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G2-3

Survey of Results for Ionic Crystals and Metallic Oxides, Carbides and Nitrides

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A survey is made of X-ray powder work which has been done since 1960 to obtain information on electron states and electron charge distributions. The investigations are classified into three groups, depending upon their aims. Then the following three subjects are described: electron state of metallic nitrides, especially of Fe₄N, deformation of charge cloud in ionic crystals and comparison of measurements on MgO.

Introduction

A considerable number of investigations have been made on the compounds to be surveyed in the present paper. Much of the older work is cited in the paper by Witte & Wölfel (1958) and in a review article recently written by Brill (1967). Therefore, only the work done since 1960 will be mentioned. Although every investigation was carried out for various purposes more or less of its own, it may not be unreasonable to classify these investigations into the following three groups.

In group 1, shown in Table 1, the main concern is to determine the ionicity, or the number of electrons transferred to or from an individual atom, by careful

intensity measurements of reflexions in a small angle region. Among them, six compounds from Cu₂O to Mo₂C in Table 1 have reflexions, especially in the small angle region, which are contributed mostly by light atoms alone. Such compounds are especially suitable for this kind of study. In this group, some electron diffraction work is also quoted.

It is perhaps worth while to mention here that the inner reflexions are apt to be reduced because of various effects due to extinction, preferred orientation, porosity, surface roughness, incident beam divergence and other possible phenomena. Therefore, deliberate care has been taken in measuring the intensity of these reflexions.

Table 1. *List of compounds*

Group 1		
MnO	Kuriyama, M. & Hosoya, S.	1962, 1963
MnO		1963 a
NiO	Uno, R.	1963 b
CoO		1965
CaF ₂	Togawa, S.	1964
TiC	Arbyzov, M. P. & Khaenko, B. V.	1966 a, b
VN	Hosoya, S., Yamagishi, T. & Tokonami, M.	1968
Cu ₂ O	Suzuki, T.	1961
Mn ₄ N	Kuriyama, M., Hosoya, S. & Suzuki, T.	1963
Fe ₄ N	Elliot, N.	1963
	Nagakura, S.	1968 (E. D.)
ϵ -Fe ₂ N	Nagakura, S. & Tanehashi, K.	1968 (E. D.)
ζ -Fe ₂ N		
Mo ₂ C	Nagakura, S., Kikuchi, M. & Oketani, S.	1966 (E. D.)

E.D.: electron diffraction.

Table 2. *List of compounds*

Group 2		
NaCl	Vihinen, S.	1960
	Korhonen, U. & Vihinen, S.	1961
	Kurki-Suonio, K. & Fontell, L.	1964
	Linkoaho, M.	1968
NaCl	Mansikka, K.	1961
KCl		
RbCl		
RbCl	Järvinen, M. & Inkinen, O.	1967
KBr	Meisalo, V. & Inkinen, O.	1967 a
LiF	Merisalo, M. & Inkinen, O.	1966
CaF ₂	Kurki-Suonio, K. & Meisalo, V.	1966
AgCl	Korhonen, U. & Linkoaho, M.	1964, 1966
AgBr	Vogl, E. & Waidelich, W.	1967
NiO	Inkinen, O. & Meisalo, V.	1965
MnO		
CoO		
	Meisalo, V. & Inkinen, O.	1967 b

In group 2 shown in Table 2, the main concern is to determine the number of electron charges and ionic radius, and further to detect whether the electron cloud is deformed, or deviates from spherical symmetry.

Table 3. *List of compounds*

Group 3		
CaF ₂	Togawa, S.	1964
	Maslen, V. W.	1967
MgO	Uno, R. (unpublished data)	1963 c
	Togawa, S.	1965
	Burley, G.	1965
	Raccah, P. M. & Arnott, R. J.	1967
NaF	Meisalo, V. & Merisalo, M.	1966

In group 3, shown in Table 3 the precision of measurement is high enough to enable us to judge which theoretical atomic scattering factor seems to be the more accurate or at least the more reasonable.

In the following paragraphs, several selected topics are described.

Electron state of metallic nitrides

Among group 1, the isomorphous compounds Fe₄N and Mn₄N seem to be worthy of mention. In these compounds, metal atoms occupy three face-centre positions and one corner position of each unit cell, and each nitrogen atom occupies a centre of the cell. The magnitude of the magnetization of Fe₄N was measured by Guillaud & Creveaux (1946). In order to explain the magnitude of its ferro- or ferrimagnetic magnetization, two theoretical models of the electron state were proposed, as shown in Table 4. One model is by Zener (1952) and the other by Wiener & Berger (1955). These two models are rather different, because each nitrogen atom is an electron acceptor in the former model and a donor in the latter. Then Frazer (1958) determined the magnetic moment of each atom by neutron diffraction. His results were clearly contrary to the Zener model and supported the model of Wiener & Berger.

A big difference in the electron state of nitrogen (3- and 3+) should easily be distinguished by measuring the intensities of 100 and 110 reflexions for X-ray diffraction. In fact, Elliot (1963) carried out the measurement, and found that the Zener model is right, which is contrary to the result by neutron diffraction. These results have been left inconclusive.

Recently Nagakura (1968) has measured the structure factors by use of electron diffraction and concluded the electronic structure to be around Fe⁰(Fe^{1/3+})₃N¹⁻. As is well known, the atomic scattering factor for electron diffraction is very sensitive to the electronic state in the low angle region. This sensitivity seems to cover the lack of precision in the intensity measurement.

It is not intended to discuss here which of the two is right, the result by X-ray diffraction or that by electron diffraction. It is still interesting to know that a new model proposed by Nagakura can explain the experimental results, (1), (2) and (3) or (1), (2) and (3') in Table 4. This model, however, can be considered only by discarding the widely accepted Hund rule. Namely, this model requires that the 3d band should begin to be filled with down spins even before all possible levels are completely filled with up spins. This idea does not seem to be allowed in usual metals and alloys, but might not be rejected in interstitial compounds such as Fe₄N. With this model, the above contradiction disappears and further, even one degree of freedom is left. That is, there remains one unknown parameter corresponding to the number of electrons transferred to the 4s band. If this parameter is determined by other physical measurements, electron states are determined. To be more exact, however, the partition of 4s electrons transferred from the atom at the corner and those at the face centres is not yet determined.

A similar contradiction was found also in Mn₄N. According to X-ray diffraction work (Kuriyama, Hosoya & Suzuki, 1963), nitrogen atoms in this compound are in the state N⁰~N¹⁻, but this result is not consistent with any of the donor and acceptor theories which

were considered to explain the observed magnetization (Guillaud & Wyart, 1946). On the other hand, neutron diffraction work has been carried out (Takei, Shirane, & Frazer, 1960; Takei, Heikes & Shirane, 1962). In this case, it is also possible to find the model which is consistent with all experimental results.

In general, however, interstitial compounds are known to have properties intermediate between ionic, covalent and metallic bondings. Therefore, the above working hypothesis may be too simple and might not be a reasonable assumption for interpreting experimental results. If, for instance, there are some covalent electrons, the apparent neutrality in chemical formulae need not necessarily hold. In such a case, the present argument should be drastically changed. In this sense, it is hoped that more details of electron distribution will be studied by X-ray diffraction.

In conclusion, the diffraction method can supply very valuable information for determining the electron state, especially in compounds of such a kind.

Deformation of charge cloud in ionic crystals

Among materials, typical ionic crystals such as NaCl have been studied most extensively. Even if only typical ionic crystals are chosen, there are already too many reports to be surveyed. In this paper, therefore, only a few comments are made.

Because these structures are comparatively simple, the main concern is with details of charge cloud. Therefore, precise measurements of intensity values needed for the reflexions up to as high an angle region as possible, often supplemented by measurements on a single crystal.

In order to obtain information about anisotropy or deformation of the electron charge distribution, the number of total charges belonging to an individual atom and its ionic radius, the following three methods are used.

(1) The first method is to use the usual Fourier synthesis. In this case, the unobserved data in the high angle region are replaced by theoretical values often expressed in analytical form. If those values are used, in unobserved regions, the Fourier map thus obtained may not be accurate in details of electron distribution, although the atomic scattering factor in the high angle region is very insensitive to the state of outer electrons. It may be difficult, however, to assess to what extent the map obtained is affected by the theoretical terms.

When Fourier summation is taken over a finite number of terms, the resultant map is accompanied by ripples due to termination. Using a numerical example Weiss (1966) showed how the ripples appear especially in the region halfway between atoms depending upon the region in reciprocal space used, and he also showed how the convergence is improved by taking the charge density averaged over a small volume in real space.

The number of electrons belonging to an atom can be obtained by integrating electron charge over the volume surrounding the relevant atom. For example, in a review article by Brill (1967), an explicit expression is given for the case where the volume has an orthorhombic shape. The boundary of this volume should be set at the surface where the charge density has a minimum. This can be done by calculating the number of electrons as a function of the size of the region, and by finding the inflexion point.

(2) The second method is the difference Fourier synthesis, which is an alternative method to (1). This can be used for determining values of temperature factors for individual atoms, and also for detecting the deviations from spherical symmetry of the electron cloud around atoms more sensitively than by the method (1). However, it is still necessary to remember that unobserved values are not completely cancelled by F_{cal} 's, unless the observed region is wide enough.

(3) The third method is 'non-approximate analysis of electron distribution' by Kurki-Suonio (1962*a*, 1962*b*) and Kurki-Suonio & Fontell (1963). The essential point is to consider the scattering factor f_T for electrons distributing in the region T which may have any form with an atom at the centre of symmetry. This region T may correspond to the generalized region of the simplest orthorhombic shape mentioned in (1) above. The merit is that the f_T can be expressed by observed structure factor values F_{obs} and the Fourier transform of the region T . Thus the comparison can be made in reciprocal space without being affected by termination errors.

By these methods, deviations of the electron cloud from spherical symmetry have been detected for various compounds. For example, such a deformation has been found in the halogen ions of NaCl (Korhonen & Vihinen, 1961; Kurki-Suonio & Fontell, 1964), LiF (Merisalo & Inkinen, 1966) and RbCl (Järvinen & Inkinen, 1967) and also in the anions and cations of CaF₂ (Kurki-Suonio & Meisalo, 1966) and KBr (Meisalo & Inkinen, 1967*a*). In conclusion, there is a

Table 4. Summary of work on Fe₄N

Model	Measurement	(1) Guillaud & Creveaux (1946) magnetization	(2) Frazer (1958) neutron diffraction	(3) Elliott (1963) X-ray diffraction	(3') Nagakura (1968) electron diffraction
Zener (1952)	Fe ⁰ (Fe ⁺) ₃ N ³⁻	○	⊗	○	
Wiener & Berger (1955)	Fe ⁰ (Fe ⁻) ₃ N ³⁺	○	○		
Nagakura (1968)	Fe ⁰ (Fe ^{1/3+}) ₃ N ⁻	○	⊙		○

tendency for the electron cloud to shrink in the direction connecting neighbouring atoms. Mathematical problems in obtaining the information about deformations are discussed in a recent paper by Kurki-Suonio (1968).

It was also found that the traditional values of ionic radii are sometimes not valid. For instance, the ionic radii for Rb and Cl atoms in RbCl were found to be 1.71 and 1.58 Å in contrast to the traditional values 1.49 and 1.80 Å, respectively. This difference seems to be rather significant.

In this connexion, it should be added that the experimental results clearly show the difference between typical ionic crystals and silver halides. According to the detailed study on AgCl (Korhonen & Linkoaho, 1964, 1966) and the preliminary study on AgBr (Vogl & Waidelich, 1967), electron states $\text{Ag}^{2+}\text{Cl}^0$ and Ag^+Br^0 respectively are suggested. In AgCl, the eight electrons supplied by the four Ag atoms per unit cell are reported to be localized at all the 24 interstitial positions on {100} planes with an average occupancy of $\frac{1}{3}$ of an electron. It is interesting to consider that such a characteristic electron distribution should be closely connected with the marked difference of silver halides from alkali halides in physical and chemical properties.

Comparison of measurements on MgO

At least four independent measurements have so far been carried out on MgO. The measurement by Togawa (1965) was carried out on an absolute basis, while Burley (1965) determined the absolute scale by mixing rock salt powder in the specimen. The measurements by Uno (1963*c*, unpublished data) and by Racciah & Arnott (1967) were carried out on a relative basis.

As shown in Table 5, all investigators used the theoretical f value for Mg^{2+} calculated by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). As for a theoretical f value for oxygen, there are at least four different values:

- (1) f_{cal} for O^- ion in free state calculated by Freeman (1959),
- (2) f_{cal} for O^{2-} in +1 potential well by Suzuki (1960),
- (3) f_{cal} for O^{2-} in +2 potential well by Suzuki (1960) and
- (4) f_{cal} for O^{2-} in MgO by Tokonami (1965).

The differences between the last three f_{cal} values are very small but systematic. These f_{cal} values will be referred to by their numbers in the above.

Togawa reported in his paper that the experimental results showed a good agreement with f_{cal} for Mg, and as for O, a better agreement with (4) f_{cal} than with (3). On the other hand, Burley remarked that the agreement was good for (3) but not good for Mg. When Burley wrote his paper, (4) f_{cal} was not available. Racciah & Arnott, who later obtained a similar result to that by Togawa, concluded that the difference between Togawa's and Burley's results is due to the difference in f_{cal} they used rather than due to the measured values themselves.

Therefore, these four measurements have been compared with each other, dealing with the data in the same way. Because both Mg^{2+} and O^{2-} ions have ten electrons, the reflexions with odd indices, which are determined by the difference of f values of Mg and O, are weak in intensity. It is, therefore, difficult to obtain f_{obs} values for Mg and O from F_{obs} values by interpolation. The comparison was, therefore, made for F_{obs} values including dispersion corrections but without taking thermal diffuse scattering into consideration. The results are shown in Fig. 1, where almost all F_{obs} values show a good agreement with each other, especially for reflexions with even indices. Among the reflexions with odd indices, the data for the 111 reflexion show large percentage deviations which are positive or negative depending upon which f_{cal} values are used. Theoretical values in an inner region are generally less reliable, corresponding to less accurate information about the states of outer electrons. The same f_{cal} , however, was used for Mg^{2+} , though this is not very accurate. It is, therefore, most probable that (3) f_{cal} is smaller and (4) f_{cal} is larger than the true value for the 111 reflexion.

Further, the discrepancy of a few per cent for this reflexion among F_{obs} values is beyond the standard deviations estimated by those authors. It is hoped that both a more elaborate calculation and a more accurate measurement will be carried out, particularly for the 111 reflexion.

Table 5 shows the reliability index, or R factor, for various combinations of theoretical and experimental values. Naturally the R factor cannot be a good criterion in the present case. As shown in Fig. 1, the

Table 5. Comparison of R factor (in %) for MgO

f_{cal} (Mg)	Berghuis <i>et al.</i> (1955)			
	(1) Freeman (1959) O^- free	(2) Suzuki (1960) O^{2-} in +1 well	(3) Suzuki (1960) O^{2-} in +2 well	(4) Tokonami (1965) O^{2-} in MgO
f_{cal} (O)				
Uno (1963 <i>c</i>)	2.71	1.52	1.16	1.14
Togawa (1965)	1.33	0.71	0.57	0.62
Burley (1965)	2.04	1.11	0.71	0.52
Racciah & Arnott (1967)	2.32	1.19	0.91	0.66

R factor used here is $\Sigma |F_{\text{obs}}|^2 - |F_{\text{cal}}|^2 / \Sigma |F_{\text{obs}}|^2$.

111 reflexion shows an exceptionally large deviation from any of the calculated F_{cal} values. This makes the R factor very large, even if other reflexions show a good agreement. In Togawa's case, if the value of the 111 reflexion is omitted, the R factors become 0.52 and 0.38 for (3) and (4) f_{cal} respectively. In conclusion, the f_{cal} values (1) and (2) are worse than (3) and (4). The difference between (3) and (4) is very slight, but the latter seems to be better than the former.

In other cases, the difference is often big enough to allow one to judge which f_{cal} is definitely better. For example, in CaF_2 (Togawa, 1964), f_{cal} for F^- ion by Freeman (1959) or by Boys (1962) shows a better agreement with f_{obs} than that by Berghuis *et al.* (1955).

Generally speaking, f_{cal} values obtained with better theoretical assumptions and approximations are preferred, when compared with accurate measurements. This is a reasonable result and implies that the measurements are fairly reliable.

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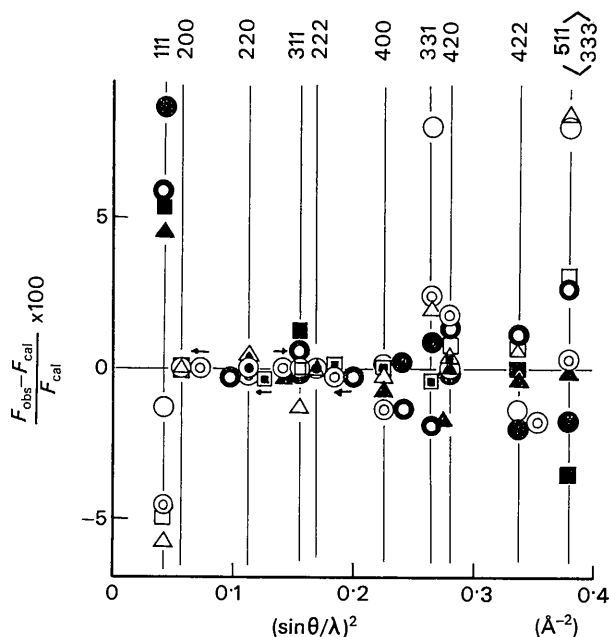


Fig. 1. Comparison of measurements on MgO. The meanings of various marks in the figure are shown below.

Measurement	f_{cal} for oxygen used in F_{cal}	
	(3) Suzuki (1960)	(4) Tokonami (1965)
Uno (1963c)	○	⊙
Togawa (1965)	○	●
Burley (1965)	□	■
Racchah & Arnott (1967)	△	▲

Solid and thick marks for the 200 reflexion are omitted because they practically fall on open marks.

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DISCUSSION

HERBSTEIN: I notice that of the two different temperature factors which you deduce from the two sets of experimental data for MgO, one leads to a Debye temperature which is considerably closer to that obtained by other methods. I would regard this agreement as a better assessment of the experimental data than the *R* factors.

HOSOYA: I had not taken notice of this feature. However, according to our experience, for instance, on MnO (Hosoya & Yamagishi, 1966, p. 2641) a Debye temperature value is apt to be heavily affected by the difficulty in taking a suitable range of background to be subtracted, when a sample is subject to heavy strain. The agreement in a Debye temperature value, therefore, may not always be a good criterion.

DR B. DAWSON then discussed a comparison of the available experimental evidence on MgO with a variety of models, using the same temperature factors for both atoms. This discussion appears in the written version of his paper in the present proceedings.

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Charge Density and Momentum Density - A Comparison Between Theory and Experiment

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X-ray structure factors and Compton line shape measurements provide complementary information on charge and momentum density, the latter measurement evidencing very much greater sensitivity to the valence electrons. Theoretical calculations of structure factors and Compton line shapes for solids have been sparse and have probable errors in excess of 3%. When these errors are compounded with experimental errors of several per cent the cases for which comparison between theory and experiment is meaningful are presently limited to diamond, silicon, germanium, MgO, LiH, Li, Be, Mg, Al and perhaps a few others. In diamond the 111 and 222 structure factors are in agreement with theory as are the 111 structure factors of LiH and MgO. The experimental momentum densities in Li, Be, Mg, and Al do not agree with conventional band calculations since these are unable at present to account for a significant electron-electron correlation effect.

This paper is concerned with a comparison between X-ray measurements and theoretical calculations of electron charge and momentum density. Some of this material has already been considered in a previous publication (Weiss, 1966) and therefore emphasis will be placed on recent developments.

Introduction

For the past 35 years, and especially since World War II, experimental efforts in X-ray diffraction have shown little success in providing reliable details of valence electron distributions in solids, in sharp contrast to the enormous success in crystal structure determinations. The reason, of course, is that the valence electron contribution to structure factors is overwhelmed by the inner electron contribution so that, at the very least,

measurements of absolute structure factors must be in error by no more than 1% to provide even the barest of information. In a few cases (like the 'forbidden' 222 reflection in diamond) such restraints on the errors are considerably relaxed but the information gained is limited and is only useful in comparing various theoretical calculations of the charge density. One might have thus guessed from the Heisenberg uncertainty principle that a large indeterminacy in valence electron positions would be compensated by a well-defined determination of their momenta. This, indeed, is the case and X-ray Compton line profile measurements have revealed significant details of momenta distributions. Furthermore, the problems inherent in structure factor measurements like extinction, absolute scale, termination errors, and Debye-Waller factor are absent from Compton line profile measurements.