Localized and delocalized models in the theory of polarization: perovskite oxides

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Abstract. Possibilities of working out the theory of polarization in perovskite-type oxides in frameworks of localized and delocalized models are analysed. Born effective charges are used as a criterion of correlating these models. It is shown that taking into account gradients of effective electric fields on anions and high electric permittivity ensures the adequate description of polarization in these crystals by using the Slater localized (static) model. The results of our calculations in the framework of the Slater model are given and compared with *ab initio* calculation data.

1. Introduction

The classical theory of crystal polarization has been developed on the basis of localized models [1–4], in which ions of the crystal lattice have been presented as a point charge assembly with dipole moments induced by an external electric field or sublattice displacements. In perovskite-type ABO_3 oxides a strong electrostatic interaction of these moments leads to the very large local (internal) electric fields on the B and O_1 ions. The large internal fields are the cause of crystal instability provoking the ferroelectric phase transition. A flaw of the localized models is that, as a rule, they eliminate the mixed ion–covalent character of chemical bonds resulting in the delocalization of the electronic charge. The delocalization effects are taken into account in *ab initio* calculations [5–8], the authors of which suppose that the anomalously large transfer of the delocalized electronic charge by the change of the length of the chemical bonds is representative for the considered crystals.

The present paper is devoted to a comparative analysis of the results of application of the localized and delocalized models to the perovskite crystals in the cubic paraelectric phase. The main attention is given to the calculation of the effective dynamical Born ion charges, which are the quantitative measure of the Coulomb interaction in the crystals. For this aim we have generalized the classical Born dynamical model [4] for the perovskite-type ABO_3 crystals. The Born charges for the $BaTiO_3$, $SrTiO_3$ and $KNbO_3$ crystals in the cubic paraelectric phase have been calculated for the standard set of electronic polarizabilities [2, 3] and also for the case of variable effective polarizabilities of cations and anions. The corresponding set of the electronic polarizability values permitting us to reach a satisfactory fitting to the Born charges defined in the delocalized models [5–8] has been also found.

2. Results and discussion

In the classical Born model [4] the dynamical effective ion charges Z_j^* for the binary NaCl-type cubic crystals ($j = 1, 2$) can be expressed as

$$Z_j^* = Z_j(\partial E_j^{HF}/\partial E)_{E=0} \tag{1}$$

where Z_j is the static ion charge of the jth ion, $E_j^{HF} = (\varepsilon_\infty + 2)E/3$ and E_j^* are the local Lorentz fields on the ions of the jth sublattice induced by the weak high-frequency or low-frequency macroscopic field E, respectively, and ε_∞ is a relative high-frequency (electronic) dielectric permittivity which is equal to the square of the refractive index. The equation (1) gives us the possibility to express the Born effective charges Z_j^* in terms of appropriate local fields.

In the binary NaCl-type crystals $E_1^{HF} = E_2^{HF}$, $E_1^* = E_2^*$ and there is no difference between E_j^* in nondisplaced and displaced ion positions. Our generalization of relation (1) for the perovskite-type ABO$_3$ crystals is found by taking into account:

(i) the difference of the local fields E_j^* on the ions belonging to the different sublattices [3];

(ii) the local field gradients $\partial E_j^*/\partial z$ which do not equal zero for the certain ion sublattices [9]. The latter circumstance is equivalent to taking into consideration a change of the E_j^* value by the ion displacements [10–12].

In this case the polarization of the crystal P induced by the local fields E_j^* and ionic displacements U_j from the equilibrium positions is

$$P = \sum_{j=1}^n P_j = \sum_{j=1}^n N_j \left[\alpha_j \varepsilon_0 \left(E_j^* + \frac{\partial E_j^*}{\partial z} U_j \right) + Z_j e U_j \right]. \tag{2}$$

Here P_j, α_j, N_j, $n = 5$, ε_0 and e are the polarization, the electronic polarizability, numbers of the jth type ions in a volume unit and of different ion types in the crystal, permittivity of free space and the elementary charge, respectively. In equations (2) E_j^* and $\partial E_j^*/\partial z$ represent the local fields and their gradients on the nondisplaced (symmetrical) ion positions corresponding to $U_j = 0$. All the local fields are equal to zero in absence of the external field and displacements of ion sublattices.

A connection of the local fields E_j^* with the sublattice polarizations P_j and the external electric field can be defined by using the well known relation [3]

$$E_j^* = E + \frac{1}{\varepsilon_0} \sum_{k=1}^n \left(c_{jk} + \frac{1}{3} \right) P_k \tag{3}$$

where c_{jk} are the structural coefficients of the local field which have been calculated by Slater [3]. All the c_{jk} coefficients in the cubic paraelectric phase can be determined by using two constants, $p = 0.6898$ and $q = 2.394$ [3]. The substitution of E_j^* from equation (3) into P_j from equation (2) allows us to obtain the set of linear equations for P_j. After finding and summing P_j we obtain the crystal polarization in the form

$$P = \varepsilon_0(\varepsilon_\infty - 1)E + \sum_{j=1}^n N_j Z_j^* e U_j \tag{4}$$

where the effective dynamical Born charges Z_j^* are calculated by using a relation

$$Z_j^* = -\frac{1}{N_j \alpha_j} \left(Z_j + \frac{\alpha_j \varepsilon_0}{e} \frac{\partial E_j^*}{\partial z} \right) \sum_{k=1}^n \left\| c_{lm} + \frac{1}{3} - \frac{\delta_{lm}}{N_l \alpha_l} \right\|_{jk}^{-1} \tag{5}$$

(l, $m = 1, \ldots, 5$, δ_{lm} is the Kronecker symbol). The first term in the right-hand part of equation (4) represents an electronic contribution to the crystal polarization P.

The local field gradients $\partial E_j^* / \partial z = (\partial E_j^* / \partial z)_{dip} + (\partial E_j^* / \partial z)_{mon}$ are the sum of the point dipole and monopole (point charge) components. It is easy to show that for all the ion sublattices the dipole components $(\partial E_j^* / \partial z)_{dip} \equiv 0$. Therefore we must calculate only the monopole component. It can be done by using the usual formula for E_j^* arising due to Coulomb interaction of the point charges,

$$E_i^* = \frac{1}{4\pi\varepsilon_0} \sum_{j \neq i} Z_j e z_{ij} r_{ij}^{-3} \qquad (i, j = 1, \ldots, 5). \tag{6}$$

Here the static ion charges $Z_j = s Z_j^{nom}$ are products of an ionicity s and nominal ion charges $Z_1^{nom} = 2$, $Z_2^{nom} = 4$, $Z_3^{nom} = Z_4^{nom} = Z_5^{nom} = -2$ for the $BaTiO_3$ and $SrTiO_3$ crystals and $Z_1^{nom} = 1$, $Z_2^{nom} = 5$, $Z_3^{nom} = Z_4^{nom} = Z_5^{nom} = -2$ for the $KNbO_3$ crystals. The summation extends over all the ions of the crystal except the ith ion type, r_{ij} is the distance between the ith and jth ions and z_{ij} is a projection of r_{ij} on the z axis. Then one may derive

$$\frac{\partial E_i^*}{\partial z} = \frac{1}{4\pi\varepsilon_0} \sum_{j \neq i} Z_j e \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5}. \tag{7}$$

The equation (7) can be represented with the use of the coefficients c_{jk} [3] as

$$\frac{\partial E_i^*}{\partial z} = -\frac{e}{\varepsilon_0 a^3} \sum_j c_{ij} Z_j \tag{8}$$

where a is the unit-cell parameter and the summation extends over all the ion types in the crystal. The field strength gradients on the cation positions are $\partial E_1^* / \partial z = \partial E_2^* / \partial z = 0$. In the case of the equality of Z_j to the normal ion valence, we obtain for the anions

$$\frac{1}{2} \frac{\partial E_3^*}{\partial z} = -\frac{\partial E_4^*}{\partial z} = -\frac{\partial E_5^*}{\partial z} = \frac{2(p-q)e}{\varepsilon_0 a^3}. \tag{9}$$

In a general case, the local field gradient values should be changed by the ionicity s multiplication. Before calculating the Born charges Z_j^* we inverted the matrix in equation (5) for arbitrary α_j by using the Maple V Release 3 system. Then the substitution of $\partial E_j^* / \partial z$ from (9) into (5) allowed us to calculate Z_j^* using different α_j and s values. We have obtained a best fitting to the *ab initio* calculation data by using the value $s = 0.55$ for all the studied crystals. The ionicity is close to a value evaluated earlier for the $BaTiO_3$ crystal [9].

The calculated Born charges for the standard α_j values [2, 3] are presented in the first line of table 1. Both the cation charges Z_1^* and Z_2^* which do not contain the field gradient contributions are practically equal to the corresponding *ab initio* charges. They do not differ substantially from the 'classical' Born charges calculated using equation (1). The proximity of Born cation charges to $(\varepsilon_\infty + 2)Z_j/3$ values was established earlier by Axe [11]. The small difference between $Z_{1,2}^*$ and $(\varepsilon_\infty + 2)Z_{1,2}/3$ arises owing to the well known difference of $E_{1,2}^*$ from the Lorentz field [3]. It is interesting to note that $Z_{Sr}^* = 2.55$ for $SrTiO_3$ only is somewhat greater then $Z_{Sr}^* = 2.39$ for the SrO crystal [13]. The large Z_2^* is caused by large values $\varepsilon_\infty \geqslant 5$ and nominal charges $Z_2 = 4$–5.

As to anion Born charges, as seen from table 1, the localized Slater model gives $|Z_3^*|$ larger and $|Z_4^*|$ much less than the corresponding charges from *ab initio* calculations on the basis of the delocalized model. Consequently the localized Slater model allows us to obtain the large values Z_2^* and $|Z_3^*|$ only due to the large values of ε_∞ and $|\partial E_{3,4}^* / \partial z|$ without any

Table 1. Electronic polarizabilities (in $4\pi \times 10^{-30}$ m^3 units) and effective Born and Scott charges of the BaTiO$_3$, SrTiO$_3$ and KNbO$_3$ cubic crystals with the ionicity $s = 0.55$.

Crystal	α_1	α_2	α_3	$\alpha_4 = \alpha_5$	Z_1^*	Z_2^*	Z_3^*	$Z_4^* = Z_5^*$
BaTiO$_3$	1.95	0.19	2.41	2.41	2.64	7.12	−8.68	−0.540
($a = 0.401$ nm,	5.25	0.60	1.95	0.98	2.63	7.16	−5.51	−2.14
$\varepsilon_\infty = 5.76$)	*ab initio* Born charges				2.75	7.16	−5.69	−2.11
	ab initio Scott charges				1.15	2.98	−2.37	−0.879
SrTiO$_3$	1.60	0.19	2.25	2.25	2.55	7.44	−8.97	−0.505
($a = 0.3905$ nm,	4.60	0.50	1.87	0.97	2.59	7.10	−5.65	−2.02
$\varepsilon_\infty = 5.66$)	*ab initio* Born charges				2.54	7.12	−5.66	−2.00
	ab initio Scott charges				1.07	2.99	−2.38	−0.841
KNbO$_3$	1.14	0.25	2.40	2.40	1.11	9.40	−8.78	−0.484
($a = 0.4022$ nm,	3.85	0.50	2.16	1.21	1.10	9.56	−6.66	−1.60
$\varepsilon_\infty = 5.00$)	*ab initio* Born charges				1.14	9.23	−7.01	−1.68
	ab initio Scott charges				0.510	4.13	−3.13	−0.751

specific microscopic suppositions. But the Slater model gives a relation $Z_3^*/Z_4^* \approx 16$–18 which arises owing to the high $|\partial E_{3,4}^*/\partial z|$ values and is very large in comparison with the *ab initio* ratio $Z_3^*/Z_4^* \approx 3$–4. Such a situation with the anion charges may be improved by using the known result [13] that in Clausius–Mossotti [1, 2, 4] and Slater [3] type formulae the effective electronic polarizabilities should be used instead of the usual ones. The reason is overlapping electronic shells of the nearest ions in crystals with the ion–covalent character of chemical bonds. The calculations by the authors of [13] have shown that, in such binary AO oxides as CaO, SrO and BaO, the effective electronic polarizabilities of the cations were decreased in contrast with the effective electronic polarizabilities of the anions which were increased in comparison with the usual α_j values [2, 3]. However it is obviously that in the ABO$_3$ oxides the situation can be substantially different due to the gradients of the local fields on the oxygen ions. Therefore we have varied α_j in assumption of the possibility of the anisotropy of the oxygen polarizabilities in order to obtain the values of Z_j^* nearest to [6] (the second line in table 1). For all the α_j combinations the high-frequency dielectric permittivities ε_∞ of the crystals are chosen near the known experimental data for the cubic phase in a vicinity of the Curie point.

Z_1^* and Z_2^* were little changed due to α_j variation; meanwhile Z_3^* and Z_4^* were changed enough, directed to decreasing the Z_3^*/Z_4^* ratio. In the third and fourth lines of table 1 we placed the *ab initio* Born charges Z_j^* [6] and the corresponding Scott [14] charges $Z^S = Z^*/\sqrt{\varepsilon_\infty}$.

The main result of our variation of the α_j values is the anisotropy of the oxygen electronic polarizabilities $\alpha_3/\alpha_4 \approx 1.8$–$2$. The presence of such anisotropy in the ABO$_3$ perovskite crystals is obvious due to an asymmetrical environment of the oxygen ions. Anisotropy of the same character ($\alpha_3/\alpha_4 > 1$) was earlier described in a series of works fulfilled in the framework of both a polarizable point-charge model [15] and a non-linear shell model [7, 16, 17]. However our Z_j^* values are substantially nearer to the *ab initio* ones than the values calculated by using the shell model [7]. The second result is decreasing the α_3 and α_4 in comparison with the corresponding Slater values. It is the consequence of multiplying the $\alpha_{3,4}$ values by the large $|\partial E_{3,4}^*/\partial z|$ values in formula (5) for $Z_{3,4}^*$. Decreasing the α_3 and α_4 values leads to increasing the α_1 and α_2 ones in order to keep $\varepsilon_\infty = $ constant. But these α_j variations do not change the cation Born charges Z_1^* and Z_2^*.

So, the very large effective Born charges Z_2^* and $|Z_3^*|$ are characteristic of both the delocalized and localized polarization models for the ABO_3 type perovskite crystals. Especially the large $|Z_3^*|$ values come out by using the standard (Slater) set of electronic polarizabilities [3]. A microscopical mechanism of the large Z_2^* and $|Z_3^*|$ values arising is studied by the authors of [5–8] who connect it with the well known hybridization effect between O 2p and Ti 3d (or Nb 4d) states (see, for example, [18]). The hybridization can be changed during a variation of the length of B–O_1 bonds and this dynamical effect can be interpreted as the large charge transfer between the B and O_1 ions.

Therefore the presence of considerable covalency in the B–O_1 bonds of the ABO_3 perovskites is not in doubt. However a quantitative evaluation of covalency (ionicity) is very difficult because the static ion charges Z are unknown and the Born effective charges are not suited for this aim. In the case of the binary NaCl type cubic crystals the Scott charges $Z^S = Z^*/\sqrt{\varepsilon_\infty}$ [14] can be used for the evaluation of the ionicity. Experimental data for ε_∞ [1] and equation (1) allow us to conclude that the difference between Z^S and Z is less than 3%.

However *ab initio* data for the Z^S charges of the ABO_3 perovskites (the fourth lines in table 1) have a principal difference from the corresponding data for the NaCl type crystals that is manifested in $|Z_3^S| > |Z_3^{nom}|$ and in the large anisotropy Z_3^S/Z_4^S. Both these circumstances are impossible for the real static charges. To explain these results it is quite enough to use relation (5). Because of the fact that the $E_j^*/(\sqrt{\varepsilon_\infty}E)$ value has only an insignificant difference from 1 [3], Z_j^S and Z_j are close only for the cations. As to the anions, the signs of $\partial E_3^*/\partial z < 0$ and $\partial E_4^*/\partial z > 0$ as well as the large field gradients lead to the Z_3^S and Z_4^S values which are shown in table 1. In our opinion the local field gradients can be considered as an additional source of the charge transfer.

The delocalized and localized models can be regarded as mutually supplementary approaches to the problem of the crystal polarization.

3. Conclusions

(i) The large Born effective dynamical charges of the B and O_1 ions can be interpreted in the frameworks of the delocalized and localized models of the crystal lattice.

(ii) For the interpretation of the large transfer of the delocalized electronic charge it is necessary to take into account the effective field gradients and the large ε_∞ value in the framework of the localized Slater model.

(iii) The Slater theory has general character and can be used for crystals with ion–covalent chemical bonds. However, instead of the usual values of the electronic polarizabilities, the effective ones should be used.

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