



B STRUCTURAL SCIENCE CRYSTAL ENGINEERING MATERIALS

ISSN: 2052-5206 journals.iucr.org/b

X-ray diffraction study of the atomic interactions, anharmonic displacements and inner-crystal field in orthorhombic KNbO₃

Adam I. Stash, Ekaterina O. Terekhova, Sergey A. Ivanov and Vladimir G. Tsirelson

Acta Cryst. (2021). B77, 728-739



Author(s) of this article may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see https://journals.iucr.org/services/authorrights.html

research papers



STRUCTURAL SCIENCE CRYSTAL ENGINEERING MATERIALS

ISSN 2052-5206

Received 2 June 2021 Accepted 5 July 2021

Edited by O. V. Yakubovich, Moscow State University, Russian Federation

Keywords: X-ray diffraction; electron density; inner-crystal field; ferroelectricity; atoms in molecules; anharmonicity; potassium niobate; perovskite.

CCDC reference: 2094437

Supporting information: this article has supporting information at journals.iucr.org/b



X-ray diffraction study of the atomic interactions, anharmonic displacements and inner-crystal field in orthorhombic KNbO₃

Adam I. Stash,^a Ekaterina O. Terekhova,^b Sergey A. Ivanov^c and Vladimir G. Tsirelson^b*

^aA.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova str., Moscow 119991, Russian Federation, ^bQuantum Chemistry Department, D.I. Mendeleev University of Chemical Technology, Miusskaya Square, 9, Moscow 125047, Russian Federation, and ^cDepartment of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russian Federation. *Correspondence e-mail: vtsirelson@yandex.ru

An X-ray diffraction study aimed at establishing the subtle details of the electron density and anharmonicity of the atomic vibrations in a stoichiometric monodomain single crystal of potassium niobate, KNbO₃, has been conducted at room temperature (orthorhombic ferroelectric phase Amm2). The cation and anion displacements obtained from the experiment are weakly anharmonic without any manifestation of structural disorder. The chemical bond and interatomic interactions inside and between crystal substructures at the balance of intracrystalline forces are characterized in detail. The role of each of the ions in the formation of the ferroelectric phase was studied and the features of the electron-density deformation in the niobium and oxygen substructures, and the role of each of them in the occurrence of spontaneous polarization are established. The position-space distribution of electrostatic and quantum forces in $KNbO_3$ is restored. It is emphasized that for the completeness of the analysis of the nature of the ferroelectric properties it is necessary to consider both static and kinetic electronic factors, which are of a quantum origin. The experimental results and theoretical estimations by the Kohn-Sham calculation with periodic boundary conditions are in reasonable agreement, thus indicating the physical significance of the findings of this study.

1. Introduction

KNbO₃ (KNO) is a canonical example of a ferroelectric material with a perovskite structure, differing from other representatives of this family by the high values of the spontaneous polarization, piezoelectric and electro-optical coefficients (Lines & Glass, 2001; Shirane et al., 1954; Hewat, 1973; Wang et al., 2020). It is the only ferroelectric with the same set of phase transitions as BaTiO₃, but with more noticeable structural distortions and enthalpy changes in the observed phase sequence. At the temperature T > 591 K, KNO is a paraelectric with a cubic unit cell (space group Pm3m). The K⁺ ions occupy positions at the vertices of the unit cell, the Nb ions are at its centre and O^{2-} anion sites are at the centres of the cube faces, forming a perfect octahedron around Nb. With decreasing temperature, the crystal undergoes a series of structural phase transitions: from the cubic phase to the ferroelectric phase at T = 591 K (space group P4mm), then at T = 498 K to the second ferroelectric phase with the space group Amm2, which is stable at room temperature, and finally, at T = 238 K, into the rhombohedral phase R3m (Shirane *et al.*, 1954; Hewat, 1973; Yamanaka et al., 2009). Commonly, this phase sequence is considered to be a result of a shift of the

electronic reprint

ferroelectric active central Nb ion in the [001] and [011] directions, respectively, in the tetragonal and orthorhombic phases relative to the cubic aristotype (Hewat, 1973), a highly symmetric structure that is an idealized version of the lowest symmetric structure. Considering the mechanism of phase transitions in KNO by X-ray absorption fine structure (XAFS) spectroscopy, Shuvaeva et al. (1998) concluded that structural disorder appears near the phase transition points, as well as in high-temperature phases, when the positions of the Nb cations are noticeably disordered. At room temperature, this effect is negligible. According to the Landau theory of phase transitions, an explanation of the ferroelectric properties of KNO has been suggested (Lines & Glass, 2001). The thermodynamic Gibbs potential near the ferroelectric transition point was presented in the form of an expansion in a Taylor series in powers of a small order parameter, for which the spontaneous polarization \mathbf{P}_{s} was chosen.

The average and local atomic and electronic structure of potassium niobate, its optical and ferroelectric properties, the mechanism of phase transition and spontaneous polarization have been studied using a wide set of experimental and theoretical methods (Hewat, 1973; Wang *et al.*, 2020; Yamanaka *et al.*, 2009; Shuvaeva *et al.*, 1998; Liang & Shao, 2019; Stash *et al.*, 2017; Nakamoto *et al.*, 2006; Bozinis & Hurrell, 1976; Kalinichev *et al.*, 1993; Postnikov & Borstel, 1994; Cochran, 1969; Currat *et al.*, 1989; Fu *et al.*, 1999). The KNO electronic band structures and the densities of states (DOS) and their link to the mechanism of polarization have also been investigated (Fu *et al.*, 1999; Schmidt *et al.*, 2017).

In the highly symmetric phases of perovskites, a multimode distribution of atomic positions is observed with respect to the average atomic site (Abramov *et al.*, 1995*a,b*; Zhurova *et al.*, 2000). The temperature dependency of the displacement parameters of the cation and anion subsets of KNbO₃, revealed by the powder X-ray diffraction method, has shown that there are noticeable anharmonic vibrations of the Nb ions (Ivanov *et al.*, 1979, 1984). Thus, ferroelectric phase transitions



The orthorhombic unit cell and NbO₆ octahedron in the KNbO₃ crystal.

in KNbO₃ are intrinsically linked with anharmonicity of the Nb-ion displacements (Xu *et al.*, 2018).

At the atomic level, the instability of the highly symmetric phase is associated also with the partially covalent Nb-O bonds in the NbO₆ octahedron. According to Hewat (1973), the NbO₆ octahedron may be represented as a rigid unit having a set of low-frequency vibration and libration modes at high temperatures. The first ones, condensing with decreasing temperature, lead to ferroelectric distortions, while the latter manifest themselves in the anisotropy of displacements or in the splitting of the positions of O atoms in the equatorial plane of the Nb octahedron. In the language of the phonon model (Cochran, 1969; Currat et al., 1989), with decreasing temperature, the frequency of the 'soft' mode decreases nonlinearly. Near the phase-transition temperature, $T_{\rm c}$, this frequency tends to zero, and at $T = T_c$ the soft mode 'freezes' in the extreme position specified by its eigenvector. Spontaneous displacement of Nb cations occurs and its oxygen octahedron is distorted; the Nb-O bonds of the octahedron are no longer equivalent and spontaneous polarization P_s arises (Lines & Glass, 2001). In this phenomenological picture, the polarization vector averaged over the unit cell is directed along the c axis of the unit cell (space group Amm2). To estimate the spontaneous polarization, both experimental and computational methods have been used, but the results obtained so far are not reliable, as discussed by Maksimov et al. (2004). The magnitude of polarization in orthorhombic KNO, estimated by various experimental methods, is in the range 20-49 μ C cm⁻² (see, for example, Wang *et al.*, 2020). Calculations by the Berry phase approach gave \mathbf{P}_{s} values ranging from 34 to 41 μC cm⁻² (Fu et al., 1999; Wang et al., 2020; Yamanaka et al., 2009).

The phonon model considers normal harmonic vibrations, while the displacements of atoms in a crystal occur in the position space. In addition, the probability distribution functions (PDF) for displacements of atoms from equilibrium positions are anharmonic (Shuvaeva et al., 1998; Postnikov & Borstel, 1994; Cochran, 1969; Currat et al., 1989; Zhurova et al., 2000). Anharmonicity is taken into account in X-ray and neutron structural analyses by introducing additional displacement parameters into the electron-dynamic structural model, which is then optimized for a set of experimental diffraction intensities. This allows the atomic PDF accounting for anharmonic motion of atoms to be reconstructed. However, X-ray diffraction studies which consider anharmonicity in perovskites are rare (Ohgaki et al., 1992; Postnikov & Borstel, 1994; Zhurova et al., 2000; Zhurova et al., 1992; Abramov et al., 1995a,b; Yamanaka et al., 2017; Ohgaki et al., 1992; Ivanov et al., 1999; Tsirelson et al., 2000; Zhurova & Tsirelson, 2002; Kibalin et al., 2021; Voufack et al., 2019). Furthermore, the electron distribution of potassium niobate in the position space was analyzed previously using total and deformation electron density (ED) and electrostatic potential (Yamanaka et al., 2009; Kawamura et al., 2013). Powder X-ray diffraction (PXRD) was commonly used. Unfortunately, this technique is less accurate than single-crystal diffractometry. Therefore, the powder diffraction data do not allow all the subtle features of the electron density in a crystal to be reliably studied. Actually, the simplest indicator of the precision of available KNO experiments, the discrepancy factor R is usually \sim 3–5% for these studies (Kawamura *et al.*, 2013; Boutaoui et al., 2008; Chen et al., 2011). The difficulties in establishing the electron-dynamic structural model of KNO using single-crystal X-ray structural analysis are also known. The problems are associated with the (commonly) complex microscopic (domain) structure of the grown KNO samples and their diffraction quality. Incomplete accounting for the interference of X-rays in a sample (extinction) leads to distortion of the electron density and atomic displacement parameters. Therefore, it is important to study a suitable KNO crystal with optimal diffraction properties described within the framework of kinematic diffraction theory (Tsirelson & Ozerov, 1996).

Thus, it should be admitted that the nature of the ferroelectricity of KNO has not yet been fully elucidated and contradiction in a number of details remains. Also, with regard to the details of the electron density, its relation to the polarization properties of potassium niobate and numerical estimates of the anharmonic atomic displacements, the available results differ. The aim of this article is to make this issue clearer. We will present a detailed analysis of the distribution of electron density, chemical bonding and the anharmonicity of atomic displacements in the ferroelectric phase of KNO based on the results of a precise X-ray diffraction experiment on a perfect stoichiometric single crystal, and also a detailed study of the picture and nature of the distribution of the innercrystal field in this crystal based on the approach described by Tsirelson & Stash (2020, 2021), Shteingolts et al. (2021) and Bartashevich et al. (2021). The experimental data are compared with the results of the theoretical calculation of KNO by the Kohn-Sham method with periodic boundary conditions.

2. Experimental

The KNO single crystals were grown according to the method considered in detail by D'yakov *et al.* (2004). Stoichiometric control of the cationic and anionic subsets in a crystal did not reveal deviations from the nominal values within the standard deviations. The as-grown KNbO₃ crystals were poled under the applied electric field of 2 kV cm⁻¹ in oil. The electric field was applied to crystals after heating them to 200 °C, followed by cooling. The domain configuration of each poled KNbO₃ single crystal was investigated under a polarized light microscope. The single-crystal sample, which was almost in a single-domain state (the correct *c*-axis orientation of the crystals was determined by the Laue method), was chosen for further analysis. This crystal, with a size of $0.20 \times 0.12 \times 0.04$ mm, did not show twinning in the entire range of the reflection angles.

The diffraction intensities were collected at T = 293 K on a four-circle automatic Enraf–Nonius CAD-4 diffractometer equipped with a point detector (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, β -filter). 11 554 reflection profiles were measured in the $\omega/2\theta$ -scanning mode in the range $10 < 2\theta < 120^{\circ}$; Ψ -scanning was additionally carried out to avoid the multiple

scattering. All the reflection peak profiles were remeasured repeatedly to attain the necessary precision. They were also checked visually to make sure that our crystal is almost in the monodomain state. The 11 544 X-ray reflection peaks were integrated using the *PANDSC* program (Stash *et al.*, 2015); all the data were then averaged and scaled using the *SORTAV* program (Blessing, 1995). The number of symmetry-equivalent reflections in each group varied from 4 to 16, and the discrepancy factor, averaged over the entire reflection set after the absorption correction, was $R_{int} = 0.032$. A numerical absorption correction was applied according to the indexed crystal faces.

From 1098 symmetry-independent structure factors, only two did not fit the condition $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ is the s.u. deduced from the diffraction intensities as it followed from the linearized theory of random errors (Tsirelson & Ozerov, 1996).

The refinement of the crystal structure within the spherical atom model with anisotropic harmonic motion was carried out using the *SHELXL2014* software package (Sheldrick, 2015). The Hansen & Coppens (1978) multipole model of electron density was then refined at the hexadecapole level for Nb and the octupole level for O atoms. The *XD2006* program (Volkov *et al.*, 2006) was used. Relativistic basis wavefunctions were used for all atoms (Macchi & Coppens, 2001). In the initial structural model, a single valence electron of the K (4s1) atom was divided between the O atoms; the monopole and higher-order multipoles of the K⁺ ion were set to zero. The extinction in the sample was corrected according to Becker & Coppens (1974) and had the following characteristics: isotropic secondary extinction, type I, Lorentz distribution, block disorientation of 237 s and block sizes of 0.98×10^{-6} cm.

The initial anharmonic parameters of the atomic displacements were obtained by high-angle least-squares refinement, followed by the all-angle refinement of the joint 'multipole model + fourth-order Gram–Charlier model' (Tsirelson & Ozerov, 1996). The weighting scheme for the refinement was chosen according to Sheldrick (2015); it minimizes the differences in the errors for reflections of different intensities. This protocol was also applied in the refinements over 1198, 1097 and 1096 reflections; no noticeable difference in the results was detected and the refinement over 1096 reflections with $F_o^2 > 3\sigma(F_o^2)$ was recognized as the appropriate one.

The obtained anharmonic parameters of the K^+ and O^{2-} ions proved to be statistically insignificant, while the nonzero components of the third- and fourth-rank tensors for the Nb atom are as follows:

 $C^{333} = -0.00008 (12), C^{113} = 0.00012 (11) \text{ and } C^{223} = 0.00008 (5) Å^3;$

 $D^{1111} = -0.00067 (15), D^{2222} = -0.00039 (3), D^{3333} = -0.00033 (4), D^{1122} = -0.00066 (2), D^{1133} = -0.00020 (3) and D^{2233} = 0.00008 (1) Å^4.$

Thus, the third-rank anharmonic parameters were determined with s.u. $\leq 1\sigma$, *i.e.* the probability of their statistical significance is not higher than 67%. The fourth-rank parameters are determined much more precisely. That defines a significance of the corresponding components of the atomic

 Table 1

 Characteristics of the X-ray experiment and refinement for the potassium niobate crystal.

Parameter	Value
Temperature (K)	293 (2)
Crystal size (mm)	$0.20 \times 0.12 \times 0.04$
Crystal shape	Prism
Colour	Colourless
Radiation source	Μο Κα
Wavelength, λ (Å)	0.71073
Space group	Amm2
a(A)	3.9719 (7)
$b(\dot{A})$	5.6943 (9)
$c(\dot{A})$	5.7209 (9)
$V(\dot{A}^3)$	129.39 (4)
Z	2
No. of reflections collected	11 554
No. of independent reflections with $I > 2\sigma(I)$	1097
Completeness of data	1.0
R _{int}	0.032
$\sin\theta_{\rm min}/\lambda$ (Å ⁻¹)	0.124
$\sin\theta_{\rm max}/\lambda ({\rm \AA}^{-1})$	1.217
Spherical atom model (1097 reflections $[I > 2\sigma(I)]$ 1	9 parameters}
R(F)	0.007
$wR(F^2)$	0.017
S	1 078
Weighting scheme	1.070
$w = 1/[\sigma^2(F_o^2) + (0.0110P)^2 + 0.0047P]; P = (F_o^2 + 2F)^2$	$(c_{c}^{2})/3$
Multipole model [1006 reflections $[I > 3\sigma(I)]$ 24 par	ametersl
R(F)	0.007
W(I) W(I)	0.007
S S	1 003
Weighting scheme	1.005
$w^{2} = 1/[\sigma^{2}(F_{o}^{2}) + (0.01P)^{2}]; P = (0.3333F_{o}^{2} + 0.6667F_{o}^{2})$	² ₂)
Multipole model + anharmonic {1096 reflections [I >	$> 3\sigma(I)$], 60 parameters}
R(F)	0.007
$wR(F^2)$	0.016
2	1.073

PDF for the Nb displacements, reconstructed from those parameters.

0.258 / - 0.317

It is not a trivial task to estimate the uncertainty of anharmonic parameters. A comprehensive nonlinear theory of random errors in X-ray diffraction analysis does not exist (Tsirelson & Ozerov, 1996). In particular, correlations between experimental X-ray intensities, as well as between the parameters of the structural model, can not be estimated and are always ignored. That means that the s.u. values of the parameters estimated for most refinements are biased and should be taken with caution. In the supporting information, different statistical indicators of the structural models mentioned above are given. They provide a full representation of the reliability and statistical significance of the obtained model parameters. Comparison of the experimental (multipole) and calculated density functional theory (DFT) electron densities (see below) demonstrates the appropriate determination of the multiple-model parameters as well. In summary, we may conclude that the fourth-rank anharmonic parameters of the Nb atom, deduced from our experiment, are quite reliable.

It is interesting that the heavier Nb atoms in $KNbO_3$ exhibit anharmonic displacements, while the lighter atoms do not. We have not yet found an explanation for this behaviour.

The detailed characteristics of the experiment, as well as the parameters of the refinement of different structural models, are presented in Table 1. Further calculations of the experimental electron density, one-electron potentials and the corresponding forces, as well as the atomic PDF for Nb, were carried out in the *WinXPRO* and *3DPlot* programs (Stash & Tsirelson, 2014, 2020).

3. Theoretical calculations

Since independent information is always useful for providing confidence in experimental data, we calculated the electron wavefunctions of the potassium niobate crystal and the electron-density distribution by the Kohn–Sham/B3LYP method with the imposition of periodic boundary conditions. The software package *CRYSTAL17* (Version 1.0.1; Dovesi *et al.*, 2018, 2020) was used. The calculation level was chosen according to Dovesi *et al.* (2020) and Sophia *et al.* (2013) as HAYWSC-31 (31d)G for Nb and TZVP for O and K. The parameters of the orthorhombic unit cell and the initial coordinates of the atoms were taken from our experiment.

During the structure optimization, the atomic positions were varied at fixed unit-cell parameters. The calculation parameters were as follows: TOLDEG = 0.0003 (r.m.s. gradient deviation) and TOLDEX = 0.0012 (r.m.s. bias deviation), TOLDEE = 12 (energy convergence criterion), TOLINTEG = 10 10 10 10 20 (cutoff criterion for two-electron integrals). The number of Monkhorst–Pack points in the irreducible part of the Brillouin zone was set at SHRINK 16 32. The vibrational IR frequencies calculated at the Γ point of the Brillouin zone turned out to be positive; this confirms the correspondence of the found structure with the PES minimum.

According to the calculations, the fundamental band gap in KNO is 4.51 eV, which is in satisfactory agreement with the experimental value of 3.17 eV deduced from the absorption spectrum (Schmidt *et al.*, 2017; Kang *et al.*, 2016).

Then, using the Berry phase approach (Resta, 2000, 2018), the value of spontaneous polarization $|\mathbf{P}_{\rm s}| = 42.1 \ \mu \text{C cm}^{-2}$ was calculated. This result is in agreement with the data available for the orthorhombic KNO phase, which are in the range $\mathbf{P}_{\rm s} = 20-49 \ \mu \text{C cm}^{-2}$ (Yamanaka *et al.*, 2009; Fu *et al.*, 1999; Wang *et al.*, 2020).

4. Results and discussion

4.1. Anharmonic PDF of the Nb atom

In the ferroelectric phase Amm^2 , the NbO₆ octahedron in KNO is noticeably distorted; the interatomic distances are 1.996 (1) (the axial direction Nb-O1 in the octahedron) and 1.873 (1) and 2.171 (1) Å [the equatorial plane Nb(O2)₄ of the octahedron or the *bc* plane of the unit cell] (Fig. 1). The O1

Residual electron densities (max/min)

 $w^2 = 1/[\sigma^2(F_0^2) + (0.01P)^2]; P = (0.3333F_0^2 + 0.6667F_c^2)$

Weighting scheme

and O2 atoms occupy unsplit positions and their anisotropic thermal vibrations can be represented by prolate spheroids oriented along the c axis. The strictly positive total PDF of the Nb atom and its anharmonic components, retrieved from the X-ray diffraction data, are shown in Fig. 2. The anharmonic part of the PDF does not show any displacement of the gravity centre along the c axis relative to the equilibrium position. The total PDF has a single-mode character and is somewhat compressed in the *ab* plane of the unit cell due to the anisotropy of the harmonic vibrations and due to the fourth-order anharmonicity. These distortions do not coincide with the Nb-O lines in the NbO₆ octahedron and, therefore, they do not mimic the anisotropy of the atomic ED distribution. The disorder component of the Nb displacements has not been detected in the Amm2 phase, in agreement with a previous polarized XAFS study (Shuvaeva et al., 1998).

4.2. Electron density and atomic interactions

The experimental ED was found to be strictly positive and normalized to the number of electrons in the unit cell. This means that the obtained ED is physically significant (Tsirelson & Stash, 2020, 2021). Let us consider the distribution of the ED in the main structural element of potassium niobate, the NbO₆ octahedron. We direct the *z* axis of the local coordinate system from the Nb atom to the O1 atom in the octahedron, while the *x* and *y* axes are oriented to the O2 atoms (Fig. 3). The electronic configuration of the outer 4*d* subshell of Nb in the superposition of spherical atoms (procrystal) looks like $(d_{z^2})^{0.0}(d_{x^2-y^2})^{0.0}(d_{xy})^{1.0}(d_{yz})^{1.0}$. The deformation ED maps [see Tsirelson & Ozerov (1996) for definition] in Fig. 3 show that when the chemical bonds are formed, the electrons leave the $4d_{xy}$, $4d_{xz}$ and $4d_{yz}$ orbitals of the Nb atom in a procrystal. These orbitals themselves 'expand' asymmetrically, reflecting the actual spatial distortion of the octahedron. At the same time, the $4d_{z^2}$ orbital is 'compressed' and accumulates some part of the electrons. Simultaneously, electrons are distributed asymmetrically on the $4d_{x^2-y^2}$ orbital.

The electron populations of the 4*d* orbitals of the bonded Nb ion, estimated by least squares from the experimental ED within the framework of the crystal-field theory scheme (Holladay *et al.*, 1983), quantitatively supplement the found spatial distribution of electrons. The valence 4*d* configuration of the bonded Nb ion is $(d_{z^2})^{0.160}(d_{x^2-y^2})^{0.510}(d_{xy})^{0.693}$. ($d_{xz})^{0.597}(d_{yz})^{0.697}$. We conclude that a simple crystal field theory is not appropriate for the description of the bonding situation in a distorted NbO₆ octahedron and the covalent bonding here deserves separate consideration.



Figure 2

The orthorhombic KNbO₃ crystal: probability density distribution function for displacements of Nb from the equilibrium position. (a) 3D image of PDF and its components; isosurfaces are $\pm 300 \text{ Å}^{-1}$; (b) 2D image of the anharmonic part of PDF; the step of isolines is 1000 Å⁻¹. All PDFs are depicted within a volume of $0.3 \times 0.3 \times 0.3 \text{ Å}$. Positive PDF values are marked in orange and negative ones are marked in violet. The directions of the unit cell axes are also indicated.

The O2 atoms are pairwise differently shifted from the Nb ions along the bc plane of the unit cell. It is not surprising that the ED distribution shows that these ions in the equatorial plane are differently involved in coordination bonds with neighbouring Nb atoms. The O2 atoms separated by a shorter Nb-O2 distance of 1.873 (1) Å make a larger contribution to the covalent bond. The O1 atoms are somewhat polarized along the c axis of the unit cell and are more obviously involved in electrostatic interaction with Nb in the axial direction of the octahedron (the ionic component of the bond).

The theoretical deformation ED [Fig. 3(b)] yields independent confirmation of the experimental results presented above. The quantitative discrepancies can be attributed to the intrinsic errors of both methods and to the use of different basis wavefunctions. Thus, the electron density of KNbO₃ is reconstructed from the experiment rather reliably. On the whole, judging by the deformation ED, the deviations in the 4*d*

orbital populations of the Nb atom from the simplified scheme of crystal-field theory originate from their displacement in the ferroelectric phases from the ideal position in the aristotype. The electron-density polarization in the oxygen subsets results from both chemical bond effects and inner-crystal influence.

As is known, it is impossible to calculate the electric polarization of ferroelectrics from the continuous periodic distribution of the electron density due to the impossibility of an unambiguous choice of the unit cell (Martin, 1974; Maksimov *et al.*, 2004). However, it is possible to establish the role of individual atoms in the formation of the unit-cell polarization. Indeed, the multipole model has shown that the electron densities of the Nb and O^{2-} ions in the orthorhombic unit cell have statistically significant dipole and quadrupole terms. Images of the corresponding densities (Fig. 4) reveal that the Nb and O1 atoms are polarized along the *c* axis of the unit cell (and in the opposite direction). The dipole contribution of the O2 ions to the polarization along the *c* axis is



Figure 3

Deformation electron density in the NbO₆ octahedron along the Nb–O1 and Nb–O2 lines: (a)/(c)/(d) are experimental maps and (b) is a theoretical map. Areas of 2D electron-density accumulation relative to a procrystal are shown in blue. The step of the isolines is 0.1 e Å⁻³. (e) The 3D image of the experimental deformation density consists of two surfaces: red (-0.3) and blue (0.3 e Å⁻³).

Table 2

Characteristics of BCPs in KNO derived from experiment and theoretical calculations.

The local axis, corresponding to λ_3 , is directed along the bond pass lines. Exp. is experiment. Theor. is theoretical.

		d_{M-O}	ρ	λ_1	λ_2	λ3	$\nabla \rho^2$
Bond		(Å)	(a.u.)	(a.u.)	(a.u.)	(a.u.)	(a.u.)
Nb-O1	Exp.	1.996	0.111	-0.161	-0.153	0.896	0.583
	Theor.	2.005	0.113	-0.163	-0.162	0.827	0.502
Nb-O2	Exp.	1.871	0.163	-0.320	-0.254	1.306	0.732
	Theor.	1.855	0.164	-0.251	-0.250	1.231	0.730
	Exp.	2.173	0.070	-0.108	-0.090	0.591	0.392
	Theor.	2.196	0.070	-0.095	-0.094	0.504	0.315
K-O1	Exp.	2.976	0.009	-0.008	-0.007	0.064	0.049
	Theor.	3.038	0.010	-0.008	-0.006	0.056	0.042
	Exp.	2.745	0.016	-0.016	-0.015	0.117	0.086
	Theor.	2.684	0.019	-0.018	-0.017	0.123	0.088
	Exp.	2.849	0.012	-0.012	-0.010	0.087	0.065
	Theor.	2.913	0.013	-0.011	-0.009	0.074	0.054
K-O2	Exp.	2.879	0.011	-0.010	-0.009	0.076	0.057
	Theor.	2.853	0.014	-0.012	-0.011	0.085	0.061
	Exp.	2.787	0.014	-0.014	-0.013	0.101	0.074
	Theor.	2.756	0.017	-0.015	-0.014	0.104	0.075

insignificant, while the quadrupole contribution is quite noticeable. These facts shed light on the subatomic nature of the stabilization of the low-symmetry *Amm*² phase and provide an argument in favour of the consideration of ferroelectrics with phenomenological structural models starting from deformable ions (Tolpygo, 1961; Abarenkov & Antonova, 1970; Maksimov *et al.*, 2004). They also support the assumption about the important role of multipole distortions of ionic electron density at the semiempirical level describing the properties of KNO (Yatsenko & Yatsenko, 2003).

It is pertinent to note that all the ED features discussed above are located at ~0.5 Å from the positions of the Nb, O1 and O2 atoms, while the maxima of the PDF of Nb (Fig. 2) appeared at a distance of 0.10–0.15 Å. Thus, the asphericity of the atomic electron densities and the anharmonicity of Nb vibrations are well separated in our structural model and do not distort each other.

Valuable quantitative information is provided by Bader's (1990) quantum topological theory of atoms in molecules (QTAIM). The features of the electron concentrations along interatomic lines largely determines the type and details of the chemical bonding. They, as a rule, are estimated at the bond (saddle) critical points (BCPs) of the ED at the zero-flux boundaries between atoms. The characteristics of the BCPs in KNO, derived from experiment and theoretical calculations, are given in Table 2. First, we note the excellent agreement of the same characteristics obtained by different methods. This provides an independent check of the validity of the results of this work. Also, it can be seen (Table 2 and Fig. 5) that in KNO all the atomic interactions are formally of the closed-shell type, demonstrating, however, specific features. We will consider these in detail.

Localization of electrons is associated with their local kinetic energy, *i.e.* with the square of their local momentum. Due to the Heisenberg uncertainty principle, it is impossible to simultaneously assign the exact values to the coordinate r and

the local electron momentum $p(\mathbf{r})$ in the position representation. However, a set of values of r allows an expression for the average value of the quantum fluctuations of the electron momentum at this point to be obtained (Luo, 2003): $p(\mathbf{r}) = -\frac{1}{2} [\nabla \rho(\mathbf{r}) / \rho(\mathbf{r})]$ [atomic units are used; $\rho(\mathbf{r})$ is electron density]. The contours of the scalar function $p(\mathbf{r})$, near the critical points, in which $\nabla \rho(\mathbf{r})$ goes to zero, form ellipsoids centred at these points; their semiprincipal axes are equal to $a = \nabla \rho(\mathbf{r}) / \lambda_1(\mathbf{r}), \ b = \nabla \rho(\mathbf{r}) / \lambda_2(\mathbf{r}) \ \text{and} \ c = \nabla \rho(\mathbf{r}) / \lambda_3(\mathbf{r})$ (Bohórquez & Boyd, 2010). Thus, the BCPs can be characterized by both the signs of the three principal values of the curvature of the ED λ_i (*i* = 1, 2 or 3) at the BCP, and their absolute values. Moreover, the shape of the bond ellipsoids visually characterizes atomic interactions of different types. For example, the BCP of an ordinary covalent bond is characterized by a Laplacian of ED $\nabla^2 \rho = \lambda_1 + \lambda_2 + \lambda_3 < 0$ and by the ratio $\lambda_3 < |\lambda_1|, |\lambda_2|$. That means that c > a, b and the



Figure 4

(a) Dipole and (b) quadrupole components of the total experimental electron density in the NbO_6 octahedron. The unit-cell axes are shown.

Table 3 Volumes of the atomic basins at $\rho(\mathbf{r})$ and $\upsilon_{kin}(\mathbf{r})$ for KNbO₃ and Bader's atomic charges.

Atom	Atomic basin	volume Ω (Å ³)		
	$\rho(\mathbf{r})$	$v_{ m kin}(r)$	Bader charge, (e) Q	
K	16.392	21.234	+0.914	
Nb	9.914	16.944	+2.223	
O1	12.772	7.907	-1.258	
O2	12.781	9.365	-0.938	

corresponding ellipsoid should be extended along the bond line. For closed-shell covalent bonds and for noncovalent interactions, $\nabla^2 \rho > 0$ and $\lambda_3 > |\lambda_1|$, $|\lambda_2|$, *i.e.* c < a, b, and the corresponding ellipsoid is transformed into a disc perpendicular to the bond line. Weaker bonds correspond to discs of a larger diameter.

In KNO (Table 2 and Fig. 5), the thickness and diameter of the discs on the lines of the same closed-shell type depends on their nature. The thickness of the bond paths in Fig. 5 is proportional to the electron density at the BCP. The Nb-O coordination bonds in the octahedron do not show elongated ellipsoids, although the corresponding discs are somewhat thickened along the internuclear lines. Nevertheless, the consideration of BCPs alone is insufficient to cover all the features of the Nb-O coordination bonds. These bonds cannot be completely characterized by the charges of the atoms. The charges, calculated within QTAIM (Table 3), differ noticeably from the formal integer values of charges on atoms; they give an electrically neutral structural unit of KNbO₃ with



Figure 5

BCP ellipsoids in the KNbO₃ crystal. The symmetry-independent bond paths are shown. The thickness of the bond paths is proportional to the electron-density value at the BCP. The c axis of the unit cell is oriented upwards.

an accuracy of 0.003 e. The obtained values not only convey the charge distribution in the unit cell, but also take into account the fact that the O1 and O2 atoms are different with respect to structure and charge. This fact completely removes any consideration based on the formal ionic charges. Fortunately, the combination of deformation ED (Fig. 4), the charges on atoms and the QTAIM parameters of coordination bonds turns out to be quite informative.

The K–O bonds $(\lambda_3 \gg |\lambda_1|, |\lambda_2|)$ correspond to discs of average transverse size, compressed along the interaction lines. In combination with the data of Table 3, they characterize the K–O bonds in KNO as ionic ones.

4.3. One-electron force field analysis in KNO

Of particular interest for research is the inner-crystal field, which determines the ferroelectric properties of potassium niobate. We studied it by following the orbital-free quantum crystallography approach developed by Tsirelson & Stash (2020, 2021). For this, we wrote the Euler equation of DFT (Dreizler & Gross, 1990) as

$$\mu[\rho] = v_{\rm kin}[\rho] + v_{\rm paem}[\rho]. \tag{1}$$

Here μ is a chemical potential. The one-electron kinetic potential is the sum of the Pauli kinetic potentials, $v_{\rm B}$ and the Weizsäcker potential, $v_{\rm W}$ (Ludeña, 1983):

$$v_{\rm kin}(\mathbf{r}) = v_{\rm P}(\mathbf{r}) + v_{\rm W}(\mathbf{r}) \tag{2}$$

The static potential acting on an electron in a molecule/crystal is the sum of the electrostatic and exchange components:

$$v_{\text{paem}}(\mathbf{r}) = -v_{\text{esp}}(\mathbf{r}) + v_{x}(\mathbf{r}), \qquad (3)$$

In this approximation, the force acting on an electron in a crystal at the point \mathbf{r} is written as $\mathbf{F}(\mathbf{r}) = -\nabla \mu(\mathbf{r})$. For a real crystal, the bonded atoms are in statistical equilibrium, the chemical potential is constant and the average value of the total force acting on the electron at any \mathbf{r} is $\mathbf{F}(\mathbf{r}) = 0$. The local balance of kinetic and static inner-crystal forces $\mathbf{F}_{\rm kin}(\mathbf{r}) = -\mathbf{F}_{\rm paem}(\mathbf{r})$ is described by the expression:

$$\boldsymbol{F}_{\mathrm{P}}(\boldsymbol{r}) + \boldsymbol{F}_{\mathrm{W}}(\boldsymbol{r}) + \boldsymbol{F}_{\mathrm{esp}}(\boldsymbol{r}) + \boldsymbol{F}_{x}(\boldsymbol{r}) = 0. \tag{4}$$

The Weizsacker force, F_{W} , arises as a result of the manifestation of the particle-wave duality and spin-independent fluctuations of electrons, obeying the Heisenberg uncertainty principle. The Pauli force, $F_{\rm P}$, appears as the correction to the electron kinetic energy for the antisymmetry property of the many-electron wavefunction (Tsirelson et al., 2013; Tachibana, 2017). The kinetic forces are heterotropic and directed away from the nuclei (see Tsirelson & Stash, 2020). Electrostatic force F_{esp} is generated by nuclear and electron charge density, and F_x is associated with electron exchange. These forces are homotropic and directed towards the nuclei. Thus, the balance of forces in a stable system is due to the superposition of the manifestation of the electrostatic interaction of electrons and nuclei, the wave properties of electrons (de Broglie relation), the Heisenberg uncertainty principle and the Pauli principle (Tsirelson & Stash, 2020, 2021).

research papers

All the indicated components of potentials and forces were expressed in terms of the orbital-free DFT *via* the electron density and its derivatives (Tsirelson & Stash, 2020, 2021). Potential $v_x(\mathbf{r})$ was taken in the van Leeuwen & Baerends (1994) approximation. This opened up the possibility, in a



Figure 6

Superpositions of atomic basins, gradient fields, bond paths in the distributions $\rho(\mathbf{r})$ (blue gradient lines) and $v_{kin}(\mathbf{r})$ (orange lines), and critical points observed in these fields for (a) the (011) plane and (b) the (101) plane. BCPs in $\rho(\mathbf{r})$ are indicated as orange circles and dark-green circles for $v_{kin}(\mathbf{r})$, ring CPs in $v_{kin}(\mathbf{r})$ are green triangles, and cage CPs are blue and orange rhombs for $\rho(\mathbf{r})$ and $v_{kin}(\mathbf{r})$, respectively. The traces of the ED basin boundaries are shown in blue and those for $v_{kin}(\mathbf{r})$ are burgundy.

justified approximation, of calculating the characteristics of the inner-crystal field through the experimental ED.

Gradient fields of scalar functions v_{kin} and ρ form atom-like volumes around nuclei, limited by surfaces obeying the conditions:

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \forall \mathbf{r} \in \mathbf{S}_i(\mathbf{r})$$

$$\nabla \nu_{kin}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0, \forall \mathbf{r} \in \mathbf{P}_i(\mathbf{r})$$
(5)

where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to the surfaces S_i and P_i at \mathbf{r} . In contrast, the gradient field $v_{\text{paem}}(\mathbf{r})$ does not show closed volumes around nuclei (Tsirelson & Stash, 2020). The kinetic forces $\mathbf{F}_{\text{P}}(\mathbf{r})$ and $\mathbf{F}_{\text{W}}(\mathbf{r})$ are directed within the atomic basins from the nuclei and the static forces are directed to the nuclei. At the boundaries of basins, P_i , forces change their direction. There are also points of zero gradient of scalar functions $v_{\text{kin}}(\mathbf{r})$ and $v_{\text{paem}}(\mathbf{r})$; these critical points, which are called Lagrange points (Tachibana, 2017), have the following property: in these points, $\mathbf{F}_{\text{kin}}(\mathbf{r}) = 0$ and necessary, and $\mathbf{F}_{\text{paem}}(\mathbf{r}) = 0$.

In Fig. 6, the atomic basins, gradient lines and CPs in $\rho(\mathbf{r})$ and $v_{kin}(\mathbf{r})$ in KNO are given. 3D atomic basins in $\rho(\mathbf{r})$ and $v_{\rm kin}(\mathbf{r})$ are shown in Fig. 7, and their volumes are given in Table 3. First, the Lagrange points in $v_{kin}(\mathbf{r})$ give a picture similar to the CP picture in the ED. Moreover, the Lagrange points are found on both bond lines in the NbO₆ octahedron and on the K-O lines, the topological characteristics of which are similar to those in the CP bonds in the ED. Second, the basin boundaries in $\rho(\mathbf{r})$ and $\upsilon_{kin}(\mathbf{r})$ do not coincide. The volumes of the v_{kin} - and ρ -basins in potassium niobate are related as follows: for K and Nb atoms, $\Omega(v_{kin}) > \Omega(\rho)$, and for O atoms, $\Omega(v_{kin}) < \Omega(\rho)$. That is, the kinetic forces arising in the basins of the cations penetrate the surface of the ρ -basins of the anions and press the former against the latter. On the other hand, the forces $F_{esp}(r)$ and $F_x(r)$ keep electrons in the atomic basins. This ensures the statistical equilibrium of the ions in the KNO structure.





The spatial arrangement of ρ -basins (solid coloured surfaces) and v_{kin} basins (mesh surfaces) in KNbO₃.

 Table 4

 The atomic dipole moments (Debye) computed as integrals over the zero-flux atomic basins.

Atom	p_x	p_y	p_z	Total
K	-0.001	0.000	-0.012	0.012
Nb	-0.011	0.000	0.442	0.442
O1	0.000	0.000	-0.245	0.245
O2	-0.002	-0.455	0.366	0.584

Axis z is directed along the c axis of the orthorhombic unit cell.

The fact that local forces change their direction at the boundaries of the atom-like basins in $v_{kin}(\mathbf{r})$ reveals the following conceptual circumstance. Polarization in ferroelectrics is usually associated with electrostatic interactions. However, speaking of electronic polarization, it is more accurate to consider the total static force $F_{\text{paem}}(r)$ acting on each electron. Fig. 8 shows the vector field of this force, reconstructed from the X-ray diffraction intensities, in a layer in the plane of the orthorhombic unit cell formed by K atoms and perpendicular to the c axis of a KNbO₃ crystal. As can be seen, this field is highly nonuniform and inner-crystal forces clearly distinguish the sublattices of the K⁺ ions and the NbO₆ octahedron. Furthermore, the forces $F_{paem}(r)$ in the individual atomic basins are directed towards the nuclei and do not clearly line up in a direction. Nevertheless, the dipole moments of the bound atoms, computed as integrals of the first charge-density moments over the Bader zero-flux volumes (Table 4), are not zero, and their components along the axes of the orthorhombic unit cell give numerical values consistent with the detailed picture of ion deformation in the KNO crystal field, as considered above. They also emphasize that the data obtained provide an experimental substantiation

of the modified theoretical Gordon–Kim model (Kim & Gordon, 1974; Muhlhausen & Gordon, 1981), based on the representation of the crystalline electron density in the form of a superposition of deformed ions. The advantage of the last approach lies in its clarity and link with existing crystal–chemical concepts.

5. Conclusions

The X-ray diffraction study of the orthorhombic ferroelectric phase of potassium niobate has shown that weak anharmonic PDFs for the displacements of the Nb atom, reconstructed from the experiment, do not show traces of the displacement and order-disorder transitions observed in high-temperature phases. The distribution of electron density, the features of the chemical bonds of potassium niobate and the characteristics of the force fields in a crystal have been restored. The role of each of the ions in the Amm2 ferroelectric phase is established and the details of the electron-density deformation in the NbO₆ octahedron and the contribution of the potassium, niobium and oxygen substructures to the electronic distribution are established. The subset of K⁺ ions contributes to the overall crystal stability, but not to the electronic polarization of KNO; these ions are not polarized explicitly. The Nb ions make a rather ionic contribution to the polarization, undergoing a noticeable shift relative to the cubic aristotype during phase transitions. Their electronic shells are polarized along the c axis of the unit cell only weakly. The O^{2-} ions play a noticeable but different role in the stabilization of the lowsymmetry Amm2 phase. They are non-equivalent with respect to the Nb position in the unit cell and this is reflected in the atomic charges and in the picture of the electron-density deformation. The O1 atoms are polarized along the c axis of



Figure 8

Static vector field $F_{\text{paem}}(r)$ in a layer, with a height of 0.6 Å, in the *ab* plane of the orthorhombic cell of KNbO₃. The arrows indicate the directions of the forces at each point, while the colour reflects their magnitude.

the unit cell (or in the opposite direction), but the dipole contribution of the O2 ions to the polarization along the c axis is insignificant. At the same time, the quadrupole electron-density contribution to polarization along the c axis is quite noticeable.

These facts shed light on the subatomic nature of stabilization of the low-symmetry *Amm*² phase and provide an argument in favour of the consideration of ferroelectrics with phenomenological structural models starting from deformable ions (Tolpygo, 1961; Abarenkov & Antonova, 1970; Maksimov *et al.*, 2004). Also, our observations substantiate the validity of the early assumptions about the role of multipole ED deformations of the O^{2-} ions in KNO and support the ferroelectric models based on the representation of the ED of a crystal in the form of a superposition of deformed ions (the Gordon– Kim type model). The advantage of such an approach lies in its clarity and link with the existing crystal chemical models.

At a level of detail previously inaccessible to the X-ray diffraction method, the features of the arrangement of atomic basins and the distribution of the electron kinetic potential in the KNO crystal were studied, and their atomic basins were characterized. It was established how exactly the balance of forces is realized in the KNO crystal, due to the joint action of electrostatic forces, wave properties of electrons, the Heisenberg uncertainty principle and the Pauli principle. It is concluded that the formation of the actual electronic structure in KNO occurs with the participation of both static and kinetic factors of a quantum nature. The kinetic electronic forces, arising in the v_{kin} -basins of the cations and directed to their boundaries, penetrate through the surface of the ρ -basins of the anions and press the cations to anions. This is how a balance of forces is achieved, which ensures the stabilization of the KNO crystal structure. The resulting picture clearly demonstrates the link of the features of the electronic structure and interatomic interactions in potassium niobate to its properties.

6. Related literature

The following references are cited in the supporting information: Abrahams & Keve (1971); Meindl & Henn (2008).

Acknowledgements

AIS acknowledges the support of the Ministry of Science and Higher Education of the Russian Federation.

Funding information

The following funding is acknowledged: Russian Foundation for Fundamental Investigations (grant No. 19-03-00141a to VT).

References

Abarenkov, I. V. & Antonova, I. M. (1970). *Phys. Status Solidi B*, **38**, 783–797.

Abrahams, S. C. & Keve, E. T. (1971). Acta Cryst. A27, 157-165.

- Abramov, Y. A., Reznik, I. M., Tsirelson, V. G. & Okamura, F. P. (1995a). Physica C, 254, 189–192.
- Abramov, Yu. A., Tsirelson, V. G., Zavodnik, V. E., Ivanov, S. A. & Brown, I. D. (1995b). Acta Cryst. B51, 942–951.
- Bader, R. F. W. (1990). In *Atoms in Molecules: A Quantum Theory*. Oxford: Clarendon Press.
- Bartashevich, E., Stash, A., Yushina, I., Minyaev, M., Bol'shakov, O., Rakitin, O. & Tsirelson, V. (2021). *Acta Cryst.* B77, 478–487.
- Becker, P. J. & Coppens, P. (1974). Acta Cryst. A30, 129-147.
- Blessing, R. H. (1995). Acta Cryst. A51, 33-38.
- Bohórquez, H. J. & Boyd, R. J. (2010). *Theor. Chem. Acc.* **127**, 393–400.
- Boutaoui, N., Benabbes, A. & Ramdane, K. (2008). *Int. J. Mod. Phys. B*, **22**, 2169–2176.
- Bozinis, D. G. & Hurrell, J. P. (1976). Phys. Rev. B, 13, 3109-3120.
- Chen, H., Zhang, Y. & Lu, Y. (2011). Nanoscale Res. Lett. 6, 530.
- Cochran, W. (1969). Adv. Phys. 18, 157-192.
- Currat, R., Buhay, H., Perry, C. H. & Quittet, A. M. (1989). *Phys. Rev. B*, **40**, 10741–10746.
- Dovesi, R., Pascale, F., Civalleri, B., Doll, K., Harrison, N. M., Bush, I., D'Arco, P., Noël, Y., Rérat, M., Carbonnière, P., Causà, M., Salustro, S., Lacivita, V., Kirtman, B., Ferrari, A. M., Gentile, F. S., Baima, J., Ferrero, M., Demichelis, R. & De La Pierre, M. (2020). *J. Chem. Phys.* **152**, 204111.
- Dovesi, R., Saunders, V., Roetti, C., Orlando, R., Zicovich-Wilson, C. M., Pascale, F., Civalleri, B., Doll, K., Harrison, N., Bush, I., Llunel, M., Causà, M., Noël, Y., Maschio, L., Erba, A., Rérat, M. & Casassa, S. (2018). *CRYSTAL17 User's Manual*. University of Torino, Italy.
- Dreizler, R. M. & Gross, E. K. (1990). In *Density Functional Theory:* An Approach to the Quantum Many-Body Problem. Berlin: Springer Science & Business Media.
- D'yakov, V. A., Podshivalov, A. A. & Syrtsov, V. S. (2004). Vestn. Mosk. Univ. Ser. 3 Fiz. Astron. 5, 24–28.
- Fu, L., Yaschenko, E., Resca, L. & Resta, R. (1999). Solid State Commun. 112, 465–470.
- Hansen, N. K. & Coppens, P. (1978). Acta Cryst. A34, 909-921.
- Hewat, A. W. (1973). J. Phys. C, 6, 2559-2572.
- Holladay, A., Leung, P. & Coppens, P. (1983). Acta Cryst. A**39**, 377–387.
- Ivanov, S. A., Mikhal'chenko, V. P. & Venevtsev, Yu. N. (1979). Dokl. Akad. Nauk SSSR, 248, 865–867.
- Ivanov, S. A., Ter-Mikaelyan, G. B. & Venevtsev, Yu. N. (1984). *Ferroelectrics*, 56, 25–28.
- Ivanov, Y., Zhurova, E. A., Zhurov, V. V., Tanaka, K. & Tsirelson, V. (1999). Acta Cryst. B55, 923–930.
- Kalinichev, A. G., Bass, J. D., Zha, C. S., Han, P. D. & Payne, D. A. (1993). J. Appl. Phys. 74, 6603–6608.
- Kang, P. G., Yun, B. K., Shin, S., Ko, J. H., Lee, D. J., Lee, Y. S. & Jung, J. H. (2016). *Mater. Sci. Eng. B*, **210**, 19–23.
- Kawamura, S., Magome, E., Moriyoshi, C., Kuroiwa, Y., Taniguchi, N., Tanaka, H. & Wada, S. (2014). *Ferroelectrics*, 462, 1–7.
- Kibalin, I., Voufack, A. B., Souhassou, M., Gillon, B., Gillet, J.-M., Claiser, N., Gukasov, A., Porcher, F. & Lecomte, C. (2021). Acta Cryst. A77, 96–104.
- Kim, Y. S. & Gordon, R. G. (1974). Phys. Rev. B, 9, 3548-3554.
- Leeuwen, R. van & Baerends, E. J. (1994). Phys. Rev. A, 49, 2421–2431.
- Liang, Y. & Shao, G. (2019). RSC Adv. 9, 7551-7559.
- Lines, M. E. & Glass, A. M. (2001). In Principles and Applications of Ferroelectrics and Related Materials. Oxford: OUP.
- Ludeña, E. V. (1983). J. Chem. Phys. 79, 6174-6181.
- Luo, S. (2003). Phys. Rev. Lett. 91, 180403.
- Macchi, P. & Coppens, P. (2001). Acta Cryst. A57, 656-662.
- Maksimov, E. G., Zinenko, V. I. & Zamkova, N. G. (2004). Phys.-Uspekhi, 47, 1075–1099.

Martin, R. M. (1974). Phys. Rev. B, 9, 1998–1999.

Meindl, K. & Henn, J. (2008). Acta Cryst. A64, 404-418.

- Muhlhausen, C. & Gordon, R. G. (1981). Phys. Rev. B, 23, 900-923.
- Nakamoto, Y., Ohi, K., Okada, T., Nagai, T. & Yamanaka, T. (2006). *Ferroelectrics*, 337, 189–195.
- Ohgaki, M., Tanaka, K. & Marumo, F. (1992). Mineral. J. 16, 150-160.
- Postnikov, A. V. & Borstel, G. (1994). Phys. Rev. B, 50, 16403-16409.
- Resta, R. (2000). J. Phys. Conds. Matter, 12, R107-R143.
- Resta, R. (2018). Eur. Phys. J. B91, 100.
- Schmidt, F., Landmann, M., Rauls, E., Argiolas, N., Sanna, S., Schmidt, W. G. & Schindlmayr, A. (2017). *Adv. Mater. Sci. Eng.* 2017, 1–13.
- Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.
- Shirane, G., Danner, H., Pavlovic, A. & Pepinsky, R. (1954). Phys. Rev. 93, 672–673.
- Shteingolts, S. A., Stash, A. I., Tsirelson, V. G. & Fayzullin, R. R. (2021). Chem. Eur. J. 27, 7789–7809.
- Shuvaeva, V. A., Yanagi, K., Yagi, K., Sakaue, K. & Terauchi, H. (1998). Solid State Commun. 106, 335–339.
- Sophia, G., Baranek, P., Sarrazin, C., Rérat, M. & Dovesi, R. (2013). *Phase Transit.* 86, 1069–1084.
- Stash, A. & Tsirelson, V. (2020). Quantum Crystallography Online Meeting, 27–29 November, 2020, CentraleSupélec (CS), France. Book of Abstracts, p. 34.
- Stash, A. I., Ivanov, S. A., Stefanovich, S. Y., Mosunov, A. V., Boyko, V. M., Ermakov, V. S., Korulin, A. V. & Kalyukanov, A. I. (2017). *Crystallogr. Rep.* 62, 31–39.
- Stash, A. I., Ivanov, S. A., Stefanovich, S. Y., Mosunov, A. V., Boyko, V. M., Ermakov, V. S., Korulin, A. V., Kalyukanov, A. I. & Isakova, N. N. (2015). *Crystallogr. Rep.* 60, 620–628.
- Stash, A. I. & Tsirelson, V. G. (2014). J. Appl. Cryst. 47, 2086–2089.
- Tachibana, A. (2017). In New Aspects of Quantum Electrodynamics. Singapore: Springer.

- Tolpygo, K. B. (1961). Sov. Phys. Usp. 4, 485-497.
- Tsirelson, V., Ivanov, Y., Zhurova, E., Zhurov, V. & Tanaka, K. (2000). *Acta Cryst.* B**56**, 197–203.
- Tsirelson, V. & Ozerov, R. (1996). In *Electron Density and Bonding in Crystals*. Bristol, Philadelphia: IOP.
- Tsirelson, V. & Stash, A. (2020). Acta Cryst. B76, 769-778.
- Tsirelson, V. & Stash, A. (2021). Acta Cryst. B77, 467-477.
- Tsirelson, V. G., Stash, A. I., Karasiev, V. V. & Liu, S. (2013). Comput. Theor. Chem. 1006, 92–99.
- Volkov, A., King, H. F., Coppens, P. & Farrugia, L. J. (2006). Acta Cryst. A62, 400–408.
- Voufack, A. B., Kibalin, I., Yan, Z., Claiser, N., Gueddida, S., Gillon, B., Porcher, F., Gukasov, A., Sugimoto, K., Lecomte, C., Dahaoui, S., Gillet, J.-M. & Souhassou, M. (2019). *IUCrJ*, 6, 884–894.
- Wang, D., Wang, G., Lu, Z., Al-Jlaihawi, Z. & Feteira, A. (2020). Front. Mater. 7, 91.
- Xu, Y.-Q., Wu, S.-Y., Wu, L.-N. & Zhang, L.-J. (2018). Mater. Sci. Semicond. Process. 75, 253–262.
- Yamanaka, T., Ahart, M., Mao, H. & Suzuki, T. (2017). Solid State Commun. 249, 54–59.
- Yamanaka, T., Okada, T. & Nakamoto, Y. (2009). Phys. Rev. B, 80, 094108.
- Yatsenko, A. A. & Yatsenko, A. V. (2003). Glass Phys. Chem. 29, 406– 409.
- Zhurova, E. A., Ivanov, Y., Zavodnik, V. & Tsirelson, V. (2000). *Acta Cryst.* B**56**, 594–600.
- Zhurova, E. A. & Tsirelson, V. G. (2002). Acta Cryst. B58, 567-575.
- Zhurova, E. A., Zavodnik, V. E., Ivanov, S. A., Syrnikov, P. P. & Tsirelson, V. G. (1992). *Russ. J. Inorg. Chem.* **37**, 1240–1244.