A FURTHER TEST OF THE NISHINA THEORY OF X-RAY ABSORPTION

T H E S I S

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In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

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Pasadena, California

1 9 2 9

S U M M A R Y

Aoyama, Kimura, and Nishina have given a theory for the displacement of the x-ray K_1 absorption edge in chlorides. The theory is derived by carrying out a cyclic process in which a K electron is removed from the chlorine ion in a lattice, followed by the removal of the resulting argon-like Cl^- ion. An attempt is made to keep track of all the energy changes while the ion is being brought back to its original state, and after neglecting small terms the conclusion is reached that the change in absorption frequency with compound, where the compounds have similar crystal structure and chemical bond, should be a linear function of the lattice energy. Four experimental points are plotted to a straight line, but the experimental error is too great and the points lie too close together to justify the conclusion that the experiments check the theory.

For a further test of the theory, more points have been secured by taking x-ray spectrograms of chlorides in which larger absorption edge shifts were to be expected. Lattice energies have been calculated, and the resulting data plotted. The points lie approximately on a straight line, but not in such a way as to check the theory. The extrapolations of all such lines should converge to a common intercept, and in the present case there is a divergence. The Aoyama-Kimura-Nishina work is criticised for the omission from the graph of certain points which lie far from the plotted line and which would cast much doubt on its proper location. In a paper as yet unpublished, Pauling finds theoretical objections to the theory. The conclusion is reached that the theory is not even approximately correct, that it is probably too simple, and that we do not yet know very well the mechanism of the absorbing act or the factors which enter into it.

INTRODUCTION

When a beam of x-rays passes through a slit and is let fall
on the plane surface of a crystal, it is resolved into a spectrum, the
lines of which take positions according to the law, deduced by the Braggs,

$$n\lambda = 2d \sin \theta$$

where n is the order of the spectrum, λ the wave length, d the lattice
constant of the crystal, and θ the angle made by the beam with the crystal
face. Such spectra were first obtained by the Braggs[1]. The spectrum
so obtained may be thought of as two superposed spectra--one consisting
of emission lines, which will be characteristic of the elements composing
the anti-cathode, the other being a continuous spectrum of "white"
radiation, which will be manifest by a general darkening of a photographic
plate. If between the x-ray source and the photographic plate a substance
is interposed in the path of the x-rays, the rays will be partially
absorbed in such a way as to yield another type of spectrum--the absorption
spectrum. This type of spectrum was first observed by de Broglie[2] as
a sudden change in the blackening of the plate. It is now well known
that the intensity of the x-rays which pass through the absorbing body
is a critical function of the frequency--that when a certain definite
frequency is reached the radiation is strongly absorbed, but with
frequency further increasing, the absorption falls off until another critical
frequency is attained. These discontinuities, or "absorption edges,"
have definite wave lengths which are characteristic of the absorbing
substance. Corresponding to the emission spectra, the absorption
spectra may occur in several series, with several edges in a given
series. For some time it was thought that the position of an edge is
a function only of the element to which it is due. Bergengren[3] first

discovered indications that the spectra were influenced also by the chemical combination of the atom, but his investigations were limited in scope and his conclusions erroneous. Lindh[4] continued the study and discovered that the positions of the absorption edges may vary considerably with chemical compound. The greatest single determining factor seems to be the chemical valence of the element. With increasing valence of a given element, the x-ray absorption begins at higher frequencies. Stelling[5] has explained the effect of valence as being due to the screening effect of electrons in external parts of atoms. As an example of the shift in absorption edge we may cite the sulfur compounds. The wave lengths of the principal K edge of a large number of 4-valent inorganic compounds of sulfur are separated on the average by about 8 X.U. from the corresponding edge of 6-valent compounds, and between the 2-valent and 4-valent compounds there is a wave length separation of about 13 X.U. All the substances thus far investigated show in general a similar behavior. There are still other factors influencing the edges, but to a lesser degree. In the sulfates of potassium and strontium, for example, the valence of sulfur is the same, but the edges are about one X.U. apart, due apparently to the different metals. Finally, the crystal lattice structure is known to produce small changes in the position of the edges. In investigating the latter effect it is desirable to work with a single element in several compounds in which it occurs with the same valence, and with similar crystal structure. In the following pages will be described some new work on these small shifts.

THE NATURE OF THE PROBLEM

The present investigation deals with the shifts in the principal K absorption edge of monovalent chlorine in a series of

compounds. These edges are already well known for a number of compounds, from the researches of Lindh[6] and Stelling[7]. Aoyama, Kimura, and Nishina[8] have given a theory which relates the shift in edge to the "Gitterenergie" or lattice energy of the absorbing substance. The theory as developed is limited in its application to chlorides of similar chemical binding and similar crystal structure. If the position of the K_1 edge of some standard substance--say sodium chloride--is taken as a reference, then the other chlorides of the same crystal structure and type of binding will show edges which are displaced with reference to the NaCl edge. According to the theory, this displacement should be a linear function of the lattice energy. The theory is derived by carrying out a cyclic process in which a K electron is removed from the chlorine ion in a lattice, followed by the removal of the resulting argon-like Cl⁻ ion. While the ion is being taken through the cyclic process and brought back to its original state through a series of steps, an attempt is made to follow all the energy changes incident to the process. Since the initial and the final states are the same, an equation may be written for the energy changes. This equation, after dropping two comparatively small terms, which partially cancel each other, takes the form

$$K_{XCl} - K_{Cl-} = U_1 - U_2$$

in which K_{XCl} is the energy required to remove a K electron from the chlorine ion in a lattice, K_{Cl-} the corresponding energy for the free chlorine ion (which is a constant), U_1 the lattice energy, and U_2 the energy of deformation of the lattice and the electron shells. On the assumption of a proportionality between U_1 and U_2 the equation becomes

$$K_{XCl} - K_{Cl-} = a U_1$$

where "a" is a constant. K_{XCl} is supposed to be the energy absorbed when x-rays fall on the lattice. There are good reasons for believing that $U_2 = 0$ in the actual absorbing act, as it takes place too quickly for the establishment of the equilibrium which is assumed in the cyclic process of Nishina and his colleagues. This point was not noted by them, but it would have the effect only of giving the constant "a" the value 1, and hence the line represented by the equation should have the slope 1. The authors of the theory have taken data on the chlorides of sodium, potassium, rubidium, and lithium, and on ammonium chloride--substances for which the theory is supposed to hold sufficiently closely. They have used sodium chloride as a reference material, and for the other substances have taken the shift of the edge from the NaCl value, in ν/R units. Against these values they have plotted the lattice energy, also in ν/R units, and have indeed obtained a straight line. Their curve is shown in Figure 1, below.

Fig. 1
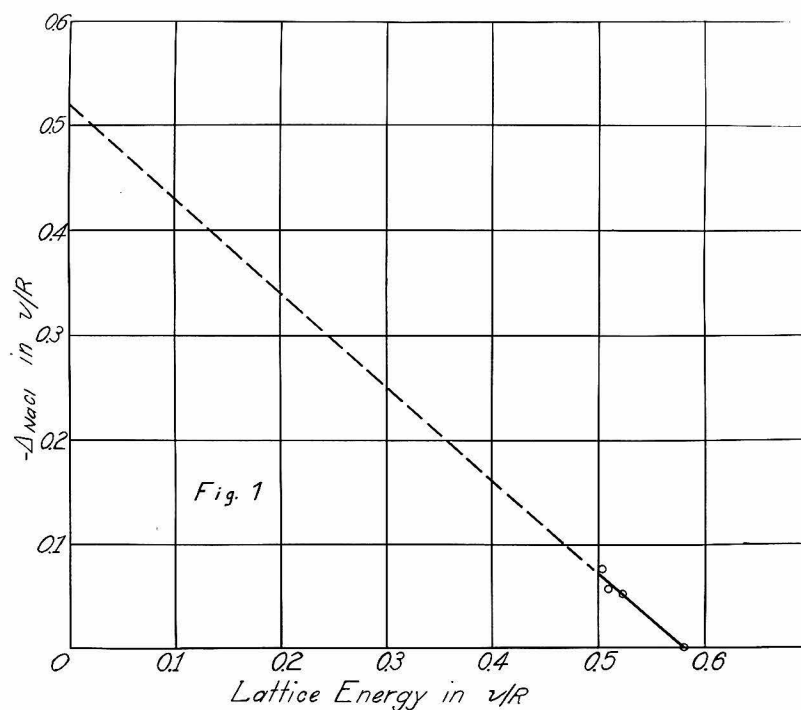
The NaCl point necessarily lies on the line, as it is the reference point. The other three points are closely bunched, and lie not far from the NaCl point. Considering the possibility of experimental error, and the ease with which almost any sort of line can be drawn near closely grouped points, it seemed to the writer that the experimental data were far too meager to justify any conclusions as to the experimental verification of the theory, and that a greater spread of points was therefore desirable. To obtain more points, under the restriction of similar crystal structure and chemical binding, it seemed that compounds similar to ammonium chloride might be used, where the hydrogen atoms are displaced by methyl or ethyl or higher carbon chain groups. A number of x-ray plates were accordingly made, using the substances just metnioned as absorbers, and also with NaCl for reference, and NH_4Cl as a check.

DESCRIPTION OF APPARATUS AND ADJUSTMENTS

The photographs were all taken with a vacuum x-ray spectrograph, similar to that described by Siegbahn in his "Spectroscopy of X-rays," pp 62 ff. This apparatus may be thought of as consisting of two rather distinct parts--a Coolidge x-ray tube, and the spectrograph proper.

The main body of the x-ray tube is hollowed out of a piece of brass, and has two ground cones projecting from it, for the attachment of glass tubes. These glass tubes serve as supports for the cathode and the anti-cathode, both of which may thus be insulated from the rest of the spectrograph if desired. For continuous operation water cooling is necessary for both cathode and target, and as an added precaution the body of the tube was itself channeled, and water

circulated continuously. The target was a copper tube, beveled to about 60°. It was slipped into a loosely fitting constricted neck of the glass tube, and sealed with sealing wax. The position of the target could be adjusted by softening the wax, and slipping the target within the glass tube. The filament distance could be adjusted by two supplementary means. The filament mounting was carried on a brass tube, similar to the target tube, but instead of a wax seal to the insulating glass tube, a ground cone joint was used, to facilitate rapid removal for change of filaments. The brass cone was itself a sleeve, fitting closely to the cylindrical tube, and capable of being sealed at any desired position by sealing wax. This served as a rough adjustment. The filament holder was attached to the cooling tube by tungsten wires of about 1 mm diameter, which could be slipped back and forth in holes drilled in the end of the cooling tube, and fastened by set screws. This served as a convenient fine adjustment. Once a satisfactory filament distance was determined, filaments could be changed without disturbing the adjustment. As the life of a filament is a matter of hours, a convenient method of making and replacing filaments is desirable. Filaments were made of 10-mil tungsten wire, wound first into a conical spiral. The winding was done on a spirally grooved spindle form made from $\frac{1}{4}$" brass rod. The conical spiral was then flattened by heating it to whiteness in a Bunsen flame, and pulling it against sheet asbestos, backed firmly by a metal plate. Several such treatments were usually necessary if the filament was to remain fairly permanently in a flat spiral. One end of the filament was grounded in the water cooling tube, and the other was insulated and led to the outside through an air tight seal. The optimum distance of filament from target is a characteristic of an individual x-ray tube

and its electrodes, and had to be determined experimentally.

The x-ray tube was fastened to the spectrograph proper with solder, a free opening communicating between the two. In front of this opening the slit was placed.

In the center of the bottom of the spectrograph were two coaxial ground cones, mounted vertically. To the internal end of one of these cones was attached an arm the outer extremity of which carried the plate holder, a simple brass frame with spring clamps to hold the plate firmly in place. By means of the cone bearing, the plate holder could be rotated to any desired position. The external end of this cone was rigidly attached to a precision angle scale, and was divided to 5' of arc over a complete circle. With the help of a microscope readings could be made to about 15" of arc. The plate holder and the slit were placed equidistant from the axis of rotation—which is necessary for good sharp lines, especially if the rotating crystal method is to be used.

The mounting of the crystal requires great care, and entails some difficulty. It is first fastened to a brass plate by some sort of wax---beeswax-rosin is good. For a particularly valuable crystal a slower but safer method was used. Beeswax was partially dissolved or softened in carbon bisulfide, and applied to the back of the crystal a little at a time and built up in layers until there was enough backing to stick the beeswax to the metal plate. This procedure obviated the danger of breaking the crystal by the heat of the melted beeswax-rosin. After the crystal is stuck to the metal plate, the plate is fastened with screws to a mounting which permits adjustments in two directions. The first adjustment is to bring the face of the crystal into parallelism with the axis of rotation of

its mounting. A screw device permits the tilting of the plane of the crystal until the desired orientation is reached. To determine when the crystal has the proper tilt, a piece of plane-parallel glass (interferometer plate) is clamped to the crystal face, one end of the glass projecting above the crystal. This glass plate is used as a mirror, in which may be viewed the image of a scale through a telescope set about two meters away, and the position of the cross hair noted. Then the crystal and glass plate are rotated through 180° and the scale again viewed, using the other side of the plate as the mirror. When this rotation produces no shift in position of the cross hair on the scale, the crystal face is parallel to the axis of rotation. It was not possible to view the glass plate directly with a telescope, as the plate was a few centimeters below the top of the spectrograph. A pair of prisms was arranged to overcome this difficulty. These prisms introduced other reflecting surfaces, and in the multiplicity of images visible it was sometimes hard to locate the right one. The next adjustment is to move the crystal parallel to its face until the face wholly contains the axis of rotation. This is accomplished by another auxiliary device which is clamped to the plate holder arm. A fine ivory point is mounted so that it can be moved with fine adjusting screws, either along or perpendicular to its axis. This point is brought into coincidence with the axis of rotation of the plate holder and crystal. When the plate holder revolves, the ivory point moves with it about the same axis. The point is viewed through a microscope, and by means of a scale in the eyepiece the position of no rotation of the tip can be observed. The point being adjusted to this position, the crystal is moved forward by a micrometer screw, a straight dovetail

groove guiding the motion so that the directional orientation of the crystal remains unchanged.   The point and its image in the crystal can be observed simultaneously, and the two are brought toward each other until they just meet, thus completing the crystal adjustment.

The crystal and plate holder must be capable of independent rotation.   This was accomplished by means of the two coaxial ground cones of brass previously mentioned.   The cones were separated by a thin conical sleeve of steel.   To exclude air most effectively, a grease made by the prolonged boiling of vaseline and the addition of finely powdered graphite was found satisfactory.   These cones could be turned from the outside, permitting the setting of plate and crystal without the loss of vacuum.   A degree scale and vernier sufficed for a rough setting of the crystal, which does not require fine adjustment for angle.   The vernier was carried on a rigid arm attached to the same cone which carried the crystal mounting.   The large circular cover (40 cm diameter) of the spectrograph rested on a rubber gasket and was fastened with screws.   This cover had to be removed for loading plates, adjusting slit, and changing crystal orientation.

For slowly rotating the crystal a gear box was used with a reducing ratio of 125,000:1.   This was driven by a small electric motor.   The slow turning of the end gear caused a nut to travel and push the vernier arm, which rotated the crystal through approximately a tenth of a degree per hour.   It was necessary to turn the crystal in order to get homogeneous plates.   With stationary crystal, the plate was covered with streaky marks, due to local irregularities, and these marks were hard to distinguish from lines and edges.

The pumps were of the usual mercury condensation type, with Hyvac fore pump, and pressure was further reduced by a trap, cooled

sometimes with liquid air, sometimes with solid carbon dioxide.

EXPERIMENTAL PROCEDURE

A problem always present in soft x-ray technique is to shut out the light inevitably given off by the x-ray tube without cutting off too much of the x-radiation. Soft x-rays are strongly absorbed by even the thinnest of paper. Several different devices were tried and discarded. One such was the making of thin celluloid films by dissolving celluloid in amyl acetate, and allowing the solvent to evaporate from the thin surface film which forms when a drop of the solution is put on a water surface. These films could be attached to a brass frame, and placed in the path of the light. But it was more difficult to render them effectively opaque to visible light. Attempts were made to use red dye, india ink, and a deposit of soot from burning camphor. The drying of the liquid usually broke the films, and the lamp black coating was hard to control. The films were extremely thin (of the order of a few wave lengths of light) and consequently very fragile, and finally other means were tried. Thoraeus[9] has described a spectrograph in which he interposed a sheet of aluminum foil between the filament and target. This not only shut out the light, but also prevented the deposit of tungsten vapor on the target, and yet permitted electrons from the filament to go through to the target with but slight decrease in velocity. This method seemed very promising, and considerable time and effort was spent on it. But it proved to be unsuccessful in our hands, and Thoraeus himself has apparently abandoned it. We finally made use of three different light absorbing screens—carbon paper, cigarette paper coated with india ink, and blackened celluloid films. All

three gave about the same results. The usual commercial liquid india ink is somewhat gummy and has a tendency to crack or "draw" when it dries. Better to the purpose is Chinese india ink--solid sticks from which a suspension can be prepared by rubbing the sticks on a piece of wetted slate. Also celluloid films (not nearly so thin as those mentioned above) were made by applying a coat of dissolved celluloid to a glass plate, and removing with a razor blade when dry. One or two such films were successfully coated with india ink and gave good results.

The preparation of absorbing screens was also the subject of considerable experimenting. Rubbing the powdered solid into the pores of tissue paper was tried, but it did not adhere very well. Then the crystals were finely pulverized in an agate mortar and made into a thin paste with celluloid dissolved in amyl acetate, and painted onto glass to dry. Some good screens were made in this way, but it is hard to make them homogeneous, and to remove them from the glass without breaking. The paste may also be applied to thin paper, but this increases the thickness of the screen. One of the best methods was to put a thin coat of the celluloid solution on thin (cigarette) paper, and then gently sift the powder on through a fine meshed screen or cloth. This method gave greater homogeneity, and the thickness of the layer was easier to control. Some of the photographs were made with such screens. With care, one side of the paper could be blackened, and the other side coated with the powder. For an ammonium chloride screen, the salt was heated until it sublimed, and by holding blackened paper in the path of the dense cloud ensuing, a deposit of extremely fine particles could be obtained in almost any desired thickness. But the substances we were particularly

interested in---tetramethyl- and tetraethyl ammonium chloride---proved to be entirely too hygroscopic for any such treatment. We finally tried moistening a paper with the concentrated solution, and found that in the evacuating process the salt had dried and left a layer, not of scattered and relatively large crystals, but thin and uniform. The appearance was much like that of the gum on postage stamps. These salt solutions were placed on the unblackened side of carbon paper, and screens so made gave good results.

The best thickness of absorbing material to use for screens has to be determined by experiment for a given material. The general tendency is to make the screen too thick.

The plates used were Eastman Speedway. Eastman X-ray were first tried, but the grain seemed coarser, and no superiority over Speedway could be noticed. On each plate a reference mark was photographed. This mark was made by a fine slit in a narrow piece of brass (about 2 mm wide) which was placed immediately in front of the plate.

It was found that a small dish containing a few grams of phosphorous pentoxide spread out to a large surface and placed in the spectrograph caused the filaments to last much longer. Without the P_2O_5 the life of a filament was about four to ten hours. With it, the life was increased to from thirty to fifty hours. This is evidently due to the absorption of water vapor which is known to have a very destructive effect on tungsten filaments when it is present in even the minutest quantities. It is desirable to have long lived filaments so as not to lose vacuum during the necessarily long exposures.

The length of exposure varied from about 15 to 35 hours. The time required to obtain a good edge seemed to vary according to

absorbing screens and light screens used, as well as with applied
voltage and current in the x-ray tube: Usually a preliminary
plate was made, and from that was inferred the exposure time requisite
to the best results. The voltage used was from fifteen to twenty
thousand. We used an ordinary x-ray transformer, with no rectifying
device. For further work, by all means a good rectifying and wave
smoothing arrangement should be installed. Currents up to fifty
milliamperes were used. With better transformers, two or even three
times that current can be used, at higher voltages, with corresponding
shortening of exposure time.

On all the plates we were interested in measuring the position
of the principal K absorption edge of chlorine. Following Aoyama,
Kimura, and Nishina, sodium chloride was used as a reference substance,
and we observed the shift in position of the chlorine edge of the
other substances from the NaCl position. To obtain this, we measured
the linear shift on the plate. We shall call this shift Δl. To
fit in with the Aoyama-Kimura-Nishina scheme, we wish the corresponding
change in wave number, which we shall call $\Delta \nu$. This was calculated
directly from measurements of Δl and the formula

$$\Delta \nu = - \frac{\cot \theta}{2r\lambda} \Delta l$$

This formula is based on the Bragg relation,

$$n\lambda = 2d \sin \theta \qquad \text{and its derivative}$$

$$n\, d\lambda = 2d \cos \theta \, d\theta, \qquad \text{the relation}$$

$$\nu = \frac{1}{\lambda} \qquad \text{and its derivative}$$

$$d\nu = - \frac{1}{\lambda^2} d\lambda, \qquad \text{and the geometrical relation}$$

$$d\theta = \frac{dl}{2r} \qquad \text{where } r \text{ is the distance from}$$

crystal to plate. For the small shifts obtained, the intrinsic

error due to the use of this formula was entirely negligible.

For convenience in calculating $\triangle(\frac{\nu}{R})$ for the shift from the

sodium chloride value of $\frac{\nu}{R}$, we may compute the coefficient $\frac{\cot \theta}{2\ R r \lambda}$

using the following constants:

θ = 46° 21' 27" (Based on 2d = 6058.08 X.U. for calcite)

R = 109,737 (Rydberg number)

= 4384.0 X.U. (Aoyama-Kimura-Nishina value)

r = 17.981 cm (Direct measurement)

The value of the coefficient is 5.5125, and we now have the simple

formula

$$\triangle \left(\frac{\nu}{R}\right)_{NaCl} = 5.5.25 \triangle l$$

which applies of course only to the special conditions of this

investigation.

The measurement of $\triangle l$ involved the comparison of each plate
with a standard NaCl plate. The edges leave something to be desired
in sharpness, as they appear rather fuzzy under the comparator.
The difficulty of determining the proper location of the edge has
been discussed by Stelling[10]. The ordinary comparator method was
used, supplemented by another method, which will be briefly described.
The two plates to be compared for shift are mounted at right angles
to each other, one of them being fixed to a carriage which can be
moved by a micrometer screw. Beams of light, after passing normally
through the two plates, are made parallel by means of a half silvered
surface between two prisms, and the two beams before entering the
prisms are cut off by straight edges in such a way that any lines or
edges to be compared are viewed directly end to end. The reference

lines can be brought easily and accurately into juxtaposition, and the shift in edge can then be measured directly by turning the micrometer screw until the edges coincide.   If the edges are of about the same degree of fuzziness (and in the present case they appeared to be so) it is no longer necessary to speculate on their proper location.   The method suffers from the difficulty usual in comparators--lack of contrast--but is rapid and direct and permitted the duplication of readings to within about two hundredths mm.   By taking a large number of readings the error was much reduced.   The comparator was made by Dr. R. J. Kennedy of this Institute, and has been used by him for measuring shifts in interference fringes.

When using either type of comparator it was found to be a decided advantage to work in a dark room, shutting out as much stray light as possible.   The use of a green filter also seemed to improve the contrast in some cases.   The sharpest edge obtained was of ammonium chloride.   To give an idea of the degree of uncertainty involved in setting on an edge and on the reference line, the following sample table is introduced:

Plate # 12   NH$_4$Cl

Position of Edge				Reference Mark
65.219 mm	.202	.224	.215	59.046 mm
.214	.215	.221	.217	.050
.199	.227	.219	.212	.047
.233	.196	.231	.220	.045
.201	.228	.212	.238	.050
.229	.221	.227	.222	.048
.210	.224	.212	.224	.044
.223	.220	.227	.209	.047
.205	.228	.210	.207	.046
.215	.211	.194	.215	.049

Mean Value   65.217 mm   59.047 mm

Difference   6.17 mm

Of the above values for edge, 87 % lie within 7.5 % of the mean value, and 75 % are within 5 % of the mean. A more complete tabulation will be given later.

For the lattice energy, the values given by Aoyama, Kimura, and Nishina were used for NaCl and NH_4Cl. Some of these were calculated from the Born formula[11], and the others were derived by Born[12] and Grimm[13] from cyclic processes, using thermochemical constants. The Born formula was also used for calculating the lattice energy of the new substances under consideration. The application of this formula to a compound requires a knowledge of its crystal structure. This structure is known for $N(CH_3)_4Cl$, but not for $N(C_2H_5)_4Cl$ so far as the author could ascertain. However, the structure is known for both the corresponding iodides, and we are thereby enabled to infer what it should be for the chloride with a probability of very little error.

Ammonium chloride and the tetramethyl ammonium halides[14] have a crystal structure very similar to that of cesium chloride. The structures are illustrated in Figs. 2 and 3.
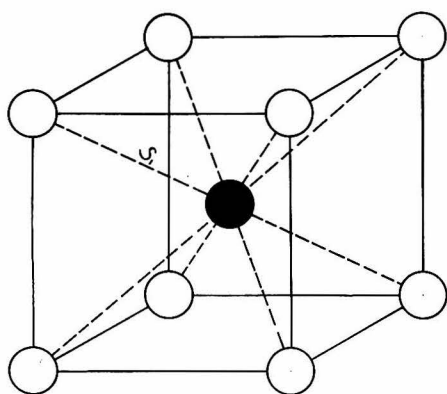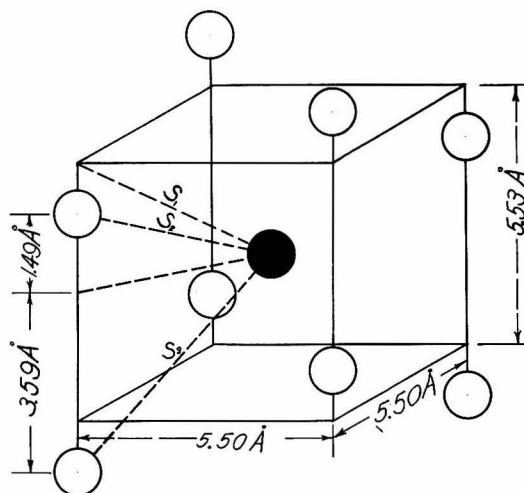

Fig. 2   Cs+   o   Fig. 3

Cl−   •

For cesium chloride[15] the Coulomb energy is

$$U' = \frac{z^2 e^2}{S} 1.7624$$

where S represents the smallest distance between oppositely charged ions, z is the number of unit charges per ion, and e the value of unit charge. The tetramethyl ammonium chloride structure differs slightly from the cubical cesium chloride structure, as will be noted from the figure. From crystal structure data we have, referring to Figure 3,

$$S_1 = 4.77 \ \overset{\circ}{A}$$

$$S_2 = 4.34 \ \overset{\circ}{A}$$

$$S_3 = 5.29 \ \overset{\circ}{A}$$

The formula given above for the energy of cesium chloride may be applied with negligible error to this distorted cesium-chloride-like structure. We show this by calculating the energy of eight chlorine ions with respect to a positive ion, both when the chlorine ions are at the corners of a cube, and when they are in the ammonium chloride position. If the Cl^- were at the corners the energy (for a single cube) would be $8 \ z^2 e^2 / S_1$, where $S_1 = 4.77 \ \overset{\circ}{A}$, or $W = 1.677 \ z^2 e^2$. But for the actual structure we have

$$W = \left(\frac{4}{S_2} + \frac{4}{S_3} \right) z^2 e^2$$

and on substituting for the S values given above,

$$W = 1.675 \ z^2 e^2$$

We therefore see that in our case we may consider the crystal to have the cesium chloride structure, since the results just calculated for W are practically identical. If we then take the energy of the methyl ammonium chloride to be

$$U' = \frac{z^2 e^2}{S} 1.7624$$

the error involved will be of the order of 0.1 %.

We infer the structure of tetraethyl ammonium chloride from that known for the corresponding iodide[16] and the methyl chloride and iodide, by assuming a proportionality. Since S_1 for $N(CH_3)_4I$ is 4.96 Å, and for $N(C_2H_5)_4I$ is approximately 5.72 Å, then on the foregoing assumption, recalling that S_1 for the methyl chloride is 4.77 Å, we get for $N(C_2H_5)_4Cl$

$$S_1 = \left(\frac{572}{496}\right) 4.77 \text{ Å} = 5.50 \text{ Å}$$

We are now in a position to calculate the energy for the methyl and ethyl ammonium chlorides. The Coulomb energy should be modified by multiplying it by the factor $(1 - 1/9)$, in order to get the lattice energy[17], the repulsion exponent being taken as 9.

Lattice Energy of $N(CH_3)_4Cl$

$$z = 1$$

$$S_1 = 4.77 \times 10^{-8} \text{ cm}$$

$$U_1 = \frac{(4.774)^2 \times 10^{-20} \times 1.767 \times 8}{4.77 \times 10^{-8} \times 9} \text{ ergs}$$

$$= 8.43 \times 10^{-12} \text{ ergs} = \underline{0.351} \quad \nu/R \text{ units}$$

Lattice Energy of $N(C_2H_5)_4Cl$

$$z = 1$$

$$S_1 = 5.50 \times 10^{-8} \text{ cm}$$

$$U_1 = \frac{(4.774)^2 \times 10^{-20} \times 1.767 \times 8}{5.50 \times 10^{-8} \times 9} \text{ ergs}$$

$$= 6.48 \times 10^{-12} \text{ ergs} = \underline{0.300} \quad \nu/R \text{ units}$$

We may now summarize the experimental data in the following table:

Substance	No. of Plates	No. of Readings	$\triangle\lambda_{NaCl}$ mm	$\triangle\left(\dfrac{\nu}{R}\right)_{NaCl}$	Lattice Energy $\dfrac{\nu}{R}$
NaCl	2	100	----	----	0.581
NH_4Cl	2	40	0.102	0.056	.504
$N(CH_3)_4Cl$	3	130	.17	.094	.351
$N(C_2H_5)_4Cl$	2	140	.22	.121	.300

The above values are plotted in Figure 4, along with the previously given plot of Aoyama, Kimura, and Nishina.
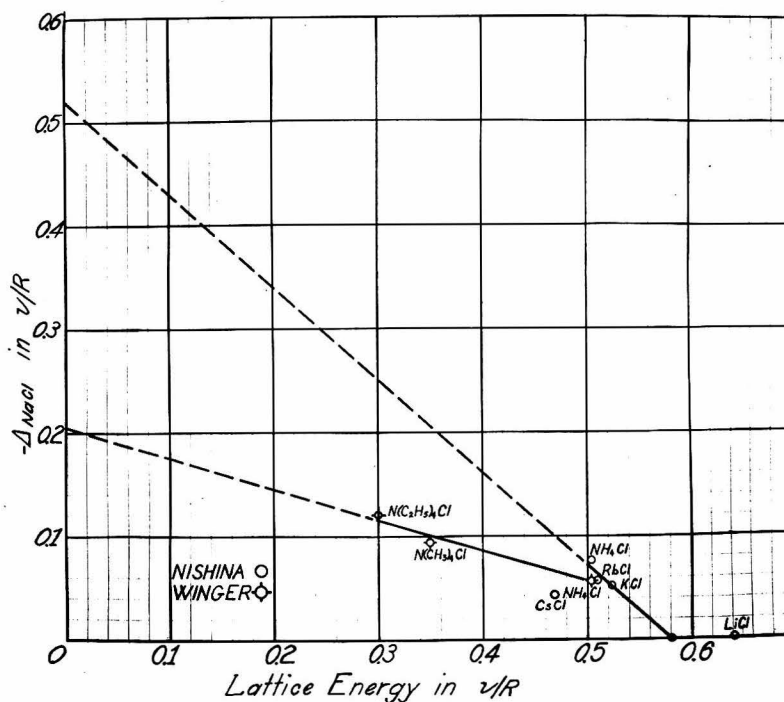

Fig. 4

D I S C U S S I O N   O F   R E S U L T S

It will be noticed at once that the new results fall somewhat off the straight line drawn by the former experimenters. Also, that their point for NH_4Cl is not checked. The difference between the two

NH_4Cl values, however, lies within the experimental error allowed by
Aoyama, Kimura, and Nishina. The shifts in edge measured are so
small for the substances they investigated that there is a very large
uncertainty in the location of their points. The new points
represent well over twice the range of displacement, and the
observational error should be reduced correspondingly. But it
would seem unduly optimistic to claim an accuracy in measurement
greater than one or two hundredths mm, which is from 10 to 20 % of
the quantity measured in the present case, and rather more than that
for the other observers, considering their small shifts, and the lower
dispersion given by their spectrograph.

In Fig. 4 appear two Aoyama-Kimura-Nishina points which
did not appear in their published graph of Fig. 1. These points
correspond to cesium and lithium chloride, and inasmuch as values
were published for those compounds, it is not easy to see why they
were not included in the graph. Cesium chloride is mentioned
among a group of other chlorides which were not plotted on the ground
that those compounds have either a different crystal structure or a
different kind of chemical bond from NaCl. But on that basis, there
is not even as much justification for their plotting of NH_4Cl, since
its crystal structure is slightly further from NaCl than is CsCl--
at least in the form at which it crystallizes at usual temperatures--
whereas CsCl has the same kind of bond as NaCl. The CsCl point lies
far from the line plotted by Aoyama, Kimura, and Nishina. Still more
difficult to understand is why the LiCl point was not plotted. Both
in crystal structure and in chemical binding it is a perfectly
orthodox member of the alkali group, and deserves the same consideration
as any of the others. When we take this point into account, much

uncertainty is thrown on the proper slope of the line.

The author has plotted his points also on a straight line, which has only about half as steep a slope as the Aoyama-Kimura-Nishina line. Moreover, all these points meet the conditions of the Nishina theory by being all of the same crystal structure and chemical binding, although they differ somewhat from the alkali group. This might be interpreted as a confirmation of the theory, as a somewhat different slope is to be expected, but there is so much similarity in the compounds that the difference should not be any way near the magnitude observed. There is a further serious flaw. The extrapolation of the lines to $U_1 = 0$ should give for the intercept the difference between the absorption frequency of free Cl^- ion and that of NaCl, hence all the possible lines should converge to the same intercept. Instead, the lines seem to diverge. Finally, in an unpublished paper, Pauling finds theoretical objections to the theory.

In view of the results above, it is the opinion of the author that the Aoyama-Kimura-Nishina theory is no longer tenable. It seems to be too simple, and the evidence indicates that at least some very important factors have been left out of consideration. We do not as yet know very well the mechanism of the absorbing act, nor the factors entering into it. A comprehensive theory will depend on more experimental data.

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