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# Chlorine-*K*-X-Ray Spectra and Electronic Band Structure of CuCl

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The $K\beta$-emission and $K$-absorption spectra of chlorine in CuCl have been obtained with a 50-cm bent-quartz-crystal vacuum spectrograph. The spectra are discussed in terms of the energy-band structure. Results are evaluated by comparing the Cl $K$ spectra with the Cu $K$ and $L$ spectra, with the x-ray photoelectron spectrum, and with the theoretical band structure. It is confirmed that the upper valence band arises primarily from the $3d$ state of copper and the lower band predominantly from the $3p$ state of chlorine. The low-energy part of the conduction band arises from the $4s$ state of copper. The $p$-type states in the conduction band are located at several eV above the bottom.

## I. INTRODUCTION

CuCl is a compound semiconductor which crystallizes in the zinc-blende structure at room temperature. The electronic energy-band structure has been deduced experimentally by many investigators on the basis of the interpretation of the fundamental ultraviolet absorption spectra,[1,2] the soft x-ray emission and absorption spectra,[3–5] and the x-ray photoelectron spectrum.[6] It has also been calculated theoretically by Song.[7] It is reported that the valence band consists of two bands separated by a forbidden band, and the upper and the lower bands arise primarily from the $3d$ state of copper and the $3p$ state of chlorine, respectively. The former seems to be accepted generally, while the latter has not been confirmed unambiguously. For the conduction band, it is supposed that its low-energy part arises from the $4s$ state of copper.

As is well known, x-ray valence-band emission and absorption spectra give information about the density of states in the valence and conduction bands, respectively. For example, the Cl $K\beta$-emission and $K$-absorption spectra of CuCl reflect the distributions of the $p$-type states in the valence and conduction bands, respectively, and the Cu $L\alpha$-emission and $L_{III}$-absorption spectra reflect the distributions of the $s$- and $d$-type states. The Cu $L$ spectra have been investigated by Bonnelle[3] and discussed in relation to the electronic structure. However, the Cl $K$ spectra have not yet been reported, except for the present author's short note.[4] The purpose of the present study is to delineate the Cl $K\beta$-emission and $K$-absorption spectra and to obtain information on the electronic band structure.

On the other hand, the $K$-absorption spectrum of copper in CuCl has been observed by several investigators.[8–10] Beeman *et al.*[8] have measured the spectrum by the use of a double-crystal spectrometer with high resolving power and analyzed the absorption structure near the $K$ edge into component absorption lines. The most intense absorption maximum was regarded as being due to excitation of the $K$ electron into the $4p$ level of the $Cu^+$ ion.

## II. EXPERIMENTAL

A 50-cm bent-quartz-crystal vacuum spectrograph[11] was used in the present investigation. Both the $K\beta$-emission and the $K$-absorption spectra were recorded on a Fuji A1 photographic film in the first-order reflection for the $(11\bar{2}0)$ plane of the crystal. The dispersion of the spectrograph was 5.23 xu/mm (xu is for "x-ray units") or 3.10 eV/mm on the film.

CuCl specimens used for both emission and absorption studies were prepared by Ueta and his coworkers. They were chemically purified and zone refined.[12] The emitter used to obtain the emission spectrum was powdered CuCl rubbed into a tungsten target of a demountable x-ray tube.[11] The operating conditions of the x-ray tube were 5 kV and 3 mA. The exposure times were about 10 min.

Absorption measurements were made on an evaporated film. The film, about 5 $\mu$ in thickness, was prepared by the use of an evaporation apparatus placed in the vacuum spectrograph tank. Radiation with a 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 2 h. The pressure of the spectrograph tank during the experiments was $1\times10^{-5}$ Torr. The wavelength values were calibrated by comparing the $K\beta$-emission and the $K$-absorption spectra with three emission lines, Pd $L\alpha_1$ (4358.62 xu),[13] Pd $L\alpha_2$ (4366.81 xu),[13] and Cl $K\beta_1$ (4394.91 xu)[14] of KCl.

## III. RESULTS AND DISCUSSION

The $K\beta$-emission and $K$-absorption spectra of chlorine in CuCl are shown in Fig. 1. The wave-

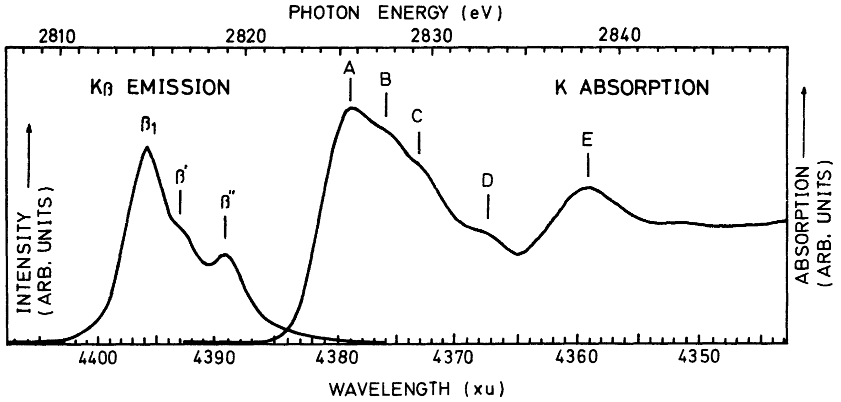

FIG. 1. $K\beta$-emission and $K$-absorption spectra of chlorine in CuCl.

length and photon energy values of the characteristic points in these spectra are listed in Table I. The $K\beta$-emission spectrum consists of a prominent peak $\beta_1$ with a shoulder $\beta'$ and a less prominent $\beta''$. The $K$-absorption spectrum has several structures. These emission and absorption spectra are similar to those of chlorine in LiCl.[15]

X-ray photoelectron spectroscopy is useful for obtaining information on the valence bands of solids. Recently, Kono *et al.*[6] found two separate valence bands for CuCl from the x-ray photoelectron measurement and reported that the major part of the upper band arises from the 3*d* state of copper and the major part of the lower band from the 3*p* state of chlorine. In Fig. 2, comparisons of the Cl $K\beta$-emission and $K$-absorption spectra, the Cu $L\alpha$-emission and $L_{III}$-absorption spectra,[3] the x-ray photoelectron spectrum,[6] and the theoretical energy-band structure[8] are shown, where the main peak in the photoelectron spectrum and the prominent peak $L\alpha$ are associated with the upper valence band and the prominent peak $\beta_1$ is associated with the lower band. The two bands in the photoelectron spectrum as well as the two bands $L\alpha$ and $\alpha$ in the $L\alpha$-emission spectrum correspond well to the two separate valence bands calculated by Song. Here, the small shoulder $\alpha$ is probably related to the lower band, because the mixing of the *d* state to the lower band is about 20%, according to the calculations by Song[7] and Kono *et al.*[6]

The structure $\beta'$ or $\beta''$ in the $K\beta$-emission spectrum does not correspond well to the main peak in the photoelectron spectrum, to the $L\alpha$ peak, or to the upper valence band. However, the two structures $\beta'$ and $\beta''$ correspond well to two satellites $\beta_x$ and $\beta_5$ on the high-energy side of the $K\beta_1$-emission band of Cl$^-$ ion in alkali chlorides LiCl,[15] NaCl,[16] KCl,[17] and RbCl.[18] Moreover, they can be fairly well assigned in terms of two satellite groups[19] ($^1P \rightarrow {}^1D$, $^3P \rightarrow {}^3P$, $^1S \rightarrow {}^1P$) and ($^3S \rightarrow {}^3P$, $^1S \rightarrow {}^3P$) arising from double ionization of Cl$^-$ ion. The assignment is shown in Fig. 2. Therefore, the structure $\beta'$ or $\beta''$ probably relates to the satellite groups. However, the intensity ratio of $\beta_1$ to $\beta''$ (0.45) is much larger than the ratio (0.18) of $\beta_1$ to $\beta_5$ for LiCl. This discrepancy seems to suggest that the structure $\beta''$ consists of a superposition of the satellite band and the emission band related to the *p*-type state in the upper valence band, because the mixing of the *p* state to the upper band is 10–20%, according to the calculations by Song[7] and Kono *et al.*[6] It should be noted that the intensity relation between the two bands $\beta_1$ and $\beta''$ in the $K\beta$-emission spectrum is reversed, as compared with the relation between the two bands $\alpha$ and $L\alpha$ in the $L\alpha$-emission spectrum. From these experimental results, it can be concluded that the upper valence band arises primarily from the 3*d* state of copper and the lower band predominantly from the 3*p* state of chlorine.

Let us next compare the Cl $K$-absorption and the Cu $L_{III}$-absorption spectra with the theoretical conduction band. The shoulder *A* and the peak *B* in the $L_{III}$ absorption correspond well to the lowest band (derived from the 4*s* state of copper) and the next lowest band (derived from the 4*s* state of chlorine), respectively, and the peak *C* corresponds well to the *d*-type state $K_2$ (derived from the 3*d* state of

TABLE I. Wavelength and photon energy values of the characteristic points of the $K\beta$-emission and $K$-absorption spectra of chlorine in CuCl.

| Notation | Wavelength (xu) | Photon energy (eV) |
|---|---|---|
| $\beta_1$ | 4395.6 | 2814.7 |
| $\beta'$ | 4393.0 | 2816.4 |
| $\beta''$ | 4389.2 | 2818.8 |
| *A* | 4378.5 | 2825.7 |
| *B* | 4375.4 | 2827.7 |
| *C* | 4373.0 | 2829.3 |
| *D* | 4367.3 | 2833.0 |
| *E* | 4359.0 | 2838.4 |

chlorine). On the other hand, the structures $A$, $B$, and $C$ in the $K$-absorption spectrum correspond to the $p$-type states $L_3$, $\Gamma_{15}$, and $W_3$ (derived from the 4$p$ states of copper and chlorine) located at several eV above the bottom $\Gamma_1$. From these comparisons, we can conclude that the low-energy part of the conduction band arises from the 4$s$ state of copper. The $p$-type states in the conduction band are located at several eV above the bottom.

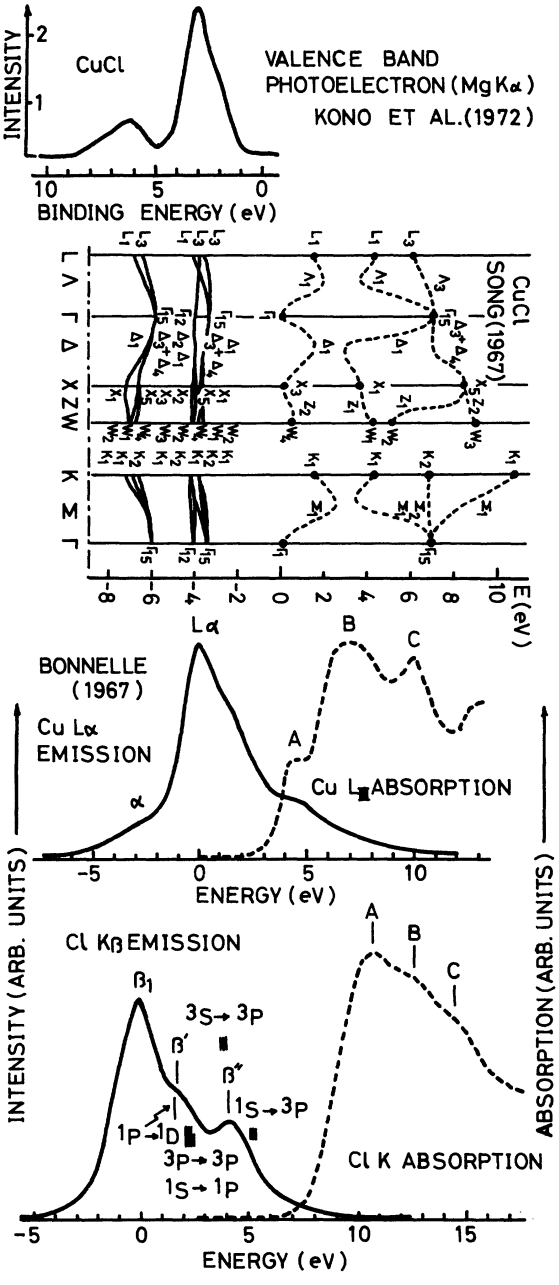

FIG. 2. Comparisons of the Cl $K\beta$-emission and $K$-absorption spectra of CuCl, the Cu $L\alpha$-emission and $L_{\rm III}$-absorption spectra from Bonnelle (Ref. 3), the x-ray photoelectron spectrum from Kono *et al.* (Ref. 6), and the energy-band structure of Song (Ref. 7). The structures $\beta'$ and $\beta''$ in the Cl $K\beta$-emission spectrum are assigned in terms of the transition arrays for the $\mathrm{Cl}^-$ ion calculated by Deslattes (Ref. 19). The transitions marked with longer vertical lines are expected to have greater intensity than the others.

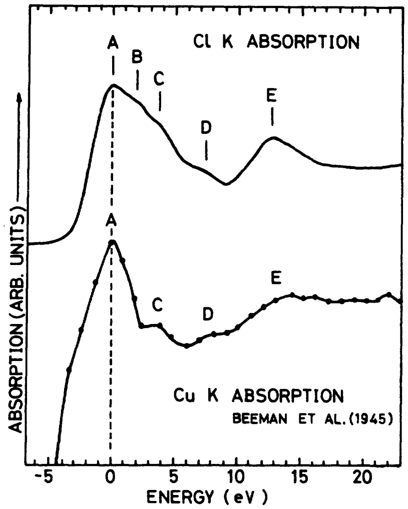

FIG. 3. Comparison of the Cl $K$-absorption spectrum of CuCl and the Cu $K$-absorption spectrum obtained by Beeman *et al.* (Ref. 8).

In Fig. 3, the Cl $K$-absorption spectrum obtained in this study is compared with the Cu $K$-absorption spectrum of Beeman *et al.*[8] As can be seen, the absorption curves agree well in the positions of the maxima but there is a distinctive difference in the relative heights. This difference is probably due to the different transition probabilities, because the variation in the absorption coefficient is related to the product of the transition probability and the density of states. Such a result has been observed for the $K$-absorption spectra of both $\mathrm{Li}^+$ and $\mathrm{Cl}^-$ ions in LiCl.[15]

## IV. SUMMARY

The $K\beta$-emission and $K$-absorption spectra of chlorine in CuCl have been shown and discussed in relation to the energy-band structure. Results are evaluated by comparing the Cl $K$ spectra with the Cu $L$ spectra, with the x-ray photoelectron spectrum, and with the theoretical band structure. It is confirmed that the upper valence band arises primarily from the 3$d$ state of copper and the lower band predominantly from the 3$p$ state of chlorine. The low-energy part of the conduction band arises from the 4$s$ state of copper. The $p$-type states in the conduction band are located at several eV above the bottom. The Cl $K$-absorption spectrum is compared with the Cu $K$-absorption spectrum and a good correspondence is found in the positions of the maxima.

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# Thermodynamic Properties of the Alkali-Halide Crystals[*]

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The equilibrium properties of fourteen alkali halides in the NaCl lattice structure are calculated by using an expression for the pair potential given by Tosi and Fumi. The calculations are based on the quasiharmonic lattice-dynamic method and the unsmeared Lennard-Jones-Devonshire cell model. The latter provides numerical estimates of anharmonic contributions which are neglected in the former. Comparison of the calculations with the available experimental data as well as the Monte Carlo data of Woodcock and Singer shows reasonable agreement for the cohesive energy, the pressure, the specific heats, the coefficients of thermal expansion, and the Grüneisen $\gamma$'s, but relatively poor agreement in the case of the elastic constants. Our results indicate that the interionic potential for the alkali halides has a stiffer repulsive core and a stronger attractive tail than the expression given by Tosi and Fumi, and that the anharmonic corrections are generally small and should be described accurately by the two lowest terms in a suitable perturbation series. Further discussion is given on the accuracy of using an existing approximate theory for the elastic constants and on the self-consistency of making the quantum and anharmonic corrections introduced here.

## I. INTRODUCTION

The alkali-halide crystals hold a certain fascination for experimentalists and theoreticians alike. Theoreticians like them because of their simple crystal structure, because their binding energy is predominantly ionic, and because of the availability of good experimental data. Furthermore, because the NaCl phase is stable over an extended temperature range, and the melting temperature is usually much larger than the Debye temperature, the distinctly anharmonic temperature interval and the distinctly quantum temperature interval are separate, permitting one to exercise and test these aspects of a theoretical model individually. Experimentalists have been attracted to alkali halides because of the availability of large, high-quality single crystals, because of the relative ease of handling them, and because of the active theoretical interest.

As a result of this interest a large amount of information has been obtained on alkali halides, in view of which it should be possible to determine how well the interionic forces in the alkali halides can be systematically represented by means of two-body central forces which are the sums of contributions from distinct atomic interactions, such as the Coulomb interaction, the van der Waals attraction, and the Born-Mayer repulsion. Fragmentary answers to this question do, in fact, exist. For example, it appears from the work of Szigetti,[1] Lyddane and Herzfeld,[2] and Lyddane, Sachs, and Teller[3] that such a force law cannot reproduce the phonon dispersion curves obtained from neutron scattering data. On the other hand, it is well known[4] that such an approach does provide a very