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$K\beta$ X-Ray Emission and K X-Ray Absorption of Cl^- in NaCl

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The $K\beta$ emission and the K absorption spectra of Cl^- ion in NaCl have been obtained with a 50-cm bent-quartz-crystal vacuum spectrograph. The obtained spectra are compared with the density of states calculated by Fong and Cohen and by Lipari and Kunz. The $K\beta$ satellites are accounted for in terms of the Deslattes model. A shoulder at the threshold of the K absorption is observed for the first time and its origin is discussed in terms of the core exciton.

I. INTRODUCTION

It has been argued by many investigators that the sharp structure near the threshold of the K, L, M, or N absorption of atom in ionic crystals is due to either the core exciton or the density of states of the conduction band. Recently, Haensel *et al.*[1] and Nakai *et al.*[2,3] measured the Na^+ $L_{2,3}$ absorption spectra of sodium halides including NaCl and explained the sharp doublet at the threshold in terms of the core excitons with holes in the $2p$ level of sodium. Moreover, Haensel *et al.*[4] presented direct evidence for the existence of the core excitons from a photoemission study of NaCl. The Cl^- $L_{2,3}$ absorption spectra of alkali chlorides including NaCl have been also studied by many investigators[5-9] and the sharp peaks near the threshold were explained in terms of the core excitons with holes in the $2p$ level of chlorine, except for the explanation given by Brown *et al.*,[8] who gave concepts that these peaks are due to maxima in the final density of states, rather than to exciton phenomena. Besides, Lipari and Kunz[10] explained fairly well the Cl^- $L_{2,3}$ absorption spectrum of NaCl in terms of the joint density of states.

The core (or x-ray) excitons have been first suggested by Cauchois and Mott,[11] and then an investigation was performed experimentally by Parratt and Jossem[12,13] in the case of the K absorption spectra of K^+ and Cl^- ions in KCl. Muto *et al.*[14] discussed theoretically the possibility of existence of such x-ray excitons in the case of KCl. But the question of whether or not an exciton peak appears in the K absorption seems to be still not clarified, because the position of the bottom of the conduction band can not be determined accurately on the K absorption spectrum and the absorption structure is relatively broad. Hence, we shall consider this question in the case of the Cl^- K absorption spectrum of NaCl.

The Cl^- $K\beta$ emission spectrum of NaCl was investigated by Valasek[15] and by Vainshtein *et al.*,[16] and the Cl^- K absorption spectrum was investigated by Kiyono and Sugiura,[17] and by Mazalov *et al.*[18] Recently, the present author measured these spectra and reported a part of the results.[19]

Regarding Cl^- $K\beta$ satellites, Deslattes[20] measured in detail the $K\beta$ emission spectra of argon gas compared with K^+ and Cl^- ions in KCl, and explained satisfactorily the first high-energy satellite in terms of a double-ionization model. Åberg[21] developed the theory of x-ray satellites based on the sudden approximation. He found a good agreement between his theory and Deslattes's measurements[20] for the $K\beta$ satellites of argon and KCl. Recently, Best[22] discussed details of the $K\beta$ emission spectra of KCl in the light of the observations made by Deslattes.[20] Here we shall also explain the Cl^- $K\beta$ satellites of NaCl with the aid of the Deslattes model.[20]

Recently, the energy-band structure of NaCl has been calculated by several investigators[10,23-26] using the augmented-plane-wave (APW) method, the orthogonalized-plane-wave (OPW) method, the empirical-pseudopotential (EP) method, and the mixed-basis (MB) method. The density-of-states curves for the valence band and the conduction band have been given by Fong and Cohen[25] and by Lipari and Kunz.[10] The valence band consists of the $3p^6$ state of the Cl^- ion, and the conduction band consists of the $3s$ and $3p$ states of the Na^+ ion and the $3d$, $4s$, $4p$, etc., states of the Na^+ and Cl^- ions. The bottom of the conduction band Γ_1 is an s-like state. The theoretical width of the valence band is wide, 4.38 eV, in the case of the MB calculation by Lipari and Kunz,[10] whereas it is narrow in the case of the other calculations, which for example, are 1.35 eV in the case of the OPW calculation of Kunz[23] and 0.57 eV in the case of the APW calculation of Page and Hygh.[26] The calculated band gaps are 7.4,[23] 12.08,[10] and 9.96 eV[10] (with correlation effects), values of which differ from the experimental band gaps, 8.6 eV[27] and 8.97 eV.[28] We shall compare the $K\beta$ emission and the K absorption spectra of Cl^- ion in NaCl with the results of these band calculations.

II. EXPERIMENTAL

The measurements were carried out using a 50-cm bent-quartz-crystal vacuum spectrograph.[29]

Both the $K\beta$ emission spectrum and the K absorption spectrum were recorded on a Fuji-A1 photographic plate in the first-order reflection for $(11\bar{2}0)$ plane of the crystal. The dispersion of the spectrograph was 5.23 xu/mm or 3.10 eV/mm on the photographic plate for the spectral region (4335–4410 xu) investigated.

The emitter used for the $K\beta$ emission spectrum was powdered NaCl rubbed onto a tungsten target of a demountable x-ray tube.[29] The operating condition of the x-ray tube was 5 kV and 3 mA. The exposure times were about 10 min. The wavelength values were determined by comparing the $K\beta$ emission (or K absorption) spectrum with three emission lines Pd $L\alpha_1$, Pd$L\alpha_2$, and $\mathrm{Cl}^-K\beta_1$ of KCl at 4358.62 xu,[30] 4366.81 xu,[30] and 4394.91 xu,[15] respectively.

The absorption measurement was made on an evaporated film. The film, about $7\,\mu$ in thickness, was prepared by means of an evaporation apparatus placed in a vacuum spectrograph tank.[31] Radiation with continuous spectrum was obtained from the x-ray tube with a tungsten target, operating at 5.5 kV and 20 mA. The exposure times were about 3 h. The pressure of the spectrograph tank during the experiments was 1×10^{-5} Torr.

III. RESULTS

The $K\beta$ emission and K absorption spectra of Cl^- ion in NaCl are shown in Fig. 1. The wavelength and photon energy values of the characteristic points in these spectra are given in Table I with the designations of lines following Valasek for the $K\beta$ spectrum. The $K\beta$ emission spectrum consists of two prominent peaks β_1 and β_x, and of a small peak β_5. The wavelength values and spectral profile are in good agreement with those of the fluorescence spectrum obtained by Valasek[15] and Vainshtein *et al.*,[16] but the spectrum obtained by Vainshtein *et al.* has no small peak β_5. The K absorption spectrum consists of a shoulder A, obtained for the first time in the present work, the intense and broad absorption band with three structures B, C, and D, three small structures E, F, and G, a relatively intense and broad band H, and neighboring weak and broad structures I, J, K, etc. The spectral profile and wavelength values are in good agreement with the results of Kiyono and Sugiura[19] except for the shoulder A. They also agree with those of Mazalov *et al.*[16] except for the shoulder A and the weak structures G, J, and K.

IV. DISCUSSION

It is well known that the intensity distribution of an x-ray valence-emission band, as well as the variation in the absorption coefficient, is related to the product of the density of states and the transition probability and so does not give a direct picture of density of states. Nevertheless, certain features of the density of states, such as the total width of the valence band and energy positions of maxima and minima in the density of states of the valence band and the conduction band, can be determined from the good x-ray data. Therefore, it is significant to compare the $K\beta_1$ emission band (which is due to the transition $3p\rightarrow 1s$ within the Cl^- ion) and the K absorption of Cl^- ion in NaCl with the calculated density of states of the valence band and the conduction band, respectively.

In Fig. 2, the $K\beta$ emission and the K absorption spectra are compared with the density-of-states curves for the Cl^- $3p$ valence band and the conduction band, where the peaks labeled B in both the absorption curve and the density of states given by Fong and Cohen[25] are tentatively associated with each other. Two density-of-states curves for the conduction band are not in very good agreement with each other. The peaks labeled B, C, D, and E in the absorption curve and in the density-of-states curves (note that the curve given by Lipari and Kunz has no peak B) correspond to each other, but their relative heights are different. This discrepancy is due to the fact that the K absorption reflects the p-like states in the conduction band, whereas the density of states includes s-, p-, d-, and f-like states. The region labeled d in the density-of-states curves (Γ'_{25}, Γ_{12} at the center of the Brillouin zone) consists of the d-like states associated primarily with the $3d$ states of Cl^- ion.

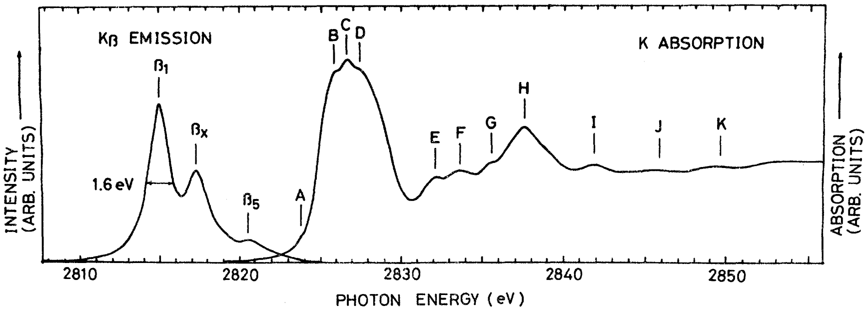

FIG. 1. $K\beta$ emission and the K absorption spectra of Cl^- ion in NaCl.

TABLE I. Wavelength and photon energy values of the characteristic points of the $K\beta$ emission and K absorption spectra of Cl$^-$ ion in NaCl.

Notations	Wavelengths in xu	Photon energies in eV
β_1	4395.01	2815.11
β_x	4391.65	2817.26
β_5	4386.4	2820.6
A	4381.4	2823.9
B	4378.4	2825.8
C	4377.1	2826.6
D	4375.7	2827.5
E	4368.7	2832.1
F	4366.2	2833.7
G	4363.3	2835.6
H	4360.4	2837.5
I	4353.5	2841.9
J	4347.5	2845.9
K	4341.7	2849.7

Consequently, the K absorption spectrum has no peak corresponding to the peak d, because the transitions to the d-like states from the 1s-core state of Cl$^-$ ion are forbidden in the dipole selection rules.

The parent band β_1 in the $K\beta$ emission spectrum corresponds to the main peak p_1 in the density-of-states curve of the valence band but has no peak corresponding to the second peak p_2. The total width of the density of states, 4.38 eV, seems to be broader than that of the parent band β_1, whereas the other theoretical bandwidths, 1.35[23] and 0.57 eV,[26] are narrower than the experimental half-width, 1.6 eV, of the parent band β_1. If this experimental width, 1.6 eV, is corrected for both the half-width of the 1s state of chlorine, 0.45 eV,[12] and the instrumental broadening, it becomes narrower and approaches the theoretical widths.

Let us consider the structure on the high-energy side of the parent band β_1. This structure has no corresponding branch in the calculated valence bands.[10,23-26] Besides, the energy difference between two peaks β_1 and β_x, 2.15 eV, is in good agreement with the satellite ($^3P \rightarrow {}^3P$, $^1S \rightarrow {}^1P$)-parent separations, 2.34, 2.38, 2.45, and 2.50 eV for Cl$^-$ ion calculated by Deslattes,[20] and the difference between β_1 and β_5, 5.5 eV, also is in good agreement with the calculated satellite ($^1S \rightarrow {}^3P$)-parent separations,[20] 5.14, 5.19, and 5.26 eV. Therefore, the two peaks β_x and β_5 are probably two satellite complexes arising from double ionization of the Cl$^-$ ion. Moreover, as the difference for the shoulder near the photon energy 2819 eV also seems to agree well with the calculated satellite ($^3S \rightarrow {}^3P$)-parent separations,[20] 3.92, 3.96, and 4.04 eV, this shoulder also is probably the satellite complex. In Fig. 2, the observed structure is shown together with the locations of the calculated satellite arrays.[20] Thus, the high-energy structure is the satellite complexes and can be fairly well accounted for in terms of the Deslattes model. Recently, such satellites have also been observed by the present author in the case of the $K\beta$ spectra of Cl$^-$ ion in the other alkali chlorides.[32]

Let us now consider the location of the bottom of the conduction band of NaCl on the Cl$^-$ K absorption spectrum and the origin of the shoulder A. The position of the bottom of the conduction band is not clear on the K absorption spectrum. The photon energy of the emission band β_1, 2815.11 eV, plus the optical band gap 8.97 eV[28] equals 2824.08 eV. This value is larger by 0.2 eV than the photon energy 2823.9 eV of the shoulder A. Moreover, in consideration of the width of the emission band β_1 it is clear that the bottom of the conduction band is located at a position between the shoulders A and B. The final level of the shoulder A is located below the bottom of the conduction band. According to the calculation for the x-ray exciton by Muto *et al.*,[14] as the region of possible occurrence of the exciton absorption is

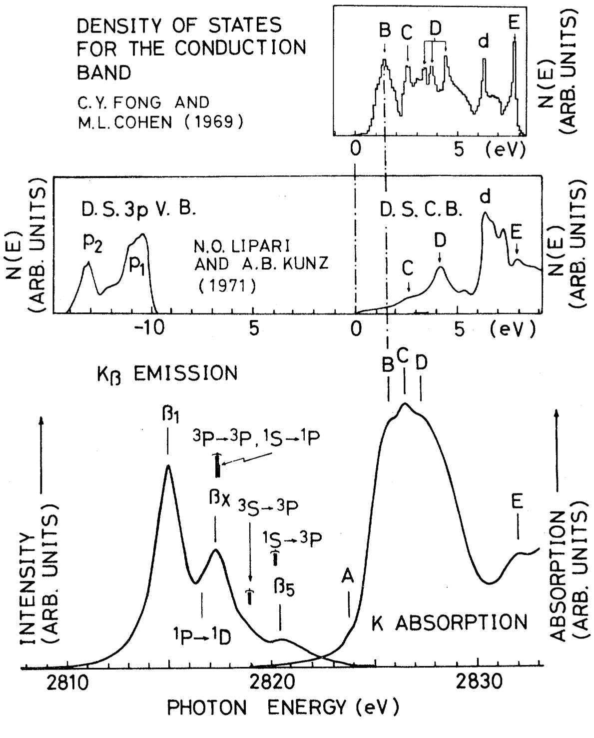

FIG. 2. $K\beta$ emission and the K absorption spectra of Cl$^-$ ion in NaCl are compared with the density of states for the Cl$^-$ 3p valence band (D.S. 3p V.B.) and the density of states for the conduction band (D.S.C.B.). The $K\beta$ satellites are assigned in terms of the transition arrays for Cl$^-$ ion calculated by Deslattes (Ref. 20). The transitions marked with longer vertical lines are expected to have greater intensity than the others.

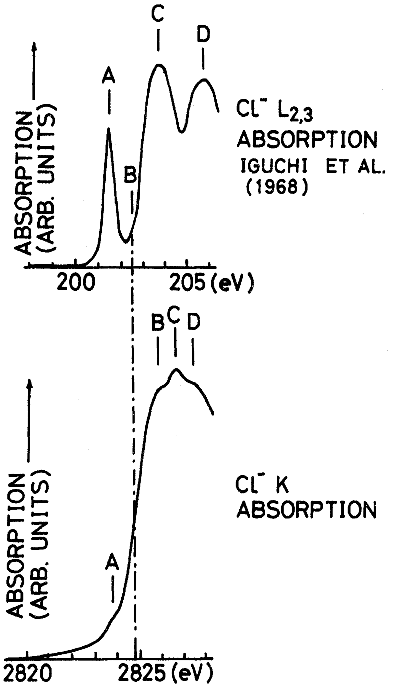

FIG. 3. Comparison between the K absorption and the $L_{2,3}$ absorption (Ref. 7) (at room temperature) of Cl$^-$ ion in NaCl. These two absorptions are joined by the photon energy (2622.23 eV) (Ref. 35) of the Cl $K\alpha_1$ line of NaCl.

around the shoulder A on the K absorption, this shoulder A may be ascribed to the occurrence of a core exciton with a hole in the 1s level of the Cl$^-$ ion. Furthermore, the transition probability from the Cl$^-$ core 1s level to the excited p-type level of x-ray excitons located below the bottom of the conduction band can be supposed to become sufficiently small according to the similar considerations to those of the case of optical exciton.[14] Such a shoulder has also been observed in the Cl$^-$ K absorption spectra of the other alkali chlorides[32] and in the Na$^+$ K absorption spectrum of NaCl.[33,34]

A comparison between the K absorption and the $L_{2,3}$ absorption[7] (at room temperature) of the Cl$^-$ ion in NaCl is shown in Fig. 3, where these two absorptions are joined by the photon energy (2622.23 eV)[35] of the Cl $K\alpha_1$ line of NaCl. As can be seen, the position of the shoulder A in the K absorption is located at the 0.9-eV lower-energy side compared with that of the shoulder B (at 202.56 eV)[36] in the $L_{2,3}$ absorption. As already suggested by many investigators,[6,7,9] if the peak A (at 201.50 eV)[36] in the $L_{2,3}$ absorption is ascribed to the Γ exciton associated with the transition from the L_3 level to the bottom Γ_1 of the conduction band and also the shoulder B corresponds to the onset of the core-level-to-band transition, the position of the bottom of the conduction band on the K absorption must be located at a position between the shoulders A and B. The final level of the shoulder A is located at 0.9 eV below the bottom of the conduction band. This level is probably the p-type exciton level located below the bottom of the conduction band.

V. CONCLUSIONS

The $K\beta$ emission and the K absorption spectra of Cl$^-$ ion in NaCl have been recorded and compared with the calculated density of states of the valence band and the conduction band. There is a tolerable matchup between some maxima and minima in the spectral curves and the density of states, but there are also some discrepancies. The shoulder A at the threshold of the K absorption may be ascribed to the occurrence of a core exciton with a hole in the 1s level of chlorine. The high-energy structure of the $K\beta_1$ emission band is the satellite complex and can be fairly well accounted for in terms of the Deslattes model.

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