# X-RAY DIFFRACTION ANALYSIS OF THE IONIC STATE

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# Abstract

A critical review is given of methods used in determinating the ionic state of crystal atoms from X-ray structure amplitudes. The necessity of defining the atoms as local objects on the basis of the composite charge density is emphasized. The radius of best separation of the atom from its surroundings is defined as the radius $R$ corresponding to minimum $4\pi r^2 \varrho_0(r)$, where $\varrho_0$ is the spherical average charge density around the atom. Definition of the atomic charge as the integrated electron count within this radius has a conceptual indeterminacy of the order of $4\pi R^2 \varrho_0(R)$. For calculation of these quantities a method is suggested based on analytic integration of Fourier series and on analytic treatment of a Gaussian model crystal to eliminate termination errors. Methods based on extrapolation of atomic factors or on comparison of structure factors with different models suffer from undefined basic concepts. They are unable to distinguish the effect of the ionic state from the influence of atomic distortions and they give a misleading picture of the problem, because the charges of the free model atoms cannot be interpreted as the atomic charges of the model crystals. The alkali halides KBr, LiF and NaF and the metal oxides MnO, CoO and NiO are treated as examples. The experimental data are seen to indicate single and double ionization for halides and oxides, respectively, with a larger conceptual indeterminacy in the latter case.

# 1. Introduction

X-ray diffraction provides information on charge distributions and is therefore one of the most direct means for studying the ionic state of atoms in solids. This has been clear since the early history of X-ray diffraction. In 1918 DEBYE and SCHERRER [34] stated definitely the possibility of studying the bonding in solids in this way. They also made the first attempt to derive the atomic charges in some alkali halides particularly in LiF from the low order reflexions. Several authors, *e.g.* GERLACH and PAULI (1921) [42], MARK and TOLKSDORF (1925) [77] and ZINTL and HARDER (1931) [117] applied the same reasoning, which actually was an elementary version of the conventional method based on extrapolation of atomic factor curves to zero diffraction angle.

In 1926 COMPTON [28] presented a more sophisticated method, where by assumption of sphericity the radial charge density of the atom was represented as a Fourier series in terms of the atomic scattering factor. The atomic charge was then obtained by numerical integration. This work

was followed by further applications of this method by HAVIGHURST [45] and BEARDEN [7]. These works seem to represent the first initiative towards evaluation of the atomic charges directly from the charge distribution or from different projections of it. In this context the difficulty caused by the considerable width of the electron clouds or by their overlap was noted for the first time. Attempts to avoid this were made by use of a large artificial lattice constant in calculating the radial charge density, but then the problem once again turned into the difficulty of extrapolating the atomic factor curves.

In 1939 BRILL, GRIMM, HERMANN and PETERS [18], made the first serious attempt to observe the influence of the bonding type on the electron distribution. The difficulty caused by the overlap was described as being properly solved (in the case of NaCl) by use of smooth atomic factor curves derived graphically from the experimental structure amplitudes. This procedure is indeterminate and as such it must be regarded as an unsatisfactory makeshift. This difficulty with its different manifestations has been a source of continual confusion. Particularly in the case of LiH the results obtained with the graphical method by BIJVOET and FREDERIKSE [10] in 1929, ZINTL and HARDER [117] in 1931, and AHMED [3] in 1951 were contradictory. Sharp criticism was therefore presented by WALLER and LUNDQVIST [111] in 1952 and by BIJVOET and LONSDALE [11] in 1953, who came to the completely negative conclusion that the state of ionization cannot at all be determined by X-ray diffraction.

Meanwhile, it had become a common practice to estimate atomic charges from the Fourier maps by numerical integration; [cf. 23, 24, 74]. In connexion with this method the same overlap problem made its appearance and led to a series of critical articles by TAYLOR (1954) [105], BLACK (1955) [12] and BLACK and TAYLOR (1958) [13] referring particularly to studies of some transition metal alloys [36, 89, 97]. In addition to certain experimental problems three difficulties were mentioned: 1) imperfect resolution of the atoms, i.e. overlap of the outer regions, 2) outer electrons affect only low order reflexions and even there the differences between different models are small [cf. 103], 3) the atomic factor curves used do not correspond to the electron content of the atom which they are supposed to represent [cf. 25]. In fact, however, these are different manifestations of the same problem. Also in this context a rather pessimistic view was adopted.

Another view of the problem was presented by COCHRAN [26, 27] (1958, 1961), who emphasized the necessity of careful definitions of the concepts of charge transfer or ionic charge, and in 1962 by CALDER, COCHRAN, GRIFFITHS and LOWDE [21], who showed in their thorough and careful work that the distribution of charges in LiH indicates single ionization of

the atoms inspite of the negative conclusion of BIJVOET et. al. [11]. In fact, although the paper does not so state explicitly, this work shows that

1. the two types of methods, the atomic factor method and direct integration of charges, are definitely non-equivalent,
2. the integration method arises in a natural way from definition of the basic concepts and leads to a realistic description of the situation in a solid and
3. the state of ionization can be a meaningful concept even in cases where no conclusions about it can be made from the atomic factor method.

Still, some confusion seems to be prevailing in the treatment of this problem in the literature. Both methods have been applied continually side by side, with several improvements in the calculation techniques, as can be seen from the more recent review articles by SIROTA and GOLOLOBOV [101], SIROTA [100], BRILL [17] and HOSOYA [48], but the origin and nature of their differences and of their uncertainties coupled particularly to the atomic factor method seem not always to have been fully realized. Through this paper, besides giving a review on the development of this problem, we therefore wish, to call attention back to the nature of the problem, to the foundations of these methods and to their basic limitations in order to attain a proper appreciation of the significance of the results obtained.

## 2. Nature of the problem

Basically the ionic state is a *parameter of the separate atom model*, as are many other parameters conventionally treated in crystal analysis. Such parameters have significance only in so far as it is meaningful to speak about atoms in a solid. If we can define the atom, we immediately also get all atomic parameters, and, *vice versa*, any determination of such parameters necessarily involves some definition for the atom, the significance of the results depends on the relevance of this definition.

Because the first aim is to obtain experimental information about the atoms, we must have some kind of an operational definition, *i.e.* we must not start from the abstract idea of an atom but from the experiment [cf. 26]. Each type of experiment or phenomenon then creates naturally its own definition of 'atom' which is the 'effective atom' in this particular phenomenon. The agreement or disagreement between the values of atomic parameters obtained in different contexts is an interesting question in itself indicating the degree of relevance of the atomic concept [cf. 27]. Here we shall concentrate on the 'effective atom' of X-ray diffraction.

In the case of one given atom, the atomic charge $Z$ can be expressed unambiguously either in terms of the charge density $\varrho(\mathbf{r})$ or in terms of the scattering amplitude $f(\mathbf{b})$:

(1)
$$Z = \int \varrho(\mathbf{r})d^3r = f(0) .$$

This simplicity is apparently preserved in the separate atom model, *i.e.*, in a crystal built by superposition of atoms. Since in such a model we know the charge distributions $\varrho_n(\mathbf{r})$ and scattering amplitudes $f_n(\mathbf{b})$ of the individual atoms beforehand, we can immediately express the charge density and structure amplitudes of the composite system in terms of them through the equations

(2)
$$\varrho(\mathbf{r}) = \sum_n \varrho_n(\mathbf{r} - \mathbf{r}_n)$$

(3)
$$F_j = \sum_n f_n(\mathbf{b}_j) \, e^{2\pi i \mathbf{b}_j \cdot \mathbf{r}_n}$$

where we understand the effect of thermal motion to be included in $\varrho_n$ and $f_n$. Here $\mathbf{r}_n$ are the atomic positions and $\mathbf{b}_j$ the reciprocal lattice vectors; the first summation runs through all atoms while the latter refers to one unit cell.

This construction is somewhat misleading, because in the true problem the primary system is the composite one, and not the atoms as in the model. To write the charge density and the structure amplitudes in the form of eqs. (2) and (3) means decomposition of the crystal into atoms, and this is not possible without first defining the atoms in some way. It is clear from the requirement of operational definition that this must arise from a study of the crystal itself, and in this context particularly from the experimental structure factors or from any quantities mathematically derived from them *e.g.* the charge density. The free atom is a completely different system and can therefore not provide a basis for this purpose. The crystal as a whole is a complicated quantum mechanical system of a vast number of electrons. From a theoretical point of view the division into atoms is artificial and no unique definition can be given as emphasized by LUNDQVIST [75] in 1954 and later by WESTIN, WALLER and LUNDQVIST [115], MANSIKKA and KULMALA [76] and AIKALA and MANSIKKA [4]. Consequently, there will always be a basic *conceptual indeterminacy* in all atomic parameters, including the ionic state of the crystal atoms.

Although we do not know exactly how to define the atoms, there are certain conditions which must be fulfilled to make the definition reasonable. For example, we must introduce the requirement of locality [63, 64] as a basic property of our 'effective atom'. This is quite a natural requirement from the point of view of the abstract idea of an atom. It says simply that no distant parts of the charge distribution will be assigned to the atom; an electron cannot be said to belong to some particular atom for any other reason than for being close enough to its nucleus. This requirement is

directly applicable to the operational definitions desired in this context, because it refers to the charge distribution.

It should be noted that this discussion applies also to any model crystal. It is often stated that superposition of theoretical free atoms gives a good approximation for X-ray diffraction analysis. This is true, but it concerns exclusively the composite charge density of the crystal. It does not imply that the parameters of the free model atoms used would represent the situation in the composite model crystal in any sense. Consistency already requires that we use the same definitions for the model quantities as for the experimental ones. Their deviations from the theoretical free atom values are important for understanding the nature of the model used. If eventually the experimental values obtained lie close to the free atom values, it is, in principle, just a fortunate coincidence. On the other hand, serious or irregular deviations from the free atom values would indicate that the concept of an atom is no more fully usable.

All methods applied in the determination of the ionic state must be judged on the basis of the propriety of the atomic definitions inherent in them. The conventional methods fall naturally into two categories according to the principle followed in dividing the crystal into atoms. This division is effected either as a decomposition of the charge density according to eq. (2) or as a decomposition of the structure amplitudes according to eq. (3). The results are then correspondingly based on either of the definitions (1) of the atomic charge; [cf. 17]. In the following we shall call these two groups of methods the *integration* methods and the *extrapolation* methods, respectively.

# 3. The integration method

## a) *General*

The integration method is based on the simple idea of relating the total charges in suitable parts of the unit cell, as calculated from the experimental charge distribution, to the atomic charges; [cf. 27]. In these methods the requirement of locality is taken into account automatically. If the atom were surrounded by a region of zero charge density, the volume taken up by the atom would be well defined and integration over this volume would yield an unequivocal definition for the atomic charge. This is, in fact, never the case. But, in any event, the charge distribution shows directly the degree of atomic separation, and we can still use the electron count of the atomic peak as the 'effective charge' defined by our experiment; its dependence on the size of the region will show the conceptual indeterminacy

coupled to this definition [cf. 21]. In this way such calculations will provide a realistic picture of the atomic charges.

The applications of the integration method vary in the technique of integration, in the choice of atomic regions, and in the treatment of the residual term problem and obviously in many technical details.

### b) *Technique of integration*

*Numerical integration* of the charge distribution has been done most frequently from two, or even one, dimensional projections [6, 23, 24, 36, 56, 89, 97, 98, 101]. When the three dimensional charge density has been used, the calculation has been based on values in one direction and on the assumption of sphericity or on some average of several different directions [5, 45, 90, 116].

The method of COMPTON [28] is also based on numerical integration. However, the radial charge distributions of the atoms used there are calculated from the experimental atomic factors, which must first be evaluated from the experimental structure amplitudes. Therefore this method and other comparable calculations [7, 18, 20, 45, 54] fall rather into the class of extrapolation methods. It should be noted in this context that the average radial charge distribution around a nucleus can also be calculated without any intermediate steps and without the assumption of sphericity directly from the structure amplitudes of the crystal from the series

$$(4) \qquad \varrho_0(r) = \frac{1}{V} \sum F_j \frac{\sin 2\pi b_j r}{2\pi b_j r} \,,$$

where the relevant nucleus is assumed to lie at the origin [50, 62, 63, 72, 85]. This would provide the most direct means for numerical integration of the atomic charge.

*Analytical integration* of the Fourier series has certain practical advantages due to avoidance of the tedious preliminary calculation of the charge density. The electron count of an arbitrary region $T$ is given by the series

$$(5) \qquad Z_T = \frac{1}{V} \sum F_j \sigma_T^*(\mathbf{b}_j) \,,$$

where $\sigma_T(\mathbf{b})$ is the shape transform of $T$ [60]. For a sphere of radius $R$ centered at the origin eq. (5) takes the form

$$(6) \qquad Z(R) = \frac{4\pi R^3}{V} \sum F_j \frac{j_1(2\pi b_j R)}{2\pi b_j R} \,.$$

Except for spherical regions, which are used most frequently [51, 55, 61, 67—70, 73, 81, 82, 84, 93, 110], use of an ellipsoid [55, 61, 110], or a cube

[17, 21, 26, 85, 113], or a parallelpiped [30] have all been proposed. The analytic method is similarly applicable to the projections of charge density; COCHRAN [23] and BROWN and WILKINSON [19] give the expressions for a rectangular region and a circle, respectively, separated from a two dimensional projection. The analytic calculation of electron counts and the estimation of the effect of known experimental uncertainties [cf. 23, 30, 64, 113] is in all these cases straightforward.

### c) Choice of atomic regions

Obviously, the choice of atomic regions must correspond to the shape and width of the atomic peaks shown by the charge distribution. If we want to share all of the charge between the atoms, we must divide the unit cell into parts and assign each part to one atom. In this way we may obtain regions of rather complicated shapes [cf., e.g., 23, 24] for which numerical integration is preferable. CALDER et. al. [21], WEISS [113] and MERISALO et. al. [85] have followed this principle in the case of NaCl structure by simply dividing the unit cell into equal cubes of side $a/2$. This, of course, is an easy way to gain some idea of the charge transfer from one atomic site to the other, but it does not even tend to find the most proper atomic regions.

It is often more expedient to consider some electrons as not belonging to any of the atoms. For instance, attempts have been made to count from the charge distribution the number of electrons contributing to a covalent bond [cf., e.g., 15, 16, 22, 43, 80]. Similarly, a distinction has been attempted between the conduction electrons and the core electrons, thereby motivating statements concerning the state of ionization of the atoms in a metal [cf. 2, 8, 44]. The electron distribution may also indicate occurrence of separate electron aggregates in the interatomic space [55, 110].

Because of such possibilities it is advisable in more precise studies to define the atomic region for each atom independently by seeking the most natural way to separate it from its surroundings. An obvious solution is to let the surface of the region go through the minimum charge density in all directions. This procedure, however, is unnecessarily tedious. The regions would have irregular shapes that require the use of numerical methods, and they would be rather sensitive to termination errors. It is much more practical to take regions of some regular shape and to determine their size such that the surface follows the minima as well as possible. We can then use analytical integration, whereby the differences due to the shape of the region will be nonessential and will remain within the limits of conceptual indeterminacy of the atomic charge.

A sphere is certainly the most natural shape to be used for any structure,

because it takes the requirement of locality into account isotropically. The problem is then to find the most proper atomic radii. It has been common practice to let the minimum value of charge density on the line connecting nearest neighbours determine the radii [55, 56, 110, 116]. This principle has the disadvantage of giving one direction a special position. Therefore KURKI-SUONIO and FONTELL [68] suggested another choice based on the average radial charge densities around the atoms, which can be calculated from eq. (4). To avoid overlapping of regions the sum of the two radii was still kept equal to the nearest neighbour distance, and the criterion was to have equal average charge density on the surfaces [50, 51, 73, 81, 82, 84, 85, 93]. The minima of the $\varrho_0(r)$, in all these cases, lie far beyond these radii, which indicates that the neighbours, in fact, have little effect on the integrated charges, unless the spheres are taken very large [cf. 50, 63]. Therefore, the limiting condition of having the spheres just touching each other leads to an underestimation of the radii as well as of the atomic charges [cf. 101]. However, in terms of total charges attached to the peaks of the charge distribution the minimum of $4\pi r^2 \varrho_0(r)$, rather than of $\varrho_0(r)$, will show the *radius of the best separation of an atom from its surroundings*. This would be equal to the value of $R$ where $Z(R)$ has an inflexion point, and the corresponding value of $Z(R)$ is the natural operational definition of the atomic charge in the crystal. The value of $4\pi R^2 \varrho_0(R)$ will be a measure of its conceptual indeterminacy. This definition can be used for all atoms independently and will always lead to slight but unimportant overlapping of the atomic spheres.

In the case of the NaCl structure BRILL [17] has suggested a corresponding procedure with cubes. This worked well for the positive ions. However, the charges around the negative ions were too diffuse to produce an inflexion point until the cubes corresponding to ions of the same kind overlapped considerably. Therefore the region of the negative ion was defined simply as the complement of the cube corresponding to the positive ion. In this way the definitions for the two ions were unique, but different, and dependent on each other. These difficulties do not show up when spheres are used.

### d)  Treatment of the termination problem

The termination problem is less serious for the integrated charge than for the charge density [cf. 63, 64]. One way to take termination into account is to use eq. (5) as a difference series. The result then shows the deviation of $Z_T$ from that of the model crystal [cf., e.g., 61, 73, 85, 89]. This, however, does not give direct information on the ionic state of the atoms, because, as first emphasized in 1953 by COCHRAN [24, 25], the theoretical values of

$Z(R)$ may deviate strongly from the electron counts of the model atoms [cf. also 12, 13, 67].

Moreover, the $Z_T$ values of the model crystal show little correlation with the ionic state of the model atoms used, [64, 113], so that no conclusions seem possible without actually calculating the residual term.

In calculating the residual term a Gaussian representation of the theoretical atomic factors is useful. It can be used like any other analytic form [cf. 91] to create crystal structure factors at large $b$ values and, thus, to provide continuation of series (5) or (6) until a reasonable convergence is reached [17, 51, 55, 67, 68, 81, 82, 84, 110]. For a Gaussian crystal we also have the much simpler possibility of calculating $Z(R)$ directly on the basis of the analytic expression. This procedure has been used since 1953 in charge density calculations, first by Hosemann and Bagchi [46, 47], then by several others [8, 56, 90, 102, 116], to replace Fourier series, and for calculation of $\varrho_0(r)$ instead of series (4) by Inkinen and Järvinen [50] and by Merisalo et. al. [85].

It is important that the Gaussian representation is accurate at large values of $b$, where we can assume the theoretical free atomic scattering factor to be reliable. If the fit is not good enough at small values of $b$, the Gaussian results must be corrected by the difference series with coefficients $F_{obs} - F_{Gauss}$ to yield the experimental values of $Z(R)$ and by another difference series with coefficients $F_{theor} - F_{Gauss}$ to give the model values.

## 4. The extrapolation method

The idea of the extrapolation method is most apparent in those special cases where it is possible to assign some of the structure amplitudes to certain atoms, on the basis of some simplifying assumptions, or to decompose them approximately into contributions from different atoms [cf. 65]. We then have atomic factor values at some of the points $\mathbf{b}_j$ and the evaluation of the atomic charges appears to be a matter of extrapolation to $\mathbf{b} = 0$. To be able to do this we must know the behaviour of the atomic factor near the origin, [27]. At this point the definition of the atom is included in the method.

The extrapolation is sometimes explicit, [3, 47, 95]. More often it is replaced by a comparison of the atomic factor values $f(\mathbf{b}_j)$ deduced from the data with the theoretical values derived for different ionic states of the free atoms [20, 57—59, 86—88, 104, 107]. Estimates of atomic charges have also been based on comparison of the experimental structure amplitudes with model values corresponding to different degrees of ionization of the constituents [29, 35, 37, 49, 78, 96, 99, 101]. Basically these methods

contain the implicit idea of extrapolation according to free-atom-like behaviour of the atomic factors.

The nature of the problem is here somewhat obscured by the intimate connexion with the separate atom model, where the initial atomic factors are definite functions at all values of $\mathbf{b}$. This gives the impression, often referred to, that the experimental information, which is concentrated at the reciprocal lattice points, would be critically defective [11, 106, 115]. However, all information we can have as the starting point of the analysis, even in principle, is included in the structure amplitudes $F_j$. To get more information can only mean in this context to collect more complete and more accurate data on $F_j$. The apparent lack of information must rather be understood as a consequence of the conceptual indeterminacy of the atomic definition. This concerns the uncertainty in decomposition of the structure amplitudes $F_j$ into atomic factor values $f(\mathbf{b}_j)$ as well as the uncertainty in the interpolation or extrapolation of these values to regions between the points $\mathbf{b}_j$, particularly to $b = 0$.

This decomposition, interpolation and extrapolation of scattering amplitudes is not arbitrary. There are certain limitations due to the need to define the atoms in a reasonable manner. It is sometimes assumed that these limitations are taken into account when the atomic factors are derived graphically as smooth curves [18]. However, the important requirement of locality in particular, is of a more definite nature [63, 64], and such an undefined procedure is not sufficient to satisfy it.

If we start by decomposing the structure amplitudes into atomic contributions according to eq. (3), we must be sufficiently careful not to rely on the sphericity of atoms [cf. 33, 38, 63, 64, 114]. At least we must take into account the possibility of having some small deformation contributions which violate the conventional extinction rules [65]. The first few reflexions, on which the extrapolation must be based, are most sensitive to distortions caused by bonding [21]. Even if the decomposition into atomic contributions were unambiguous, they would provide rather unreliable initial values for the extrapolation. Spherical changes, *e.g.*, overall compression or extension of the atom, will cause the atomic factors to deviate from the free atom values at the first reflexions, thus making the initial values either too high or too low. Nonsphericities, on the other hand, cause a selective increase or decrease of the reflexions and may therefore give a misleading initial slope for the extrapolation. If we want to take this effect into account in this method, we must realize that we can no more represent the atomic factor by just one curve, but that we have slightly different curves for different directions of $\mathbf{b}$, which means considerable complication and additional uncertainty in the extrapolation.

In general the effect of deformations on the structure amplitudes is

small. The examples in which it has been possible to analyze them nevertheless show that they may be of observable magnitude. At least, they cannot be neglected without careful consideration of their order of magnitude [cf. 31, 32, 49—51, 69, 70, 72, 81, 84].

It has been stated many times that the differences between atomic factors corresponding to different ionic states are very small even at the first reflexions. These differences should be compared, first, with the experimental possibilities, which during recent years have been subject to international projects [1, 52, 53, 66, 92], and secondly, with the effects of deformations, which may well be of the order of a few percent. If we were to assume that such differences characterize the accuracy required for determination of the ionic state by X-ray diffraction, we have but one possible conclusion: the task is impossible. The difficulty of reaching a definite conclusion in favour of any of the models with different states on the basis of comparison with experimental results is evident in numerous relevant studies [11, 21, 49, 58, 59, 103, 104, 107, 115]. It is instructive that this difficulty is not restricted to metals, or to covalent crystals, where we might consider that the bonding makes the ionic state indefinite, but it concerns similarly even the most obvious ionic crystals such as the alkali halides. This leads us to suspect that such a view of the problem is overpessimistic.

There are cases where certain structure amplitudes of models with different states of ionization differ markedly [35, 37]. Furthermore, electron diffraction is more sensitive to differences at low scattering angle, because the scattering amplitude for electrons is proportional to $Z - f$. It therefore provides a means for more accurate comparison with different models [86—88]. The experimental accuracy then seems to be sufficient to allow us to state which of the models is in accord with the experimental value of the reflexion studied. The conclusion is still uncertain, because the effect of the atomic distortions on the intensity is correspondingly greater, quite possibly greater than the influence of the degree of ionization [21].

In the above considerations we have been concentrating on the reliability of the initial values of extrapolation provided by the first few reflexions. This is only a part of the problem. An obvious objection can be raised against the whole idea of free-atom-like extrapolation, which is the essence of these methods. The ionic state is a matter of the state of the outer electrons, which also determines the behaviour of the atomic factor at small $\sin \theta / \lambda$. The state of the outer electrons, however, undergoes considerable changes when the atom becomes part of a solid. This is clear, since the charge distributions of free atoms, particularly those of negative ions, often extend rather far from the nucleus, [17, 21, 24, 25, 79, 111, 115]; see further, for instance, the tables by Froese-Fischer [41] on Hartree-

Fock atoms. At least that part of the atomic charge distribution which by superimposing the atoms comes into or close to the region of the neighbouring atoms, will change completely, which already may significantly affect the atomic factor near the origin [13, 25, 115].

In such cases the free-atom-like extrapolation also violates the restrictions imposed by the requirement of locality. Thus the assumption of free atom behaviour is a poor one. In particular the extent of its poorness depends strongly on the state of ionization of the model atom. Therefore, the comparison of data with different models cannot give any realistic view of the problem.

These considerations indicate that even in the model crystals we cannot define the crystal atoms as the free atoms from which the crystal is built. A definition based on the composite charge density or on the structure factors may yield atomic parameters with values significantly different from those of the free constituents. Thus, for instance, the statements of WEISS [113] concerning the very small differences in the integrated electron counts of $Mg^0O^0$, $Mg^{1+}O^{1-}$ and $Mg^{2+}O^{2-}$, do not necessarily imply that the atomic charges of the crystal are completely indeterminate, but only that in the model they are largely independent of the ionic state of the free model atoms.

## 5. Examples

To clarify the above considerations we shall discuss a few examples, where the construction of separate atom models with different ionic states is possible on the basis of existing theoretical calculations and where relatively good data are available. In this way we come to two kinds of examples, the alkali halides KBr, NaF and LiF and the metal oxides MnO, CoO and NiO. The following data were used: for KBr the data of MEISALO and INKINEN [82], for NaF the data of MEISALO and MERISALO [83] and for LiF the data of MERISALO and INKINEN [84], while for the three oxides the data of UNO [109] were introduced.

For each crystal one model was constructed from neutral atoms and another from ions, singly ionized in case of the alkali halides and doubly ionized in case of the oxides. The following theoretical atomic factors were adopted:

| atom | reference |
|---|---|
| Li, Li$^+$, K, F, F$^-$ | FREEMAN [38], |
| Na, K$^+$ | BERGHUIS et. al. [9] |
| Na$^+$ | BOYS [14] |
| Br, Br$^-$ | FREEMAN and WATSON [40] |

Mn, Co, Ni                Freeman and Watson [39]
$Mn^{2+}$                  Piper [94]
$Co^{2+}$, $Ni^{2+}$       Watson and Freeman [112]
O, $O^{2-}$                Tokonami [108]

The calculations were performed according to the principles sketched in the discussion on the integration method. The temperature factors obtained in the analyses presented in the references [82—84] were used for the model crystals of the alkali halides. For the metal oxides the temperature factors obtained by Meisalo and Inkinen [81] were used. The Gaussian representations for $Na^+$, $K^+$, $F^-$, $Br^-$, Mn, $Mn^{2+}$, Co, $Co^{2+}$, Ni, $Ni^{2+}$ and $O^{2-}$ were taken from the paper by Kurki-Suonio, Meisalo, Merisalo and Peltola [71] and for $Li^+$ from the work of Merisalo and Inkinen [84]. For the neutral atoms Na, K, F, Br and O the Gaussian representations were chosen equal to those of the corresponding ions, which necessitated correction of the Gaussian results by difference series, as described in sec. 3.

To obtain on a local basis an idea about how the electrons are distributed among the two components in these crystals and in the corresponding models the electron count $Z(R)$ was calculated in spheres around both kinds of atoms according to eq. (5). The results are shown in figures 1 to 6. In these figures the radii are measured from the left for the metal atoms and from the right for the halogen or the oxygen atoms. Curves 1 correspond to the neutral models, curves 2 to the ionic ones, and curves 3, the broken lines, are the experimental values with error bars showing the standard errors.

The values $f(000)$ or $f_T(000)$ given by Meisalo and Inkinen [82] for KBr and by Merisalo and Inkinen [84] for LiF, as well as the values $N_0$ of Meisalo and Inkinen [81] for the three metal oxides are completely equivalent to $Z(R)$, although they are obtained by summation of a long series (5). The theoretical values given in these references correspond to our ionic model, but some differences can be observed. The only major discrepancy, a matter of almost one whole electron in the case of oxygen in NiO, turned out to be a misprint in some earlier stage of the calculations. In KBr, MnO and CoO there are physically meaningless deviations, which are numerically too large to be attributed to inaccuracies in the calculations. They could be traced back to the fact that some adjustment of the observed structure amplitudes of KBr and refinement of temperature factors were made after the calculation of electron counts[1]).

Each of the curves has an inflexion point, which shows the distance of the lowest radial charge density from the center of the atom. (Its exact

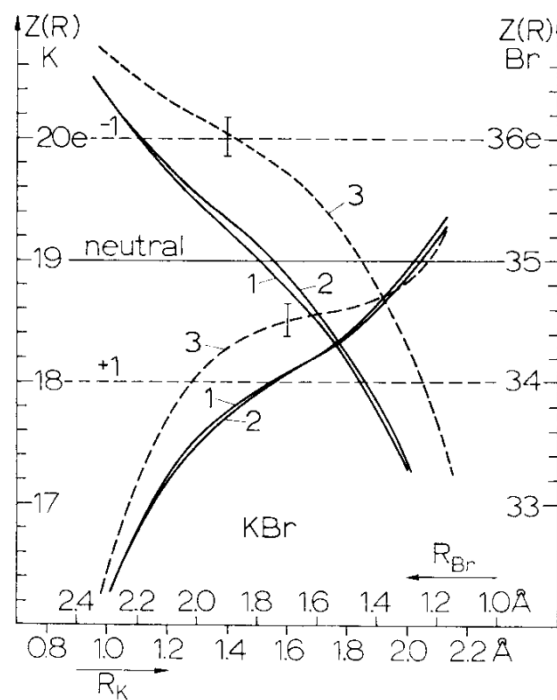---

[1]) Meisalo, private communication

Figure 1. Integrated electron counts in spheres around K and Br atoms in a KBr crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from free ions $K^+$ and $Br^-$ and 3. experimental data of MEISALO and INKINEN (1967b).
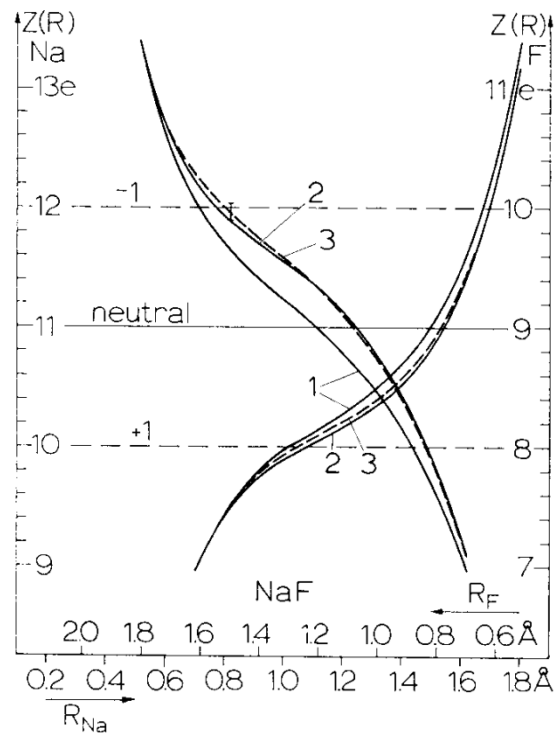
Figure 2. Integrated electron counts in spheres around Na and F atoms in a NaF crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from free ions $Na^+$ and $F^-$ and 3. experimental data of MEISALO and MERISALO (1966).
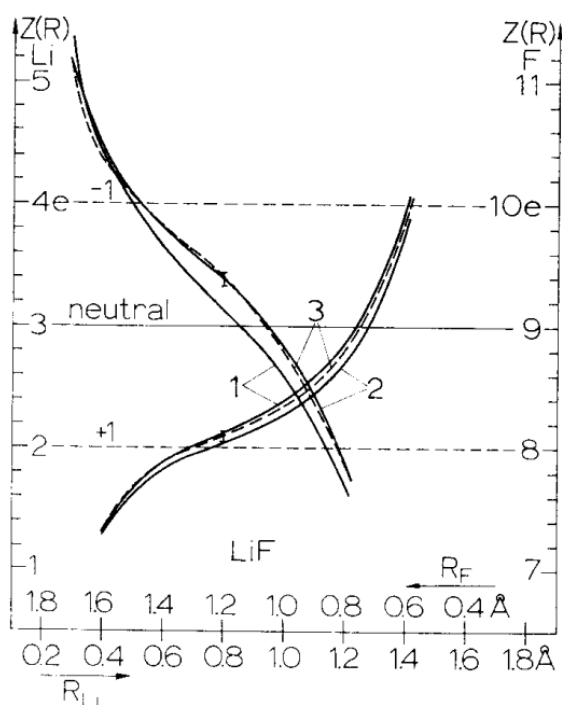
Figure 3. Integrated electron counts in spheres around Li and F atoms in a LiF crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from free ions $Li^+$ and $F^-$ and 3. experimental data of Merisalo and Inkinen (1966).

position is more easily seen by calculating $4\pi r^2 \varrho_0$ from eq. (4).) This defines the atomic radius $R_i$ as the radius of best separation of the atom from its surroundings. The value of $n = Z - Z(R_i)$ is then the corresponding ionicity of the atom.

It is obvious from the curves and from the corresponding numerical values given in table 1 that the charges of the free model atoms do not correspond to the situation in the model crystals. The differences in the charge distributions of the two models are much less than would be expected on the basis of the free constituents. The electron counts in equal spheres differ at most by 0.05 to 0.15 e and by 0.1 to 0.3 e for the alkali and halogen atoms, respectively, instead of by one electron as expected. In the metal oxides the corresponding differences are 0.4 to 0.5 e and 0.6 to 0.7 e instead of two electrons. Thus overlapping of model atoms in the crystal destroys to a large extent the differences in outer electron configuration, and the atomic charge, if defined on the basis of the composite charge distribution, has little dependence on the state of the free constituents.

We realize that, in fact, the neutral model cannot be understood to represent a crystal with neutral crystal atoms. The one or two outer electrons of the free metal atoms are too far from the nucleus to remain in the possession of the atoms after superposing the charge densities. The charges
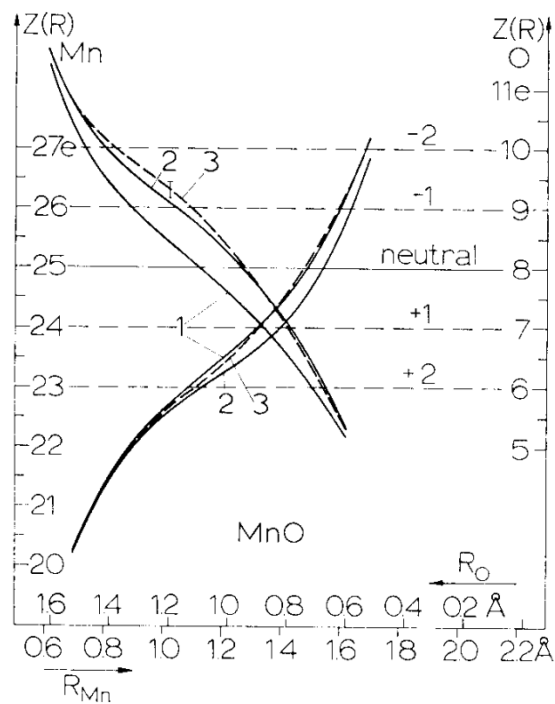
Figure 4. Integrated electron counts in spheres around Mn and O atoms in a MnO crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from ions $Mn^{2+}$ and $O^{2-}$ and 3. experimental data of Uno (1965).
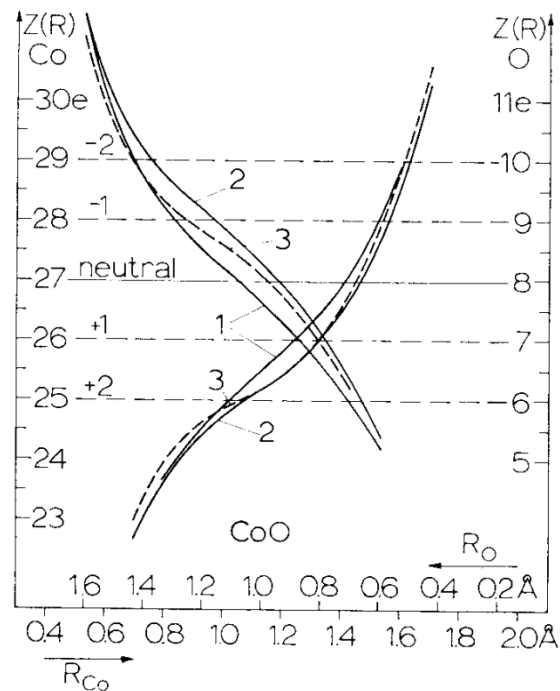


Figure 5. Integrated electron counts in spheres around Co and O atoms in a CoO crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from ions $Co^{2+}$ and $O^{2-}$ and 3. experimental data of Uno (1965).
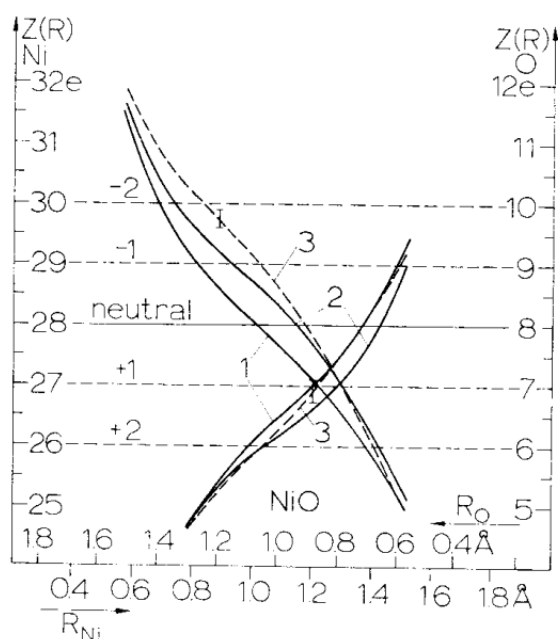
Figure 6. Integrated electron counts in spheres around Ni and O atoms in a NiO crystal as a function of radius. The curves correspond to 1. a model crystal built from free neutral atoms, 2. a model built from ions $Ni^{2+}$ and $O^{2-}$ and 3. experimental data of Uno (1965).

of the halogen and oxygen atoms in the crystal come much closer to the values of the neutral atoms, although the runaway electron of the other atom does make a contribution.

The ionic model is much closer to a crystal with ionized crystal atoms. In this case it is the negative ion which is slightly too diffuse to play quite credibly the role of a singly or doubly charged negative crystal atom [cf. 17, 21, 111, 115].

The experimental values indicate a more compact and thus a better defined negative ion than that of the ionic model except for CoO where the oxygen is more diffuse, according to these data. We observe that the differences $n^+ - n^-$ come reasonably close to the ideal values 2 and 4 corresponding to the completely ionized states, again with the exception of CoO. In this context it can be noted that the scale of the KBr data must be somewhat high because the total number of electrons in the two spheres comes out too large. However, the difference $n^+ - n^-$ is independent of this and indicates a similar state of ionization as in the cases of the other two alkali halides.

The inflexion points of the curves are not sharp, but there is for each atom a longer interval of lower slope. This shows clearly the natural uncertainty of the atomic charge in a crystal and the different degrees of it for different kinds of crystals. As a relative measure of this conceptual indeterminacy of the ionicity we give in table 1 also the differences $\Delta n$

## Table 1.

The degrees of ionization $n^+$ and $n^-$ of the atoms and their differences $n^+-n^-$ as obtained from the inflexion points of the curves in figs. 1 to 6 corresponding to neutral and ionic free atom models and to experimental data. The values $\Delta n$ are not experimental errors but show the degree of conceptual indeterminacy. The radii of best separation and their overlap ratios correspond to the experimental values.

| | neutral | | | ionic | | | experimental | | | | | radii of best separation | | $\dfrac{R^++R^-}{d}$ |
| | $n^+$ | $n^-$ | $n^+-n^-$ | $n^+$ | $n^-$ | $n^+-n^-$ | $n^+$ | $\pm\Delta n^+$ | $n^-$ | $\pm\Delta n^-$ | $n^+-n^-$ | $R^+[\text{Å}]$ | $R^-[\text{Å}]$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KBr | +0.8 | −0.2 | 1.0 | +1.0 | −0.4 | 1.4 | +0.45 | ±0.03 | −1.15 | ±0.07 | 1.6 | 1.67 | 1.97 | 1.10 |
| NaF | +0.9 | −0.2 | 1.1 | +0.9 | −0.6 | 1.5 | +0.85 | ±0.07 | −0.75 | ±0.10 | 1.6 | 1.14 | 1.40 | 1.10 |
| LiF | +0.9 | −0.3 | 1.2 | +1.0 | −0.6 | 1.6 | +0.95 | ±0.05 | −0.70 | ±0.09 | 1.65 | 0.77 | 1.35 | 1.05 |
| MnO | +1.8 | −0.2 | 2.0 | +2.0 | −1.2 | 3.2 | +2.0 | ±0.20 | −1.7 | ±0.20 | 3.7 | 1.08 | 1.29 | 1.07 |
| CoO | +1.5 | −0.1 | 1.6 | +1.9 | −1.0 | 2.9 | +2.0 | ±0.13 | −0.7 | ±0.16 | 2.7 | 1.05 | 1.17 | 1.04 |
| NiO | +1.3 | 0.0 | 1.3 | +1.9 | −1.0 | 2.9 | +2.1 | ±0.27 | −1.8 | ±0.25 | 3.9 | 1.00 | 1.20 | 1.05 |

corresponding to $\Delta R = \pm\ 0.05$ Å at the inflexion point. The slope is much lower for the alkali halides than for the metal oxides, which indicates better separability of the atoms, and hence a clearer ionic nature for the bonding in the former case. We clearly observe that the positive alkali ions are more exactly definable as independent entities than any of the other atoms considered in these examples. Yet the slope is in no case so low that we could speak about a unique definition of the atoms. The radii of the best separation indicate some overlapping of atomic spheres as seen from the ratio $(R_i^+ + R_i^-)/d$. The conventional way of choosing the atomic radii corresponds to the value 1.0 for this ratio. This ratio has larger values in cases where the space between the atomic peaks is emptier and hence the overlap of the atoms in the conventional sense is smaller.

## 6. Discussion

The two main types of methods are clearly non-equivalent, and there are several reasons for preferring the integration methods over the extrapolation methods.

First of all, the integration method is based on calculation of a well defined quantity. Secondly, this quantity is closely related to a definition of the ionic state on the basis of the composite system studied. In this way the problem is rather well isolated from other interpretational problems connected with the separate atom model, and is thus unaffected by, say, possible atomic deformations. The problem about the significance of the results is in this way clearly divided into two different questions, the accuracy of the quantities calculated, and the relation of these quantities to the concept studied, which can be treated separately.

The idea of extrapolation, on the other hand, leaves the concept of ionic state undefined. It merely correlates the atomic charges in some vague manner to the charges of the free constituents of the model. This connection makes it difficult to cast aside impressions and ideas based on the separate atom model or even the spherical model, and the deficiencies of these models appear therefore as inaccuracies of the method. Moreover, there is no obvious connection between these quantities and the experimental data and hence there cannot be any unique way to derive them from the data. As demonstrated by the examples, the charges of the free model atoms correspond poorly to the atomic charges in the model crystal as defined by integration. Therefore, when using this method, we may obtain at worst a completely misleading picture of the whole problem. We could consider that it is the first few structure amplitudes which are here the definite quantities derived from the data, and the whole problem would

then be concentrated to a study of their relation to the ionic state. There is no direct relation; moreover, these quantities depend strongly on other parameters of the model. Thus the problem of ionic state is not sufficiently well isolated in this method.

In actual fact, the ionicities can be deduced much more accurately than one would expect on the basis of comparison of different models. There is, for instance, no doubt that the alkali halides and the metal oxides treated as examples are close to the singly and doubly ionized states. This statement cannot be reached by the extrapolation method, but is rather obvious from considerations based on the integration method. We realize that it is strongly coupled to the geometry of the crystal. Since the geometry of a crystal certainly depends on the state of its constituents, it is natural that, *vice versa*, conclusions on the ionicities can be traced back to the geometry.

It should also be noted that the integration method requires a whole set of structure amplitudes, whereas the extrapolation method involves only the first few. Our considerations thus emphasize the necessity of measuring complete and accurate sets of structure amplitudes. Very little information can be obtained from a measurement of only one or two reflexions.

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