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A Proof of Aspherical Valence Charge Parts in the Rock-Salt Structure Compounds by Means of an X-Ray Bond Charge Model

By

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The aspherical valence charge parts are deduced for the rock-salt structure compounds NaF and MgO by means of a bond charge (BC) model. The valence charge density is described by spherical atoms and an additional particle near the anions in the $\langle 100 \rangle$ directions. The BC amount is smaller according to the dielectric theory, but the other parameters as position and extension follow its tendency. The anharmonic core vibrations of atoms, the asphericity of the bond charge and its dynamical properties are essential for the zincblende to rock-salt phase transition.

Für die in der Kochsalzstruktur kristallisierenden Verbindungen NaF und MgO werden asphärische Valenzladungsanteile mit Hilfe eines Bindungsladungsmodells nachgewiesen. Die Valenzladungsdichte wird aus der spherischer Atome und einem nahe dem Anion lokalisierten und au der $\langle 100 \rangle$ Achse befindlichen zusätzlichen Teilchen beschrieben. Die erhaltenen Bindungsladungsbeträge sind kleiner als die theoretisch aus der dielektrischen Theorie erhaltenen. Die Parameter Position und Ausdehnung der Bindungsladung folgen aber den theoretisch erwarteten Trends. Die anharmonischen Gitterschwingungen der Atome, die Asphericität der Bindungsladung und deren dynamische Eigenschaften werden als ausschlaggebend für den Zinkblende–Kochsalzstruktur-Phasenübergang angesehen.

1. Introduction

From the general point of view the valence charge of the rock-salt structure compounds is spherically arranged around the atoms. Because of the tendency of filling the octet shells the chemical bond is realized by means of the Coulomb interaction between the positive and negative ions.

The invalidity of the Cauchy relation for most of them stands in contradiction to this picture. These relations are accomplished for a realization of central forces only. The atoms must be arranged in the centrosymmetric points of the structure. This is not true for an aspherical charge distribution around the atoms.

On the other hand, we cannot understand the phase transition under pressure from the covalently bound compounds to the ionic ones without a dominant role of the aspherical charge parts of both structures. Moreover, the tendency of filling the octet shells known for the ionic compounds seems to be in conflict with the screening concept of ionic pseudopotentials by means of transferred valence charge in a semicovalent compound.

In recent years some publications tempted to show the aspherical charge parts and to determine the ionization states of the rock-salt structure compounds from the X-ray structure data. Weiss [1] has submitted a difference of the scattered intensities reflected at the same q-value ($q = 4\pi \sin \theta / \lambda$) for LiH. This might be taken as a charge

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concentration in the $\langle 100 \rangle$ direction only. For LiF Merisalo and Inkinen [2] indicated a charge concentration of 0.15 electrons/Å^3 between next neighbours.

Other papers demonstrate the cation symmetry to remain spherical, whereas the anions are deformed in most cases [3 to 5]. This state can be described by cubic harmonic functions in the $\langle 100 \rangle$ direction. But their absolute values are small.

A deformation of the anion charge distribution appears in self-consistent pseudo-potential calculations by the Thomas-Fermi approximation for NaCl, too [20].

For different rock-salt structure compounds Kurki-Suonio and Fontell [6] determined the effective charge of the constituents. They pointed out a different absolute charge amount of anion and cation, respectively. These results base on the X-ray powder data. The accuracy of the structure amplitudes is limited. From single crystal data those analyses were not made in an extended manner.

This work describes the aspherical charge parts of NaF and MgO by means of a bond charge model tested for semiconductor compounds [7 to 9]. A theoretical reconstruction of the experimentally determined X-ray single crystal data is possible with the same accuracy as from exact calculations with spherical ionic scattering factors. Some comments are given of the zincblende to rock-salt phase transition on the basis of a general bond charge concept.

2. Model

The aspherical part of the valence charge distribution can be analysed by means of the reflection group $h + k + l = 4n + 1$ (h, k, l are the Miller indices). The spherical part of these reflections depend on the difference of the ordinary numbers of the constituents. The structure amplitude can be given by the following relation:

$$F_{\text{obs}}(hkl) = 4(f_A T_A - f_B T_B) + \alpha_{\text{BC}} f_{\text{BC}} . \tag{1}$$

The f_i are the scattering factors of the A, B atoms listed in the tables [10]. The values are corrected for dispersion [11]. The valence part of the scattering factors must be reduced by the charge part necessary for building up the bond charge (BC). The T_i are the temperature factors calculated by an ordinary Debye-Waller formalism. The α_{BC} stand for the structure factors of the BC scattering factor f_{BC} which measures the contribution of the aspherical scattering power to the structure amplitude. For the rock-salt structure α_{BC} is real only and depends on the position of the BC scattering centre on the connection line between next neighbours along $\langle 100 \rangle$, measured from the cation.

The BC scattering factor contains the temperature dependence and is constructed by a Gaussian,

$$f_{\text{BC}}(hkl) = \frac{A\pi^{3/2}}{a^3} \exp{(-q^2/4a^2)} . \tag{2}$$

The BC amount, $A\pi^{3/2}/a^3$, and the half-value width are fitted. The agreement between theoretical and experimental data is controlled by the R-factor

$$R = \frac{\sum |F_{\text{obs}} - F_{\text{calc}}|}{\sum |F_{\text{obs}}|} . \tag{3}$$

The calculation problems are treated in [7, 9] in an extended manner.

3. Data Analysis and Results

The X-ray single crystal data were taken from Howard and Jones [12] and Sanger [13] for NaF and MgO, respectively. The asphericity of the valence charge distribution is visible from the differences of the (600)/(442) and (333)/(511) reflection intensities,

Table 1

Experimental and calculated structure amplitudes for NaF and MgO

	hkl	F_{exp} [12]	F_A	F_0	F_{BC}
NaF	111	5.12	5.11	5.29	5.12
	311	6.40	6.35	6.49	6.20
	331	4.98	4.99	5.00	4.98
	333	3.58	3.69	3.63	3.63
	511	3.63	3.69	3.63	3.67
	531	2.69	2.71	2.70	2.67
	533	1.99	2.00	1.98	1.98
	R-factor		0.0093	0.0140	0.0123
	hkl	F_{exp} [13]	F_2	F_0	F_{BC}
MgO	111	11.28	11.42	12.20	11.28
	311	12.32	12.72	12.29	12.32
	331	9.55	9.69	9.56	9.55
	511	7.15	7.16	7.16	7.06
	333	7.41	7.16	7.16	7.24
	531	5.34	5.34	5.37	5.33
	R-factor		0.0109	0.0235	0.0051

The F_A are calculated from [14] for NaF. The F_0 are the neutral spherical scattering factors and the F_2 represent twice ionized spherical scattering factors for MgO calculated from [10]. The F_{BC} are calculated on the basis of the BC-like analysis.

respectively, scattered at the same q-value. For NaF the (600)/(442) ratio and (333)/(511) ratio are 1.6% and 1.1%, respectively. For MgO the ratios are 1.4% and 6.9%, respectively. The experimental errors turn out to be 1%.

For NaF the theoretical structure amplitude is calculated by means of the Hartree-Fock scattering factors from the International Tables and the Aikala ionic scattering factors [14]. These are compared with a BC-like aspherical analysis of the valence charge distribution. For MgO the BC corrected data are compared with those from free neutral Hartree-Fock form factors and from twice ionized Hartree-Fock form factors. The temperature factors of atoms were taken from the literature.

The results of both substances are indicated in Table 1. The BC-like analysis is a possible description of the X-ray data. There is a direct correlation with the existence of aspherical valence charge parts around the anion scattering centres. For NaF the best R-factor appears when using the Aikala scattering factors. But the right tendency finds its expression in the BC analysis. It can explain the different scattering power of the (511) and (333) reflections only. This coincides with the results presented by Meisalo and Merisalo [15].

For MgO the theoretical and experimental values match more closely the BC-like analysis. These results remain valid on application to other ionization states of the compound [16, 17].

4. Discussion

The fitted BC data are listed in Table 2. In comparison with the dielectric theory by Phillips and van Vechten [18, 19] the BC amount of a compound depends on the static dielectric constant ε_0 calculated from $2/\varepsilon_0$ for a bond. The extension of the BC in the

Table 2

Fitted BC parameter in comparison with those determined by the dielectric theory. The BC position is normalized to a half lattice constant

parameter	NaF	MgO	comment
BC amount	0.52 ± 0.02	0.37 ± 0.01	in electrons
$2/\varepsilon_0$	1.18	0.42	in electrons [18]
a	2.05 ± 0.03	2.32 ± 0.03	in Å^{-1}
k_F	2.11	2.32	in Å^{-1} [18]
BC position	0.45 ± 0.01	0.42 ± 0.01	$a_0/2$

elementary cell is correlated to the Fermi wave number k_F. The latter conforms with the experimental parameter a. However, the determined BC amount is smaller than that from theory. The tendency of the increased BC amount appears at rising ionicity, but the absolute values are too small. The shift of the BC position is increased in the direction of the anion from MgO to NaF. This agrees with the increased ionicity, too. Principally a complete description of the $A^n B^{VIII-n}$ compounds is possible by the use of a BC model. The valence charge distribution can be calculated by means of spherical atomic scattering factors and an additional scattered particle for the group IV and $A^{III}B^V$ and $A^{II}B^{VI}$ compounds. The BC is shifted in direction of the anion at increased ionicity. Additionally the anions contribute more electrons to the BC. However, the BC shift expresses the charge transfer from cation to anion.

Hübner [21] used a BC point charge model to point out the phase transition from zincblende to rock-salt. Accordingly the increased ionicitiy induces the BC to dip in the anion core for zincblende compounds. The repulsion of the anion core requires the phase transition. This suggestion does not correspond to an extended BC. For each ionicity some BC parts are localized inside the anion core. For the phase transition the following points of view must be taken into account:

a) Following the dielectric theory the BC amount increases with rising ionicity. But for rock-salt structure compounds the BC charge part in $\langle 100 \rangle$ direction is smaller compared to the theory. Therefore, we assume a second charge centre in $\langle 111 \rangle$ direction.

b) The mean square displacements and the anharmonic core vibrations are increasing with rising ionicity for the zincblende compounds [22]. The zincblende to wurtzite phase transition of CuI was discussed by Matsubara [23] by means of the anharmonic core vibrations of the copper atoms, for instance. Besides the static BC change the dynamical BC properties will be essential. For stretching of a bond axis BC is transferred from this bond to the compressed one [24]. Therefore, the force constants of the compound are not constant.

c) Due to the different wave functions of both constituents the overlap region between next neighbours is deformed [25]. For increased ionicity the charge parts outside of the connection line between next neighbours will be of importance. This can explain the decrease in the ratio of the bond bending and bond stretching constants within the valence force field model [26].

For the phase transition the BC balance between the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions must be analysed near the phase transition point. Obviously then the aspherical BC's from $\langle 111 \rangle$ are overlapping in the $\langle 100 \rangle$ direction. This can be analysed from very exact structure data for CdO (ionicity ≈ 0.78), for instance. A first analysis of the charge distribution was taken from Linkoaho [27] and Rantavuori [28].

A second point of view is the fundamental understanding of the dynamical BC properties in an experimental and theoretical manner. Both problems will be tackled in the future.

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