

SECOND ORDER CHLORINE K-VALENCE BAND SPECTRA OF CHLORIDES

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(Plate IV)

ABSTRACT. Chlorine K-valence band spectra ($3p \rightarrow 1s$) in the second order *i.e.*, in the region of 9 A. U. were studied by a concave (gypsum crystal) spectrograph for the alkali-chlorides, alkaline-earth chlorides, CdCl_2 , ZnCl_2 , CuCl_2 , AgCl etc. The resolving power is about 2X. U. per mm. or 1.0 e.v. per mm. on the photometer records. The energy differences of '3p' emission structures from the chlorine K-absorption edge of the corresponding chloride obtained from Stelling's data have been calculated for various chlorides and the differences are found to agree well with the ultra-violet absorption bands obtained by Pohl and Hilsch for the corresponding chlorides. As to the origin of ultra-violet absorption bands in various chlorides, a new explanation has been offered and that put forward by Von Hippel has been criticised. The 3p band widths of various chlorides have been estimated and are related to the ratio of ionic diameters of the constituent elements of the chlorides. The experimental results obtained are better explained by the band scheme due to Bloch than by atomic model due to Heitler-London.

INTRODUCTION

In the first paper (K. Das Gupta, 1946) of the series, an account of the soft X-ray absorption and emission spectra of Mg, Al, Si and their oxides has been given. In the present paper, second order emission spectra of chlorine from LiCl , NaCl , KCl , RbCl , CsCl ; CaCl_2 , SrCl_2 , BaCl_2 ; CdCl_2 , ZnCl_2 , CuCl_2 , AgCl in the region of about 9 A. U. have been described.

Chlorine $L_{2,3}$ spectra ($3, 1s \rightarrow 2p$, p being doublet) have been studied by Siegbahn and Magnusson, O'Bryan and Skinner (1940). They have found that $L_{2,3}$ lines of these chlorides *viz.*, η and l lines are accompanied by other two lines η' and l' in the neighbourhood. The intensities of η' and l' are found to be different for various chlorides but the voltage difference between them (η' and l') is the same as that found for η and l *viz.*, 1.6 volts. There is no doubt as to the presence of other satellites on both sides of the main lines for which no satisfactory explanation has been offered. O'Bryan and Skinner suggest that of the two groups (η , l and η' , l') the strongest pair η , l are from ionic chlorine centres, while the other which is relatively displaced to the shorter region are from 'neutral atomic centres' of chlorine in the lattice. It has, however, been observed by O'Bryan and Skinner

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that the third order $L_{2,3}$ spectrum of chlorine in LiCl consist of two bands only and of Cl in CsCl taken by Siegbahn and Magnusson consists of two bands with a very faint band near about the middle. The absence of weak band in CsCl has been ignored in the 'neutral atomic hypothesis' of Skinner and in the case of LiCl the absence of satellites has been attributed to the lack of resolution due to the greater breadth of lines.

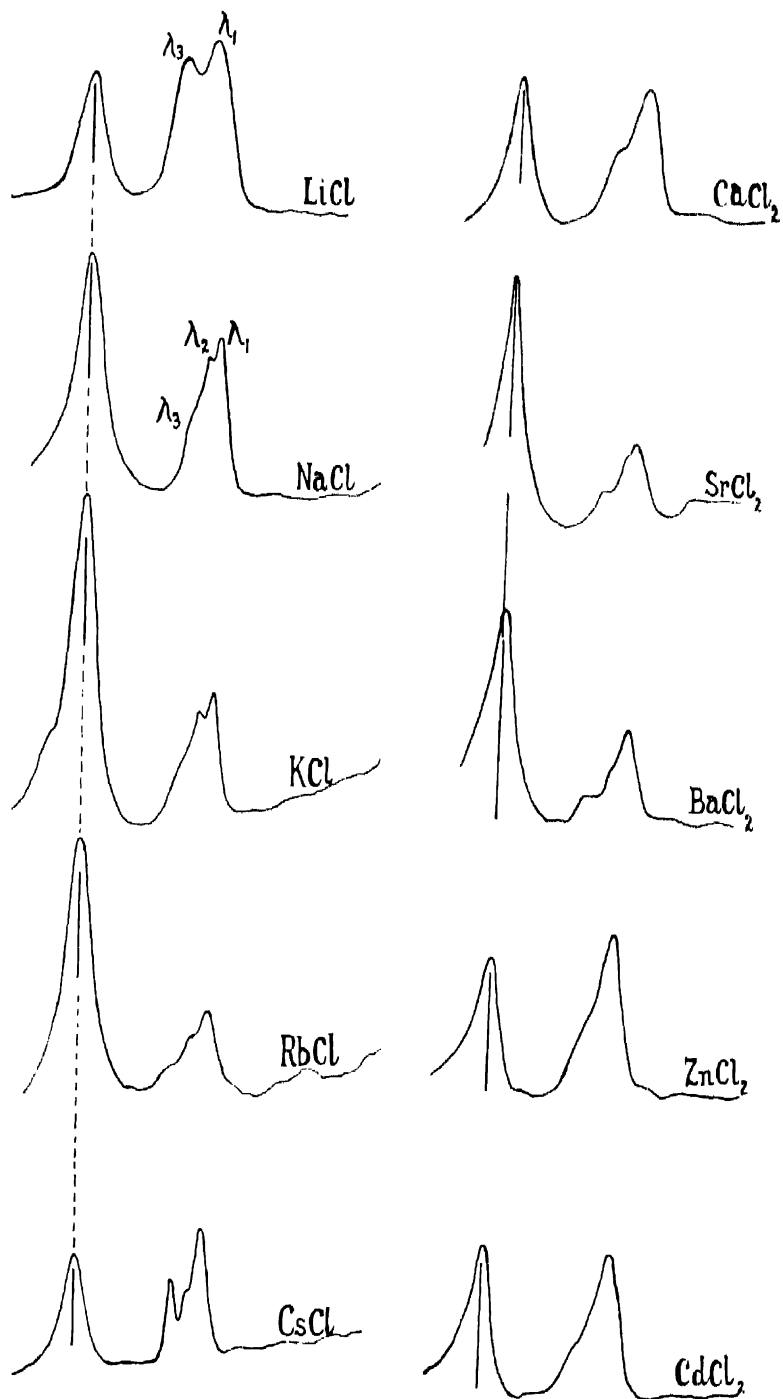
The K level in compounds is very much sharper than that of the valence band and thus the structure of K band ($3p \rightarrow 1s$) gives us a direct measure of the influence of the lattice on the energy breadth of 3p level. O'Bryan and Skinner have drawn some '3s' bands of Cl from $L_{2,3}$ spectra ($3s \rightarrow 2p$) assuming that the breadth of the levels 2p is small compared to that of 3s. Our experimental results throw some new light on Cl K-valence spectra ($3p-1s$) and in the case of 3p band one is more justified to neglect the width of 1s level due to chemical binding.

The energy differences of 3p emission structure from the Cl K-absorption edge of the corresponding chloride obtained from Stelling's data have been calculated for NaCl, KCl, RbCl, CsCl, CaCl₂, BaCl₂, CuCl₂, AgCl and it is very interesting to note that the differences are found to agree well with the ultra-violet absorption bands obtained by Pohl and Hilsch for the corresponding chlorides.

Slater and Schockley (1936) have theoretically calculated the total breadth of Cl 3p band of NaCl which comes out about 4.5 e.v. for which experimentally observed data are not available. The present experimental data on the chlorides give 3p band width and it has been found that the observed 3p band width of Cl in NaCl is 6.5 volts, resolving power in this region being 1 e.v. per mm. More accurate experiments in third order spectra, with better resolution are necessary to measure accurately the 3p band width. It has been found that the structure of all alkali chlorides are similar while it is different from those of alkaline-earth chlorides. For alkaline-earth chlorides, however, 3p band spectra are similar amongst themselves.

EXPERIMENTAL RESULTS AND TECHNIQUE

In the previous paper (K. Das Gupta, *loc.cit.*) the experimental details have been given. It must be mentioned here that the emission spectra taken by direct excitation by electron impact are not satisfactory. It has been found that the effect of a particular metal forming the anti-cathode target on the investigating sample can be practically avoided, but still the electrons from the filament strike the substance causing some undesirable change. Most of the alkali-chlorides become coloured green, blue, violet etc., due to the electron impact in the X-ray tube, the colour is also formed by X-ray irradiation. Secondary fluorescence method has just been adopted to study the emission spectra of chlorides in the second order, that is in the region of about 9 Å. U. to avoid electron impact. For some less stable chlorides it is very difficult to maintain the order of vacuum of the spectrograph, as the electron impact under the



2nd order Cl K-valence band Spectra.
 See $1/\beta$, reference line on extreme left

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experimental conditions cause some reduction of the sample and Cl gas comes out. In such cases there is always a discharge current in the tube and the rate of suction of the pump, as well as, the cooling of the anticathode had to be increased to minimise the discharge. The blackening of the film due to exposure to the discharge glow was avoided by using a very thin aluminium

TABLE I
K-Valence Band Spectra of Chlorine in Chlorides

Specimen	Wavelength in Å. U.		
	λ_1	λ_2	λ_3
LiCl	4395.8 S (Strong)	4386.9 W (Weak)
NaCl	4398.1 S	4395.2 W	4390.1 V. W. (Very Weak)
KCl	4399.1 S	4396.1 W	4391.2 V. W.
RbCl	4899.0 S	4395.1 V. W.	4387.1 W.
CsCl	4397.1 S	4392.7 V. W.	4388.1 W.
CaCl ₂	4396.9 S	4388.7 W	4376.8 V. W.
SrCl ₂	4397.0 S	4391.2 W	4387.7 V. W.
BaCl ₂	4397.1 S	4391.0 W	4385.6 V. W.
CdCl ₂	4395.9 S	4385.6 V. W.
ZnCl ₂	4395.1 S	4386.6 V. W.
CuCl ₂	4397.3 S	4391.8 W	V. V. W.
AgCl	4398.0 W	4393.6 S	4387.7 W.

foil screen. To study the effect of metal target on the Cl spectra, NaCl was pressed on copper target and silver target successively and there was no detectable change of Cl 3p band structure.

GENERAL INTERPRETATION OF RESULTS

K β or K-valence band spectra of Cl give a direct measure of the influence of the lattice on the energy breadth of 3p level, neglecting the breadth of 1s of Cl in chlorides. Plate IV shows original microphotometer records and in Table I, wavelengths of K β band of various chlorides have been given.

In LiCl, the peaks of the two bands λ_1 and λ_2 are separated by 5.7 e.v. and the stronger one is on the lower energy side. Intensities of the two bands are approximately of the same order of magnitude. If we assume the stronger one (low energy part) to be due to Cl ion, the other must be

assumed, according to O'Bryan and Skinner, to have emitted from neutral Cl. The question of relative intensity between the bands raises a serious doubt whether in these ionic crystals, percentage of neutral chlorine can be so large.

In NaCl, beginning from the low energy part of the spectrum, of the three bands the first λ_1 , λ_2 , λ_3 is the strongest while the last one λ_3 is distinctly weaker than the middle one. In NaCl spectrum, the energy difference between the two extreme bands is almost the same as found for the two bands for Cl in LiCl. If we explain the origin of the band on the short wave side due to neutral Cl centres we are faced with difficulty to explain the intermediate band.

The structure of K band of Cl in KCl is similar to that found for NaCl. In CsCl, which is body centred cube, the number of bands is the same as found for NaCl and KCl with the difference that the band having shortest wave-

TABLE III
Total Band-width of Cl K β band in Chloride:

Width in e.v.	LiCl	NaCl	KCl	RbCl	CsCl
e.v.	9.18	7.71	7.10	6.37	5.40
Ratio of ionic diameters ...	Cl ⁻ /Li ⁺	Cl ⁻ /Na ⁺	Cl ⁻ /K ⁺	Cl ⁻ /Rb ⁺	Cl ⁻ /Cs ⁺
.....	3.0	1.90	1.36	1.22	1.07
Width in electron volt	CaCl ₂	SrCl ₂	BaCl ₂	ZnCl ₂	CdCl ₂
.....	10.0	9.2	7.71	10.72	9.72
Ratio of ionic diameters ...	Cl ⁻ /Ca ⁺⁺	Cl ⁻ /Sr ⁺⁺	Cl ⁻ /Ba ⁺⁺	Cl ⁻ /Zn ⁺⁺	Cl ⁻ /Cd ⁺⁺
.....	1.82	1.60	1.34	2.40	1.86

length is stronger than the middle one. The main point of similarity in Cl K β spectra of alkali halides is that the spectra begin for each of them with the strongest band on the long wavelength side and its wavelength in chlorides in the same periodic column is almost the same. The wavelength and intensity of the remaining band in each spectra differ. It means that the influence of the lattice is much more felt by the outer portion of the 3p level while the energy value of the deepest part of the valency level remains less affected.

Ca, Sr and Ba are in the same column of the Periodic Table, having same crystal structure for their chlorides and their spectra are similar. This is also the case with Cd and Zn. In the case of CdCl₂ and ZnCl₂, the K β spectra of Cl are similar, but they are different from those of alkali-chlorides and alkaline-earth chlorides. Thus different groups of elements have different structure of K-band but the structure for the chlorides of elements in the same column and having same crystal structure are similar.

It has been found that within 5-10 minutes the alkali halides become coloured green, blue, violet under electron impact in the existing condition

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of the tube. Cl in the form of gas comes out of chlorides and stoichiometric excess of alkali metals thus produced is responsible for the development of colour. Similar colour can be developed if the particular halide be heated for a sufficient time in presence of the corresponding alkali vapour.

The widths of chlorine K β band of chlorides, have been calculated and in Table III, the values as against the ratios of ionic diameters Cl^-/R^+ are given. It will be seen that as the ratio of ionic diameters increases, the width of Cl K β band also increases. When the radii of the metal ion are large, the halide ions are pushed farther apart and they overlap less with each other, the

TABLE II
Soft X-ray K-Absorption and Emission Spectra and Ultra-violet Absorption bands of Chlorides

Specimen	K-valence band spectra of Cl		Cl K-absorption edge in e.v. (Steiling)	K-edge- λ_2 in e.v.	1st Ultra-violet absorption band (Hilsch & Pohl)	K-edge- λ_1 in e.v.	2nd Ultra-violet absorption band (Hilsch & Pohl)
	λ_1 e.v.	λ_2 e.v.					
NaCl	2806.0	2808.7	2815.9	7.2	7.8	9.0	9.6
KCl	2806.2	2808.1	2815.2	7.1	7.6	9.0	9.1
RbCl	2806.3	2808.8	2815.1	6.3	7.4	8.8	8.9
CsCl	2807.3	2810.3	2815.0	4.7	7.5	7.6
CaCl ₂	2807.6	2812.0	2815.6	2.7	8.0	8.1
BaCl ₂	2807.6	2809.5	2815.9	9.4	7.7	8.3	9.1
CiCl ₂	2807.3	2810.9	2816.0	5.1	6.4	8.7	8.2
AgCl	2807.0	2809.7	2811.3	1.6	1.8	7.3

width depending on the amount of overlapping. A similar interpretation applies to the oxide and fluoride band widths obtained by Skinner. In alkaline-earth chlorides the width of K band is greater compared to alkali-chlorides for the same value of the ratio of ionic diameters, showing thereby that the overlapping does not depend only on the ratio of the ionic diameters but also on the arrangements of the atoms in the crystal.

Table II shows that the ultra-violet absorption bands of various chlorides can be indirectly obtained, if we know accurately the K-absorption edge of Cl in different chlorides, the latter being taken by Steiling. If we calculate the energy difference of the peak λ_1 and of the peak λ_2 of Cl emission spectra of a chloride from Cl K-absorption edge of the corresponding chloride, we

get the values of the two ultra-violet absorption bands. The energy difference between λ_1 and λ_2 peaks of Cl spectra in a chloride agrees well with the difference between the first and second ultra-violet absorption bands of the corresponding chloride.

An explanation as to the origin of Cl $K\beta$ spectra in various chloride is put forward. In solid physics, mainly there are two schemes, the Heitler-London scheme, in which the solid is pictured as being made up of separate atoms or ions which interact with each other. The second is due to Bloch in which the electrons in the outermost shell of the atoms concerned are not supposed to be bound to their individual atoms, but are supposed to be free to move through the lattice. This is known as the collective electron model.

In an atomic picture, the eight valence electrons per unit cell of the alkali-halides completely occupy the outer 's' and 'p' shells of the negative ions. In the band scheme, the same electrons occupy four zones, one of which connect with the ionic 's' level and the three others of which connect with ionic 'p' level. Fig. 1 illustrates the manner in which the ionic

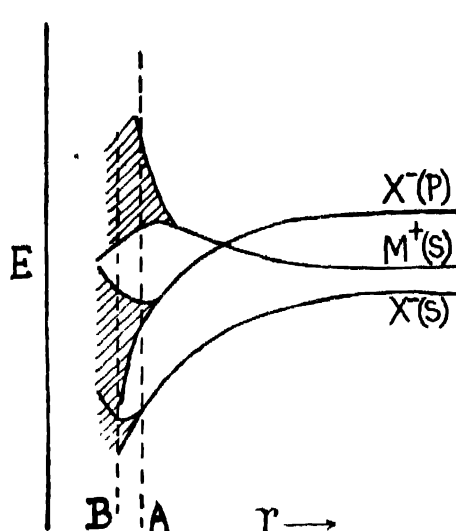


FIG. 1

Schematic representation of the manner in which the ionic levels of the constituents of ionic crystals break into the bands in the band approximation. At A the s and p bands of the negative ions are separate, whereas at B they overlap.

level broaden into bands of the zone theory, as the ions are brought together. The levels of the negative ions are depressed and those of the positive ions are raised because of the Madelung field. In addition, the levels break into bands when ions begin to overlap. At the observed lattice distance of NaCl, the 's' and 'p' bands are separated from one another and from the higher unfilled band which connects with the lowest level of the metal ion. The ionic level does not split into bands in the Heitler-London approximation but remains discrete, roughly following the centre of gravity of the bands. The chlorine '3p' band is superposition of $3p_1$ and $3p_2$ electrons and thus the

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transition probability to vacant K level for them are different. This gives rise to two peaks, the longest wavelength peak of Cl spectra is due to the transition of electrons from the bottom of the valence $3p$ band having $3p_1$ characteristic and the next one, on the short wave side is due to ' $3p_2$ ' electrons from the top of the $3p$ band. The energy difference between the two consecutive peaks beginning from long wave side is found to be fairly constant for all the alkali chlorides and is of the order of 2 e. v. In the band scheme $3p_1$ level, as well as, $3p_2$ level broaden into band and the width of $3p$ band determined experimentally in the case of NaCl spectra is of the order of 6.5 e. v. Although, in the ground state the doublet separation for Cl atom is 0.11 e. v. only, considering both the transition probability, as well as, the density of state of $3p_1$ and $3p_2$ electrons in $3p$ band it is quite possible to get two peaks at the observed 2 volts energy difference. In chemical combination, both $3p_1$ and $3p_2$ level are affected and displaced downwards in the energy (negative) scale and it is quite possible that $3p_1$ and $3p_2$ electrons are not equally affected when chemical combination takes place. This is supported by the experimental fact that the longest peak for most of the chlorides has got nearly the same wavelength. The width of $3p$ band, which depends on to what extent the electrons overlap, will also be different for $3p_1$ and $3p_2$ electrons. The absence of two peaks having energy difference equal to 2 volts in LiCl is attributed to the overlapping of $3p_1$ and $3p_2$ bands, centres of gravity of p_1 and p_2 band possibly come very close to each other. The width of Cl long wave band in LiCl being greater than 5 e. v.

The origin of the weakest band having shortest wavelength may be due to electrons coming from the colour band above the $3p$ band. The colour is formed due to stoichiometric excess of alkali metals. The energy gap between the short wavelength band and the $3p$ band qualitatively accounts for the green, blue, violet colours observed with different halides. To establish definitely this point, sample of KCl was changed at an interval of 10 minutes so that Cl $K\beta$ spectra may be taken mostly from uncoloured salt. From the microphotometer record it was seen that the weakest band on short wave side has almost disappeared.

This explanation as to the origin of the structure of Cl K-valence band spectra *viz.*, from $3p_1$, $3p_2$ and the 'colour band' electrons may also be extended to explain the ultra-violet absorption bands of chlorides. Of course, in the same apparatus, by the same experimenter both the emission and absorption spectra are to be obtained, which work has already been undertaken. Von Hippel (1930) has calculated the position of the first absorption band in the alkali-halides on the assumption that an electron is removed from a halogen ion to a neighbouring metal ion. Passing to the absorption band of shorter wavelength, attempts have been made to assign these to a process in which an electron is transferred from a halogen ion to one of the next nearest metal ions. According to Mott and Gurney (1940) there is no reason

why the electron should stay on a particular one of these more distant ions. Theory put forward as to the origin of the ultra-violet absorption bands in chlorides (at least) is that electrons in the valence band, which is superposition of $3p_1$ and $3p_2$ electrons, absorb energy and jump into the first vacant band, which according to the zone scheme, is the 's' band of metal ion. In X-ray K absorption spectra, the absorption begins at an wavelength corresponding to the transition of K electrons to the same vacant 's' band of metal ion. From above explanation it is at once evident that the energy difference between p_1 and p_2 peaks in Cl K-spectra will agree with the energy difference between the first and second ultra-violet absorption bands.

DISCUSSION

The second order Cl K-valence band spectra with gypsum crystal is unsatisfactory because of poor resolving power *viz.*, 1 e.v. per mm. To establish definitely the theory put forward to explain the ultra-violet absorption bands in chlorides, third order spectra in emission, as well as, in absorption are being taken with a concave mica grating spectrograph. The longwave band in LiCl has been attributed to the overlapping of $3p_1$ and $3p_2$ band and the energy difference between the peaks as obtained in other chlorides is so small in LiCl that the peaks are not resolved by the spectrograph. This conclusion is supported by the fact that amongst the alkali-chlorides it is only in LiCl that the two ultra-violet absorption bands are least separated and the separation is 1 e.v. which, according to the theory put forward, is the energy difference between $3p_1$ and $3p_2$ peaks of LiCl. The resolving power of the spectrograph in this region being 1 e.v. per mm. on the microphotometer record. It is expected that in the third order spectra with better resolving power some fluctuation of intensity in the long wave band of Cl in LiCl will be observed.

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