Inelastic neutron scattering study of lattice dynamics in α-ZnCl$_2$

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Abstract. Inelastic neutron scattering experiments have been carried out to measure the phonon density of states in polycrystalline α-ZnCl$_2$ at Dhruva, Trombay. Lattice dynamical calculations, based on an interatomic potential model, are accomplished to study phonons associated with this otherwise extremely hygroscopic compound. Our calculated data are found to be well-compatible with the available measured ones.

**Keywords.** Inelastic neutron scattering; lattice dynamics; phonons.

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1. Introduction

Crystalline ZnCl$_2$, which is of extremely hygroscopic nature, possesses in general four different structurally determined forms at ambient pressure [1,2], viz. α (I$\bar{4}$2d, $Z = 4$), β (P2$_1$/c, $Z = 12$), γ (P4$_2$/nmc, $Z = 2$) and δ (Pna2$_1$, $Z = 4$). In the γ form, Zn^{2+} ions lie in tetrahedral sites between alternate sheets of Cl$^-$ ions, while in the α and β forms, Zn^{2+} ions are found between all chloride sheets to provide a cross linking effect which is, however, more pronounced in α-ZnCl$_2$. Upon compression, the α phase transforms into the δ phase at 2.1 GPa [2]. Several studies [2–4] on such pressure-induced structural phase transitions in polymorphous (including glassy) ZnCl$_2$ make it an interesting system to study its local dynamics at the atomic level. The present work elucidates the neutron inelastic scattering measurements of phonon density of states carried out at Dhruva, Trombay, for the α form of ZnCl$_2$. Complementary lattice dynamical calculations have been accomplished to help interpret the various measured data [2,5,6].

2. Structure and model potential

α-ZnCl$_2$ crystallizes to a cristobalite type three-dimensional network of corner-linked tetrahedra (figure 1). In the present model, Born–Mayer repulsive and weak attractive van der Waals interactions among different pairs of atoms are incorporated within the framework of quasi-harmonic approximation. Because of the
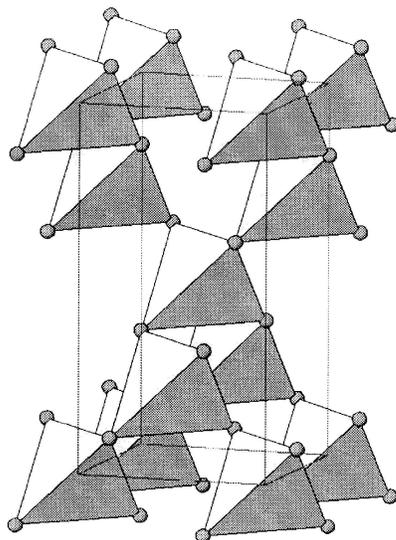
Figure 1. Crystal structure of α-ZnCl$_2$. The small circles represent Cl atoms, while Zn atoms are located inside (not visible here) the ZnCl$_4$ tetrahedra.

covalent nature of the Zn–Cl bond, a stretching term has to be included further in our potential function. The actual model thus turns out to be

$$V(r) = a \exp \left\{ -b \left(\frac{r}{R(k) + R(k')} \right) \right\} - \frac{C_{ij}}{r^6} - D \exp \left\{ -\frac{n(r - r_0)^2}{2r} \right\},$$

(1)

where a (=1822 eV) and b (=12.364) are the constants, $R(k)$ and $R(k')$ refer to effective radius parameters for Zn and Cl atoms, C_{ij} accounts for van der Waals terms between the Zn and Cl atoms, r_0 is the equilibrium bond length, D and n are two adjustable parameters. At zero pressure and temperature, the empirical parameters were so adjusted as to give nearly zero net force on each individual atom. The eigenvalues, $\omega_j^2(\boldsymbol{q})$, have also to be all positive as an essential requirement for the dynamical stability. Necessary computations have been accomplished using DISPR [7] developed at Trombay.

3. Experiments and results

The reagent grade chemical ZnCl$_2$ (purity 98%) was purchased from Merck Chemical Co. (Germany), which was dried (due to its excessive hygroscopic nature) at 100°C for a constant period of 8 h. It was then transferred into the glove box under dry argon atmosphere for filling into different containers. About 30 g of the so-obtained polycrystalline ZnCl$_2$ sample was placed in a thin-walled aluminum sample holder of circular shape for the inelastic neutron scattering (INS) study.
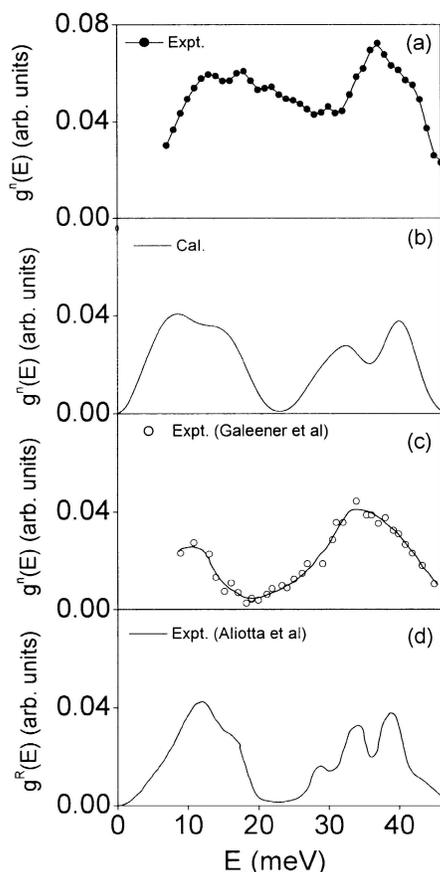
Figure 2. Graphical representation of (**a**) experimental and (**b**) calculated neutron weighted phonon density of states for α-ZnCl$_2$ along with (**c**) experimental neutron weighted phonon density of states for vitreous ZnCl$_2$ (ref. [10]) and (**d**) Raman density of states for the molten ZnCl$_2$ (ref. [11]). The multiphonon contribution has not been subtracted from the experimental data in (**a**). The corresponding calculated spectrum in (**b**) has been convoluted with the energy resolution of the instrument. The line in (**c**) is drawn as guide to the eye.

INS measurements were carried out using a medium resolution triple-axis spectrometer [8] at the Dhruva reactor, Trombay. The instrument used a monochromated beam of neutrons produced by Bragg scattering from the (1 1 1) planes of a copper crystal. Neutrons scattered inelastically by the sample were again Bragg diffracted by a pyrolytic graphite (0 0 2) analyzer and subsequently detected in a ^{10}BF$_3$ proportional counter. All the measurements were made in the energy loss mode with constant momentum transfer (Q). The elastic energy resolution was about 15% of the initial energy. Several scans were performed with final energy (E_f) value of 30 meV. These were recorded by stepping the incident energy (E_i)

Table 1. Zone-center mode assignments in α-ZnCl$_2$.

	Optical phonon modes (cm^{-1})			
	Present calculation	Experimental data		
Modes		Ref. [5]	Ref. [6]	Ref. [2]
A$_1$	223	233	245	226
A$_2$	147			
	301			
B$_1$	94	113	117	
	273			
B$_2$	111	128	128	
	325			
E	75	82	80	76
	99	103	103	100
	263			
	327			

between 100 meV and 20 meV in steps of 1 meV and counting for fixed monitor counts at each setting.

In the present calculation, the neutron weighted phonon density of states, $g^n(E)$, is obtained from the measured scattering function $S(Q, E)$ through the following relation [9]:

$$g^n(E) = A \left\langle \frac{\mathrm{e}^{2W(Q)}}{Q^2} \cdot \frac{E}{n(E,T)+1} \cdot S(Q,E) \right\rangle$$

$$= B \sum_p \frac{4\pi b_p^2}{M_p} g_p(E), \tag{2}$$

where $n(E,T) = [\exp(E/KT)-1]^{-1}$, A, B are normalization constants, b_p, M_p, and $g_p(E)$ refer respectively to the neutron scattering length, mass and partial density of states of the pth atom in the unit cell. The quantity within $\langle \cdots \rangle$ represents the average over all Q values. $2W(Q)$ is the Debye–Waller factor. The factor $4\pi b_p^2/M_p$ turns out to be 0.063 and 0.474 barn/a.m.u. for Zn and Cl atoms respectively.

The experimental phonon density of states is shown in figure 2 along with the calculated spectrum. Our calculations show that there exist at least two broad bands in α-ZnCl$_2$, which are separated by a small band gap around 25 meV. However, the band gap in the experimental data is observed to be not so significant due partly to the water contamination in the sample and partly to the poor instrumental resolution. Detailed calculations on the partial phonon density of states (not shown here) further bring out that Zn atoms contribute considerably below 10 meV, while from 10 meV to 25 meV it is the vibration of Cl atoms that dominates. In the higher energy range (above 25 meV), the contributions from both the atoms seem to be equally significant. Experimental optical phonon data (even though available scantily) are also observed to be in fair agreement with our calculated results (table 1).

4. Conclusions

Our proposed covalent interatomic potential model appears to be quite realistic in the sense that it has been able to mimic the measured phonon density of states, at least qualitatively. To further justify our model, we need to carry out a subsequent extension of this potential to the other crystalline polymorphs of ZnCl$_2$, which is, however, underway.

Acknowledgments

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