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THE POLARIZABILITY ANISOTROPY OF OXYGEN ATOMS AS A POSSIBLE REASON FOR THE FORMATION OF ANTIFERROELECTRICITY IN PEROVSKITES

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Abstract. The paper analyzes the structural features of perovskite-like ABO_3 type materials responsible for the formation of antiferroelectric phases. For this purpose, the descriptions of some single crystals have been compared using three models: the adapted Slater dipole model (I), the Cowley shell model (II) and the Born – Karman model supplemented with consideration dipole-dipole forces and parameterized basing on *ab initio* calculations by Ghosez (III). The parameters of model I were found at which qualitative agreement with the data on inelastic X-ray scattering obtained by experiments with lead hafnate was observed. An analysis of all the results led to the conclusion that model I and the Ghosez parameterization confirmed the hypothesis about the key role of the lateral component of the oxygen atoms' polarizability over its axial component for the antiferroelectricity formation. However, model II data did not support this.

Keywords: structural phase transition, antiferroelectric, shell model, dipole-dipole interaction

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АНИЗОТРОПИЯ ПОЛЯРИЗУЕМОСТИ АТОМОВ КИСЛОРОДА КАК ВОЗМОЖНАЯ ПРИЧИНА ФОРМИРОВАНИЯ АНТИСЕГНЕТОЭЛЕКТРИЧЕСТВА В ПЕРОВСКИТАХ

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Аннотация. В работе проанализированы особенности структуры перовскитоподобных материалов вида ABO_3 , ответственные за формирование антисегнетоэлектрических фаз. С этой целью сопоставлено описание ряда монокристаллов с помощью трех моделей: адаптированной дипольной Слэтера (I), оболочечной Каули (II) и модели Борна – Кармана, дополненной учетом диполь-дипольных сил и параметризованной на основе первопринципных расчетов Госеза (III). Определены параметры модели I, при которых наблюдается качественное согласие с данными по неупругому рассеянию рентгеновского излучения из экспериментов с гафнатов свинца. Анализ всех результатов привел к заключению, что модель I и параметризация Госеза подтверждают гипотезу о ключевой роли латеральной компоненты поляризуемости атомов кислорода над ее аксиальной компонентой для формирования антисегнетоэлектричества. Однако результаты использования модели II этого не подтверждают.

Ключевые слова: структурный фазовый переход, антисегнетоэлектрик, оболочечная модель, диполь-дипольное взаимодействие

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Introduction

Structural instabilities in perovskites are the focus of much attention, since perovskite crystals and thin films based on them find numerous technical applications in electromechanical sensors and drives, pyroelectric sensors, electrocaloric coolers, energy storage and memory devices [1–5].

When the crystal becomes unstable with respect to one of the phonon modes, a structural phase transition occurs. This process can be described as follows. A crystal consisting of N atoms has $3N$ degrees of freedom associated with displacements of these atoms from fixed equilibrium positions (three degrees of freedom for each atom).

The internal energy can be expressed in quadratic form in the harmonic approximation:

$$\frac{1}{2} \mathbf{u}^T \cdot \mathbf{U} \cdot \mathbf{u}, \quad (1)$$

where \mathbf{u} is the displacement vector with the length $3N$, \mathbf{U} is the matrix of force constants for the vector \mathbf{u} .

Some quadratic eigenvalues are necessarily zero, for example, the eigenvalues corresponding to homogeneous displacement of the crystal as a whole. However, the remaining eigenvalues must be positive so that the crystal tends to return to the state of equilibrium under an external perturbation. This theory is outlined in a number of papers and textbooks on lattice dynamics [6, 7]. When a structural phase transition from a cubic phase to a low-symmetry phase (characterized by some kind of distortion of the crystal lattice) occurs in perovskite-like crystals, the eigenvalue corresponding to this distortion becomes zero or negative. As for ferroelectric phase transitions, then this eigenvalue should correspond to the zero wave vector, i.e., the Γ point of the cubic Brillouin zone. The eigenvalues for other transitions, for example, antiferroelectric, correspond to another point in the Brillouin zone.

Thus, the question of why Perovskites undergo phase transitions and why all these transitions are so different can be broken into more specific questions, namely, why some of the eigenvalues could turn out to be negative and why this negative number corresponds exactly to this, and not to any other point in the Brillouin zone. For example, an approach outlined in John Slater's study [9] for barium titanate BaTiO_3 proposes to divide all forces acting on ions into two groups.

The *first group* includes short-range repulsive forces arising (in the simplest interpretation) because electron clouds of the ion crystal tend to reduce the degree of mutual overlap. These repulsive forces tend to stabilize the high-symmetry cubic phase, in other words, preserving all eigenvalues of the quadratic energy form positive.

The *second group* of forces are dipole–dipole forces resulting from the Coulomb interaction. Unlike the first group, dipole–dipole forces are long-range. If the influence of such dipoles on each other is taken into account, it turns out that such dipoles tend to line up along the O–B bonds in the ABO_3 structure in perovskite-like crystals. Such a tendency towards forming bonds by dipole–dipole forces can lead to a negative value of the eigenvalue corresponding to this distortion. The above-mentioned distortion induces ferroelectricity, since the displacements are arranged identically in each of the ABO_3 cells. This structural rearrangement is formed due to predominant influence of dipole–dipole forces specifically on the center of the Brillouin zone [8].

Thus, Slater's theory answers both questions posed for a ferroelectric such as BaTiO_3 : why an eigenvalue becomes negative, and exactly which one it is.

However, John Slater's views have been regularly re-examined critically since the 1990s. For example, it was discovered through advances made in quantum mechanical calculations that these crystals are far from absolutely ionic, i.e., the overlap of electron clouds leads not only to repulsion but also to attraction due to orbital hybridization and formation of partially covalent bonds. In other words, destabilization of the cubic phase occurs not only due to the action of dipole–dipole forces, but also due to the influence of partial covalence of the bond. The role of dipole–dipole forces is preserved in this case, since covalent forces are short-range. Otherwise, it is difficult to explain exactly how long-range ordering of the structure can be achieved and establish the specific point of the Brillouin zone that the resulting distortions correspond to.

A recent paper by Burkovsky [10] uses the Slater model [9] to describe mismatched anti-ferroelectric phases: it is found that dipole–dipole forces can enhance not only homogeneous polarization (center of the Brillouin zone) but also incommensurate distortions; however, this requires more complex characteristics of short-range forces that could cancel the tendency of dipole-dipole forces towards enhancing polarization along O–B bonds. This is possible if the crystal structure is such that it is extremely energetically unfavorable to form a dipole along such a bond even in the presence of dipole–dipole forces. For example, considerable energy costs are required if the ions are packed very closely and cannot shift much along these O–B bonds, and their electron clouds also cannot stretch in this direction. The tolerance factor acts as a measure of atomic packing for perovskite-like crystals: when its values are less than unity, the atoms are tightly packed along the O–B chains [11]. The tolerance factor for a PbZrO_3 crystal of the lead zirconate family is equal to 0.756, corresponding to the following case: the ionic radius of the B-ion (Zr^{4+}) is large, and the oxygen anions O^{2-} are 'sandwiched' between zirconium cations. If the ability to form O–B dipole bonds is suppressed, other pathways emerge for dipole ordering. For example, if strong polarizability of oxygen atoms in the O–A planes (perpendicular to the O–B bonds) is combined with strong polarizability of ion A, such loss of cubic symmetry for which the dipoles form an incommensurate modulation wave propagating in the O–A plane may be energetically favorable.

Slater's model is by no means the only one capable of explaining why incommensurability and antiferroelectricity arise in perovskites. We should consider the shell model describing the total energy of the lattice rather than that of its dipole subsystem as well as the Born–Karman model taking into account dipole–dipole forces, also used earlier to parameterize the lattice energy of perovskite-like crystals. These two models have not been compared before, and we propose to take the first steps in this direction.

Objectives and experimental procedure

To find out how significantly the combination of the polarizability of oxygen atoms in the O–A planes with the strong polarizability of ion A affects the formation of experimentally observed disproportionate and antiferroelectric phases in crystals of the lead zirconate family, we compare the values of the polarizability of various groups of atoms in the cubic phase of lead hafnate (PbHfO_3). To this end, we analyzed experimental data on inelastic X-ray scattering on single crystals of lead hafnate antiferroelectric in the framework of two models: dipole [10] and shell [12, 13].

In our opinion, the mathematical framework based on the shell and dipole models, used to describe the phenomena under consideration, is too extensive to be considered in its entirety in this paper, especially since an explicit mathematical representation of these models was given by Cowley [13] and Burkovsky [10]. We compare the existing results with the polarizabilities obtained from the first-principle (*ab initio*) quantum mechanical calculations by Ghosez et al. [14].

The shell model was first proposed by Dick and Overhauser [15] and adapted for the Perovskites by Cowley [13]. Polarizability consists of the sum of ionic and electronic polarizabilities within the framework of the model. The first one is associated with displacement of the entire ion from the equilibrium site. The displacement of an ion under the action of external forces is prevented by short-range forces between the ion shell and the shells of its neighbors. In addition to displacement of the entire ion, the charged core is displaced inside the electron shell. This process is equated to the second, electronic, polarizability.

The dipole model is considered a simplification of the shell model. The simplification is that it is sufficient to account for the long-range forces and only parts of short-range ones describing the polarizability of atoms in the crystal lattice to describe the internal energy in the crystal [10].

The study by Ghosez et al., with whose results we compare the polarizabilities, performed decomposition of interatomic interactions into short- and long-range components for several perovskite-like crystals: antiferroelectric lead zirconate (PbZrO_3) and ferroelectrics barium titanate and lead titanate (BaTiO_3 and PbTiO_3). We recalculated the polarizabilities from the Ghosez parameters as Z^2/k , where Z are the Born effective charges and k are the corresponding force constants.

The main results of the analysis are presented below.

Experimental phonon dispersion curves and their description based on the shell model are shown in Fig. 1, *a* and *b* [12]. Apparently, the shell model adequately reproduces the anisotropy of phonon dispersion curves for transverse phonons.

The acoustic phonon branches were converted into dipole stiffness α using the dipole model to describe the experimental data (see Fig. 1, *a*, *b*) by the formula

$$\alpha = CE^2,$$

where E , J , is the phonon energy; C , $\text{C}^2/\text{J}^2\cdot\text{m}^3$, is the dimensional coefficient.

We consider this conversion to be fairly reasonable, since the frequency of transverse acoustic phonons and dipole stiffness are symmetric quantities: the higher the value of dipole stiffness, the greater energy the phonons creating such dipole waves should have. Fig. 1, *c* shows a three-dimensional graph of dipole stiffness in the $hk0$ plane of the Brillouin zone: qualitative agreement with experimental data on inelastic scattering by single crystals of lead hafnate was achieved at $C = 0.12 \text{ C}^2/(\text{J}^2\cdot\text{m}^3)$. To represent stiffness within the framework of the dipole model in this manner, the polarizability of the A-ion α_A should be higher than the polarizability of the B-ion α_B ; it is obtained that the anisotropy parameter of oxygen atoms $\delta = \alpha_{\text{O-A}}/\alpha_{\text{O-B}}$ is equal to 1.40 in this case.

Analyzing the results in Fig. 1, we can conclude that both models adequately reproduce the anisotropy of phonon dispersion curves along different directions, which means that a certain coincidence can be expected when dipole and shell models are used.

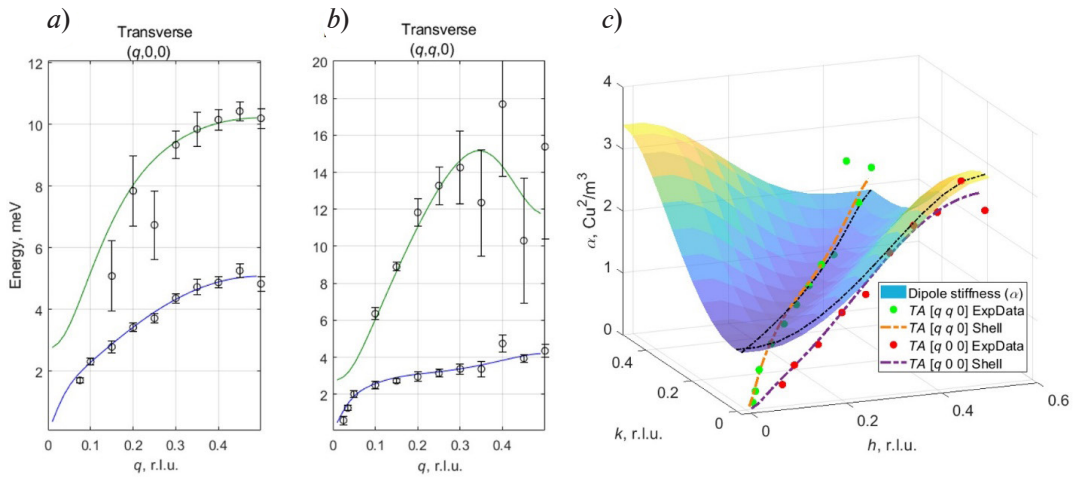


Fig. 1. Experimental phonon dispersion curves of lead hafnate in cubic phase (symbols) and their approximations by the shell model (solid lines) for transverse phonons propagating in the directions [100] (a) and [110] (b); description of acoustic phonon branch (TA) by the dipole model (c)

The table shows the polarizabilities of atoms obtained by the three models, as well as similar data for barium titanate BaTiO_3 obtained by Turik and Khasabov [16] using the shell model and the Slater model [9].

Table

Comparison of polarizabilities obtained by different calculation models for the oxygen anion in two crystal sites and for various cations

ABO_3	Model	Polarizability, \AA^3			
		α_A	α_B	$\alpha_{\text{O-A}}$	$\alpha_{\text{O-B}}$
PbHfO_3	Shell [12, 13]	4.90	0.37	2.74	3.63
	Dipole [10]			3.90	2.78
PbZrO_3	<i>Ab initio</i> calculations by Ghosez [14]	177.43	22.33	55.80	12.48
PbTiO_3		89.86	52.73	21.70	32.39
BaTiO_3		10.07	52.17	9.97	38.86
	Shell [16]	1.95	0.18	0.64	3.80
	Slater [9]	1.94	0.19	2.38	

Notations: α_A , α_B are the polarizabilities of the A^{2+} and B^{4+} cations; $\alpha_{\text{O-A}}$, $\alpha_{\text{O-B}}$ are the polarizabilities of the O^{2-} anion in O–A planes and along O–B bonds. Note. The values of electronic polarizability are given for the shell model, and those of total polarizability for the other models.



According to our estimates, the polarizabilities α_A and α_B of A- and B-cations in lead hafnate turned out to be very similar for the dipole and shell models (the case in the table when they are strictly equal is accidental), but the polarizabilities of oxygen anions are different. Moreover, different predictions were obtained for the ratio of polarizabilities of oxygen atoms along different directions within the framework of the two models: the anisotropy parameter $\delta = \alpha_{O-A}/\alpha_{O-B} = 0.75$ for the shell model, and $\delta = 1.40$ for the dipole model.

This is an unexpected result, which can be explained by the simplification of the shell model, namely, that the dipole model does not account for all the particulars of the effect of short-range forces on atoms. However, the problem requires extensive research, and it is impossible to make an unambiguous choice in favor of any model at this stage.

According to the *ab initio* calculations by Ghosez, the value of the anisotropy parameter δ of oxygen atoms exceeds unity only for antiferroelectric PbZrO_3 , while for ferroelectrics BaTiO_3 and PbTiO_3 this parameter is less than unity. This suggests that the anisotropy of oxygen polarizability, when dipole formation along the O–B bonds is suppressed and enhanced in the O–A planes, is a major factor in the origin of antiferroelectricity.

Notably, there is a large numerical difference between the polarizabilities obtained by Ghosez by calculations from first principles (*ab initio*) and those based on model predictions. In our opinion, the reason for the difference may lie in the instability of the crystal assumed by the Ghosez model (in contrast to the assumptions of the dipole and shell models), implying that the polarizabilities obtained by this model may be higher. In addition, we used Born charges to calculate polarizabilities using the Ghosez model; however, constraints are sometimes imposed on such charges in calculations of local crystal properties, which include the polarizability of individual atoms.

Discussion

In this paper, we analyzed the particulars of the structural configuration of perovskite-like materials to identify its specific properties inducing antisegetoelectric states during structural phase transitions.

To this end, we described the experimentally observed phonon spectrum of lead hafnate (PbHfO_3) using two models: shell [12] and dipole [10]. These models are essentially similar: the internal energy of the crystal structure consists of two forces of a different nature that affect ions, the short-range and long-range ones. The former arise due to overlap of electron clouds of neighboring ions and include both repulsive forces aimed at maintaining the highly symmetric phase in the crystal and attractive forces caused by hybridization of electronic orbitals and the formation of partially covalent bonds. The latter, i.e., long-range forces are Coulomb in nature, determining the internal organization of the crystal at long distances, due to the ordering of dipoles in the crystal. The dipole model is a certain rationalization of the shell model and is convenient for representing incommensurate phases in antiferroelectrics. The simplification is that the description of internal energy in the crystal is limited, only accounting for a part of the short-range forces affecting the polarizability of the atoms of the crystal lattice (accounting for the long-range forces remains).

In general, both models adequately reproduce the experimental data, the descriptions are in agreement with respect to the polarizabilities of A- and B-cations, however, they yield different estimates for the polarizability of oxygen anions: according to the shell model, the polarizability of oxygen atoms α_{O-A} along the O–A planes is less than that for oxygen atoms along the O–B bonds; the results turn out to be exactly the opposite within the framework of the dipole model.

Comparison of the obtained parameters with the results of *ab initio* calculations by Ghosez et al. [14] for ferroelectric and antiferroelectric perovskites confirms the hypothesis of the key role that the special nature of polarizability anisotropy of oxygen atoms in the crystal plays in the structural phase transition into antiferroelectric or incommensurate phase. According to the results obtained by *ab initio* calculations, as well as by the dipole model, the value of α_{O-A} must exceed the value of α_{O-B} to achieve the transition of the crystal to the antiferroelectric phase. At the same time, there is no quantitative agreement between the parameters: the parameter values obtained by Ghosez are much higher than those for the dipole–dipole model. We attribute this discrepancy to the fact that we used Born charges to calculate local polarizabilities by the Ghosez model, which, strictly speaking, are determined for displacements of entire sublattices, and not individual ions, i.e., the polarizability calculated using Born charges may be significantly overestimated.

Conclusion

Each of the model descriptions obtained has some advantages over the others. The benefit of the dipole model is that the role of each of the parameters governing the experimental three-dimensional distribution of dipole stiffness is clear. The benefit of the shell model is that the calculated results can be directly compared with the experimental data on inelastic X-ray scattering. Meanwhile, the description by the Born–Karman model accounting for dipole–dipole forces allows to correlate the experimental data with the results obtained by calculating the electronic structure of many-particle systems (based on density functional theory (DFT)), i.e., DFT calculations.

The reasons for incommensurability and antiferroelectricity in perovskites are yet to be fully understood; attempts at interpretation include macroscopic models and atomistic models with varying degree of detail [10, 17–21]. In this paper, we limited ourselves to three models for which we were able to establish the role that the ratio of polarizabilities of various atoms plays in the given phenomenon. The predictions of two models are similar in this aspect, but contradict the predictions of the third one. So far, it seems premature to make an unambiguous choice in favor of any of the models, since each has its advantages with sound arguments to support them.

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