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PHOTO-IONIZATION IN LIQUIDS AND CRYSTALS AND THE DEPENDENCE OF THE FREQUENCY OF X-RAY ABSORPTION EDGES ON CHEMICAL CONSTITUTION

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ABSTRACT

The mechanism giving rise to the electron affinity E of a liquid or a crystal is discussed, and it is shown that the relation

$$E \cong \alpha W_0$$

should hold, in which α is a numerical factor lying between 1/2 and 1, and W_0, the average potential energy of a free electron in the liquid or crystal (with the sign changed), is related to the specific diamagnetic susceptibility of the liquid or crystal by the equation

$$W_0 = -6.43 \times 10^6 \kappa \text{ (in volt-electrons)}.$$

Franck and Scheibe's interpretation of the ultra-violet absorption of aqueous solutions of halides as showing photo-ionization of halide ions is used in deducing a value of 3.81 v.e. for the electron affinity of water, corresponding to $\alpha = 0.82$.

Observed values of long wave-length limits for ultra-violet absorption leading to photo-ionization in crystals of five alkali halides lead to electron affinities for the crystals corresponding to values of α of about 0.80.

Assuming the relation $E = 0.80\ W_0$ to hold in general it is found that the diamagnetic susceptibilities of the silver halides are of the correct order of magnitude to give electron affinities of the crystals sufficient to allow photo-ionization of the halide ions by visible light. This is presumably the primary process in photosensitization of the photographic plate.

The equation

$$h\nu_{\text{abs}} = h\nu_0 + e\Phi^{(1)} - E_{\text{crystal}},$$

in which ν_{abs} is the x-ray absorption edge of an ion in a crystal, ν_0 that for a free ion, $\Phi^{(1)}$ the electrostatic potential at the center of the ion due to surrounding ions, and E_{crystal} is given by $E \cong 0.80\ W_0$, is used to predict shifts in the K edge of chlorine in various crystals and of potassium in its halides. The predicted shifts agree well with those observed for the series LiCl, NaCl, KCl, RbCl and KF, KCl, KBr, KI, supporting the contention that the factors of importance in producing shifts of the edges in these cases are the electrostatic potential and the electron affinity of the crystals.

I. INTRODUCTION

A PHYSICAL concept of great importance for the interpretation of many phenomena has been recently introduced by Sommerfeld.[1] This is the so-called *outer field*, or, to use what seems a better name, the *average potential* within a condensed substance. In Sommerfeld's electron theory of metals the energy of a metallic electron or "free" electron is represented

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[1] A. Sommerfeld, Naturwiss. **15**, 825 (1927).

as the difference of two energy quantities, $W_i - W_0$. W_0 is the average potential energy of the electron as it moves around in the metal, and W_i is its average kinetic energy. W_0 is equal to eV_0, where V_0 is the average potential within the metal.

Bethe[2] has obtained a theoretical expression for the average potential in a liquid or solid substance; it is

$$V_0 = \frac{2\pi e N}{3v} \sum_k \overline{r_k^2}, \tag{1}$$

in which

$$\overline{r_k^2} = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^2 \psi_k \psi_k^* r^2 \sin\theta \, dr d\theta d\phi. \tag{2}$$

Here r, θ, and ϕ are the spatial polar coordinates of an electron in an atom relative to the nucleus, so that $\overline{r^2}_k$ is the quantum mechanics average value of r^2 for the kth electron. The sum is to be taken over all the electrons in an atom. N is Avogadro's number and v is the molal volume.[3]

Rosenfeld[4] has pointed out that V_0 for a given substance is related to its specific diamagnetic susceptibility. The Pauli formula for the molal diamagnetic susceptibility is

$$\chi = -\frac{Ne^2}{6m_0c^2} \sum_k \overline{r_k^2}, \tag{3}$$

which when combined with Eq. (1) gives

$$V_0 = -\frac{4\pi m_0 c^2 \chi}{ev}, \tag{4}$$

or, on writing in place of χ/v the specific susceptibility κ and introducing the numerical value of the constants,

$$\begin{aligned} V_0 &= -6.43 \times 10^6 \kappa \quad \text{(in volts)} \\ W_0 &= -6.43 \times 10^6 \kappa \quad \text{(in volt-electrons)}. \end{aligned} \tag{5}$$

Thus a knowledge of the diamagnetic susceptibility of a liquid or solid substance permits the prediction of the average potential energy of a free electron in the substance. The total energy of the electron will be $T_a - W_0$, in which T_a is the average kinetic energy of the electron. It is probable that even in the lowest state T_a is not zero for a free electron in, say, a

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[2] H. Bethe, Ann. d. Physik **87**, 55 (1928).

[3] Bethe applied this formula in evaluating V_0 for nickel, obtaining $\overline{r_k^2}$ by the use of screening constants given by L. Pauling, Proc. Roy. Soc. London **A114**, 181 (1927). He used the wrong constants, however; introduction of the correct diamagnetism screening constants in his formula leads to $V_0 = 16.38$ volts, which is in better agreement with experiment than the value of 18.93 volts which he obtained.

[4] L. Rosenfeld, Naturwiss. **17**, 49 (1929).

crystal of sodium chloride. The electron as it wanders from ion to ion penetrates into each ion, traversing an orbit which is in part similar to a Kepler orbit. For a Kepler orbit T_a is equal to one-half the average potential energy, with the sign changed; that is, to $\frac{1}{2}W_0$. On the other hand an electron moving in a region of constant potential, such as Sommerfeld assumes in his electron theory of metals, has in the lowest state $T_a=0$. Hence the total energy of a free electron in the lowest state is to be expected to lie somewhere between $-W_0$ and $-\frac{1}{2}W_0$; in other words, the electron affinity E of the liquid or crystal should lie between $\frac{1}{2}W_0$ and W_0. It will be shown in the following sections that a number of observed phenomena indicate that E is uniformly equal to about 0.80 W_0.

2. PHOTO-IONIZATION OF HALIDE IONS IN AQUEOUS SOLUTION

Franck and Scheibe[5] have interpreted the absorption of light in the far ultra-violet region by aqueous solutions containing halide ions as resulting in the removal of an electron from a halide ion. By means of a calculation similar to the following one they evaluated the electron affinity of water as about 18.5 Cal/mole, or 0.8 v.e. Accepting their interpretation of the phenomenon in the main, but introducing a significant change, we shall obtain 88 Cal/mole or 3.8 v.e.

Both the initial state and the final state are different for a free halogen ion in aqueous solution. The final state, consisting of a halogen atom and an electron, lies lower by an amount E_{H_2O} equal to the electron affinity of water. It is assumed here that the free electron is in its lowest state; hence the absorption frequency which corresponds is that of the long wave-length limit of absorption.[6] In addition the upper level is shifted by an amount equal to the heat of hydration of the neutral halogen atom, estimated by Franck and Scheibe at 5 Cal/mole. We shall neglect this quantity.

The lower level is shifted by an amount equal to the potential energy of the electron in the electrical field of the water dipoles about the ion. The following argument shows that this is equal to twice the contribution of the water dipoles to the heat of hydration of the halide ion. Let $\beta\epsilon$ be the potential produced at the center of the ion by the charge ϵ. The work done in adding the element of charge $d\epsilon$ to the charge already present is then $\beta\epsilon d\epsilon$, and the total work involved in moving a charge e from a region outside the liquid to the liquid is $\int_0^e\beta\epsilon d\epsilon=\frac{1}{2}\beta\epsilon^2$. But the potential energy of the charge e in the potential βe due to the surrounding dipoles is βe^2, and this much energy must be supplied if the charge is to be removed so rapidly as not to allow the water dipoles time for reorientation. Since the hydration energy of a halide ion is due almost entirely to orientation of the water dipoles (the contribution of electronic deformation composing only about 3 percent of the dielectric constant), we may take $2H_{X^-}$ as the shift of the lower level.[7]

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[5] J. Franck and G. Scheibe, Zeits. f. physik. Chemie **139**, 22 (1928).

[6] Franck and Scheibe made their calculation for the maximum in the absorption curve.

[7] As a matter of convenience only this entire energy quantity $2H_{X^-}$ is considered as changing the lower level. This is equivalent to considering the surrounding water dipoles not

Thus we obtain the equation

$$E_X = h\nu + E_{H_2O} - 2H_{X^-}\,, \tag{6}$$

in which E_X is the electron affinity of a free halogen atom. In Table I are given values of E_X calculated by Born's method, but with the use of the thermal data given in the International Critical Tables.[8] The crystal energies were obtained from the Born equation, n being placed equal to 9 throughout. For H_x Webb's values[9] are taken, and the $h\nu$ values are from Franck and Scheibe's published curves.

TABLE I. *Photo-ionization of dissolved halide ions.*

	E_X	H_X	$h\nu$	E_{H_2O}
Cl^-	90 Cal/mole	70 Cal/mole	138 Cal/mole	92 Cal/mole
Br^-	81	66	126	87
I^-	72	61	108	86

The agreement among the three values for the electron affinity of water is satisfactory. The average value is 88 Cal/mole or 3.81 v.e.

The introduction in Eq. (5) of the known specific magnetic susceptibility of water, $\chi = -0.72\times10^{-6}$, leads to $W_0 = 4.63$ v.e. Hence E_{H_2O} is equal to about 0.82 W_0; this fraction is entirely reasonable in the light of the previous discussion.

3. PHOTO-IONIZATION IN CRYSTALS

A similar treatment can be given the ultra-violet absorption in crystals such as the alkali halides. Here the arrangement of ions about a given ion produces a potential $\Phi^{(1)}$ at the center of that ion; and the energy $e\Phi^{(1)}$ is required to remove an electron from this potential.[10] In the case of simple crystals this energy is equal in magnitude to the electrostatic part of the crystal energy per stoichiometric molecule, being given by the equation

$$e\Phi^{(1)} = \pm Ae^2/R \tag{7}$$

in which R is the distance between adjacent ions and A is the Madelung constant, of the value 1.7476 for the sodium chloride arrangement and 1.7624 for the caesium chloride arrangement. The plus sign is to be used for an anion, the minus sign for a cation.

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as part of the system but as a mechanism producing a field. It would be more strictly correct to include the water dipoles in the system, in which case the lower level would be shifted by the amount H_{X^-}, and the upper level by the amount $-H_{X^-}$, leading to Eq. (6) unchanged.

Franck and Scheibe, instead of using $2H_{X^-}$ in Eq. (6), introduced $H_{X^-}+P$, giving P an estimated value of 7.5 Cal/mole. I feel, however, that the argument given above shows that P is nearly equal to H_{X^-}. This difference is largely responsible for the small value of the heat of hydration of the electron found by them.

[8] Born's values are $E_{Cl^-} = 86$, $E_{Br^-} = 86$, $E_{I^-} = 79$.

[9] T. J. Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

In analogy with Eq. (6), the minimum frequency leading to ionization of the anion in a crystal should be given by the equation

$$h\nu = E_X + e\Phi^{(1)} - E_{\text{crystal}}, \tag{8}$$

in which E_{crystal} is the electron affinity of the crystal. Ultra-violet absorption has been observed in the alkali halides listed in Table II; the long wavelength limits lead on substitution in Eq. (8) to the values of E_{crystal} given in the table. There are also given values of W_0 calculated by Eq. (5) from the observed specific diamagnetic susceptibilities of the crystals. *In each case* E_{crystal} *is equal to about 0.80* W_0. The agreement with the result found for water is striking, and suggests that the following approximate relation holds in general:

TABLE II. *The photo-ionization of halide crystals.*

Crystal	$h\nu$*	E_X	$e\Phi^{(1)}$	E_{crystal}	$-\chi\cdot10^6$**	W_0	E_{crystal}/W_0
NaCl	7.11 v.e.	3.90 v.e.	8.90 v.e.	5.69 v.e.	29	7.3 v.e.	0.82
KCl	6.81	3.90	7.98	5.07	38	6.8	0.78
RbCl	6.51	3.90	7.65	5.04	43	6.4	0.79
KBr	5.98	3.51	7.59	5.12	45	6.7	0.77
KI	4.94	3.12	7.11	5.29	58	7.0	0.76

* R. Hilsch, Zeits. f. Physik **44,** 421, 860 (1927).

** These values are averages of those in Landolt-Börnstein and those given by P. Pascal, C.r. **158,** 37 (1914).

$$E_{\text{crystal or liquid}} \cong 0.80\ W_0 \tag{9}$$

This relation is made the basis of the discussion of the rest of this paper.

4. THE PHOTO-SENSITIZATION OF THE SILVER HALIDES

It was suggested in 1921 by Fajans[11] and by Sheppard and Trivelli[12] that the primary process in the photo-sensitization of the silver halides is the expulsion by radiation of an electron from a halide ion; later the electron can unite with a silver ion to form a neutral silver atom. It has long been recognized that the quantum must supply energy not only to remove the electron from the halide ion itself, but also from the potential $\Phi^{(1)}$, and various subterfuges have been resorted to in order to permit a quantum of small energy to do a large amount of work.[13] The way out of the difficulty is seen from Eq. (8). *The electron affinity of the crystal helps in the process of photo-*

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[10] Some justification for assuming the electron to be in a region of effective potential equal to that at the center of the ion is provided by Gauss's mean theorem, which states that the average value of the potential over a sphere not including charges producing the potential is equal to the potential at the center of the sphere. The first order perturbation energy for an electron in a state characterized by a spherically symmetrical eigenfunction would then be just $-e\Phi^{(1)}$.

[11] K. Fajans, Chem. Zent. p. 666, (1921).

[12] S. E. Sheppard and A. P. H. Trivelli, Phot. J. **61,** 403 (1921).

[13] See, for example, S. E. Sheppard and W. Vanselow, J. Phys. Chem. **33,** 250 (1929).

ionization. In the silver halides the term $e\Phi^1$ is as large as in the alkali halides; but the high molal diamagnetic susceptibility of the silver ion increases W_0 and hence E_{crystal} to such an extent as to throw the region of absorption and photo-ionization into the visible.

In verifying Eq. (8) together with Eqs. (5) and (9) the most doubtful quantity is the diamagnetic susceptibility. Hence we may use these equations to obtain values of χ, which may then be compared with what experimental values there are. In Table III the results of such a calculation are given. There is satisfactory agreement in order of magnitude between the calculated values of χ and the observed ones. This shows that the mechanism which we have postulated suffices to account in the main for the phenomenon; the electron affinity of the crystal is of the right order of magnitude to provide the energy needed to allow photo-ionization of the halide ion by visible light. Other effects such as deformation are probably also operative but of minor significance (see the discussion in the following section).

TABLE III. *Photo-ionization of the silver halides.*

	λ_{max}	$h\nu$	$e\Phi^{(1)}$	E_{crystal}	$-\chi\cdot 10^6$*	$-\chi\cdot 10^6$observed	
AgCl	4000A.	2.93 v.e.	9.03 v.e.	10.00 v.e.	49.9	40**	51***
AgBr	4400	2.67	8.68	9.52	53.6	49	61
Ag I	4500	2.61	8.35	8.86	55.7	68	75

* From Eqs. (5) and (8).
** From Stefan Meyer, quoted in Londolt-Börnstein.
*** From P. Pascal, C.r. **158,** 37 (1914).

5. X-RAY ABSORPTION EDGES IN VARIOUS CRYSTALS

An equation similar to Eq. (8); namely,

$$h\nu_{\text{abs}} = h\nu_0 + e\Phi^{(1)} - E_{\text{crystal}}, \tag{10}$$

is applicable to the case when an *inner* electron is removed from an ion in a crystal; and as a result of variations in the quantity $e\Phi^{(1)} - E_{\text{crystal}}$ the frequency ν_{abs} of the corresponding x-ray absorption edge will vary from crystal to crystal. (In this equation ν_0 represents the absorption frequency for a free ion.)

The most striking qualitative deduction from this equation is the difference in behavior predicted for anions and cations. $\Phi^{(1)}$ is positive for anions and negative for cations, while E_{crystal} has the same effect for both anions and cations; and as a result the behavior of the chlorine K absorption edge in the alkali chlorides, for example, is quite different from that of the potassium K edge in the potassium halides.

In Table IV are given calculated values of $\Delta\lambda$, the shift in X.U. from the K absorption edge for a free chloride ion, obtained from the introduction of $e\Phi^{(1)}$ and E_{crystal} in Eq. 10. Values of E_{crystal} were calculated from the diamagnetic susceptibility with the use of Eqs. (5) and (8). The agreement between the calculated values of $\Delta\lambda_{\text{LiCl}}$ and the observed ones for the series of crystals LiCl, NaCl, KCl, RbCl is excellent, in view of the inaccuracy of both the theoretical and experimental figures,[14] and justifies the belief that the two factors of significance for the absorption edge shift in this series are the crystal potential and the electron affinity of the crystal. In NH_4Cl, CsCl, CuCl, and AgCl the agreement is not good. A small change (20 percent) in χ would suffice to remove the discrepancies; but it is probable that other factors are of significance here.

TABLE IV. *The K absorption edge of chlorine in various chlorides.* $\lambda_{Cl^- \text{free}} = 4389.3$ X. U

Crystal	Structure	$-\chi \cdot 10^6$*	E_{crystal}	$e\Phi^{(1)}$	$\Delta\lambda$	$\Delta\lambda_{LiCl}$	$\Delta\lambda_{LiCl}$ observed**
LiCl	Sodium chloride	25	6.3 v.e.	9.77 v.e.	−5.5 X.U.	0 x.u.	0 X.U.
NaCl	" "	29	5.6	8.90	−5.2	0.3	0.1
KCl	" "	38	5.2	7.98	−4.3	1.2	1.3
RbCl	" "	43	5.1	7.65	−4.0	1.5	1.4
NH_4Cl	Cesium chloride	38	5.6	7.56	−3.1	2.4	1.8
CsCl	" "	48	5.9	7.09	−1.9	3.6	1.1
CuCl	Sphalerite	38	7.4	9.88	−3.9	1.6	0.3
AgCl	Sodium chloride	45	9.0	9.03	−0.1	5.3	2.6

* Averages from Landolt-Börnstein and Pascal.
** From O. Stelling, Zeits. f. Physik **50**, 506 (1928).

In Table V a similar treatment is given the potassium *K* edge in the potassium halides. In contradistinction to the chlorine *K* edge, which showed a pronounced shift from crystal to crystal, the theory requires that the potassium edge lie at about the same wave-length in the four halides. This is actually observed. The qualitative explanation of this result is the following. In the series of potassium halides $e\Phi^{(1)}$ decreases in absolute value and E_{crystal} increases as the interionic distance increases, the magnitude of the two changes being about the same. The sum of the absolute values is of significance here, and this sum remains nearly constant, so that there results the approximate constancy of the absorption frequency.

TABLE V. *The K absorption edge of potassium in various halides.* $\lambda\ {}^{+}{}_{free} = 3415.3$ X.U.

Crystal	$-\chi \cdot 10^6$*	E_{crystal}	$e\Phi^{(1)}$	$\Delta\lambda$	$\Delta\lambda_{KF}$	$\Delta\lambda_{KF}$ observed**
KF	23	3.6 v.e.	−9.39 v.e.	12.3 X.U.	0 X.U.	0
KCl	38	5.2	−7.97	12.5	0.2	0.2
KBr	45	5.3	−7.60	12.3	0.0	0.2
KI	58	5.6	−7.10	12.1	−0.2	0

* Averages from Landolt-Börnstein and Pascal.
** O. Stelling, Zeits. f. Physik **50**, 506 (1928).

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[14] The experimental values have a probable error of about ±0.1 X.U. The principal uncertainty in the theoretical values arises from the diamagnetic susceptibilities, which in the best cases (LiCl, NaCl, KCl, RbCl, the potassium halides) are probably accurate to 5 percent. This gives an error in the calculated wave-length shifts of ±0.4 X.U., so that for these four chlorides and the four potassium halides the observed and calculated shifts agree within the limit of error.

The values of χ given in the table for NH_4Cl, CuCl, and AgCl were obtained by adding Pascal's atomic susceptibilities, so that they are subject to still greater error.

The discussion of the theory can be combined with the comparison with theories previously advanced in explanation of the dependence of the absorpe tion frequency of an element on the nature of the chemical compound. Th- proposal that this resulted from a variation in external screening due to the outer electrons of the atom and to ions about it was first made by Wentzel,[15] and discussed further by Ray[16] and Coster.[17] In the case of a crystal this effect is just that which we have treated by the introduction of the term $e\Phi^{(1)}$, which can be considered as the contribution of the external screening of the ions about the ion from which an electron is removed. This term must necessarily be introduced in any theory of the difference in absorption frequency for a free ion and an ion in a crystal. Despite his, it was omitted in a following treatment. Stelling[18] considered only the effect of the deformation of the outer electron shells of an ion or atom by surrounding ions or atoms. His results can be summarized in the following statement, quoted by Aoyama, Kimura, and Nishina: "As the deformation of the negative ions increases, the corresponding absorption edge becomes harder (shifts to shorter wave-lengths); deformation of the positive ions has the opposite effect."

The effect of the electrostatic action of surrounding ions in ionic crystals was again recognized by Aoyama, Kimura, and Nishina,[19] who attempted to explain the observed shifts by this effect alone.

The theory which we have developed can be considered as an extension of that of Aoyama, Kimura, and Nishina. It differs from theirs on two points. They took into consideration the effect of the changed positions of the ions in a crystal when the attraction of a negative ion is eliminated by the removal of a photoelectron. This is incorrect, however, for in the very rapid process of the absorption of a quantum of radiation by an electron the final state of the electron is not the equilibrium state of the entire system, but rather a quantized electronic level for the system with the atomic nuclei in their original positions. The conception that the nuclei remain practically stationary during an electronic transition was introduced originally by Franck[20] in the consideration of band spectra, and applied by Franck and Scheibe[5] in the photo-ionization of a halide ion in aqueous solution; discussions on the basis of the quantum mechanics have been given by Born and Oppenheimer[21] and by Condon.[22] It is evident that these considerations apply also to photo-ionization of an ion in a crysta . The second point of difference between our theory and that of Aoyama, Kimura, and Nishina is that we take into consideration the difference in energy of the final state for an ion in a crystal and a free ion. This leads to the introduction of the

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[15] G. Wentzel, Naturwiss. **10,** 464 (1922).

[16] B. B. Ray, Phil. Mag. **50,** 505 (1925).

[17] D. Coster, Zeits. f. Physik **25,** 83 (1924).

[18] O. Stelling, Zeits. f. anorg. Chemie **131,** 48 (1923); Zeits. f. physik Chemie **117,** 161, 175, 194 (1925); Ber. d. D. Chem. Ges. **60,** 650 (1927).

[19] S. Aoyama, K. Kimura, and Y. Nishina, Zeits. f. Physik **44,** 810 (1927).

[20] J. Franck, Trans. Faraday Soc. **21,** 536 (1925).

[21] M. Born and J. R. Oppenheimer, Ann. d. Physik **84,** 457 (1927).

[22] E. U. Condon, Phys. Rev. **32,** 858 (1928).

electron affinity of the crystal, which we calculate with the aid of values of the diamagnetic susceptibility.

The two factors which we have taken into account, the electrostatic crystal potential and the electron affinity of the crystal, must be included in any theory of the x-ray absorption frequency in ionic crystals. We have applied it to crystals in which we expect other effects to be of minor significance—univalent chlorides and potassium halides—and have found quantitative agreement for the two series LiCl, NaCl, KCl, RbCl and KF, KCl, KBr, and KI. Hence we are allowed to contend that in these cases other effects are negligible, and that in particular deformation phenomena can be ignored. This is in agreement with the success attending previous efforts[23] to account for the properties of the alkali halides without the use of the concept of deformation, which is undesirable on account of the present impossibility of giving it quantitative application.

In NH_4Cl and CsCl, crystals with a structure other than the sodium chloride structure, the agreement with experiment is not very good. While this may be due in part to error in the values of χ assumed, it is probable that the crystal structure is also in some degree responsible. Thus our assumption that $E_{\mathrm{crystal}} = 0.80 W_0$ may not be universally applicable; it is conceivable that the numerical factor may vary from structure to structure.

In CuCl and AgCl the cation is an eighteen-shell ion, and as a consequence is expected to exert a large deforming action on the outer electrons of neighboring anions. The deformation will reduce the external screening of the outer electrons of the anion, and so will cause a shift to shorter wavelengths. This effect is to be added to those already considered. Some idea of its magnitude can be obtained from a discussion of the crystal energy. The crystal energy of AgCl as obtained thermochemically is about 1 v.e. greater than that given by the Born formula, based on a lattice of non-deformed ions. This suggests that a similar energy change $h\Delta\nu$ is to be expected, which corresponds to $\Delta\lambda = -2$X.U., about. Just such a shift is required to cause agreement between the calculated values of $\Delta\lambda_{\mathrm{LiCl}}$ and the observed values. It seems probable that a measurable deformation effect in addition to the effect of the crystal potential and the crystal electron affinity is to be anticipated in every crystal containing a deformable anion and an eighteen-shell cation.

Fajans, in the effort to support Stelling's contention that deformation is responsible for shifts in absorption edges, has pointed out the existence of an analogy between shifts in x-ray absorption edges and variations in the mole refraction of crystals. Having found empirically that changes in the mole refraction in a series of similar ionic crystals vary inversely as the fourth power of the interionic distance, he has shown that a similar relation seems to hold approximately for x-ray absorption edge shifts. From this he has drawn the following conclusion:[24] "The dependence of changes of the ionic refraction on a high (4th) power of the interionic distance is considered a

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[23] Linus Pauling, Zeits. f. Krist. **67,** 363 (1928); J. Am. Chem. Soc. **49,** 765 (1928).

[24] K. Fajans, Zeits. f. Physik **50,** 531 (1928).

sign that these changes represent an attendant phenomenon of the mutual *polarization (deformation) of the ions in the lattice.* Should the validity of the same power law be further substantiated for the changes in the x-ray spectrum also, it would be possible to interpret these changes in the same way, and consequently to consider them, as has already been done by Stelling on the basis of qualitative relations, as well as many other properties as a proof that the ions in the lattice deform each other."

Accepting the analogy between changes in mole refraction and shifts of absorption edges, we can still reject the conclusion that these effects are due to polarization or deformation of the ions in the crystal. The crystal potential term $e\Phi^{(1)}$ and the electron affinity E_{crystal} of a crystal, in addition to producing a shift in the x-ray absorption edge of the anion, also change the position of the ultra-violet absorption of the anion, as was discussed in Section 3. Since it is this absorption frequency which determines the essential features of the dispersion of light by the crystal, as was shown by Herzfeld and Wulf,[25] the analogy becomes evident. *But the changes in both mole refraction (that is in the dispersion formula) and x-ray absorption frequency result from a cause independent of deformation of ions in the crystal; namely, from the crystal potential and the electron affinity of the crystal.* Neither phenomenon need be interpreted as showing polarization or deformation of unexcited ions in the crystal.

The classically non-existent phenomenon of two ions identical in their immediate environment having different mole refraction values and dispersion curves is easily understandable in the quantum mechanics. The quantum mechanical dispersion formula involves terms having as denominators $\nu^2-\nu_i^2$, where ν is the frequency of light striking the ion and ν_i a characteristic frequency, equal to $(1/h)(W_i-W_0)$, with W_i the energy of the ion in an excited state and W_0 its energy in the normal state. The normal state depends essentially on the potential field in the immediate neighborhood of the ion, which may not be changed much by introducing the ion into a crystal, but the excited states, in particular states in which an electron is removed from the ion, are affected very much by the addition of a potential such as the crystal potential. Thus the introduction of an ion in a crystal changes the quantity $W_{\text{ionized}}-W_0$ by the amount $e\Phi^{(1)}-E_{\text{crystal}}$; as a result the dispersion formula and mole refraction of the ion are changed significantly, *even though the electron orbits (that is, the eigenfunction) for the normal state are not appreciably affected.* It is obviously not correct to speak of deformation of the electron orbits here.

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[25] K. F. Herzfeld and K. L. Wulf, Ann. d. Physik **78, 57,** 195 (1925). Herzfeld and Wulf interpreted the first absorption in the ultra-violet as the resonance frequency of the anion, instead of as the ionization frequency, as we have done. It is highly improbable that these negative ions have a resonance frequency differing very much from the ionization frequency (see Franck and Scheibe, reference 5). They also considered the crystal potential only to influence the absorption frequencies; the work should be repeated taking into account the electron affinity of the crystal.