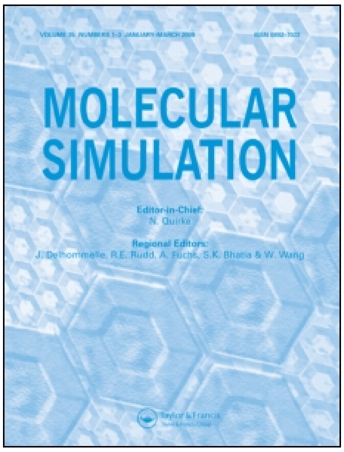

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Preliminary Communication

DERIVING AN EMPIRICAL POTENTIAL FOR FERROELECTRIC $LiNbO_3$

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We describe the derivation of a potential model for ferroelectric lithium niobate, by means of fitting parameters in the potential to the experimentally determined structure and properties of the material. In doing so we highlight the strengths and limitations of the technique, compared to theoretical methods for calculating the parameters. We also see that it is important to include ionic polarisation directly in the fit, owing to the role of polarisation in stabilising the ferroelectric structure.

KEY WORDS: Lithium niobate, ferroelectric, atomistic simulation, potential model, polarisation

INTRODUCTION

This preliminary communication describes the derivation of a potential model for ferroelectric lithium niobate. Atomistic simulation studies will undoubtedly prove valuable in understanding the defect chemistry of this technologically important electro-optic device material; hence the requirement for a good potential model. The importance of polarisation in stabilising the structure is demonstrated.

STRUCTURE OF $LiNbO_3$

The structure is based on that of corundum. It consists of chains of O_6 octahedra. The cation occupation of the octahedra follows the sequence of niobium-vacancy-lithium along the c-direction, as shown in Figure 1. The 'electrostatic equilibrium' position of the Li ion is in the oxygen plane midway between the Nb ions. However, due to oxygen close packing, the lithium site is displaced into the oxygen octahedron. The resulting non-centrosymmetric charge distribution gives rise to ferroelectricity in the

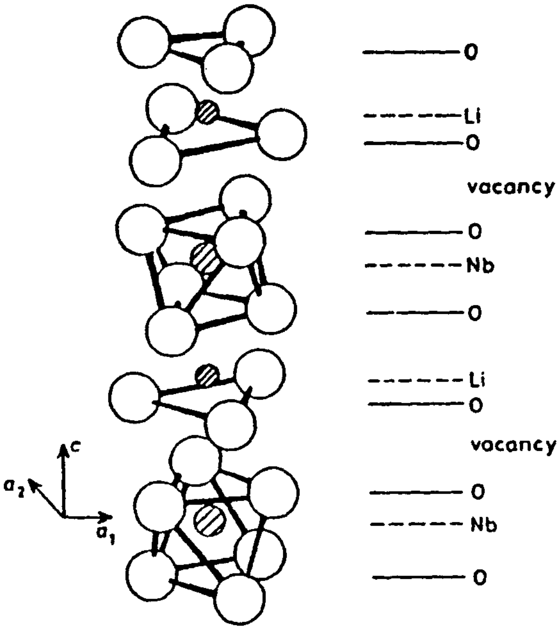

Figure 1 The structure of $LiNbO_3$ (after ref. [1]).

poled crystal. Above the ferroelectric transition temperature, expansion of the a-parameter allows the Li to occupy the oxygen plane.

POTENTIAL MODEL FOR $LiNbO_3$

Parameters were initially transferred from the binary oxides (Li_2O, Nb_2O_5). The energy of the structure was minimised using the THBREL code of Leslie. In the resulting equilibrium structure the Li ions were located in the oxygen plane (i.e. high temperature structure). Empirical fitting, using the THBFIT code (Leslie), was therefore used to obtain a potential model which reproduced the ferroelectric phase. A wide range of observables are available for $LiNbO_3$; it has been extensively studied owing to its importance in fibre optic applications. The directly fitted potentials initially also failed to reproduce the ferroelectric structure of $LiNbO_3$. The Li ion always relaxed into the oxygen plane upon energy minimisation. This happened despite the apparent excellence of the fit of the potential to the experimental structure and properties. The explanation for this may be inferred from Figure 2, which shows schematically the potential experienced by the Li ion at temperatures related to T_c as shown.

Above T_c the potential may be described by the top figure, whereas below T_c the potential has minima on either side of the oxygen plane as shown. However in the fitting procedure, where the residual forces on ions are minimised by adjusting the potential, it is easier to reproduce the situation described by the middle diagram, i.e. a wide flat single well. This will yield low residual ion strain in the fit, yet the potential has no maxima between the oxgyen plane and the Li positions and a finite gradient

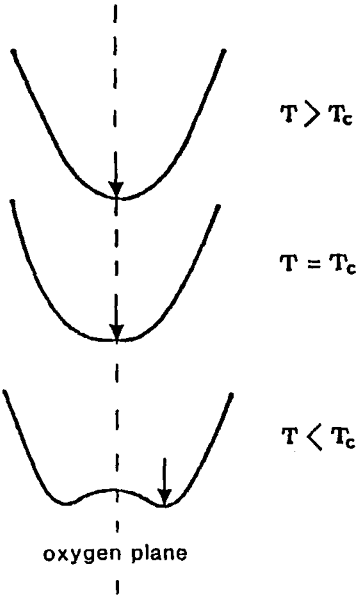

Figure 2 Schematic representation of the potential well experienced by Li in LiNbO$_3$, as a function of temperature. Arrows denote Li site.

in the direction of the oxygen plane. Hence the Li ion will still relax into the oxygen plane upon energy minimisation.

The problem arises because of the importance of polarisation in stabilising the ferroelectric phase. However, it can be overcome within the shell model [2] by including the shell co-ordinates as parameters in the fitting process. When this is done, the crystal polarisation is updated at every iteration of the fit, along with the parameters in the potential. Thus it is possible to obtain an equilibrium simulated structure that agrees well with the experimental structure of the ferroelectric phase, with Li located within the oxygen octahedra. The parameters in the final potential model are shown in Table 1.

The calculated and experimental crystal properties are shown in Table 2. We note the apparently poor agreement for the dielectric constant, a feature which is discussed below.

DISCUSSION AND FUTURE WORK

We described above how fitting may be used to develop a potential model which gives excellent agreement between calculated and experimental observables. However, the process will necessarily result in a residual in the fit, simply because we are fitting parameters in an imperfect model. The residual takes the form of small residual ion and bulk strains, and small differences in the calculated and observed crystal properties. A stage is normally reached where further optimisation is impossible; although it is possible, by adjusting the weights given to different residuals in the fit, to improve the agreement in one set of properties at the expense of others.

Table 1 Potential parameters for $LiNbO_3$

(*i*) *Short-range Parameters*

Interaction of the form:

$$V(r) = A \exp(-r/\varrho) - C/r^6$$

interaction	*A/eV*	*ϱ/Å*	*C/eVÅ*$^{-6}$
O...O	22764.3	0.149	27.879
Nb...O	1113.3	0.38815	0.0
Li...O	816.3	0.26086	0.0

(*ii*) *Core-Shell Parameters*

Interaction of the form:

$$V(r) = \frac{1}{2}K_1r^2 + \frac{1}{24}K_2r^4$$

ion	shell charge	K_1/eVÅ^{-2}	K_2/eVÅ^{-4}
O^{2-}	−4.656	462.04	10^5
Nb^{5+}	4.022	17.85	10^5
Li^+	0.0	∞	∞

(*iii*) *Three-body Parameters*

Interaction of the form:

$$V(r) = \frac{1}{2}K(\theta - \theta_o)^2$$

interaction	K/eV rad^{-2}	θ_o/°
O...Nb...O	0.5776	90.0

When the structure is allowed to relax to equilibrium within the derived potential, all of the residual ion strain is removed. This will cause a degraded agreement between calculated and experimental crystal properties. This is especially true for materials with high dielectric constants such as lithium niobate, because high dielectric con-

Table 2 Comparison of experimental and calculated crystal data for $LiNbO_3$

property	*experiment* *see refs [3] and [4]*	*calculated*
elastic constants/Dyne.10^{11}.cm^{-2}		
C_{11}	20.3	25.7
C_{12}	5.3	12.5
C_{13}	7.5	10.6
C_{14}	0.9	−2.2
C_{33}	24.5	27.6
C_{44}	6.0	8.8
C_{66}	7.5	6.6
dielectric constants		
e_{11}	84.1	29.7
e_{33}	28.1	61.8

stants are such sensitive functions of any structural parameter. The agreement between calculated and observed properties shown in Table 2 is thus probably the best that can be obtained with current fitting techniques.

This study highlights a strength of the empirical procedure for obtaining parameters for ferroelectric materials, namely that crystal polarisation can be included effectively in the fitting procedure. This is probably essential in view of the importance of polarisation in stabilising these complex structures.

The study also indicates how improvements in the potential may be made. The two most important are, we suggest:

1) Improved functions, e.g. a function which contains the double well shown in Figure 2 implicitly.
2) A fitting algorithm in which the lattice is equilibrated at every stage of the fit, and the potential adjusted to minimise the difference between the observed and calculated structures. At present the forces on the ions are minimised, so until the potential is tested by energy minimisation, the true quality of the potential cannot be evaluated properly. This procedure would of course increase the computational time per iteration, but would also lead to greater efficiency and improved potentials.

Acknowledgements

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