

Lattice dynamics of lithium oxide

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Abstract. Li_2O finds several important technological applications, as it is used in solid-state batteries, can be used as a blanket breeding material in nuclear fusion reactors, etc. Li_2O exhibits a fast ion phase, characterized by a thermally induced dynamic disorder in the anionic sub-lattice of Li^+ , at elevated temperatures around 1200 K. We have carried out lattice-dynamical calculations of Li_2O using a shell model in the quasi-harmonic approximation. The calculated phonon frequencies are in excellent agreement with the reported inelastic neutron scattering data. Thermal expansion, specific heat, elastic constants and equation of state have also been calculated which are in good agreement with the available experimental data.

Keywords. Lattice dynamics; phonons; thermodynamic properties.

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1. Introduction

Lithium oxide (Li_2O) belongs to the class of superionics, which allow macroscopic movement of ions through their structure. This behavior is characterized by the rapid diffusion of a significant fraction of one of the constituent species within an essentially rigid framework of the other species. In Li_2O , Li is the diffusing species, while oxygens constitute the rigid framework [1,2]. This material finds several technological applications ranging from lightweight high power-density lithium-ion batteries to being a possible candidate for blanket material in future fusion reactors [3,4]. Li_2O crystallizes in the anti-fluorite structure with a face-centered cubic lattice and belongs to the $\text{Fm}\bar{3}\text{m}$ (O_h^5) space group [1,2], lithium being in the tetrahedral coordination. Like other fluorites [5], this also shows a decrease in the elastic constant C_{11} [6] with temperature around the transition to the fast ion phase. In several other fluorites, the fast ion phase is characterized by a specific heat anomaly [7], a Schottky hump in the specific heat. However, no such anomaly has been observed in Li_2O [6,8,9].

This paper reports the lattice dynamics calculations done to understand dynamics of anti-fluorite Li_2O . Lattice dynamics calculations have been done to calculate the phonon spectrum, specific heat and elastic constants of the oxide. These results are in very good agreement with the available experimental data [6,9–11].

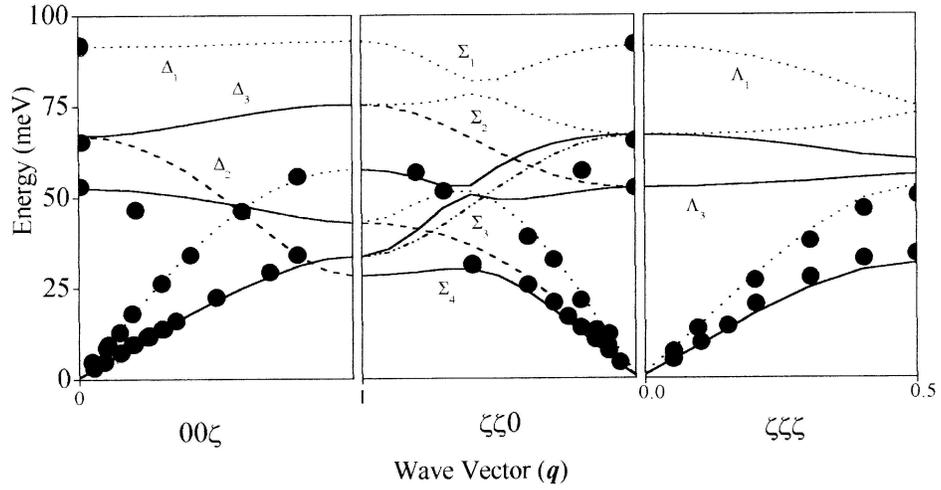


Figure 1. Phonon dispersion relation in Li_2O . Solid symbols are the experimental data from inelastic neutron scattering [10].

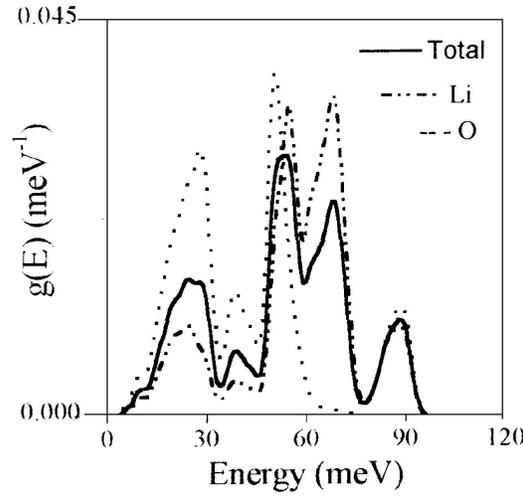


Figure 2. Phonon density of states in Li_2O , along with the partial densities of lithium and oxygen atoms.

2. Lattice dynamics calculations

Calculations have been carried out in the quasi-harmonic approximation using interatomic potential consisting of both long and short-range terms, using DISPR [12]. The form of the potential is given below:

$$V(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z(k)Z(k')}{r^2} + a \exp \left[\frac{-br}{R(k) + R(k')} \right],$$

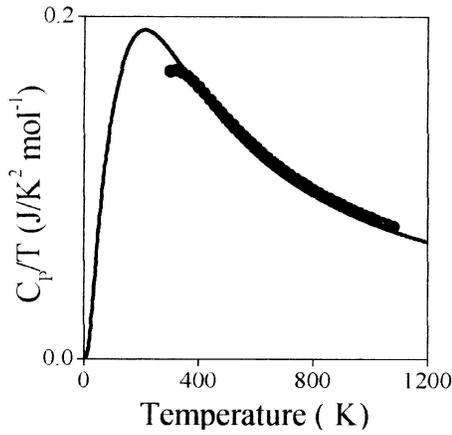


Figure 3. Specific heat of Li_2O . Solid symbols denote the experimental data [9].

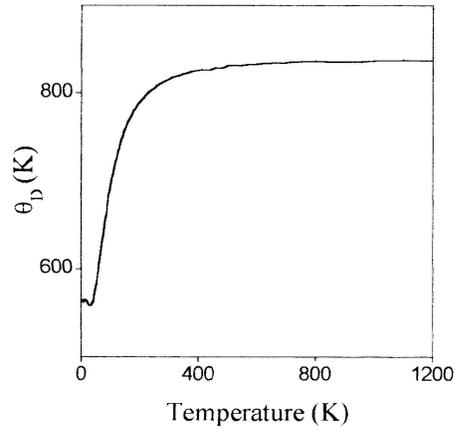


Figure 4. Variation of the Debye temperature with temperature.

where a and b are empirical parameters [13], and $a = 1822$ eV and $b = 12.364$. Oxygen ions have been modeled using a shell model [13,14]. Group theoretical considerations classify the phonons in the entire Brillouin zone into the following representations:

$$\begin{aligned} 00\zeta: & 2\Delta_1 + \Delta_2 + 6\Delta_3, \\ \zeta\zeta 0: & 3\Sigma_1 + 2\Sigma_2 + \Sigma_3 + 3\Sigma_4, \\ \zeta\zeta\zeta: & 3\Lambda_1 + 3\Lambda_3 \text{ } (\Lambda_3 \text{ are doubly degenerate}). \end{aligned}$$

The phonon dispersion relation at ambient conditions is given in figure 1. The zone center modes and the phonons in the entire Brillouin zone are in very good agreement with the available inelastic neutron scattering data [10,11]. The phonon density of states at ambient conditions along with the partial densities of lithium and oxygen is given in figure 2. Both lithium and oxygen contribute almost in the entire Brillouin zone. Lithium's contribution is higher on the higher energy side, with a prominent peak in the region between 50 and 75 meV. Oxygen contribution is greater on the lower energy side with prominent peaks below 60 meV.

The specific heat, $C_P(T)$ can be calculated from the knowledge of the phonon density of states. The calculated ratio $C_P(T)/T$ has been compared with the experimental result in figure 3. The variation of the Debye temperature (θ_D) with temperature is given in figure 4. Table 1 gives the calculated values of the elastic constants and equilibrium lattice parameters using the model calculations as compared with the experimental results.

3. Conclusions

A shell model has been successfully used to study the phonon properties of Li_2O . The interatomic potential is able to reproduce the equilibrium lattice constant,

Table 1. Comparison between calculated and experimental [6] parameters at ambient conditions. (The values in the brackets correspond to the error in the last digit.)

Physical quantity	Experimental	Calculated
Lattice parameter (nm)	0.4606(3)	0.461
C_{11} (GPa)	202.0(55)	213
C_{44} (GPa)	58.7(8)	52
C_{12} (GPa)	21.5(66)	56

elastic constants (except C_{12}) and phonon frequencies, which are in unison with the experimental data [1,6]. The phonon dispersion in the entire Brillouin zone agrees well with reported experimental data. The calculated specific heat is in good agreement with the experimental data. The interatomic potential formulated for Li_2O oxide may be transferred to other similar fluorites and antiferrofluorites like Na_2O , K_2O , UO_2 , ThO_2 etc., with suitable modifications.

References

- [1] T W D Farley, W Hayes, S Hull, M T Hutchings and M Vrtis, *J. Phys. Condens. Matter* **3**, 4761 (1991)
- [2] R W G Wyckoff, *Crystal structures*, 2nd ed. (John Wiley & Sons, New York, 1963)
- [3] David A Keen, *J. Phys. Condens. Matter* **14**, R819 (2002)
- [4] G L Kalucinski, *J. Nucl. Mater.* **141**, 3 (1986)
- [5] R B Roberts and G K White, *J. Phys.* **C19**, 7167 (1986)
- [6] S Hull, T W D Farley, W Hayes and M T Hutchings, *J. Nucl. Mater.* **160**, 125 (1988)
- [7] M Hofmann, S Hull, G J McIntyre and C C Wilson, *J. Phys. Condens. Matter* **9**, 845 (1997)
- [8] T Kurusawa, T Takahashi, K Noda, H Takeshita, S Nasu and H Watanbe, *J. Nucl. Mater.* **107**, 334 (1982)
- [9] Takaai Tanifugi, Kenichi Shiozawa and Shoichi Nasu, *J. Nucl. Mater.* **78**, 422 (1978)
- [10] T W D Farley, W Hayes, S Hull and R Ward, *Solid State Ionics* **28–30**, 189 (1988)
- [11] T Osaka and I Shindo, *Solid State Commun.* **51**, 421 (1984)
- [12] S L Chaplot, Report BARC-972 (1978); unpublished (1992)
- [13] S L Chaplot, N Choudhury, S Ghose, M N Rao, R Mittal and P Goel, *Eur. J. Mineralogy* **14**, 291 (2002)
- [14] G Venkataraman, L Feldkamp and V C Sahni, *Dynamics of perfect crystals* (MIT Press, Cambridge, 1975)
P Bruesh, *Phonons, theory and experiments I* (Springer-Verlag, Berlin, 1986)