

Relationship between x-ray spectra from some metal chlorides and their ionicity

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The $K\beta$ -emission and K -absorption spectra of chlorine in CsCl, BaCl₂, LaCl₃, and CeCl₃ have been reported. From an analysis of these data and those for other metal chlorides reported previously, it is found that the energy of a prominent peak of the Cl K -absorption spectrum measured relative to the bottom of the conduction band as well as the halfwidth of the $K\beta_1$ band, and the peak separation between the $K\beta_1$ band and its subband $K\beta_x$ are correlated to the amounts of ionic character of the bond of these chlorides. The K - and $L_{2,3}$ -absorption spectra of chlorine in CsCl have been discussed on the basis of the energy band-structure calculation by Donato *et al.* The band gaps estimated from the x-ray spectra are compared with those obtained from the optical spectra.

I. INTRODUCTION

The x-ray emission and absorption spectra have provided important information about the electronic energy-band structure in crystals. Until now, there have been many studies¹⁻¹² on the x-ray spectra for chlorides. For example, Kiyono and Sugiura⁶ studied the K -absorption spectra of chlorine in alkali chlorides. The $K\beta$ -emission and K -absorption spectra of chlorine for alkaline-earth chlorides have been studied by Sugiura.⁷ The $L_{2,3}$ -absorption spectra of chlorine have been investigated by Sato *et al.*⁸ for some metal chlorides, by Iguchi *et al.*⁹ and Aita *et al.*¹⁰ for alkali chlorides, and by Sato¹¹ for lanthanum and cerium chlorides.

In this paper we present the experimental results for Cl $K\beta$ -emission and K -absorption spectra from compounds consisting of chlorine and metal ions (Cs⁺, Ba²⁺, La³⁺, and Ce³⁺) belonging to the sixth row in the Periodic Table, making an attempt to get a systematic understanding of the electronic band structure of these metal chlorides. The spectra for CsCl (Ref. 6) and BaCl₂ (Ref. 7) have been already reported, but those for LaCl₃ and CeCl₃ are new data, which have not yet been reported. The electron configurations of these metal ions are [Xe]4 f^0 , except for a Ce³⁺ ion having a [Xe]4 f^1 configuration, where [Xe] indicates the electron configuration of a xenon atom. Their ionic radii are 1.69, 1.35, 1.15, and 1.02 Å for Cs⁺, Ba²⁺, La³⁺, and Ce³⁺, respectively.¹³ LaCl₃ and CeCl₃ have UCl₃-type crystal structure with lattice constants quite similar

to each other,¹⁴ and BaCl₂ has the PbCl₂ type, which resembles the UCl₃-type structure¹⁴; CsCl is of the so-called CsCl-type structure.

The K -absorption and $K\beta$ -emission spectra for CsCl, BaCl₂, LaCl₃, and CeCl₃ have been compared with their Cl $L_{2,3}$ -absorption spectra obtained by Sato *et al.*⁸ and by Aita *et al.*¹⁰ In particular, spectra for CsCl have been compared with theoretical results of the energy-band-structure calculation that have been obtained by Donato *et al.*¹⁵ on the basis of the pseudopotential theory. The influence of the different metal ion on the Cl $K\beta$ -emission and K -absorption spectra from some metal chlorides has been discussed in relation to the ionicity of the bond of these chlorides.

II. EXPERIMENTAL

The starting materials of the metal chlorides used here were of the commercial reagent grade and were chemically in the form of CsCl, BaCl₂·2H₂O, LaCl₃·6H₂O, and CeCl₃·6H₂O. The hydrated chlorides were heated in vacuum for several hours to remove water molecules and to obtain powders of BaCl₂, LaCl₃, and CeCl₃.

The $K\beta$ -emission and K -absorption spectra of chlorine in the anhydrous metal chlorides were obtained with the same bent-crystal spectrograph used in the previous works.³⁻⁷ The details of the experimental procedures are described in a previous paper.⁷

III. RESULTS AND DISCUSSION

The $K\beta$ -emission and K -absorption spectra of chlorine in CsCl, BaCl₂, LaCl₃, and CeCl₃ are shown in Fig. 1. The photon-energy values of the characteristic points in these spectra are listed in Table I. The spectra for BaCl₂ have been already reported by Sugiura,⁷ but the present result for K absorption differs slightly from the previous one, where the peak corresponding to peak *D* was missing.

A. Cl $K\beta$ -emission spectra

The $K\beta$ -emission spectra consist of a prominent band $K\beta_1$ and its subbands $K\beta_x$ and $K\beta_5$ on the high-energy side. With the increase of the difference in the electronegativity ($\Delta\chi$) (Ref. 16) of the metal and chlorine atoms, the halfwidth of the $K\beta_1$ band (which arises from the transition $3p \rightarrow 1s$ within the Cl⁻ ion) decreases and the energy separation between the $K\beta_1$ and $K\beta_x$ bands increases. In Figs. 2(a) and 2(b), the halfwidth of the band $K\beta_1$ and the energy separation between the $K\beta_1$ and $K\beta_x$ bands for the present results are plotted against $\Delta\chi$, together with those for other metal chlorides reported previously.^{4,5,7} They linearly change with $\Delta\chi$ in the range from 1.9 to 2.3. When $\Delta\chi$ of the chlorides is smaller than 1.9, that is, when they are largely covalent (for example, $\Delta\chi$ of MgCl₂ is equal to 1.8), their $K\beta_1$ band is so broad that their subbands are not observed.¹⁷ In CsCl, whose $\Delta\chi$ is the largest in the materials investigated, the $K\beta_1$ band is very sharp, but its subband is widely spread and the $K\beta_5$ subband is ambiguous.

The subbands on the high-energy side of the $K\beta$ emission in metal chlorides have been considered^{4,5,7,18} as being associated with a double ionization of the chlorine ion. Deslattes¹⁸ has calculat-

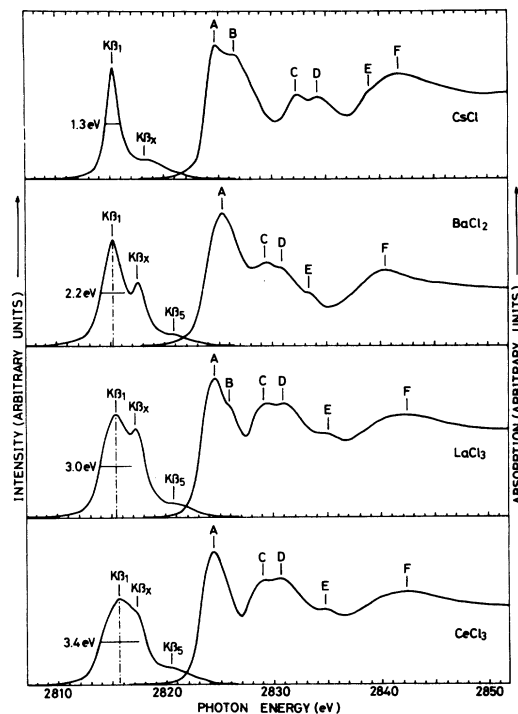


FIG. 1. $K\beta$ -emission and K -absorption spectra of chlorine in CsCl, BaCl₂, LaCl₃, and CeCl₃.

ed satellite-parent separations for Cl⁻, Ar, and K⁺ in a double-ionization model using approximate wave functions. The horizontal lines on the right in Fig. 2(b) indicate Deslattes' theoretical predictions for Cl⁻ ion. They are close to the experimental results for those materials whose $\Delta\chi$ is around 2.1–2.2. Our experimental data on the satellite-parent separation show that they depend on the metal ion. Therefore, it would be necessary to extend Deslattes' model in which effects of the crystal environment of ions or atoms are not considered, in such a way that the solid-state effects can be incorporated.

TABLE I. Photon-energy values (in eV) of the maxima of the $K\beta$ -emission and K -absorption spectra of chlorine in CsCl, BaCl₂, LaCl₃, and CeCl₃.

Notations	CsCl	BaCl ₂	LaCl ₃	CeCl ₃
$K\beta_1$	2815.2	2815.2	2815.4	2815.6
$K\beta_x$	2818.2	2817.4	2817.2	2817.3
$K\beta_5$		2820.8	2820.7	2820.4
<i>A</i>	2824.7	2825.3	2824.6	2824.4
<i>B</i>	2826.5		2826.0	
<i>C</i>	2832.1	2829.3	2829.1	2828.9
<i>D</i>	2834.2	2831.0	2831.0	2830.7
<i>E</i>	2840.0	2833.2	2835.2	2834.8
<i>F</i>	2841.7	2840.6	2842.4	2842.3

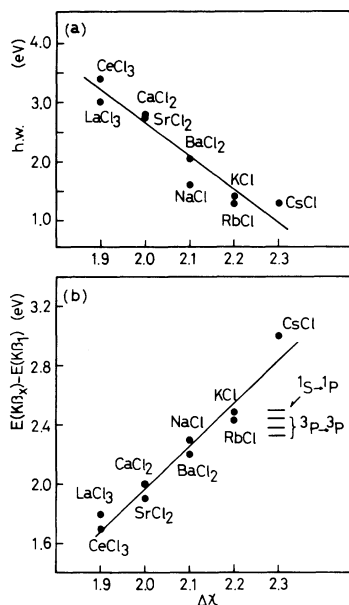


FIG. 2. (a) Halfwidth (hw) of the $K\beta_1$ band and (b) peak separation between the $K\beta_1$ band and its subband $K\beta_x$ for some metal chlorides as a function of $\Delta\chi$. Straight line fits are of the form $A\Delta\chi + B$, with $A = -5.59$ eV and $B = 13.80$ eV for hw, and with $A = 2.83$ eV and $B = -3.69$ eV for the peak separation.

B. Cl K -absorption spectra

The Cl K -absorption spectra have the characteristic features common to all materials investigated in this paper. They are the first intense peak A at the threshold, the two peaks C and D which are

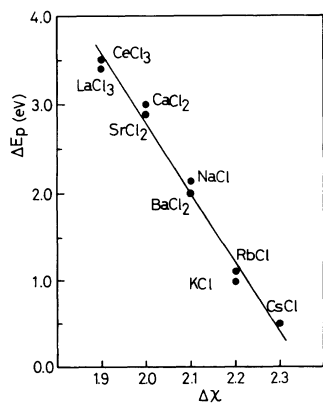


FIG. 3. Energy of a prominent peak of the Cl K -absorption spectra measured relative to the bottom of the conduction band for some metal chlorides as a function of $\Delta\chi$. The straight line is given by $\Delta E_p = A\Delta\chi + B$, with $A = -7.88$ eV and $B = 18.54$ eV.

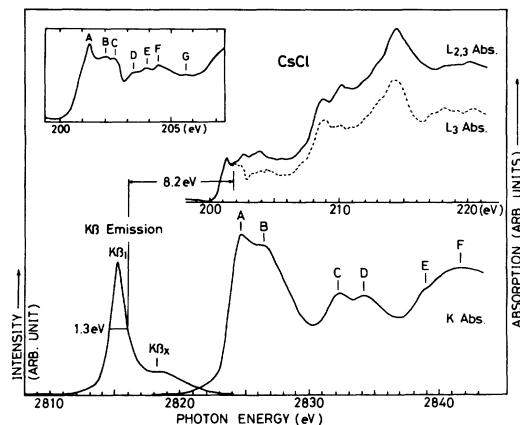


FIG. 4. Comparison of the K - and $L_{2,3}$ -absorption (taken from Ref. 10) spectra of chlorine in CsCl. Expanded L_3 -absorption spectrum is also illustrated.

separated from each other by 1.7–2.1 eV, the following peak E , and a broad peak F located in the region from 2840–2843 eV. In LaCl_3 and CsCl , the peak A has a shoulder (B) on its high-energy side. The K -absorption spectra from LaCl_3 , CeCl_3 , and BaCl_2 are greatly alike except for the shoulder B in LaCl_3 , as expected from that LaCl_3 and CeCl_3 take the same crystal structure (UCl_3 type) and BaCl_2 has the similar crystal structure (PbCl_2 type) to the trichlorides.¹⁴ The reason for the absence of the peak B in CeCl_3 is not clear at present, but we think it may be related to the fact that the La atom has a $5d$ electron, whereas the Ce atom does not, because peaks that are considered to be associated with the $3d$, $4d$, and $5d$ states have been observed in the Cl K -absorption spectra of transition-metal chlorides.^{19–23}

We will now compare the Cl K -absorption spectra with the Cl $L_{2,3}$ -absorption spectra obtained by Sato¹¹ for LaCl_3 and CeCl_3 , by Sato *et al.*⁸ for

TABLE II. Comparison between some maxima in the K -absorption spectrum for CsCl and critical points in the band structure. All quantities measured relative to peak A are in eV.

Peak	Experimental	Theoretical ^a
A	0.0	0.0 (X_4')
B	1.8	2.1 (M_5')
C	7.4	8.1 (M_5')
D	9.5	11.0 (M_4')
E	15.3	14.7 (X_4')
F	17.0	15.4 (Γ_{15})

^aReference 15.

TABLE III. Comparison between some maxima in the L_3 -absorption spectrum (Ref. 10) for CsCl and critical points in the band structure. All quantities measured relative to peak B are in eV.

Peak	Experimental	Theoretical ^a
B	0.0	0.0 (X_1)
C	0.4	0.6 (M_1)
D	1.2	1.1 (M_3)
E	1.9	2.3 (Γ_1)
F	2.4	2.4 (R_1)
G	3.6	3.5 (R'_{25})

^aReference 15.

BaCl₂, and by Aita *et al.*¹⁰ for CsCl. The general shapes of the three $L_{2,3}$ -absorption spectra except for CsCl are similar to each other. The first peak in the $L_{2,3}$ absorption is located at a lower energy than that of the K absorption, which is probably due to the transition to the lowest p -like state arising from the $4p$ state of the Cl⁻ ion, provided that the K - and $L_{2,3}$ -absorption spectra are joined by the photon energy [2622.2 eV (Ref. 24)] of the Cl $K\alpha_1$ line from these chlorides. Its energy difference is about 1.1, 1.5, 2.7, and 2.8 eV for CsCl, BaCl₂, LaCl₃, and CeCl₃, respectively. We focus our attention on the energy difference (ΔE_p) between a prominent peak of the Cl K -absorption spectrum and the bottom of the conduction band. This energy difference is shown in Fig. 3 for CeCl₃, LaCl₃, CaCl₂, SrCl₂, BaCl₂, NaCl, KCl, RbCl, and CsCl as a function of $\Delta\chi$. Here the position of the bottom of the conduction bands for NaCl, KCl, RbCl, and CsCl is determined from data by Iguchi *et al.*⁹ on the $L_{2,3}$ -absorption spectra (shoulder B). In these materials, peaks due to a core exciton are observed. For other materials that have no exciton peak, the bottom of the conduction band is determined with the assumption that the L_3 -absorption edge (decided at the midpoint of the edge) corresponds to the bottom of the conduction band. From Fig. 3 one can see that the energy of the prominent peak of the Cl K -absorption spectrum measured relative to the bottom of the conduction band is correlated to the amounts of ionic character of the bond of metal chlorides. The influence of the different metal ions is obvious, even in the Cl K -absorption spectrum. We can regard this result as a reflection of the degree of localization of atomic wave functions of the ions which constitute the metal chlorides.

Next let us make a comparison of experimental and theoretical results in the case of CsCl for which the theoretical calculation of the energy-band structure is available,¹⁵ and try to assign the maxima in

TABLE IV. Energy-band gaps (in eV), obtained from the x-ray and the optical spectra. The values of E_{optical} for LaCl₃ and CeCl₃ are taken from Figs. 2 and 3 in Ref. 11; fundamental absorptions begin at these energy values.

Metal chloride	$E_{x \text{ ray}}$	E_{optical}
CsCl	8.2	8.3 ^a
RbCl	8.2	8.50 ^a
KCl	8.3	8.7 ^a
NaCl	8.5	8.75 ^a
BaCl ₂	7.0	
SrCl ₂	7.5	
CaCl ₂	6.9	
CeCl ₃	3.7	3.6 ^b
LaCl ₃	4.2	4.5 ^b

^aReference 12.

^bReference 11.

the K - and $L_{2,3}$ -absorption spectra to the p -like states and s - or d -like states in the conduction bands, respectively. The K - and $L_{2,3}$ -absorption spectra for CsCl are shown in Fig. 4, where they are joined by the photon energy (2622.2 eV) (Ref. 24) of the Cl $K\alpha_1$ line of CsCl. In the K -absorption spectrum of CsCl, the peak of A is ascribed to the transition to X_4' state, the peaks B and C to the two M_5' states which are separated by about 6 eV from each other, the peak D to M_4' state, the peak E to X_4' state, and the peak F to Γ_{15} state. This comparison of the maxima in the K -absorption spectrum with band-structure critical points is summarized in Table II. Such a comparison for the Cl L_3 -absorption spectrum, which has many fine structures (see Fig. 4), is also made, and the result is listed in Table III. The first peak A in the $L_{2,3}$ -absorption spectrum may be attributed to an x-ray exciton at X_1 minimum point, because it is located below the bottom of the conduction band expected from the optical data.¹²

Finally we should mention band gaps estimated from the Cl $K\beta_1$ -emission and $L_{2,3}$ -absorption spectra. We have obtained the values of the band gaps, assuming that the width of the valence band, which is mainly constructed from the $3p$ state of the Cl⁻ ion, is given by the experimental halfwidth of the $K\beta_1$ band and using the values for the bottom of the conduction band used in obtaining ΔE_p in Fig. 3. They are listed in Table IV together with data obtained from the optical spectra.^{11,12} The values for alkali chlorides, CeCl₃, and LaCl₃ are in good agreement with those obtained from the optical measurements. Unfortunately, there are no data to be compared for BaCl₂, SrCl₂, and CaCl₂, as far as we know.

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