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## Atomistic simulation studies of $\text{Li}_K$ off-centre defects in $\text{KTaO}_3$ : I. Isolated defects

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**Abstract.** Details of the structures and energies of substitutional lithium ions on the potassium site in  $\text{KTaO}_3$  have been studied by shell model techniques in which empirically derived potentials have been used to represent the short-range interactions. The lithium ion is found to occupy one of six equivalent off-centre positions along the  $\langle 100 \rangle$  directions at a distance of  $0.64 \text{ \AA}$  from its on-centre location;  $\pi/2$  reorientational jumps between the equivalent sites are found to have a low activation energy of  $\sim 120 \text{ cm}^{-1}$ . Vibrational and librational energies have been calculated as  $\sim 175 \text{ cm}^{-1}$  and  $\sim 130 \text{ cm}^{-1}$ , respectively.

### 1. Introduction

Lithium off-centre impurities in  $\text{KTaO}_3$  are of special interest because of their influence on the ferroelectric properties of the host material. Pure  $\text{KTaO}_3$  has frequently been termed an *incipient ferroelectric*, describing its property of exhibiting a large static dielectric constant at low temperatures, which is not accompanied by a phase transition. Upon doping with lithium or niobium, polar phases appear [1]. In order to elucidate the physical processes leading to this behaviour a detailed investigation of isolated lithium off-centre defects and their effect on the surrounding crystal lattice as well as their interactions with its nearest-neighbour lithium defects is needed. The latter type of interaction, which to a large extent is intermediated by the crystal lattice, will be treated in a forthcoming publication. In this paper we explore isolated  $\text{Li}^+$  defects with help of a computer simulation technique.

Static lattice calculations employing the shell model have successfully been applied to off-centre defect studies in a number of alkali halides [2]. A different theoretical approach from the Mott–Littleton technique [3] employed here and in [2] has been reported by Stachiotti and co-workers [4]; this is also based on the shell model, which is, however, combined with a Green function method for calculating ionic relaxations. In contrast to our calculations, in [4] short-range interactions of ions in the host lattice are assumed to be essentially harmonic. Although using a more elaborate description of ionic polarizabilities than in our model (an anisotropic polarizability is assigned to the oxygen ion), the harmonic approximation applied to the interionic potentials is a significant drawback. The model of Stachiotti and co-workers performs well for the description of lattice dynamics of  $\text{KTaO}_3$  [5], but its validity in the case of defect calculations, where large anharmonic effects are expected, is questionable. In contrast our simulation, which is based on the shell model in combination with the Mott–Littleton approach, fully accounts for such anharmonic effects. Furthermore, we believe that the short-range Li–O interaction used by Stachiotti and

co-workers is not appropriate for simulations of Li defects within their model for  $\text{KTaO}_3$ . Their Li–O potential was taken over from an earlier MD simulation of  $\text{LiKSO}_4$  [6], where a certain partial charge was assigned to the Li ion. In the study of  $\text{KTaO}_3$  a different value for this partial ionic charge was adopted, which leads to an inconsistency; the MD Li–O short-range interaction is too weak when used within the Stachiotti model of  $\text{KTaO}_3$ . We note that only total interionic potentials are transferable and because all our potentials refer to the consistent integral charges such problems do not occur in our case.

The present paper is organized as follows. In the next section we briefly describe the shell model which was used in the calculations and list the short-range potential parameters; in section 3 we present the results of the simulations. Finally, in section 4 our main conclusions are summarized.

## 2. The method

We applied a static lattice energy minimization technique based on the shell model and a two-region strategy in defect calculations.

Within the shell model [7] each ion is represented by a charged core (charge  $X$ ) to which a charged shell (charge  $Y$ ) is coupled harmonically (force constant  $k$ ). The sum of  $X$  and  $Y$  yields the formal (integral) charge of the respective ion, which complies with the concept of a (mainly) ionic crystal. Simulations with a shell model of this type have also been applied to semi-ionic oxides as  $\text{BaTiO}_3$  [8],  $\text{LiNbO}_3$  [9] and  $\text{La}_2\text{CuO}_4$  [10].

By means of this construction the (free) electronic polarizability of an ion is modelled, the value of which is

$$\alpha = \frac{Y^2}{k}. \quad (2.1)$$

Short-range interactions are specified between ion shells which causes the (true) polarizability to become dependent on the environment: an aspect of major importance in oxide materials. As a result, the effective in-crystal ionic polarizabilities are to some extent both anharmonic and anisotropic. A common choice for the functional form of the short-range interactions is given in (2.2):

$$V(r) = A \exp(-r/\rho) - C/r^6. \quad (2.2)$$

In this Buckingham potential (2.2)  $r$  denotes the interionic (shell) distance,  $A$ ,  $\rho$  and  $C$  are parameters, which are to be determined according to empirical or theoretical schemes. The first expression on the right-hand side of (2.2) is the Born–Mayer term which represents the repulsion due to the overlap of the charge clouds of different ions. This, in turn, originates in the Pauli principle and the exponential dependence has been given a firm quantum mechanical foundation [7]. The attractive second term in (2.2) expresses the interionic electronic correlation (van der Waals interaction). This term may also include small contributions arising from covalency and other attractive forces. The short-range interactions are dominated by long-range Coulomb terms which, of course, are operative between all charged species, except for core and shell of the same ion which interact only harmonically.

The parameters used in this study were determined by empirical fitting procedures. In the empirical approach the unknown parameters are treated as variables to adjust in order to give the best agreement between calculated perfect crystal properties (crystal structure,

**Table 1.** Empirically derived potential parameters used in  $KTaO_3$ ; Li–O interaction and shell parameters from Farley and co-workers.

Interactions	Short-range potential parameters		
	$A$ (eV)	$\rho$ (Å)	$C$ (eV Å <sup>6</sup> )
$O^{2-}-O^{2-}$	22764.3	0.149	27.627
$Ta^{5+}-O^{2-}$	1315.572	0.36905	0.0
$K^+-O^{2-}$	523.156	0.34356	0.0
$Li^+-O^{2-}$	383.72	0.32415	0.0

Ion	Shell parameters	
	$Y$ (e)	$k$ (eV Å <sup>-2</sup> )
$O^{2-}$	-2.75823	30.211
$Ta^{5+}$	-4.596	5916.770
$K^+$	—	—
$Li^+$	-0.267	35.64

elastic and dielectric constants) and the corresponding experimental data. Of course, the successful application of this method presupposes that sufficient experimental data are known as is the case in  $KTaO_3$ . Empirical potentials derived this way are strictly valid only in the vicinity of the observed perfect lattice spacings, a shortcoming which does not apply to theoretically developed parameters. Since *ab initio* theoretical schemes are rather costly in terms of computer resources and empirical potentials (in spite of their limitations) often give results which are in closer agreement with experiment, the latter were used in this study, although we note an increasing interest in the use of *ab initio* derived potentials.

The potential parameters for  $KTaO_3$  given in table 1 have been obtained by fitting to the crystal structure, elastic and dielectric constants of the material. In table 2 the experimental values are compared with the respective calculated ones. Close agreement could be obtained without treating  $K^+$  as a polarizable ion, which is justified *a posteriori* by the fact that no large relaxations of these ions occur in the current situation (see table 4). Therefore the ionic polarizability of  $K^+$  is not very significant in this system and furthermore the number of parameters used in the model is reduced.

**Table 2.** Comparison of calculated and experimental properties of  $KTaO_3$  calculated with parameters from table 1. ( $C_{\mu\nu}$  are elastic constants,  $\epsilon_0$  is the static dielectric constant, and  $\epsilon_\infty$  is the high-frequency dielectric constant  $E_{lat}$  is the lattice energy). All properties except for  $E_{lat}$  have been included in the fitting procedure.

Property	Theoretical	Experimental
$C_{11}(10^{10} \text{ N m}^{-2})$	39.88	39.36 [21]
$C_{12}(10^{10} \text{ N m}^{-2})$	10.57	—
$C_{44}(10^{10} \text{ N m}^{-2})$	10.90	10.71 [21]
$\epsilon_0$	244.08	243.00 [22]
$\epsilon_\infty$	4.426	4.592 [23]
$E_{lat}$ (eV)	-174.73	-180.98 <sup>a</sup>

<sup>a</sup> Born–Haber cycle

An important aspect of our work is the use of a ‘relaxed fitting’ procedure, which involves the calculation of properties to be carried out for a relaxed lattice. This proved

**Table 3.** Off-centre displacements of  $\text{Li}_K^{\pm}$  in  $\text{KTaO}_3$ . Energy gain denotes the difference in energy for the  $\text{Li}^+$  ion residing on the lattice site (0.976 eV) and the respective off-centre position.

Direction	Energy (eV)	Energy gain (eV)	Displacement ( $\text{\AA}$ )
$\langle 100 \rangle$	-1.018	0.042	0.64
$\langle 110 \rangle$	-1.002	0.026	0.56
$\langle 111 \rangle$	-0.995	0.019	0.45

**Table 4.** Local geometry of the  $\text{Li}_K^{\pm}$  off-centre defect from calculation based on the shell model (lattice constant  $a = 3.9885 \text{\AA}$ ). The first four ions listed are at the positive end of the dipole; the others are near the negative. Because of the  $C_{4v}$  symmetry of the defect only representative ions are included in the table.

Ion	Perfect lattice position			Relaxed position			Difference
	$x_0/a$	$y_0/a$	$z_0/a$	$x/a$	$y/a$	$z/a$	
$\text{Li}^+$	0.0	0.0	0.0	0.16091	0.00000	0.00000	0.16091
$\text{O}^{2-}$	0.5	0.5	0.0	0.46788	0.47439	0.00000	0.04108
$\text{Ta}^{5+}$	0.5	0.5	0.5	0.49895	0.50188	0.50188	0.00286
$\text{K}^+$	1.0	0.0	0.0	1.00097	0.00000	0.00000	0.00097
$\text{O}^{2-}$	0.0	0.5	0.5	-0.00266	-0.51375	-0.51375	0.01962
$\text{O}^{2-}$	-0.5	0.5	0.0	-0.50738	0.51040	0.00000	0.01275
$\text{Ta}^{5+}$	-0.5	0.5	0.5	-0.49609	0.49651	0.49651	0.00630
$\text{K}^+$	0.0	1.0	0.0	-0.00251	1.00039	0.00000	0.00254
$\text{K}^+$	-1.0	0.0	0.0	-1.00259	0.00000	0.00000	0.00259

necessary for  $\text{KTaO}_3$  since minute changes of ion positions, which occur for example when residual strains on the structure are released after a conventional unrelaxed fitting, result in large changes of dielectric constants. The  $\text{Li}^+-\text{O}^{2-}$  interaction and shell parameters were taken from [11]. They were fitted to structural as well as to lattice dynamical data and have been successfully used in ion transport studies in  $\text{Li}_2\text{O}$  [12].

For defect calculations the crystal is partitioned into two regions: region I, containing the defect and  $\sim 300$  surrounding ions, atomistically treated and fully relaxed to equilibrium; and region II, the remaining crystal, in which for finding the defect-induced displacements the Mott-Littleton approximation [3] is applied.

Within the applied shell model, defect-induced relaxations are included in a most efficient manner whereby an anharmonic response of the crystal lattice in the vicinity of the defect (region I) is included. Note that within the approach used by Stachiotti and co-workers [4] the environment of the defect is assumed to react harmonically, which in our approach is true only for ions in region II. These ions are so remote from the defect that relaxations are small and a harmonic treatment is justified. With respect to defect calculations we expect anharmonic effects related to the interionic potentials to be important. For further details of the shell model used in our study see [13]. The method has been coded in the computer program CASCADE [14].

### 3. Results

Using CASCADE with the parameters given in table 1 we investigated the energy surface depending on the lithium off-centre position in certain high-symmetry directions in  $\text{KTaO}_3$ , figure 1. Clearly the off-centre displacement occurs in the  $\langle 100 \rangle$  direction. This is in

agreement with results from NMR experiments, according to which the lithium ion is shifted a distance ranging from  $0.86 \text{ \AA}$  [15] to  $1.1 \pm 0.1 \text{ \AA}$  [16] along the  $\langle 100 \rangle$  direction. The calculated  $\text{Li}^+$  off-centre displacement of  $0.64 \text{ \AA}$  is less than these values, but it should be considered that in the evaluation of the experiment assumptions concerning the environment of the defect are implicit. (The isotope  $^7\text{Li}$  with a nuclear spin of  $\frac{3}{2}$  possesses a quadrupole moment which couples to the electric field gradients. Therefore a NMR-measurement of the level splitting provides information on the local electric field gradients acting on the ion observed. On the basis of certain assumptions, for example formal ion charges, perfect lattice positions of ions, the off-centre position of the  $\text{Li}^+$  ion can be inferred from the splitting.)

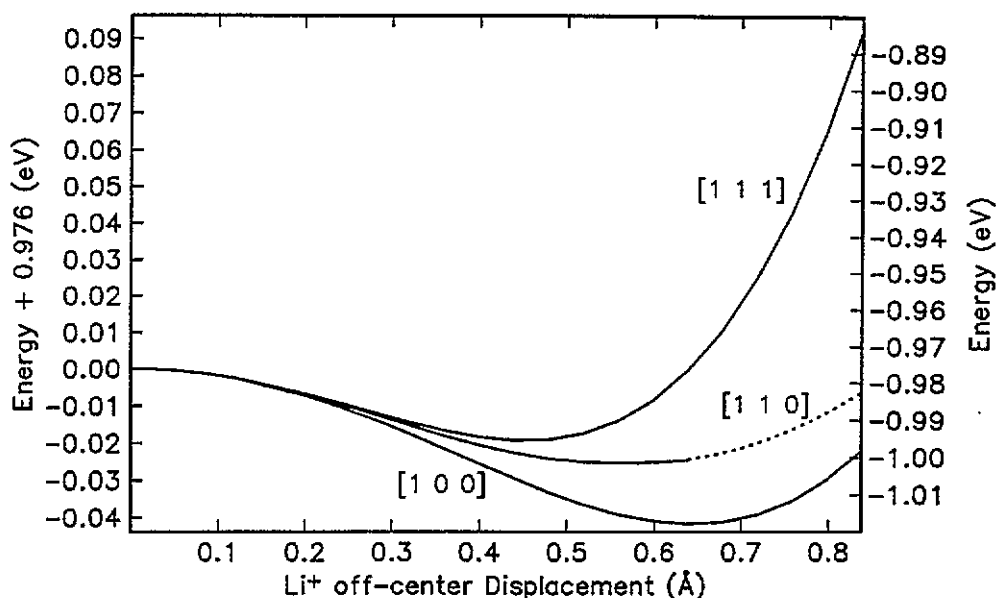


Figure 1. Defect energy against off-centre displacement for  $\text{Li}^+$  in  $\text{KTaO}_3$  in different directions. The broken part of the curve corresponds to calculations which would not converge, possibly due to the vicinity of the lithium ion to oxygen ions in this direction. The shown curve is an extrapolation of a polynomial fit to the converged part of the curve.

Borsa and co-workers [15] report a nuclear magnetic resonance frequency for the  $^7\text{Li}$  off-centre ion of  $70 \pm 2 \text{ kHz}$ , from which they deduced their value for the off-centre shift of  $0.86 \text{ \AA}$ . By calculating electric field gradients within the relaxed environment† of the  $\text{Li}$  off-centre defect and using the formula  $\nu_Q = |(1 - \gamma_\infty)eQV_{zz}|$  given in [17] (with  $Q = 0.042 \times 10^{-24} \text{ cm}^2$ ,  $(1 - \gamma_\infty) = 0.74$  and  $V_{zz}$  denoting the electric field gradient) we find that this value corresponds to an  $\text{Li}$  position of  $0.78 \text{ \AA}$ . If we conduct the calculation for the unrelaxed lattice we obtain a position of  $1.1 \text{ \AA}$  corresponding to  $70 \text{ kHz}$ . Relaxation results in a reduction of the respective calculated  $\text{Li}^+$  off-centre displacement. Conversely, for our equilibrium position of  $\sim 0.64 \text{ \AA}$  we calculate a frequency of  $25 \text{ kHz}$ . The strong variation of frequency shows the sensitivity of the NMR frequency on the  $\text{Li}$  off-centre position, which is in agreement with calculations of van der Klink and co-workers [17].

† Ions within a region I radius of 3.3 lattice units were considered.

Other theoretical values for the off-centre displacement are 1.44 Å [4] using a shell model approach of Stachiotti and co-workers and 1.35 Å [17] with a point polarizable ion model. Both of these investigations involve some inconsistencies or simplifying assumptions. In the first case the  $\text{KTaO}_3$  host crystal reacts harmonically upon the defect, but more seriously the Li–O potential is too weak to simulate an Li ion properly. Indeed, if we employ this potential in our model we obtain an off-centre displacement of about 1.5 Å together with an unphysically large energy gain of 1.5 eV. The major disadvantage of the second approach is the use of a polarizable point charge model by means of which electronic polarizations are decoupled from interionic short-range forces leading to overestimated induced dipoles. Calculations employing a shell model of the kind used in this contribution avoid the shortcomings of these two methods and provide a reliable approach to obtain defect properties.

Figure 1 also shows that  $\pi/2$  jumps crossing the  $\langle 110 \rangle$  direction are the most likely way for reorientation of the defect. Table 3 gives the details of the energy and off-centre displacement. The energy for the  $\pi/2$  reorientation is  $\sim 0.015$  eV ( $120 \text{ cm}^{-1}$ ), as can be seen by taking the difference of the energy gain on relaxing in the  $\langle 100 \rangle$  and the  $\langle 110 \rangle$  direction. This value is also found from SHG (second harmonic generation) measurements on 0.8% Li doped  $\text{KTaO}_3$  crystals [18]. In figure 2 the energy surface of the  $\text{Li}_K^x$  off-centre defect is shown against the displacement in the  $\langle 100 \rangle$  plane. Clearly the central on-centre energy maximum, the four off-centre minima along the  $\langle 100 \rangle$  directions in the plane can be seen and also the  $\langle 110 \rangle$  saddlepoint directions.

The lithium ion performs vibrational motions in its off-centre potential well around the equilibrium position. These consist of a vibration along the  $\langle 100 \rangle$  direction towards and opposite the on-centre maximum and a librational movement, essentially perpendicular to the former. By fitting a quadratic function to the respective parts of the energy surface around the equilibrium these energies can be estimated. The force constant  $k$  is of course obtained directly from the curvature and the vibrational energy from the standard expression  $E_{\text{vib}} = \hbar\omega = \hbar\sqrt{k/\mu}$ , where  $\mu$  is the reduced mass. Approximately  $\mu$  can be set equal to the mass of the lithium ion, since it is far smaller than all other ion masses present. In this way we obtain an energy of  $176 \text{ cm}^{-1}$  for the vibration and  $40 \text{ cm}^{-1}$  for the libration quanta. An earlier assignment of a value of  $40 \text{ cm}^{-1}$  for the vibration energy from Raman measurements [19] seems rather unlikely because the signal is independent of the lithium concentration [19, 20] and also on the basis of the result of our calculations. A different interpretation has been given, according to which this low-energy feature belongs to a soft mode of the host lattice [20]. The local defect geometry qualitatively resembles the picture shown in Stachiotti and co-workers [4]. The displacements indicated there, however, are considerably larger than the ones calculated here. This discrepancy might be due to the harmonic approximation applied in [4]. The general pattern is such that anions are attracted towards, and cations are repelled from, the positive ( $\text{Li}^+$ ) end of the defect dipole. The opposite movements are seen at the negative ( $V_K^-$ ) end of the dipole. The coordinates of the nearest neighbours are given in table 4. The last  $\text{K}^+$  ion listed in this table, which lies on the defect axis in the opposite direction of the  $\text{Li}^+$  displacement, does not follow the aforementioned rule. Elastic effects are responsible for its shifting away from the negative end of the dipole.

We have also investigated the off-centre behaviour of the lithium ion under various conditions: (i) without allowing for lattice relaxation, (ii) only allowing shells of the ions to relax (optical calculation), and (iii) treating  $\text{Li}^+$  as an unpolarizable (rigid) ion. If lattice relaxation is not admitted (neither cores nor shells relax) no lithium off-centre displacement occurs. This is also the case for the optical calculation, which corresponds

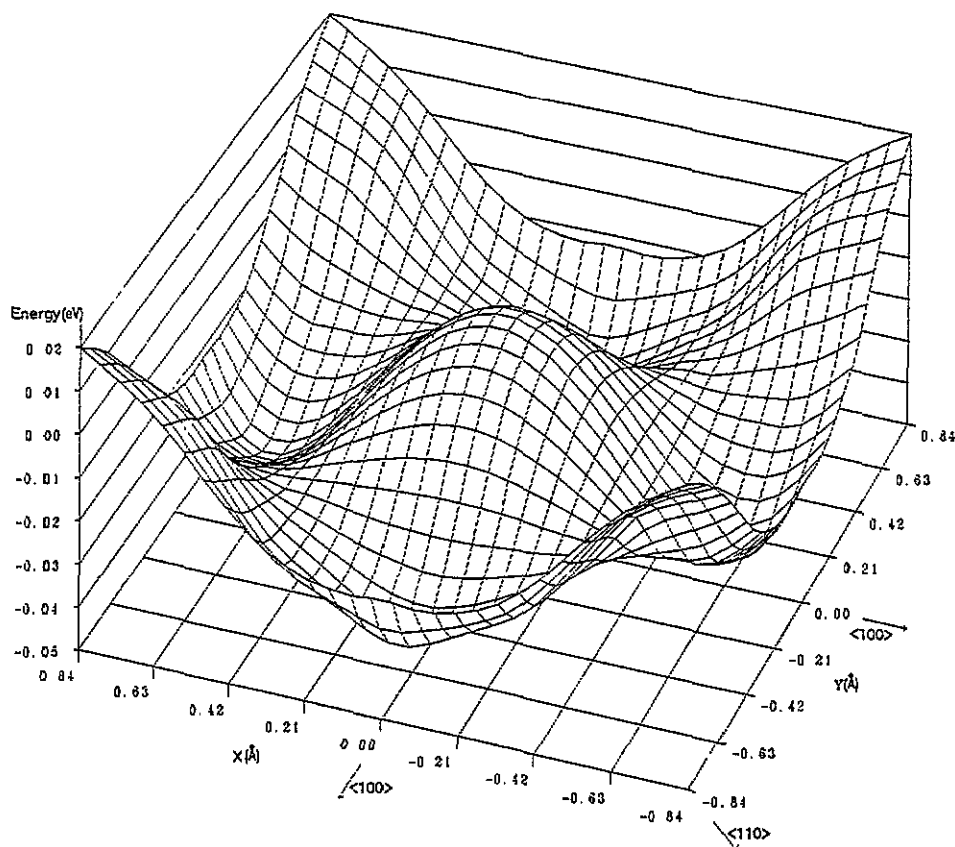


Figure 2. Defect energy against off-centre displacement for  $\text{Li}^+$  in  $\text{KTaO}_3$  over the  $\langle 100 \rangle$  plane. Four off-centre minima along  $\langle 100 \rangle$  and saddlepoint directions along  $\langle 110 \rangle$  are shown as well as the central on-centre maximum.

Table 5. Off-centre displacement of  $\text{Li}_K^+$  in  $\text{KTaO}_3$  with the unpolarizable lithium ion.

Direction	Displacement ( $\text{\AA}$ )	Energy gain (eV)
$\langle 100 \rangle$	0.258	0.0013
$\langle 110 \rangle$	0.182	0.0006
$\langle 111 \rangle$	0.170	0.0001

to a purely electronic relaxation. Therefore lattice relaxation is indispensable for any off-centre displacement. However this result, obtained from calculations based on the shell model, needs further support from explicit electronic structure calculations (for example, embedded cluster calculations), since within calculations employing the shell model the electronic degrees of freedom are only incorporated in a rudimentary fashion. The potential curves from optical calculations are considerably flatter than the ones obtained without any relaxation, figure 3. If the lithium ion is unpolarizable, off-centre displacements are still present but they are far less in extent and energy gain, see table 5. The ionic polarizability of the off-centre  $\text{Li}^+$  ion has a strong influence but not so as to prevent the ion from displacing to an off-centre position.



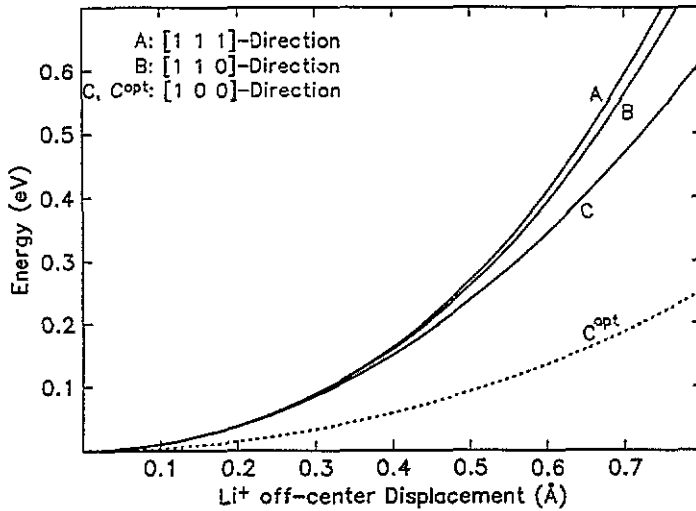


Figure 3. Defect energy against off-centre displacement for  $\text{Li}^+$  in  $\text{KTaO}_3$  without lattice relaxation for high symmetry directions. No off-centre minima occur. The curve denoted  $C^{\text{opt}}$  refers to an optical calculation for an  $(100)$  direction.

#### 4. Conclusions

In this paper it has been shown that calculations based on the shell model can bring considerable insight into physical processes occurring in connection with off-centre defects. Lattice relaxation has been recognized as being essential for the occurrence of  $\text{Li}^+$  off-centre displacements. The treatment of lithium as an unpolarizable ion results in a reduction of the off-centre displacement, but not its vanishing. Therefore ionic polarization is of less importance for the off-centre displacement than the response of the lattice.

Electrostatic as well as elastic forces need to be taken into account in order to understand the behaviour. Further questions to be resolved by this technique concern the elucidation of the dominant interactions between different  $\text{Li}^+$  off-centre dipoles, which then may provide some understanding of the microscopic basis of the cooperative behaviour of these defects leading to ferroelectric transitions in  $\text{KTaO}_3$ . These questions will be addressed in a subsequent paper.

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