganese. Similar high-energy peaks have been observed in the higher-energy region of the $K\beta_5$ spectra of the complexes or compounds of iron by Slater and Urch.²⁴ They have not observed this peak for metallic iron in agreement with our result. This peak appears to be formed by transition in a double ionized state, however it is obscure. The detailed discussion on this peak will be given elsewhere, because it is beyond the scope of the present investigation.

In summary, molecular-orbital theory provides a suitable interpretation for x-ray $K\beta$ emission spectra of the manganese oxides and manganates.

The valence bands of the manganates are mainly composed of the $4p(\pi, \sigma)$ characters of the molecular orbitals for tetrahedrally coordinated MnO_4^- , while the valence bands of the manganese oxides are composed of mainly the $4p(\pi)$ and $4p(\sigma)$ characters and also the $3d(\pi, \sigma)$ characters of the molecular orbitals for octahedrally coordinated oxides and these characters give rise to the structures in

the valence band of the manganese oxides. The peaks A which are observed in the spectra of the manganese compounds, are ascribed to the transition of mainly $1t_2$ or $t_{1u}(\sigma_g) \rightarrow 1s$. The manganates exhibit a simple $K\beta_{1,3}$ peak, while the manganese oxides show a pronounced $K\beta'$ line. It is understood according to Tsutsumi's proposal on the origin of the $K\beta'$ line.

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