

The Influence of Chemical Binding and Crystal Structure on X-Ray Absorption Edges

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An attempt is made to explain the positions and the fine structures of x-ray absorption edges, so far as these are not explained by Kronig's theory, by considering that they arise from transitions into a series of discrete states. These are states in which the electron is trapped in the region of surplus positive charge, which is created by the ejection of the electron from the inner shell of the parent ion. To calculate the energy of the trapped states we use a model in which the electron is bound to the positive ions in the neighborhood of the parent ion.

INTRODUCTION

BY THE absorption of an x-ray photon in a solid, an inner-shell electron is lifted into an excited state. Kronig¹ has suggested that we can identify these excited states of the electron with those in which the electron can move more or less freely through the lattice, somewhat like conduction electrons move in metals. Such "traveling wave" states are found to occupy separated bands in the energy spectrum. This should give rise to a sequence of maxima and minima in the absorption spectrum on the short wave side of the edge. For metals which have a relatively simple crystal structure the distribution of states is known fairly well and the calculated absorption curve agrees well with the experimental results. For ionic compounds the situation is more complex. Kronig² has also given a qualitative discussion of this problem, and has shown the difficulties caused by the presence of more than one kind of ion. The predictions of this modified theory have been verified in several cases, but contradictory results have been obtained for the structures in the immediate neighborhood of the edges of some K and Cl compounds which have been investigated under high resolving power.³

For the absolute positions of the x-ray absorption edges Pauling⁴ has developed a theory of great simplicity which agrees satisfactorily with the experimental data. In the picture adopted by Pauling, the lowest excited states of the electron are also identified with traveling wave states,

although the method of calculating the energies of these states is quite different from Kronig's. However, objection to this picture can be raised on the following grounds. The removal of the electron from one of the ions creates a region around this ion which contains a surplus positive charge. The ions in the neighborhood will therefore be polarized, and thus lower the energy of the whole system. The energy which has to be supplied by the x-ray photon is consequently reduced by this amount. The polarization energy of an ion which is within a distance r from the surplus positive charge, and which has a polarizability α , is $-\alpha e^2/2r^4$. The total polarization energy is $-e^2/2 \cdot \sum_i' \alpha_i r_i^4$ where the summation is extended over all points of the lattice. Summations of this kind have been carried through for different types of crystals by J. E. Jones and A. E. Ingham.⁵ According to these calculations we can write the polarization energy as $P = -(A'\alpha_+ + A''\alpha_-)e^2/2d^4$ in which α_+ and α_- are the polarizabilities of the positive and the negative ions and d is the distance between nearest neighbors. For crystals of the NaCl type we take from Jones and Ingham⁵ the values $A' = 13.31$, $A'' = 9.33$. In Table I we give for several compounds the hypothetical values of the energy (Rydberg units) required to remove an electron from the K shell of the free Cl ion, which would account for the observed frequencies of the edges. In the first line Pauling's original formula has been used, in the second line this formula is corrected for polarization. The energy should of course be the same in all compounds. In the second line of Table I the

¹ R. de L. Kronig, *Zeits. f. Physik* **70**, 317 (1931); **75**, 191 (1932).

² R. de L. Kronig, *Phys. Zeits.* **36**, 729 (1935).

³ G. P. Brewington, *Phys. Rev.* **46**, 861 (1934).

⁴ L. Pauling, *Phys. Rev.* **34**, 954 (1929).

⁵ J. E. Jones and A. E. Ingham, *Proc. Roy. Soc.* **A107**, 640 (1925).

TABLE I. Hypothetical K absorption edge of free Cl.

	LiCl	NaCl	KCl	RbCl	CsCl	AgCl
(Pauling)	207.62	207.63	207.60	207.61	207.73	207.75
(Pauling +polarization)	207.86	207.81	207.75	207.77	207.93	208.05

spread between the hypothetical values of the energy is quite large compared with that in the first line. This means that the consistent consideration of polarization terms spoils the good agreement of Pauling's theory with the experimental data.

The fact that the absolute position of the edge and the structure of the absorption spectrum in the immediate neighborhood of the edge do not come out properly in the present theories suggests a reconsideration of the lowest possible excited states. In this article an attempt is made to do this in the light of recent theoretical discussions,⁶ which show the existence of a few discrete energy levels below the first continuous band. The region of surplus positive charge created by the removal of the electron can trap an electron so that it cannot travel freely through the crystal. Thus one gets a series of "trapped states" which occupy separated levels below the continuum of energy states in the band. Wannier's argument that these discrete levels will not appear as discrete absorption lines because they are hidden in a superposed band is no restriction in the case of the x-ray absorption because this superposed band is that of the inner shell electrons and its width is negligible. Wannier gives an approximate formula for the energy values of the trapped states. For electrons coming from an inner shell which does not show any spread in energy one has to put $A_g = 0$ in his formula (19), and so finds that the states lie within a distance ΔE from the continuum, where ΔE is given by the formula for the electronic levels in the hydrogen atom, in which, however, the electron mass is substituted by an effective mass, which is somewhat heavier. According to this formula the splitting between the two lowest levels is more than ten electronvolts. The observed splitting is smaller however, and it will be necessary to make use of the more detailed information that one can obtain from

⁶ J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).
G. H. Wannier, Phys. Rev. **52**, 191 (1937).

an atomic picture.^{6a} An approach similar to that considered here has been used previously by von Hippel⁷ and Klemm⁸ in a theory of the ultraviolet absorption of the alkali halides.

THEORY

The states which we shall consider are those in which the ejected electron is captured into the empty place of the series electron at a positive ion. The lowest state will be that in which it is bound to the ion which is nearest to the attracting center, and the other levels arise when it is bound to ions which are farther away. We do not wish to introduce unnecessary complications by attempting to treat the problem in a very general manner, but rather shall limit ourselves to the case in which only one type of positive and one type of negative ion is present.

In case the electron is ejected from a positive ion the lowest state is that in which it stays at the same ion, merely moving to an outer orbit. In this case the considerations are rather simple. The ion does not change its charge and therefore there will be no change in the electrostatic interaction with the neighbors. But there will be a difference in the exchange interaction between the neighbors and the ion in its normal and in its excited state. In many cases this difference in exchange interaction comes out to be too small to be observed. We see for example from a list⁹ of wave-lengths of the K edge of K^+ in 27 compounds which have been measured by Stelling, that those of 14 compounds lie between 3427.5 and 3427.9 X.U., the rest are at lower wave-length. In the first group we have all the halides, in the second are typical complex compounds like $K^+[FHF]$. A complex can be suspected of having an electron distribution which is quite extended. It is probably not held together by electrostatic forces alone, since the closed shells in a structure like $F-H^+F^-$ would have large repulsions, but there is probably some Heitler-London type of attraction for which a rupture of

^{6a} Since the Coulomb interaction in a medium with the dielectric constant k is e^2/kr , N. F. Mott recently suggested the formula $\Delta E = -Ry/n^2k^2$. This formula gives the same fine structure for cation and anion, and somewhat too small values, however. N. F. Mott, Proc. Roy. Soc. **167**, 384 (1938).

⁷ A. v. Hippel, Zeits. f. Physik **101**, 680 (1936).

⁸ W. Klemm, Zeits. f. Physik **82**, 529 (1933).

⁹ A. E. Lindh, *Handbuch der Exper. Physik* **24**, 2 Chapter 10, 1 (1930).

the closed shell structure is necessary. This means an increase in volume of the electron cloud. It will then overlap strongly the wave function of the series electron moving around the K^+ and thus shift its state to a higher energy and the absorption edge to a shorter wave-length.

For the calculation of the energy difference between the initial and the final state in case the electron is captured by a different ion, we consider the following effects: (1) The interaction of the ejected electron with the rest of the ion at which it is located, (2) the electrostatic interaction of the electron with the ions to which it is not bound, (3) the polarization energy due to the unsymmetrical arrangement of charges in the final state and (4) the exchange energy. In the following section we give a detailed discussion of these four effects and of their contributions to the initial and final energy of the system, which will be denoted by the letters I and F , respectively.

(1) In the initial state the electron is in one of the lower shells. The energy I_1 with which it is bound to the ion is not affected by the presence of the surrounding ions, inasmuch as these do not affect the charge distribution and therefore the potential close to the nucleus. We conclude that I_1 is equal to the binding energy of the electron to the free ion. This may be expressed in terms of the absorption edge ν_0 of the free ion. We have then $I_1 = -h\nu_0$. It should be noted, however, that ν_0 cannot be determined experimentally. In the final state the electron is bound to the lowest unoccupied level of the cation. The binding energy F_1 is known spectroscopically.

(2) The Madelung potential at a lattice point of an ionic crystal, that is the sum of the potentials of all ions but the one at the considered point, is inversely proportional to the lattice spacing. It is expressible as $-M_+e/d$ at the positive and as M_-e/d at the negative lattice points, with d standing for the distance between nearest neighbors. M_+ and M_- depend on the crystal structure. For a NaCl type with singly charged ions, for example, they would both be equal to 1.748. For the same lattice type but with doubly charged ions as constituents (for example in CaS) this value would have to be multiplied by two. Another example is SrCl_2 with $M_+ = 7.56$ and $M_- = 4.067$.

We consider an electron which makes a transition from a negative to a positive ion. In the initial state its electrostatic interaction with the ions to which it is not bound is simply the electronic charge times the Madelung potential at the negative lattice point; that is, $I_2 = -M_-e^2/d$.

For the final state we have to remember that a "positive hole" remains in the lattice after the electron has been ejected. If the electron goes to an ion which is at a distance sd from the ion to which it was bound before the transition occurred, and which is considered as the center of a superposed Coulomb attraction, a term $-e^2/sd$ must be added to the Madelung energy in the final state, so that we obtain $F_2 = (M_+ - 1/s)e^2/d$.

The sum of the two Madelung constants ($M_+ + M_-$) can be expressed by means of the commonly used Madelung constant M which gives the energy per unit cell as $-Me^2/d$. If n_+ and n_- are the numbers of positive and negative ions per unit cell and Z_+e and $-Z_-e$ their charges, the energy per unit cell is $-\frac{1}{2}(n_+Z_+M_+ + n_-Z_-M_-)e^2/d$. Because of the neutrality of the unit cell we have $n_+Z_+ = n_-Z_-$, which leads to $\frac{1}{2}(M_+ + M_-)n_+Z_+ = M$. Thus we have $F_2 - I_2 = (2M/n_+Z_+ - 1/s)e^2/d$.

(3) In calculating the polarization energy we must consider the fact, that the state of the series electron of the positive ion which is occupied after the transition has occurred has a very high polarizability, so that under the influence of electrostatic attraction alone the electron would be drawn back strongly to the ion from which it came. This tendency is restricted of course, since the electron cannot penetrate into the region where all of the possible states are occupied, and since the unfilled place in the K shell is not available to the ejected electron because of the requirement that the excited state must be orthogonal to the normal state. Anything more than a rather crude treatment of this problem seems to be very difficult. We follow a suggestion by W. Klemm⁸ and assume that the series electron is displaced by a distance $d\delta$ in the direction of the resultant electric field so that its energy changes by an amount $F_{3a} = V((s-\delta)d) - V(sd)$. Lacking a model from which to calculate δ , we fix it arbitrarily to be $\delta = 0.5$ when the emitting and the receiving ions are direct neighbors, and $\delta = 0.3$ otherwise. The different choice in δ is

made because of the difference in radii of the ions which are in the way. The emitting ion has its K electron knocked out and therefore it has contracted to a smaller radius. One might argue that δ should depend on the relative sizes of the constituent ions, in such a way perhaps as to give a constant distance of approach for a given ion. But one must consider also the effect of the radius of the orbit of the approaching electron. A large radius of the orbit, or, quantum-mechanically speaking, a large amplitude of the wave function in the region of the ion it approaches, gives a stronger repulsion due to exchange terms, which may be supposed to compensate for the smaller radius of the latter.

In addition to the polarization of the orbit of the emitted electron itself, there should be a polarization of the rest of the ions. At this point, however, it will be necessary to extend our model. An electron bound to a positive ion in the electrically unbalanced region cannot travel freely to the ions which are not in this region, but it can travel easily between ions which are in equivalent positions with respect to the center of the superposed Coulomb field. One should therefore use linear combinations

$$\psi = \sum_s A_s f(r - R_s),$$

as first approximations to the states. The factors A_s should be so determined that the ψ 's form sets whose transformations under the rotations of the symmetry group of the crystal are given by the irreducible representations of this group. For the process of absorption of radiation the final state of the electron ejected from the K shell can only be one type of function, in order that the matrix elements giving the transition probabilities may be different from zero. In a cubic crystal these functions are written down quite easily if one considers that they must be antisymmetrical with respect to reflections in one of the principal planes. For a jump to the immediate neighbor for example

$$\psi = \sqrt{\frac{1}{2}}(f(x-d, y, z) - f(x+d, y, z))$$

will be one of the functions. While this partition of the electron on two or more ions did not affect our previous considerations, it will be essential for the following. Instead of creating an electric dipole in the lattice, the electron creates a pole

of higher order. For the jump that we consider responsible for the first absorption maximum of the K edge of a negative ion, which leads to a place halfway between the center ion and its nearest neighbors, the electric field will be rather small and we shall neglect it altogether. For the following jumps special calculations need to be made.

(4) Finally we must consider the exchange interactions. There are in principle two terms. One is the interaction of the series electron with its negative ion neighbors. The other is the change in interaction of the parent ion with its neighbors, due to its diminished size and to the increase in potential. A direct calculation of the exchange integrals, even approximately, is much too involved to be worth while, but some general statements as to their comparative magnitude can be made. The series electron is repelled by the surrounding ions since the latter do not contain any unpaired electrons. The exchange interaction of the series electron with the neighboring ions will therefore produce a shift towards higher energies. The magnitude of this shift is determined by the amount of overlapping of the respective wave functions. For the interaction of the parent ion and its neighbors, we have to consider first that the influence of the positive hole produces a shift towards higher energies in the final state, while the shrinkage in size of the parent ions has the opposite effect. It appears that the first effect will outweigh the second, so that we again expect a shift toward higher energies.

TABLE II. K edges of Cl^- and of S^{--} in several compounds (ν/R) and in the free ions (ν_0/R).

COMPOUND	STRUCTURE	d	Z	ν/R	ν_0/R
LiCl	B1	2.57	2	207.871	207.517
NaCl	B1	2.81	10	207.867	207.553
KCl	B1	3.14	18	207.810	207.515
RbCl	B1	3.28	36	207.805	207.524
CsCl	B2	3.55	54	207.820	207.553
AgCl	B1	2.78	46	207.749	207.625
SrCl ₂	C1	3.02	36	207.867	207.533
BeS	B3	2.10	2	182.17	180.85
MgS	B1	2.60	10	182.06	180.93
CaS	B1	2.84	18	182.01	180.84
BaS	B1	3.18	54	181.98	180.88
MnS	B1	2.61	23	182.05	180.98
ZnS	B3	2.35	28	182.06	181.02
CdS	B3	2.57	46	181.97	181.01
Na ₂ S	C1	2.83	10	181.90	180.87

NUMERICAL APPLICATION OF THE THEORY

The negative ions for which the influence of the chemical binding on the K absorption edge has been investigated most thoroughly are Cl^- and S^{--} . From the large number of compounds which have been investigated we select those which crystallize in relatively simple systems. In the notation employed in the Landolt Boernstein tables these are the systems $B1, B2, B3, C1$. These symbols and the distances are listed in the second and third column of Table II. The observed frequencies of the K edge which are taken from the Tables 82, 85 and 91 in Lindh's book⁹ are given in the fifth column (Rydberg units). In the last column we have the hypothetical value of the x-ray term of the free emitter, which we have to assume to account for the observed frequency of the K edge in the compound under consideration. This value is computed from the formula $h\nu_0 = h\nu - F_1 + I_2 - F_2 - F_3$ that is, with neglect of exchange energy terms. The edge ν_0 of the free ion should, of course, have the same value for all its compounds. For AgCl , MnS , ZnS , CdS , however, the values come out higher than for the other compounds. This can be interpreted as caused by the neglected exchange terms, which are more important in these ions because they overlap their neighbors more than the rest of the ions. The overlapping can be seen by comparing the internuclear distances d with the numbers Z of electrons of the positive ions (see third and fourth column of Table II). For example Ag with its 46 electrons comes closer to the Cl than Na which has only 10 electrons. For the electrons in the closed shells of the positive ion this overlapping does not bring about a higher exchange interaction, because the outer electrons in these particular ions are d electrons which have nodes in the region containing the main portion of the integrand and therefore depress the exchange interaction partly. For the series electron, however, which is an s electron in all cases, there is no counteraction due to nodes and we have to expect higher exchange energies due to the strong overlapping.

If we disregard the compounds for which an exchange interaction is to be expected the values ν_0 are fairly consistent. The discrepancy existing

in Pauling's theory in the case of CsCl has disappeared. The mean deviation of the values ν_0/R from their average is 0.014 for Cl^- and 0.025 for S^{--} . For comparison it may be noted that the mean deviation of the corresponding ν/R from their averages is 0.028 and 0.073, respectively. The average value of ν_0 for Cl^- corresponds to a wave-length of the absorption edge of the free ion $\lambda_{\text{free}} = 4395.3 \text{ X.U.}$ while Pauling's theory gives a value of 4389.3 X.U.

Next we consider the fine structure at the short wave-length side of the absorption edges. Of course only that type which is not explained by Kronig's theory is considered. We attempt to correlate the maxima to successive trapped states, to explain the structure at the K edge of Cl^- in several alkali chlorides. The compounds which have been investigated⁸ are all of the same lattice type as NaCl . The first two maxima in the absorption curve are regarded as being due to transitions to neighboring ions in positions like (100) and (111). In the experimental curves the first maximum is denoted by the letter A and the second one by B , and we shall use the same letters to denote transitions to (100) and (111). F_1 and I_1 are the same for A and B . The electrostatic energy is $F_2 - I_2 = (2M - 1)e^2/d$ for A and $F_2 - I_2 = (2M - 0.577)e^2/d$ for B . The polarization is $F_{3a} = -0.748e^2/d$ and $F_{3a} = -0.139e^2/d$, respectively. For the other part of the polarization energy we have to consider the charge distribution after the transition has taken place. Besides the charge $+e$ in the center, which is created by removing the electron from the K shell, we have the distribution of the charge of this electron. In case A half the charge, that is $-\frac{1}{2}e$ goes to each of the 2 points $((1 - \delta), 0, 0)$ and $(-(1 - \delta), 0, 0)$, or to an equivalent pair of points on one of the other two axes. In case B the charge $-(1/8)e$ goes to each of the 8 corners $(\pm q, \pm q, \pm q)$ of a cube around the parent ion, with $q = (1 - \delta/\sqrt{3})$. The corresponding polar-

TABLE III. Theoretical and experimental energy difference between the first two maxima in the absorption curve.

	LiCl	NaCl	KCl	RbCl
Δ_1	5.75	5.26	4.61	4.50
Δ_2	0.27	0.26	0.37	0.50
Δ	5.48	5.00	4.24	4.00
$B - A$	3.99	6.37	3.56	4.05

ization energies are $F_{3b} = -0.16\alpha_-e^2/d^4$ and $F_{3a} = -(2.22\alpha_+ + 0.41\alpha_-)e^2/d^4$. α_+ and α_- stand for the polarizabilities of the alkali and the halogen ion. The total energy difference between the two transitions A and B comes out to be: $\Delta = 1.032e^2/d - (2.22\alpha_+ + 0.25\alpha_-)e^2/d^4$. If we express the energy in electron-volts, d in 10^{-8} cm and the polarizabilities in 10^{-24} cm³, we obtain:

$$\begin{aligned}\Delta &= 14.8/d - (31.8\alpha_+ + 3.58\alpha_-)/d^4 \\ &= \Delta_1 - \Delta_2.\end{aligned}$$

In Table III we list Δ_1 , Δ_2 , Δ , and the experimental values $B - A$. The latter two are not equal as they should be, but they are about of the right order of magnitude, which is all we can expect in view of the fact that the polarization energies are calculated from a rather crude model and that the exchange energies are neglected altogether.

In the case of the K edge of the K^+ , for which experimental data are available too, a complication arises which makes it difficult to calculate with the above model the separate levels of the trapped states. The terms come out very nearly equal, but since the terms are diagonal

elements of the energy matrix, their difference should be large compared with nondiagonal elements. The nondiagonal elements arise from integrals containing products of series electron wave functions which are concentrated around different ions. Without knowing their values numerically, it is reasonable to assume that they are appreciable, since the overlapping of the wave functions of two series electrons from different ions is more prominent than that of closed shells, which are nearer to their respective nuclei. The overlapping of closed shells, however, is responsible for the repulsive forces between the ions, which balance the ionic attraction.

This is not an argument against the assumption that the observed maxima of absorption in the immediate neighborhood of the edge are due to transitions into trapped states, but only against the method of calculating them. Thus, the apparent failure to get a support of the "trapped states theory" in case of the K edge of K^+ does not invalidate the support that we can draw for this theory from the results in case of the fine structure of the Cl^- edge in the alkali chlorides.

A New Ultraviolet Band System of Silver Iodide

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A new ultraviolet band system of AgI has been photographed in absorption at temperatures 700–900°C. At higher temperatures the system is overlapped by strong continuous absorption, which advances gradually from shorter wave-lengths. The new system lies at 2300Å, i.e., at shorter wave-lengths than the known system, and its lower state vibrational constants agree with those given by Brice for the lower state of the longer wave-length system. The rotational structure and the very small isotope effect are not resolved. The equation for the band heads may be written

$$\begin{aligned}\nu_h &= 44,724 + 152.8(v' + \frac{1}{2}) - 1.1(v' + \frac{1}{2})^2 \\ &\quad - 205.1(v'' + \frac{1}{2}) + 0.43(v'' + \frac{1}{2})^2.\end{aligned}$$

This formula is based upon progressions from $v' = 0$ to $v' = 4$ and from $v'' = 0$ to $v'' = 11$. An additional new band system was found at 2150Å, and the wave numbers of the band heads may be represented by the following formula:

$$\begin{aligned}\nu_h &= 45,487 + 176(v' - b + \frac{1}{2}) - 2.5(v' - b + \frac{1}{2})^2 \\ &\quad - 205(v'' - a + \frac{1}{2}) + (v'' - a + \frac{1}{2})^2;\end{aligned}$$

the values of a and b could not be determined.

INTRODUCTION

FRANCK and Kuhn¹ were the first to observe bands in the spectrum of silver iodide. They

photographed bands in absorption and in resonance in the region 3100–3500Å; overlapping continuous absorption was also reported. Additional bands, diffuse in nature, at longer wave-lengths, and a weak continuum having a maxi-

¹ J. Franck and H. Kuhn, *Zeits. f. Physik* **43**, 164 (1927).