# Computer Simulation Studies of the Phase Transition in Compressible Deuteroammonium Chloride

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#### Abstract

The effects of pressure on the dynamical behaviour of an  $ND_4^+$  ion near the  $\lambda$  transition under the influence of its nearest neighbours in deuteroammonium chloride have been studied by using the computer simulation technique. The well-known Lennard Jones (6–12) potential is used as the representative interaction between  $ND_4^+$  and  $Cl^-$ . The libration frequency of the  $ND_4^+$  ion is estimated to be approximately 130 and 145 cm<sup>-1</sup> at pressures of 1 atm and 3 kbar respectively.

## 1. Introduction

It is a well-known fact that a  $\lambda$ -type transition occurs in the specific heat data of deuteroammonium chloride around 249 K. However, there has been very little previous work on measurements of heat capacities. Garland and Baloga (1977) reported a  $\lambda$ -type transition for a single crystal of ND<sub>4</sub>Cl, with 99.2% deuteration, at pressures of 1 atm  $(1.01 \times 10^5 \text{ Pa})$  and 1.5 kbar (1 bar =  $10^5 \text{ Pa}$ ) by using the high resolution a.c. calorimeter technique. It was noticed that the transition temperature is strongly dependent upon pressure, increasing from approximately 249.6 K at 1 atm to 261 K at 1.5 kbar. They also observed the diminished  $\lambda$  peak in the specific heat data at the elevated pressure. Trappeniers and van der Molen (1966) studied the effect of pressure up to 2 kbar on the  $\lambda$  transition for a powdered ND<sub>4</sub>Cl sample and noticed a reduction in the transition entropy with increasing pressure, similar to the case of NH<sub>4</sub>Cl. Yelon et al. (1974) performed detailed neutron scattering investigations of the order-disorder transition in a crystal of  $N(D_{0.93}H_{0.07})_4Cl$  as a function of both temperature and pressure. They observed that the intensity of the (221) reflection dropped considerably, approaching zero, in the vicinity of the transition temperature. At pressures of 157 bar and 4.14 kbar the intensity of the (221) reflection dropped to zero at 250.4 and 280 K respectively. Garland et al. (1975) also observed the anomalous behaviour in measurements of the piezo-electric constant and thermal expansion of  $ND_4Cl$  single crystals at 1 atm pressure. Pistorius (1969) studied the phase diagrams of the ammonium halides, including  $ND_4Cl$  with

isotopic purity of 99%, up to 40 kbar by means of differential thermal analysis. By using the experimental data, an empirical relation was suggested for the critical temperature as a function of pressure:

$$T_{c}(^{\circ}\mathrm{C}) = -23 \cdot 39 + 7 \cdot 7P - 0 \cdot 1950P^{2} + 0 \cdot 00222P^{3}, \qquad (1)$$

where P is expressed in kbar. However, the accuracy of the data was claimed only up to 10 kbar.

Similar to the case of  $NH_4Cl$ , there has been considerable uncertainty about the order of transition in  $ND_4Cl$ . A small discontinuous phase change is observed at low pressure, but the transition becomes continuous at high pressure. The nature of the phase transition in compressible solids is not yet fully understood. In an earlier communication (Pandey and Trikha 1984*a*), computer simulation studies were carried out to investigate the nature of the phase transition around 249 K in deuteroammonium chloride at 1 atm pressure for 5000 time steps with  $\Delta t = 0.05$ . The present study is an extension of the earlier work in a deuteroammonium chloride system for  $10^4$  time steps with  $\Delta t = 0.01$  at pressures of 1 atm and 3 kbar. The libration frequency of the  $ND_4^+$  ion is found to increase slightly with pressure, that is it varies from 130 to 145 cm<sup>-1</sup>. However, the present calculations do not reveal a decrease in the entropy of the system up to 3 kbar. Further, there appears to be no experimental Raman spectrum study of deuteroammonium chloride at high pressure.

## 2. Crystal Structure of Compressible Deuteroammonium Chloride

As in our earlier work we only consider a unit cell of ND<sub>4</sub>Cl and the nearest neighbour interaction of the static chlorine atoms, in order to avoid excessive computational work. The crystal structure of ND<sub>4</sub>Cl, known from the neutron diffraction study by Goldschmidt and Hurst (1951), has a CsCl-type structure with a unit cell length of 0.386 nm at 1 atm pressure. The deuterium atoms are arranged tetrahedrally around the nitrogen atom at the centre of the unit cell. There appears to be no P-V data available for the case of ND<sub>4</sub>Cl. However, from the compressibility measurements of Vaidya and Kennedy (1971), one finds that the decrease of the lattice constant,  $\Delta a$ , is directly proportional to pressure up to about 10 kbar and can be expressed as  $\Delta a/a \approx 0.002 P$ , with P expressed in units of kbar for all ammonium halides. Following this, we have estimated the size of the unit cell to be 0.384 nm at a pressure of 3 kbar. We further assume that the N–D bond length (0.103 nm) remains unaffected by the application of  $\sim 3$  kbar pressure, with the moment of inertia of ND<sub>4</sub><sup>+</sup> being  $14.2 \times 10^{-47}$  kg m<sup>2</sup>.

# 3. Interaction Potential and Mathematical Formulation

In order to compute the potential energy of the dynamical system we use the wellknown Lennard Jones (6–12) potential

$$\phi(r) = 4\epsilon \{ (\sigma/r)^{12} - (\sigma/r)^6 \}$$
(2)

as the representative interaction between  $ND_4^+$  and  $Cl^-$  under pressure up to 3 kbar;

Phase transition in ND<sub>4</sub>Cl

 $\sigma$  represents the distance of closest approach ( $\approx 0.35$  nm). The equations to be solved are

$$\dot{l}_a(t) = W(t) \times l_a(t), \qquad (3)$$

$$\dot{\mathbf{\Omega}}(t) = \boldsymbol{\tau}(t), \tag{4}$$

$$W(t) = \mathbf{I}^{-1} \cdot \mathbf{\Omega}(t) \,. \tag{5}$$

Here  $l_a$  ( $\alpha = 1, 2, 3$ ) are the unit vectors along the principal axes of the molecule at any instant of time;  $\Omega$  and W represent the angular momentum and angular velocity respectively;  $\tau$  is the torque exerted on the ND<sub>4</sub><sup>+</sup> ion by its nearest eight chlorine neighbours and I denotes the inertia tensor.

The rotational motion of  $ND_4^+$  is governed by the algorithm equations

$$I_{a}(t+\Delta t) = I_{a}(t) + \dot{I}_{a}(t)\Delta t + \frac{1}{6} \{ 4 \ddot{I}_{a}(t) - \ddot{I}_{a}(t-\Delta t) \} \Delta t^{2}, \qquad (6)$$

$$\mathbf{\Omega}(t+\Delta t) = \mathbf{\Omega}(t) + \frac{1}{6} \{ 2\mathbf{\tau}(t+\Delta t) + 5\mathbf{\tau}(t) - \mathbf{\tau}(t-\Delta t) \} \Delta t, \qquad (7)$$

where  $\dot{l}_a(t)$  and  $\ddot{l}_a(t)$  are the first and second time derivatives of the direction cosines.

The mathematical details of the calculation have been given by Pandey and Trikha (1984b). The algorithm used in the present study has been found to give both excellent stability and energy conservation over long periods of time, which are the necessary conditions for this type of computation.



Fig. 1. Average total energy against average rotational energy (in reduced units) for the ND<sub>4</sub><sup>+</sup> ion, with the Lennard Jones potential, at pressures of (a) 1 atm and (b) 3 kbar, for  $\Delta t = 0.01$ .

#### 4. Discussion and Results

In the present analysis, the ND<sub>4</sub>Cl system (consisting of a unit cell) is studied by imparting angular momentum in the range 1.0-12.0 (in reduced units) to the ND<sub>4</sub><sup>+</sup> ion about the z-axis. The effect of pressure on the rotational dynamics of the  $ND_4^+$  ion (under the influence of the eight chlorine atoms fixed at the vertices of the unit cell) has been studied up to  $10^4$  time steps. The time increment  $\Delta t = 0.01$  is expressed in reduced units and is of the order of  $10^{-13}$  s.

In Fig. 1 the variation of the average total energy  $\langle E \rangle$  (sum of the potential and rotational kinetic energy) is shown as a function of the average rotational kinetic energy  $\langle E_{RK} \rangle$  of the ND<sub>4</sub>Cl system for pressures of 1 atm and 3 kbar. Here phase III corresponds to lower values of  $\langle E \rangle$  and  $\langle E_{RK} \rangle$  before the transition, and phase II to higher values of  $\langle E \rangle$  and  $\langle E_{RK} \rangle$  after the transition. The computed values of the rotational kinetic energy appear to be pressure independent, whereas the magnitude of the potential energy of the ND<sub>4</sub><sup>+</sup> ion increases with an increase in pressure. We notice that the gradient for phase II is steeper at 1 atm than at 3 kbar, as shown by the difference between the solid and dashed lines in Fig. 1*a*. Further, for the case of 3 kbar (Fig. 1*b*), our calculations show that both the phases almost lie on a common line indicating that the discontinuous phase change at 1 atm has been converted into



Fig. 2. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the ND<sub>4</sub><sup>+</sup> ion as a function of time step for angular momenta 2.0 and 4.0 corresponding to (a) 1 atm and (b) 3 kbar for  $\Delta t = 0.01$ .

a continuous phase change. Such a situation was noticed in the case of  $NH_4Cl$  at a much higher pressure of approximately 10 kbar. However, we observe that the average total energy  $\langle E \rangle$  of  $ND_4Cl$  is found to be of the same order as that calculated for  $NH_4Cl$  (see Figs 1*a* and 1*b* in Pandey and Trikha 1984*c*).



Fig. 3. Potential energy (solid curves) and rotational kinetic energy (dashed curves) for the  $ND_4^+$  ion as a function of time step for angular momentum 9.0 corresponding to (a) 1 atm and (b) 3 kbar for  $\Delta t = 0.01$ .

From a detailed analysis of the direction cosine data of the moving frame of reference attached to the  $ND_4^+$  ion, we find that the  $ND_4^+$  ion performs a three-dimensional complex torsional oscillation corresponding to phase III. The rotational motion is mostly confined to only two quadrants, whereas the plane of vibration changes slowly. Distinct changes in the dynamics of  $ND_4^+$  are not observed with a change of pressure of ~3 kbar. For phase II, a detailed analysis of the data further reveals that the  $ND_4^+$  ion is found to be comparatively free, but still unable to perform free rotation even when the angular momentum imparted to the system is of the order of 12.0. Similar to the case of the  $NH_4^+$  ion, the  $ND_4^+$  ion is still performing a complex three-dimensional librational motion, associated with the vibrational motion, and the plane of vibration can become inverted more frequently. However, the  $ND_4$ Cl system is found to be comparatively more stable than the  $NH_4$ Cl system.

Fig. 2*a* shows the potential energy (solid curves) and rotational kinetic energy (dashed curves) of the ND<sub>4</sub>Cl system as a function of time step for angular momenta 2 and 4 (phase III) at 1 atm. In Fig. 2*b* we have plotted the energy for angular momenta 2 and 4 for 3 kbar. A comparison of Figs 2*a* and 2*b* shows that the variation of energies with respect to time step is similar, indicating the ordered motion of the ND<sub>4</sub><sup>+</sup> ion. The effect of pressure is not noticeable in terms of the fluctuations of energy (potential as well as kinetic), although the total average energy of the system increases with pressure. It may be mentioned here that the corresponding fluctuation in energy of phase III in the case of compressible ammonium chloride at 3 kbar pressure was found to be more pronounced (see Fig. 2*a* in Pandey and Trikha 1984*c*).

Corresponding to phase II, Figs 3*a* and 3*b* show the potential energy (solid curves) and rotational kinetic energy (dashed curves) for angular momentum 9.0, with  $\Delta t = 0.01$ , as a function of time step at pressures of 1 atm and 3 kbar respectively. In both these cases we notice rapid fluctuations in the potential and rotational kinetic energies of the ND<sub>4</sub><sup>+</sup> ion. Similar to the case of NH<sub>4</sub>Cl, here again, we find a dominance of potential energy. However, the nature of energy variation in ND<sub>4</sub><sup>+</sup> at 3 kbar is found to be quite different, as seen also for the compressible NH<sub>4</sub>Cl system (see Fig. 3*b* in Pandey and Trikha 1984*c*).

In Figs 4*a* and 4*b* we have plotted the energy of the  $ND_4^+$  ion for angular momentum 12.0 corresponding to pressures of 1 atm and 3 kbar. The fluctuations in energy are observed to be more pronounced with the increase of angular momentum. However, we do not notice any decrease in the magnitude of the energy fluctuation in the  $ND_4Cl$  system at 3 kbar when compared with the 1 atm case. Therefore, we cannot comment on the decrease in the entropy of the system up to 3 kbar.

We propose to carry out further work in the  $ND_4Cl$  system at higher pressures.

#### 5. Conclusions

The following conclusions can be drawn from the present study:

(i) Similar to our earlier work, the rotating model of the  $ND_4^+$  ion in the compressible deuteroammonium chloride system still supports the Pauling (1930) hypothesis with slight modification. The  $ND_4^+$  ion is found to be partially free in phase II, as depicted by the present detailed analysis of the direction cosine data. However, the free rotation of the  $ND_4^+$  ion, as envisaged by Pauling, would correspond to phase I near 448 K.



Fig. 4. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the ND<sub>4</sub><sup>+</sup> ion as a function of time step for angular momentum  $12 \cdot 0$  corresponding to (a) 1 atm and (b) 3 kbar for  $\Delta t = 0.01$ .

- (ii) The computed libration frequency of the  $ND_4^+$  ion was estimated to be approximately 130 and 145 cm<sup>-1</sup> at pressures of 1 atm and 3 kbar respectively. Contrary to our earlier interpretation of the data (Pandey and Trikha 1984*a*), the  $ND_4^+$  ion was found to perform a complex three-dimensional torsional oscillation, which is confined to only two quadrants, instead of undergoing rotation through 360° in phase III.
- (iii) Since we have assumed the structure of compressible deuteroammonium chloride to be of CsCl type in our entire calculation, the discontinuity in the  $\langle E \rangle$  against  $\langle E_{RK} \rangle$  lines (Fig. 1) therefore corresponds only to phases II and III of ND<sub>4</sub>Cl. For a pressure of 3 kbar, the two separate lines of phase II and phase III appear to be almost continuous, one of the reasons for a diminished  $\lambda$ -type peak in the specific heat data as observed at elevated pressure by Garland and Baloga (1977).
- (iv) It is important to mention here that, since it is difficult to grow a pure ND<sub>4</sub>Cl crystal, the experimental results are likely to differ. In the present calculation, we have considered 100% deuteration, whereas the experimental sample of ND<sub>4</sub>Cl crystal may have deuteration of only about 99%, thus affecting the value of the moment of inertia to some extent. The multicritical point in ND<sub>4</sub>Cl is observed at a much lower pressure than that in the NH<sub>4</sub>Cl system. The diminished  $\lambda$ -type peak in the specific heat data is found to be quite appreciable in the ND<sub>4</sub>Cl system. Moreover, there appears to be no P-V data available for the ND<sub>4</sub>Cl crystal; therefore, we have confined our study up to only 3 kbar. Still, we believe that there should be a decrease in the entropy of the ND<sub>4</sub>Cl system at higher pressure, similar to the case of the NH<sub>4</sub>Cl system.

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