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Phonon properties of $KNbO_3$ and $KTaO_3$ from first-principles calculations

A. V. Postnikov,* T. Neumann, and G. Borstel
Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

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The frequencies of transverse-optical Γ phonons in $KNbO_3$ and $KTaO_3$ are calculated in the frozen-phonon scheme making use of the full-potential linearized muffin-tin orbital method. The calculated frequencies in the cubic phase of $KNbO_3$ and in the tetragonal ferroelectric phase are in good agreement with experimental data. For $KTaO_3$, the effect of lattice volume was found to be substantial on the frequency of the soft mode, but rather small on the relative displacement patterns of atoms in all three modes of the T_{1u} symmetry. The TO frequencies in $KTaO_3$ are found to be of the order of, but somehow higher than, the corresponding frequencies in cubic $KNbO_3$.

I. INTRODUCTION

Evaluation of vibrational properties within the frozen-phonon scheme is known to be a hard test on the quality of full-potential total-energy calculations. The curvature of the total-energy surface over the manifold of various atomic displacements is much more sensitive to the details of the calculation scheme than merely the position of the total-energy minimum, i.e., the equilibrium geometry. However, in case of success (that can be easily checked by comparison with experimentally measurable phonon frequencies) the calculation provides substantial information on the microscopic driving forces behind the specific vibration patterns and may give some insight into the dynamic properties of the crystal in question. For ferroelectric materials, the interest in the phonon calculations is motivated by the apparently crucial role of zone-center phonon softening in the mechanism of ferroelectric phase transition which is subject to controversial discussions.[1–4]

An early calculation of phonon dispersion curves within the empirical shell model has been done for $KNbO_3$ by Fontana *et al.*[5] First-principles calculation of Γ phonons in $BaTiO_3$ which has the same crystal structure and exhibits the same sequence of ferroelectric transitions as $KNbO_3$ have been done by Cohen and Krakauer.[6] Liechtenstein *et al.*[7] analyzed two vibrational modes (however not related to ferroelectric transition) in another perovskite — $BaBiO_3$. Singh and Boyer[8] calculated Γ and R phonons in cubic $KNbO_3$. Recently, Zhong *et al.*[9] obtained TO and LO Γ-phonon frequencies in a number of cubic perovskite-type ferroelectrics.

In the present paper, we continue the comparative research of $KNbO_3$ and $KTaO_3$ initiated in the previous *ab initio* study of equilibrium geometry (Ref. 10, referred to further as I). In the present paper, we concentrate on phonon frequencies in these compounds making use of the same calculation scheme (full-potential linear muffin-tin orbital code by Methfessel[11,12]) and setup as discussed in I.

For $KNbO_3$, we performed the Γ-phonon calculations for the nonpolar cubic phase and for the first (as the temperature lowers) ferroelectric phase, i.e., the tetragonal one. The results are discussed in Secs. II and III. In Sec. IV, the results for $KTaO_3$ in the cubic phase for two lattice spacings are presented.

II. $KNbO_3$: CUBIC STRUCTURE

As has been pointed out in I, the calculated (from the total-energy minimum) equilibrium volume of the cubic phase of $KNbO_3$ turns out to be ~95% of the experimental cell volume (extrapolated to zero temperature). Such discrepancy is known to be typical for calculations based on the local density approximation (LDA). The effect of different volumes on the trends in total energy lowering and related equilibrium displacements is discussed at length in I. Since the curvature of the total-energy hypersurface may be affected by the error of about 5% in the cell volume, we preferred to perform our phonon calculations for the experimental lattice spacing, in order to produce results better comparable with experimentally measured phonon frequencies. Specifically, we took a=4.00 Å for the cubic phase (extrapolated value on T=0 from lattice constants of the high-temperature phase, according to Ref. 13). The measured lattice constant in the cubic phase which exists above 418 °C is about 4.02 Å, slightly increasing with temperature.[13] The variation of volume over the temperature range is therefore much smaller than the difference between experimental and theoretical volumes and is ignored in the present study.

As it is known (see, e.g., Refs. 6 and 14), Γ-phonon vibration modes in the cubic perovskite structure, after projecting out three translational modes, are split by symmetry into three T_{1u} modes and one T_{2u} mode (all of them are triple degenerate). We followed essentially the guidelines of Cohen and Krakauer[6] in projecting out the translational modes, as well as in the choice of appropriate symmetry coordinates. When constructing the force constant matrix, we performed about 30 calculations for different displacement patterns, in order to provide a good multidimensional fit for the total-energy hypersurface by a fourth-order polynomial, retaining then appropriate second derivatives. In such a way, we could obtain stable and controllable values, e.g., for off-diagonal elements of the force constant matrix.

The simplified procedure of extracting each of these elements independently from a single calculation involving particular combined displacement has been used by Cohen and Krakauer[6] and applied to $KNbO_3$ by Singh and Boyer.[8] In our opinion, this scheme may be not sufficiently reliable in case of an essentially nonquadratic shape of the total-energy hypersurface, resulting in the apparent dependence of the calculated force constants on the particular displacement chosen.

On solving the secular equation of the 3×3 lattice dynamics problem (for the T_{1u} mode),

$$[\mathbf{GF} - \omega^2]\mathbf{u} = 0$$

(Refs. 15 and 16), with **G** and **F** matrices defined as in Ref. 6, the pattern of Cartesian displacements of individual atoms is restored by back symmetry transformation. For the atoms with the fractional coordinates in the cubic perovskite cell K(0, 0, 0); Nb(0.5, 0.5, 0.5); O_1(0, 0.5, 0.5); O_2(0.5, 0, 0.5); O_3(0.5, 0.5, 0), the vibrations, e.g., along the [001] direction are given by

$$\begin{pmatrix} z_1 \\ z_2 \\ z_3 \\ z_4 \\ z_5 \end{pmatrix} = \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & -1 \\ -1 & -1 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} .$$

These displacements related to the center of mass and multiplied by square roots of individual atomic masses produce the orthogonal eigenvectors of vibrational modes, which are presented, along with the frequencies, in Table I in comparison with some experimental data.

Our calculations reproduce the measured frequencies of TO_2 - TO_4 phonon modes reasonably well, while the TO_1 mode frequency is imaginary, as can be expected for a soft mode at zero temperature. In accordance with our previous analysis of I and in agreement with the results of Singh and Boyer,[8] the eigenvector corresponding to the soft mode represents roughly a displacement of Nb with respect to the rest of the crystal. It should be noted that in I, the off-center displacement of Nb was found to be energetically favorable not only at the experimental cell volume for a =7.553 a.u., but also at the somewhat smaller optimized theoretical volume (a =7.425 a.u.). Therefore, the soft mode frequency, even if calculated at the latter volume, is expected to be imaginary. On the contrary, Singh and Boyer[8] could only obtain the energy lowering by Nb displacements at a =7.589 a.u. (the value taken in Ref. 8 for the experimental lattice constant), but not at their theoretical lattice constant of 7.448 a.u. This discrepancy is probably related to some differences in the calculation schemes and needs to be further investigated.

Our results indicate a good agreement with the experimental data in determining the frequency of the TO_2 mode, whereas the frequencies of TO_3 and TO_4 modes are systematically underestimated in both the present calculation and that of Singh and Boyer.[8] The reason may be that the TO_2 mode is essentially the vibration of K atoms against the rest of crystal. As soon as the potential well related to individual off-center displacements of K is the most parabolic comparing to potentials felt by all other atoms (it has been discussed at length in I), the harmonic approximation seems to work best for this kind of displacement. Additional evidence confirming this point is that the experimental frequencies measured for this mode are most stable over a broad temperature range. The reason why the corresponding frequency is underestimated by 15% in the calculation of Singh and Boyer[8] may be the inadequacy of their fit for the total-energy hypersurface which has been constructed only on six different displacement patterns to span all three T_{1u}-type modes.

TO_3 and TO_4 modes involve two different kinds of stretching of the oxygen sublattice which seem to give rise to a rather unparabolic total-energy surface, so the accuracy of the phonon description in the harmonic approximation is not sufficient.

Turning to a more detailed analysis of the eigenvectors, one may conclude that there is an overall agreement between the displacement patterns calculated in the present work and in Ref. 8, for the experimental lattice constant. (There is also clear similarity with the displacement patterns calculated for T_{1u} modes of $BaTiO_3$ by Cohen and Krakauer[6].) However, in our calculation the displacement of K atoms in the soft mode and in the TO_3 mode is more pronounced.

The displacement pattern within the soft mode, although calculated from the second derivatives of the

TABLE I. Calculated Γ-TO frequencies and eigenvectors in cubic $KNbO_3$.

Mode	symm.	Eigenvectors (present work)					ω calc. (cm^{-1})			ω expt. (cm^{-1})		
		K	Nb	O_1	O_2	O_3	Present	Ref. 8 [a]	Ref. 9			
TO_1	T_{1u}	0.32	−0.67	0.29	0.29	0.53	203i	115i	143i	96[b]	115[c]	139[d]
TO_2	T_{1u}	−0.81	0.12	0.36	0.36	0.27	193	168	188	198[b]	207[c]	203.5[d]
TO_3	T_{1u}	0.13	−0.14	0.45	0.45	−0.75	459	483	506	521[b]	522[c]	511[d]
TO_4	T_{2u}	0	0	1	−1	0	234	266			280[e]	

[a] For a=4.016 Å.

[b] Infrared reflectivity measurements at 710 K, Ref. 14.

[c] Infrared reflectivity measurements at 740 K, Ref. 17.

[d] Infrared reflectivity measurements at 1180 K, Ref. 14.

[e] Infrared reflectivity measurements at 585 K (in the tetragonal phase), Ref. 14.

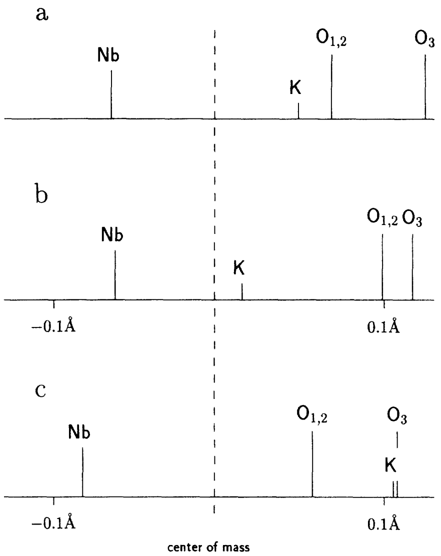

FIG. 1. Relative displacements of atoms in $KNbO_3$ along [001]: from the soft mode eigenvector in the cubic structure [(a), arbitrary scale]; from neutron diffraction measurements in the tetragonal structure, Ref. 18 (b); from geometry optimization in the tetragonal structure (c).

total-energy hypersurface in the ideal cubic structure, contains essential information about relative finite displacements of atoms in the course of cubic to tetragonal phase transition. This has been shown already by Cohen and Krakauer[6] for $BaTiO_3$. For $KNbO_3$, the relative displacements corresponding to the eigenvector of the soft mode in our calculation are presented in Fig. 1(a) in comparison with the atomic positions in the tetragonal cell as determined by neutron diffraction[18] [Fig. 1(b)]. Whereas the experimental coordinates may be interpreted as being due to opposite movement of Nb and O sublattices, with the K atoms relatively undisplaced from their positions in the center-of-mass scale, our calculations show a pronounced tendency of K atoms to remain stuck to the oxygen sublattice, so that the ferroelectric transition may be roughly considered as primarily due to net off-center Nb displacement versus the rest of the crystal. It should be noted that the K displacement has been experimentally estimated with the lowest accuracy, compared to other atoms, as has been pointed out in Ref. 18.

III. $KNbO_3$: TETRAGONAL STRUCTURE

For the tetragonal phase, the situation is complicated by the presence of strain. In I, we have shown that the tetragonal strain can be optimized, along with the off-center displacement of Nb atoms and under the constraint of constant (theoretical) cell volume, to be in fairly good agreement with the experimental estimate of $c/a \sim 1.02$. Now that we would like to proceed with the experimental lattice constant which does not provide the minimum of the calculated total energy, the optimization of the strain from first principles is no longer justified. Instead, we should take the experimental lattice constants at some temperature as an external constraint. The choice $a=4.00$ Å, $c/a=1.0165$ corresponds to what is measured at about 250°, near the lowest-temperature range of existence of the tetragonal phase.[13] Within thus predetermined crystal lattice, associated with any one type of atom (for instance, Nb), K and two nonequivalent types of O are free to relax along the [001] axis towards equilibrium positions compatible with tetragonal symmetry. Since this equilibrium geometry is not determined by symmetry as in the cubic phase, it must be found from first-principles calculations prior to further frozen-phonon analysis. This search for the global total-energy minimum over three independent parameters has been accomplished by a polynomial fitting and needed several tens of total-energy calculations to achieve sufficient accuracy.

The optimized perturbations of the fractional coordinates of atoms in the cubic perovskite cell, accounting for the off-center displacements along [001] in the tetragonal structure, are found to be the following: 0.046(K); 0(Nb); 0.034(O_1, O_2); 0.047(O_3). The arbitrary choice of unshifted Nb sublattice is taken here in order to enable a direct comparison with the experimental data of Hewat[18] which are correspondingly 0.018; 0; 0.040; and 0.044. The absolute displacements of atoms from their symmetry positions are shown in Fig. 1(c), where the center of mass has been kept fixed.

As was the case with the soft mode analysis in Sec. II, K shows, according to our calculation, a pronounced tendency to remain stuck to the oxygen sublattice. This is identical to what we have found in I for the rhombohedral phase, when considering the energetics of coupled K and O distortions. Otherwise, the main trend in the ferroelectric transition, namely that the largest displacement is that of Nb with respect to O_3, as well as the magnitude of this displacement, are in fairly good agreement with the experiment.

As the crystal space group is reduced from $Pm3m$ to $P4mm$ at the ferroelectric phase transition, the vibrations along the [001] direction are no more degenerate; three corresponding T_{1u} modes which retain the tetragonal symmetry of the crystal lattice belong now to the A_1 representation, whereas the formerly T_{2u} mode now becomes B_1. After projecting out the uniform displacement along [001], we arrive at the following symmetry coordinates (similar to those of Ref. 6):

$$\begin{array}{r} A_1\left\{\begin{array}{l} \\ \\ \\ \end{array}\right. \\ \text{transl.} \\ B_1\ \{ \end{array} \begin{pmatrix} S_1\\ S_2\\ S_3\\ \\ S_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & -1\\ 0 & 1 & 0 & 0 & -1\\ 0 & 0 & 0.5 & 0.5 & -1\\ 1 & 1 & 1 & 1 & 1\\ 0 & 0 & 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} z_1\\ z_2\\ z_3\\ z_4\\ z_5 \end{pmatrix} .$$

Vibrations normal to the tetragonal axis remain doubly degenerate; former T_{1u} and T_{2u} modes however are now mixed in the E representation, with the following symmetry coordinates (along [100]):

TABLE II. Calculated Γ-TO frequencies and eigenvectors in tetragonal $KNbO_3$.

Symm.	Frequency	Eigenvectors				
	(cm^{-1})	K	Nb	O_1	O_2	O_3
A_1	167	−0.88	0.45	0.12	0.12	0.05
	330	−0.08	−0.49	0.61	0.61	0.09
	607	−0.09	−0.20	−0.16	−0.16	0.95
B_1	248	0	0	1	−1	0
$E \parallel [100]$	$166i$	−0.35	0.67	−0.52	−0.34	−0.21
	188	−0.80	0.10	0.28	0.40	0.34
	234	−0.00	0.06	−0.02	0.64	−0.76
	456	0.13	−0.14	−0.75	0.48	0.41

$$\begin{array}{l} E\left\{\begin{array}{c} \\ \\ \\ \\ \end{array}\right. \\ \text{transl.} \end{array} \begin{pmatrix} S_1\\ S_2\\ S_3\\ S_4\\ \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & -1\\ 0 & 1 & 0 & 0 & -1\\ 0 & 0 & 1 & 0 & -1\\ 0 & 0 & 0 & 1 & -1\\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x_1\\ x_2\\ x_3\\ x_4\\ x_5 \end{pmatrix}$$

and analogously along [010].

Calculated phonon frequencies and restored orthogonal eigenvectors (individual atomic displacements, multiplied by square roots of masses) are presented in Table II; a comparison with the experimentally determined frequencies is shown in Table III. With the exception of the soft TO_1 mode, experimental frequencies are fairly stable within the temperature range of the tetragonal phase, and calculated frequencies are in all cases in reasonable agreement with them. The best agreement is obtained for the modes involving a relatively small amount of Nb vibration, which is known from our previous analysis in I to be essentially anharmonic. The most parabolic potential well, as has been already emphasized in Sec. II, is that related to the K atom; as a result, the harmonic frequency of the TO_2-E mode, which represents roughly the vibrations of K against the rest of crystal, is in fairly good agreement with experiment. The same applies to the TO_3-A_1 mode which is essentially the vibration of the basal O atom against all others. Consistent with this point of view, the experimental frequencies for these particular modes are the most stable over the temperature. Other modes either include a considerable contribution of the Nb displacement (two lowest A_1 modes), or represent essentially the stretching of the oxygen cage (B_1 and two highest E modes), in which case the harmonic approximation is less accurate, and the temperature dependence of frequencies should be noticeable.

TABLE III. Calculated and measured frequencies of Γ-TO phonons in tetragonal $KNbO_3$.

Mode	Symm.	Calculated frequency (cm^{-1})	Expt.[a]	Expt.[b]	Expt.[c]
TO_1	E	$166i$	78	53	
	A_1	330	295	275	280
TO_2	E	188	199	193	190
	A_1	167	190		200
TO_3	E	456	518		590
	A_1	607	600		600
TO_4	E	234	280		285
	B_1	248			290

[a] Infrared spectroscopy at 585 K; Ref. 14.

[b] Neutron spectroscopy at 518 K (Ref. 19); numerical values cited in Ref. 20.

[c] Raman spectroscopy at 543 K; Ref. 20.

The double degenerate soft mode exhibits the tendency of atoms to shift from their positions, which were optimized with respect to displacements along [001], but correspond to a saddle point of more general total-energy hypersurface (see I) in one or another orthogonal direction, compatible with orthorombic crystal structure. The eigenvector of the soft mode indicates that such transformation involves primarily the displacement of Nb sublattice against the rest of crystal, as was the case in the cubic to tetragonal phase transition.

IV. $KTaO_3$

$KTaO_3$, in contrast to $KNbO_3$, does not undergo a ferroelectric phase transition, remaining in the cubic perovskite structure over the whole temperature range. This crystal seems to be however at the very threshold to a ferroelectric phase transition, as is indicated by considerable softening of its TO_1 mode at low temperatures (see, e.g., Refs. 21 and 22) and by the fact that this transition can be induced by applied uniaxial stress.[23] In I, we studied the energetics of off-center displacements of different atoms in $KTaO_3$ and found the corresponding potential well to be the most anharmonic and volume dependent for Ta. We found the cubic phase to be stable at the theoretical (i.e., underestimated by ~5% as is typical with the LDA) volume, but unstable towards off-center Ta displacements at the experimental volume. In order to study in more detail the effect of combined atomic displacements near the ferroelectric threshold, we calculated the phonon frequencies and eigenvectors at both theoretical (a=3.928 Å) and experimental (a=3.983 Å) values of the lattice constant. The calculation setup (basis set, choice of radii) was the same as described in I; the symmetry analysis for phonons is identical to that in the cubic phase of $KNbO_3$.

The calculated results are shown in Table IV in comparison with the frequencies measured by several techniques. Some more experimental data, which however fall within the same limits, may be found in Refs. 21 and 27. The above-mentioned tendency of Ta to go off center, as found in the calculations performed for the experimental lattice constant, results in imaginary frequency of the soft mode, the displacement pattern of which is essentially the movement of Ta against the rest of crystal. At the theoretical volume, which is smaller, the soft mode frequency was found to be real, numerically close to the data experimentally measured at about 200 K, and consequently higher than the experimental results obtained at lowest temperatures. The real behavior of the soft mode seems to fall within the limits provided by these two cases.

In spite of the differences in the calculated soft mode frequency, the corresponding relative displacements of atoms determined for both lattice constants are very close. One can note however the difference in the vi-

TABLE IV. TO frequencies and eigenvectors in $KTaO_3$.

Symm.	Eigenvectors (calculated)					ω (cm^{-1})			
	K	Ta	O_1	O_2	O_3	Calc.	Expt.[a]	Expt.[b]	Expt.[c]
				a=3.928 Å					
T_{1u}	0.68	−0.56	0.28	0.28	0.27	71			
T_{1u}	−0.62	−0.10	0.51	0.51	0.29	227			
T_{1u}	0.12	0.02	0.32	0.32	−0.89	566			
T_{2u}	0	0	1	−1	0	294			
				a=3.983 Å					
T_{1u}	0.57	−0.57	0.31	0.31	0.40	61i	25−106	81	85
T_{1u}	−0.72	−0.02	0.45	0.45	0.29	205	196−199	199	198
T_{1u}	0.14	−0.04	0.38	0.38	−0.83	504	551−550	546	556
T_{2u}	0	0	1	−1	0	330		279	

[a] Infrared reflectivity measurements at 12−463 K, Ref. 24.

[b] Hyper-Raman scattering measurements at room temperature, Ref. 25.

[c] Raman scattering measurements at room temperature (soft mode) and at 10 K, Ref. 26.

bration of the oxygen sublattice. At the theoretical lattice constant, i.e., for the case of a nonpolar phase and real frequency, the oxygen cage remains rigid on the vibrations; as the volume increases and the ferroelectric transition develops, O_3 atoms shift further towards Ta ions than $O_{1,2}$ atoms do. The resulting slight distortion of the oxygen cage is typical for ferroelectric $KNbO_3$ according to our calculation (Table I) and for $BaTiO_3$.[6] Similar trends are seen in the calculation by Singh and Boyer[8] for two lattice constants of $KNbO_3$.

The volume dependence of the frequencies of two higher T_{1u} modes, although much less dramatic than it was for the soft mode, is nevertheless noticeable. The reason for the fact that frequencies at larger volume are systematically lower is that the potential wells related to off-center displacements of all constituent atoms become broader as volume increases, with smaller curvature at the equilibrium, as has been studied in I.

We cannot provide an explanation for the opposite tendency found for the T_{2u} mode. It seems not to be an artifact of our calculation because Singh and Boyer[8] obtained the same trends in their calculations for two lattice constants in $KNbO_3$.

The whole set of calculated frequencies lies slightly but systematically higher than those in $KNbO_3$. $KTaO_3$ therefore can be regarded to be the stiffer crystal as is also evident from its higher bulk modulus (calculated in I).

V. SUMMARY

We calculated frequencies and eigenvectors of TO Γ phonons in cubic and tetragonal $KNbO_3$ and in cubic $KTaO_3$. For cubic $KNbO_3$, the soft T_{1u} mode is characterized by an atomic displacement pattern which is close to the pattern of the off-center displacements in the ferroelectric tetragonal phase, as determined by explicit structure optimization. The frequencies of the other two T_{1u} modes and the T_{2u} mode are in good agreement with experimental data. In the tetragonal phase, the softening of an E mode indicates an instability towards the transition to the orthorombic ferroelectric phase. The frequencies of the other six A_1, B_1, and E modes are found from the calculation to be in reasonable agreement with experiment — especially for modes whose atomic displacements mostly lie in quasi-harmonic regions of the energy hyperspace. In $KTaO_3$, the TO frequencies and eigenvectors have been calculated for two values of the lattice constant in the cubic phase. Although the tendency for the ferroelectric transition and correspondingly the calculated frequency of the soft mode are found to be quite sensitive to the volume, the displacement patterns within the soft mode and other T_{1u} and T_{2u} modes are not. The frequencies are found to be close to, but systematically slightly higher than, the corresponding frequencies in $KNbO_3$.

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[*] On leave from Institute of Metal Physics, Russian Academy of Sciences, Yekaterinburg, Russia. Electronic address: apostnik@physik.uni-osnabrueck.de

[1] G. A. Samara, Ferroelectrics **73**, 145 (1987).

[2] M. D. Fontana, A. Ridah, G. E. Kugel, and C. Carabatos-Nedelec, J. Phys. C **21**, 5853 (1988).

[3] T. P. Dougherty, G. P. Wiederrecht, K. A. Nelson, M. H. Garret, H. P. Jensen, and C. Warde, Science **258**, 770 (1992).

[4] M. Stachiotti, A. Dobry, R. Migoni, and A. Bussmann-

Holder, Phys. Rev. B **47**, 2473 (1993).

[5] M. D. Fontana, G. E. Kugel, and C. Carabatos, J. Phys. (Paris) Colloq. **42**, C6-749 (1981).

[6] R. E. Cohen and H. Krakauer, Phys. Rev. B **42**, 6416 (1990).

[7] A. I. Liechtenstein, I. I. Mazin, C. O. Rodriguez, O. Jepsen, O. K. Andersen, and M. Methfessel, Phys. Rev. B **44**, 5388 (1991).

[8] D. J. Singh and L. L. Boyer, Ferroelectrics **136**, 95 (1992).

[9] W. Zhong, R. D. King-Smith, and D. Vanderbilt (unpublished).

[10] A. V. Postnikov, T. Neumann, G. Borstel, and M. Methfessel, Phys. Rev. B **48**, 5910 (1993).

[11] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[12] M. Methfessel, C. O. Rodriguez, and O. K. Andersen, Phys. Rev. B **40**, 2009 (1989).

[13] G. Shirane, R. Newnham, and R. Pepinsky, Phys. Rev. **96**, 581 (1954).

[14] M. D. Fontana, G. Metrat, J. L. Servoin, and F. Gervais, J. Phys. C **17**, 483 (1984).

[15] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill, New York, 1955).

[16] J. C. Decius and R. M. Hexter, *Molecular Vibrations in Crystals* (McGraw-Hill, New York, 1977).

[17] F. Gervais, Y. Luspin, J. L. Servoin, and A. M. Quittet, Ferroelectrics **24**, 285 (1980).

[18] A. W. Hewat, J. Phys. C **6**, 2559 (1973).

[19] M. D. Fontana, G. Dolling, G. E. Kugel, and C. Carabatos, Phys. Rev. B **20**, 3850 (1979).

[20] M. D. Fontana, G. E. Kugel, G. Metrat, and C. Carabatos, Phys. Status Solidi B **103**, 211 (1981).

[21] G. Shirane, R. Nathans, and V. J. Minkiewicz, Phys. Rev. **157**, 396 (1967).

[22] J. D. Axe, J. Harada, and G. Shirane, Phys. Rev. **1**, 1227 (1970).

[23] H. Uwe and T. Sakudo, J. Phys. Soc. Jpn. **38**, 183 (1975).

[24] C. H. Perry and T. F. McNelly, Phys. Rev. **154**, 456 (1967).

[25] H. Vogt and H. Uwe, Phys. Rev. B **29**, 1030 (1984).

[26] P. A. Fleury and J. M. Worlock, Phys. Rev. **174**, 613 (1968).

[27] C. H. Perry and N. E. Tornberg, Phys. Rev. **183**, 595 (1969).