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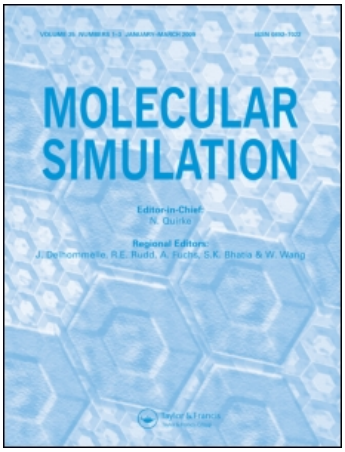

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Computer Modelling of Elastic Properties of LaF_3 Using Free Energy Minimisation Techniques

P. E. Ngoepe[a]; S. C. Parker[b]
[a] Department of Physics, University of the North, South Africa [b] University School of Chemistry, of Bath, Bath, UK

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COMPUTER MODELLING OF ELASTIC PROPERTIES OF LaF_3 USING FREE ENERGY MINIMISATION TECHNIQUES

P.E. NGOEPE

Department of Physics, University of the North, Sovenga 0727, South Africa

and

S.C. PARKER

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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An effective use of computer simulation methods in the study of solids depends on the derivation of reliable potential models. Hence, the empirically derived interionic potentials of LaF_3 were tested by free energy minimisation techniques, within the quasi-harmonic approximation. This was achieved by calculating the temperature variation of elastic constants derived directly from the shell model potentials. These changes agree reasonably well with those calculated from an experimental lattice expansion, below 800 K. However, the departure from linearity and experimental results occur in the range 800–1100 K, which is below the transition temperature to the state of high ionic conductivity. This shows how far the fitted shell model potentials can reliably predict the elastic behaviour of LaF_3.

KEY WORDS: Elastic constants, thermal expansion, LaF_3, computer simulation, free energy minimisation, interionic potentials

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INTRODUCTION

The development of reliable systems of potentials for polar solids has proceeded rapidly in the last fifteen years. Consequently, valuable insights have been shed on structural and defect properties of a wide range of halide and oxide compounds. In ionic materials, the non-Coulombic components of the potential usually referred to as the short-range potential, are represented by a number of analytic functions; these include Lennard–Jones, Morse and Buckingham functions [1]. In simulating defect properties of crystals it is necessary to include the description of ionic polarization, using representations such as the shell model. Such potential models need to be parametrized. This may be achieved by the use of a variety of theoretical techniques, including electron gas and *ab initio* Hartree–Fock methods [2]. The alternative parametrization procedure are empirical methods, where variable parameters are adjusted to known structural properties of the compound. The method is the only one currently available for determining shell model parameters.

Reliable and well developed potentials are available for crystals with a simple structure, such as alkali halides, alkaline earth oxides and alkaline earth fluorides. However, good and satisfactory potentials have also been derived for structures that are more complex, including MgF_2, $BaTiO_3$ and LaF_3. In LaF_3, with a tysonite

structure, activation and migration energies for Frenkel and Schottky defects were predicted [3]. Furthermore, the nature of the dominant type of defects in the fast-ion phase was suggested on the basis of these potentials [4]. In this paper the consistency of the empirically determined potentials of LaF_3, is tested using free-energy minimization technique. Hence a computer code, PARAPOCS, developed by Parker and Price [5], was used in an attempt to reproduce the known temperature variation of elastic constants [4] in the temperature range 100 K to 1100 K.

INTERIONIC POTENTIALS

In predicting structural and thermodynamic data of inorganic solids, the interactions between pairs of ions are described by potential functions, whose sum provides the lattice energy of the crystal, i.e.,

$$V = \sum_{i>j} \frac{q_i q_j}{r_{ij}} + \sum_{i>j} \phi_{ij} \tag{1}$$

The first term describes the Coulomb interaction and q_i and q_j are the ionic charges. The second term ϕ_{ij} includes short-range repulsive interaction between neighbouring charge clouds and van der Waals interactions to which dispersive interactions are added. The short-range potential used in this study has the Buckingham form

$$\phi(r_{ij}) = A_{ij} \exp(r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \tag{2}$$

The ionic polarizability is included by means of the shell model, where an ion is represented by a massless shell attached to a core by a harmonic spring. The polarizability of the free ion is approximated by the expression

$$\alpha_i = \frac{y_i^2 e^2}{k_i} \tag{3}$$

where $y_i e$ is the charge of shell and k_i is the spring constant. By allowing repulsive forces to act only between shells, polarization and short-range repulsions are coupled.

Lattice summations of the Coulomb terms in Equation (1) are achieved by means of Ewald procedure which transforms the sums from a slowly converging series in real space to a rapidly converging one in a reciprocal space. The short-range terms were handled in real space and had a cut off distance of 9.78 Å. The potential parameters in Equations (2) and (3) were obtained by least squares fitting to experimental data of LaF_3 [3] and are given in Table 1.

ENERGY MINIMISATION PROCEDURE

The crystal structures were equilibrated to a given temperature, by minimising the Helmholtz free-energy, (appendix A) which is the basis of the computer code PARAPOCS. This method is based on the quasi-harmonic approximation, which assumes that the vibrational motions in the solid consists of independent quantised harmonic oscillators whose frequency may vary with cell volume. The energy minimisation is achieved by adjusting the cell volume and coordinate positions until the net pressure or stress is zero. The pressure is the derivative of the free energy with

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Table 1 Parameters of the short range interionic potentials and of the shell model.

(a) Short range interaction potential parameters			
	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å^{-6})
La^{3+}–La^{3+}	53317.7	0.2206	0
La^{3+}–F^-	1476.86	0.3252	0
F^-–F^-	1127.70	0.2753	15.83
Short range potential cut-off distance: 9.78 Å			
(b) Shell model parameters			
	Y ($\|e\|$)	k (eV Å^{-2})	
La^{3+}	6.59	250.0	
F^-	−2.38	101.2	

respect to volume. However, in a non-cubic material like LaF_3, where the volume does not expand isotropically, six different strain components are considered. Hence the pressure becomes the difference in free energy for each component.

$$P_j = \frac{l}{V}\left(\frac{dF}{d\varepsilon_j}\right) \tag{4}$$

One measure of the temperature dependence of the structure is the Gruneisen parameter, as it links the microscopic properties, namely the change in frequencies

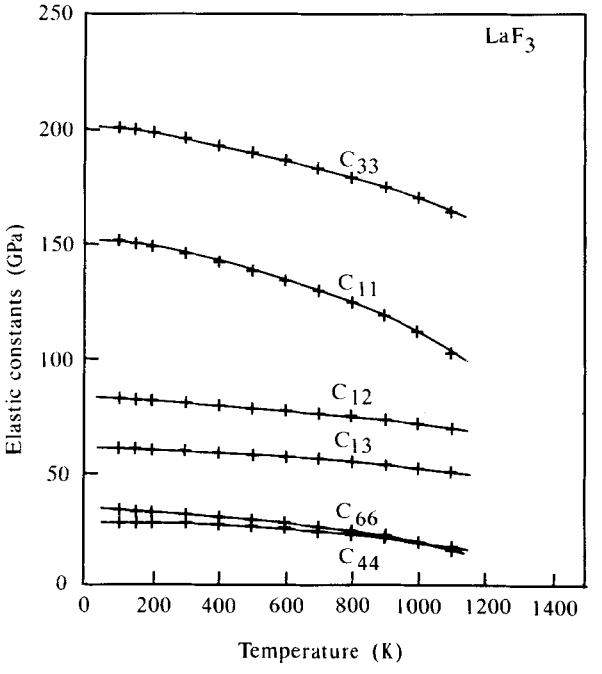

Figure 1 The variation of elastic constants with temperature calculated from free energy minimization techniques.

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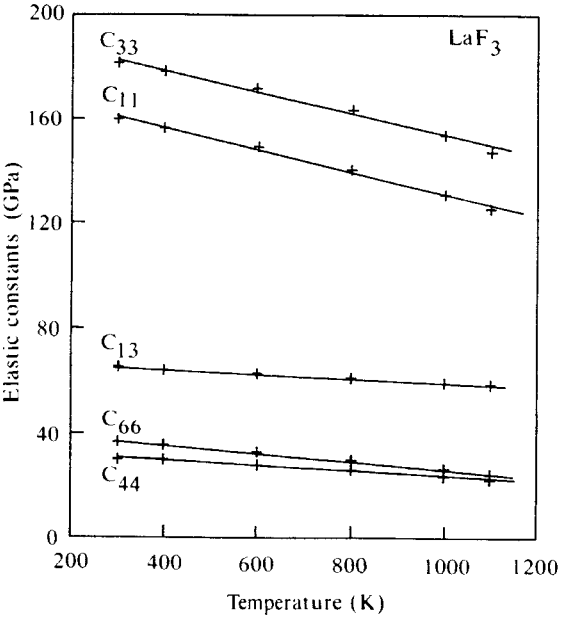

Figure 2 The variation of elastic constants with temperature calculated by allowing the lattice to expand with temperature. (after Ngoepe *et al.* [4])

with the bulk property i.e., the thermal expansion coefficient [6]. Hence the elastic constants at various temperatures were deduced from the determined coefficients of expansion. All calculations were conducted on the Cray X-MP/28, at the University of London Computer Centre.

RESULTS AND DISCUSSIONS

As mentioned in the Introduction, the aim of this study is to investigate the reliability of interionic potentials of LaF_3, using free energy minimisation methods. The results of these calculations are shown in Figure 1, where the temperature variation of elastic constants may be divided into three regions of interest. Below 200 K, nearly all elastic

Table 2 Temperature gradients of elastic constants derived from the experimental and calculated coefficients of thermal expansion.

C_{ij}	dC_{ij}/dT *Experimental (300–1100 K)* *MPa/K*	dC_{ij}/dT *Calculated (300–800 K)* *MPa/K*	% *Deviation*
C_{33}	34.8	35.8	2.9
C_{11}	37.2	40.4	8.6
C_{13}	7.6	8.8	15.8
C_{66}	13.0	13.7	5.3
C_{44}	7.6	8.3	9.2

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constants tend to a constant value as the temperature approaches zero, in agreement with the results of Laiho *et al.* [7]. This behaviour is observed in solids that have no structural phase transition in this temperature range.

A second important region lies between 300 and 800 K, where a linear reduction of elastic constants is predicted by free energy minimization calculations. Such a behaviour was noted in the Brillouin scattering results of Ngoepe *et al.* [4]. Furthermore, it was reflected by their calculation which allowed the lattice parameter to vary in accordance with the experimental coefficient of expansion (Figure 2). A reasonable agreement of the elastic constants gradients, derived from these two simulation techniques, is shown in Table 2.

The behaviour of elastic constants in the third region (800–1100 K), as predicted by our present calculations, is somewhat different. An obvious departure from linearity in all elastic constants occurs above 800 K. This is inconsistent with the results of Ngoepe *et al.* [4] where the linear behaviour persisted up to approximately 1100 K.

Thus, the test of the empirically determined interionic potentials of lanthanum fluoride, by the free energy minimisation technique, indeed confirms that potentials yield satisfactory predictions over a considerable range of temperatures. The sensitivity of these potentials appears above 800 K, where probably, there is a tendency for the severe anharmonic behaviour to commence. This may be confirmed by modifying the short-range and shell model parameters for this temperature range or by using molecular dynamics which includes the anharmonic nature explicitly – but has the disadvantage that sophisticated shell model potentials cannot be used.

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APPENDIX A

FREE ENERGY MINIMISATION BACKGROUND

The lattice dynamics approach for evaluating crystal properties, like the free energy and lattice expansion, is first to determine the phonon frequencies [5]. Thus by

defining an eigenvector problem

$$\bar{\omega}^2 n = D \cdot n \tag{A.1}$$

the vibrational frequencies, $\bar{\omega}$, may be calculated by diagonalizing the dynamical matrix D, where

$$D = m^{-1/2}(R - TS^{-1} \cdot T) \cdot m^{-1/2} \tag{A.2}$$

and R is the core–core matrix, T the core–shell matrix and S the shell–shell matrix. These matrices are second derivatives of the potential energy (Equation 1) with respect to displacements of cores and shells. The core displacements, u, are defined in terms of the diagonal matrix of core masses as

$$u = m^{-1/2} n \tag{A.3}$$

Once the phonon frequencies have been specified the free energy is determined from the following thermodynamic expression

$$F = k_B T \sum_i [x/2 + \ln (1 - \exp (-x))] \tag{A.4}$$

where $x = h\omega_i/kT$, and the summation goes over the total number of phonon frequencies and all points within the irreducible Brillouin zone. The point energy $\Sigma h\omega_i/2$ is included in Equation (A.4).

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