



REFERENCE

IC/94/366

**INTERNATIONAL CENTRE FOR  
THEORETICAL PHYSICS**

**THERMAL EXPANSION  
AND TEMPERATURE VARIATION  
OF ELASTIC CONSTANTS OF Li(H,D)  
AND Na(H,D) SYSTEMS**



**INTERNATIONAL  
ATOMIC ENERGY  
AGENCY**



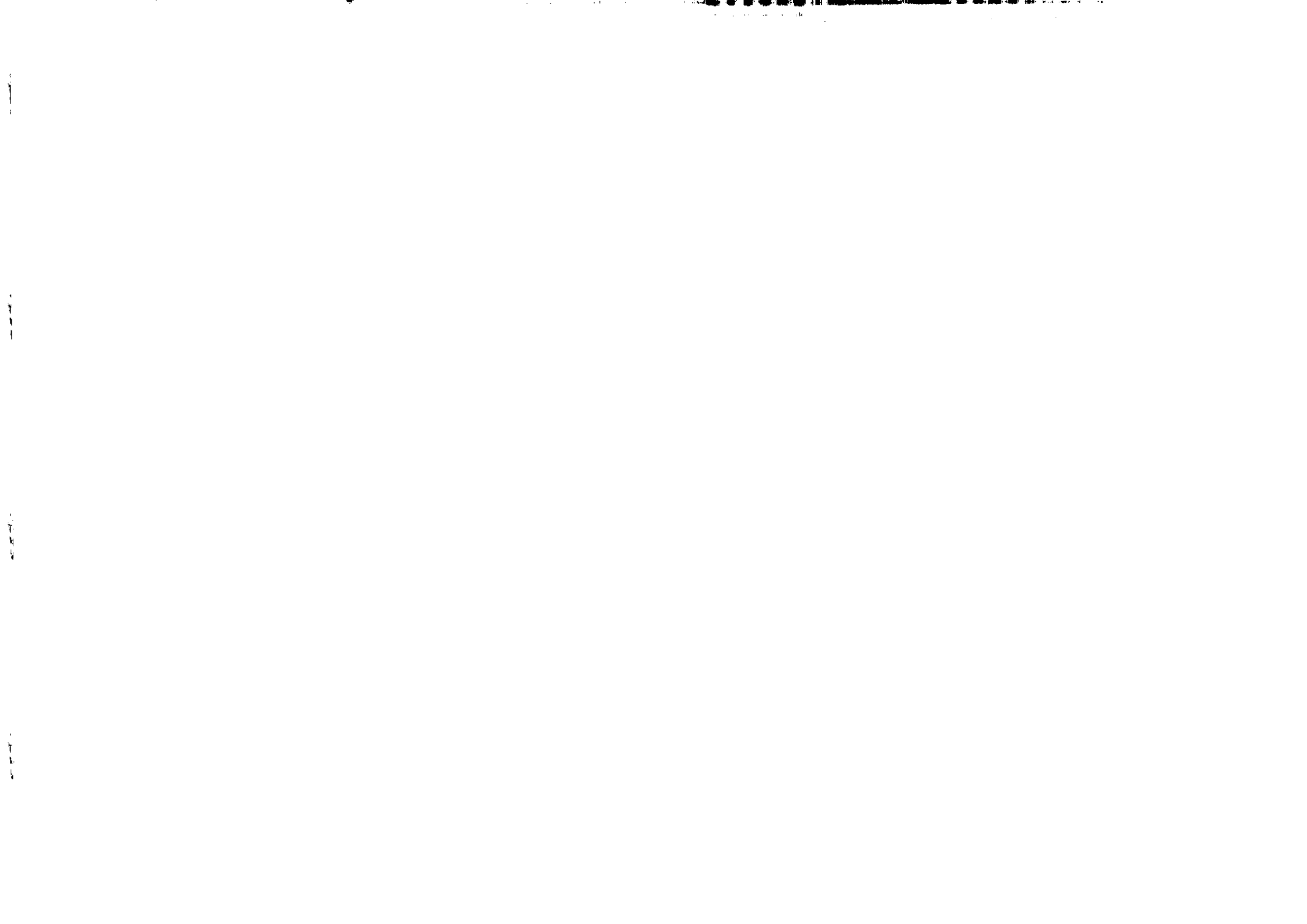
**UNITED NATIONS  
EDUCATIONAL,  
SCIENTIFIC  
AND CULTURAL  
ORGANIZATION**

**A.K.M.A. Islam**

and

**M.T. Hoque**

**MIRAMARE-TRIESTE**



International Atomic Energy Agency  
and  
United Nations Educational Scientific and Cultural Organization  
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

**THERMAL EXPANSION AND TEMPERATURE VARIATION  
OF ELASTIC CONSTANTS OF Li(H,D)  
AND Na(H,D) SYSTEMS**

A.K.M.A. Islam <sup>1</sup>

International Centre for Theoretical Physics, Trieste, Italy

and

M.T. Hoque

Department of Physics, Rajshahi University, Rajshahi-6205, Bangladesh.

**ABSTRACT**

An analysis of thermal expansion of Li(H,D) systems upto melting temperature has been performed using the theory of anharmonic lattice. The study has for the first time been extended to Na(H,D) systems where very little or no data are available. The calculated lattice constants of Li(H,D) systems show quite good agreement with experiment. The success of the present calculation with Li(H,D) and room temperature lattice constant data for Na(H,D) gives an indication of the reliability of the computed lattice constants and thermal expansion coefficients for Na(H,D) systems. The study also allows us to predict the hitherto unknown lattice constants of Na(H,D) crystal at 0K. The temperature dependence of elastic constants for Li(H,D) systems has also been evaluated. Comparison with measurements shows the reliability of the present calculations.

MIRAMARE - TRIESTE

November 1994

<sup>1</sup>Permanent address: Department of Physics, Rajshahi University, Rajshahi-6205, Bangladesh.

## 1 Introduction

The alkali halides have figured particularly prominently for which experimental investigations of specific heat, thermal expansion, elastic properties, x-ray diffraction, infrared and neutron absorption and many other such studies have been undertaken in various temperature ranges. These are coupled with the attempts to correlate the observations within the framework of different theoretical models that have met with varying degrees of success. One general conclusion which has emerged from these evaluations is that the alkali ion plays a more important role in determining the interionic forces than does the halide ion [1,2]. On purely scientific grounds it was natural, therefore, that these studies should have been extended to the hydrides and deuterides of the isotopes of lithium and sodium. Unfortunately Li(H,D) and Na(H,D) systems have not been treated in the same way as their halide counterparts. The study of thermal expansion of Li(H,D) and Na(H,D) systems is necessary because of their importance in various fields. The fuel hydrogen storage and neutron moderator in the form of metal hydrides, where the density of hydrogen in few cases exceeds that of liquid hydrogen, are the most interesting and useful practical applications. The development and fabrication of lithium hydride radiation shield of spacecraft of nuclear power station are being made. These compounds (particularly, LiH and NaH) are also used as reducing agents. The dimensional changes (or thermal expansions) are such as to minimize free energy, contributions to which can come from the static lattice, lattice vibrations, electric dipoles, nuclear spins, etc. Thermal expansion behaviour is often related to elasticity, infrared and Raman spectra, the Fermi surface, electro- and magneto-striction, phase transitions, thermal conductivity and other properties of solids. For this reason there is a need for good thermal expansion data in studies of the solid state, as well as the technical need for reliable measurements of dimensional changes with temperature.

From the experimental point of view, information on the thermophysical and other properties of Li(H,D) are available. LiH and LiD have been investigated rather extensively - the phonon dispersion in LiD [3] as well as the frequency distribution functions of LiH and LiD [4] have been determined by inelastic scattering; Raman and infrared measurements on both substances have been published [5,6] and the elastic constants [7,8] as well as the specific heat ( $C_p$ ) of Li(H,D) upto 320K [9] and the specific ( $C_v$ ) of Na(H,D) at temperature range 60-90K [10] have been measured. Pretzel et al [11] have described the preparation and properties of LiH and LiD single crystals. They have proposed models for some of the irradiation-induced point defects analogous to those in the alkali halide family using the optical absorption and electron paramagnetic resonance technique. The low-temperature variation of the elastic constants of Li(H,D) has been obtained from measurements of ultrasonic wave transit times through single crystals over the range 4.2 - 300K by James and Kheyrandish [12].

The thermal expansions of LiH and LiD have been measured by Haüssuhl and Skorzyczy [13], Zalkin [14], Laquer [15] (LiH only), Smith and Leider [16], Brückner et al [17], Anderson et al [18], , Eash [19] (LiD only). The values of linear thermal expansion coefficient from these sources have been plotted and the best curves have been drawn for both LiH and LiD [20]. The values obtained in this way are reported from 70K - 300K at 10K intervals by James and Kheyrandish [12]. But low-temperature ( $T < 70K$ ) thermal expansion data have not been reported.

Li(H,D) systems have been studied theoretically by many workers [21-31]. Thermal

expansion of all the isotopic modifications of lithium hydride have been investigated by Mel'nikova [27,28] using the theory of anharmonic lattice. Jex [24] calculated the linear thermal expansion of Li(H,D) systems using phonon data. Thermal expansion and mode Grüneisen parameters of Li(H,D) have been determined by a shell model fitted to phonon energies from inelastic neutron scattering in  $^7\text{LiD}$  [24]. But his results seem to be not correct at higher temperatures. The effect of both temperature and isotopic substitution on the distance between ions has been investigated by Tyutyunnik [32] using the rigid ion model with only NN interactions. It has also been shown that the thermal expansion may be described as a function of the Coulomb potential parameters and the cation anion reduced mass. Due to lack of data there was hardly any theoretical works on Na(H,D) systems. But these crystal systems have only recently been taken into the fold of various theoretical calculations by Haque and Islam [29], Islam [30,31,33] and Hoque [34].

Elastic constants of crystals and their temperature variation not only are of interest in themselves, but also provide much insight into the interatomic forces in solids. The low temperature  $\Theta_D$  can be calculated from the low temperature elastic data. On the other hand, the high temperature elastic data are especially useful for the study of the melting mechanism. Several other physical quantities which are useful in the characterization of the properties of solids, may be related to the elastic constants and their temperature dependence. The temperature variation of elastic constants of Li(H,D) systems has been evaluated and discussed by James and Kheyrandish [12]. But at low temperature the agreement between observation and their calculations is not satisfactory [12].

Thermophysical properties of crystals ( lattice constant, thermal expansivity, compressibility, etc ) essentially depend on the anharmonicity. The harmonic lattice does not possess thermal expansion; and only the anharmonicity brings about the isotopic dependence of all the above properties. As mentioned before detailed information on some of the properties of Li(H,D) are available but there is hardly any such data (e.g. thermal expansion etc) available for Na(H,D) systems. Thus it is of some interest to study Li(H,D) systems thoroughly in the present context and extend the method to Na(H,D) systems as far as possible.

In the present study we calculate and discuss the thermophysical properties of Li(H,D) and Na(H,D) systems on the basis of the theory of anharmonic lattice. The investigations have been undertaken in an attempt (i) to correlate between the experimental data and the theoretical calculations, (ii) to derive data for these compounds, which are essential to study the higher-order elastic constants and the anharmonic properties of crystals and (iii) to extend data to lower temperatures for these compounds.

Section 2 consists of the basis of calculation. Results and discussions are made in section 3.

## 2 BASIS OF CALCULATIONS

Grüneisen [35] was the first to make a systematic study of thermal expansion of crystalline materials. The thermal expansion is usually studied within a quasi-harmonic approximation: it neglects anharmonic terms but instead assumes the ionic vibrational frequency to be volume dependent. A measure of this volume dependence of frequency is defined as the Grüneisen's parameter:

$$\gamma = -\frac{d \ln \nu}{d \ln V} \quad (1)$$

where  $\nu$  is the frequency and  $V$  is the volume.

Thermodynamic Grüneisen function is useful in analysis of thermal expansion data, and their interpretation. It is defined by the relation:

$$\gamma(T, V) = \frac{3\alpha V}{\chi_T C_V} = \frac{3\alpha V}{\chi_a C_P} \quad (2)$$

where  $\chi_T$  and  $\chi_a$  are the isothermal and adiabatic compressibilities.  $C_V, C_P$  are the specific heats at constant volume and constant pressure, respectively.  $\alpha$  is the linear thermal expansivity and  $V$  is the volume of the unit cell. The above expression stems from the summation  $\sum C_i \nu_i / \sum C_i$  over all the excited modes, including at high temperatures both optic and acoustic phonons further away from the zone centre. Eqn (2) relates the two strongly temperature dependent quantities  $\alpha$  and  $C_V$  but is itself relatively weakly dependent on temperature [36].

In the framework of a quasiharmonic approximation, the thermal expansion coefficient can be evaluated as a function of temperature according to the relation:

$$\alpha(T) = \sum_i C_i \gamma_i / 3\chi_T V$$

where  $C_i$  is the Einstein specific heat function for  $\omega_i$  ( the frequency of the  $i$ th branch at a wave vector  $\mathbf{k}$ ). The sum extends to all normal modes. The calculated  $\alpha(T)$  at higher temperature using this method is known to deviate from experiment [43]. This can be compensated by using the available specific heat values rather than the harmonic values. We are thus led to using the simple  $\alpha(T)$  and specific heat relationship whereby higher temperature specific heat information is embedded in the procedure. Thus the thermal expansion coefficient including lattice vacancy contribution at higher temperature for Li(H,D) and Na(H,D) systems can be written as:

$$\alpha(T) = \alpha_L(T) + \alpha_{vac}(T) \quad (3)$$

where  $\alpha_L$  and  $\alpha_{vac}$  are due to lattice and vacancy contributions, respectively.

$\gamma$  of LiH is practically constant for  $T > 50\text{K}$  [12]. The values of  $\gamma$  are taken from the theoretical calculations of [28,34]. Thus following [28,34] the thermal expansion of Li(H,D) and Na(H,D) systems can be written as :

$$\alpha_L(T)_{LiH} = K_{LiH} C_P(T) \quad (4)$$

$$\alpha_L(T)_{LiD} = K_{LiD} C_P(T) \quad (5)$$

$$\alpha_L(T)_{NaH} = K_{NaH} C_P(T) \quad (6)$$

$$\alpha_L(T)_{NaD} = K_{NaD} C_P(T) \quad (7)$$

where  $K$ 's are constants appropriate for different crystals [34].

We know that the volume of a crystal varies with temperature due to anharmonic effects and to the thermal creation of vacancies. In thermal equilibrium the crystal volume is [38,39] :

$$V(T) = V(0) + nV_{vac} = V(0) + V_{vac}[V(0)/V_M]exp(S_{vac}/k_B)exp(-E_{vac}/k_B T)$$

where  $V_{vac}$ ,  $S_{vac}$  and  $E_{vac}$  are the formation volume per vacancy, entropy and formation energy of the vacancy, respectively. The two exponential factors give the equilibrium concentration  $c_{vac}$  of vacancies.

Thus the vacancy contribution to the expansion coefficient,

$$\alpha_{vac} = (1/3V)(\partial V/\partial T) = \frac{1}{3}(E_{vac}/2k_B T^2)(V_{vac}/V_M)c_{vac}$$

where  $V_M$  is the molecular volume,  $k_B$  the Boltzman's constant.

The heat capacity data  $C_P(T)$  has been measured previously for Li(H,D) systems upto 320K [9]. High-temperature heat capacity data are available only for LiH. Lang's formula [37] for the specific heat of LiH at constant pressure from room temperature to 914 K is :  $C_P$  (J/moi.K) = 15.997 + 0.0478 T. Experimental values of  $C_V(T)$  for Na(H,D) systems are available at temperature range 60 - 90K [10].  $C_V(T)$  values outside these temperatures ( ~ 20K below and ~ 200K above the ranges) are then obtained through extrapolation. The extrapolation at the higher temperature side is done upto room temperature because the graph is almost linear in this region. These data are fitted between 40 and 300K by ,  $C_V(T) = 0.0458T - 0.203$  for NaH and  $C_V(T) = 0.0585T - 0.299$  for NaD (T in Kelvin and specific heat in J/mol.K ).

We now obtain the interionic separation,  $r$  ( half the lattice constant). In this case we will defer consideration of  $\alpha_{vac}$  which will be taken up in section 3. This is because only LiH will be analysed upto melting temperature. By integrating the above eqns (4-7) we get,

$$r(T)_{LiH} = r(0)_{LiH} e^{K_{LiH}[H(T)-H(0)]} \quad (8)$$

$$r(T)_{LiD} = r(0)_{LiD} e^{K_{LiD}[H(T)-H(0)]} \quad (9)$$

$$r(T)_{NaH} = r(40)_{NaH} e^{K_{NaH}[H'(T)-H'(40)]} \quad (10)$$

$$r(T)_{NaD} = r(40)_{NaD} e^{K_{NaD}[H'(T)-H'(40)]} \quad (11)$$

where the enthalpies are given by

$$H(T) - H(0) = \int_0^T C_P(T)dT \quad ; \quad H'(T) - H'(40) = \int_{40}^T C_V(T)dT.$$

The above eqns (8-11) are without the vacancy contribution which is negligible far below the melting temperature.

The temperature dependence of elastic constants is due to the anharmonic nature of the lattice vibrations and has been treated in various ways by different workers. Leibfried

and Lüdwig [40] have shown that the dependence of the elastic constants may be represented by  $C_{ij}(T) = C_{ij}(0)(1 - D\epsilon)$ , where D is a parameter which depends on the type of the crystal or the model used and  $\epsilon$  is the mean energy per oscillator. James and Kheyrandish [12] used the method of Leibfried and Ludwig [48] to predict the temperature variation of  $C_{ij}$  of Li(H,D) systems. The method involves extrapolation proportional to the thermal energy such that slopes of  $C_{ij}$  versus T are each proportional to the heat capacity for Li(H,D). The elastic constants and the initial slopes used were the appropriate  $C_{ij}$  and  $\partial C_{ij}/\partial T$  at room temperature obtained from experiments [12]. The heat capacity data of Yates et al. [9] have been used for the purpose.

We have evaluated the temperature dependence of elastic constants in a different way. For adiabatic elastic constants we assume the following expression [28,34]:

$$\frac{dC_{ij}^a}{dT} = \frac{1}{3}\Gamma_{ij}\beta(T) = \Gamma_{ij}\alpha(T)$$

where  $\beta(T) = 3\alpha(T)$  and  $\Gamma_{ij}$  is a constant.

Writing

$$\alpha(T) = \frac{1}{r} \frac{dr}{dT}$$

we have,

$$dC_{ij}^a(T) = \Gamma_{ij} \ln[r(T)] \quad (12)$$

Integrating the above equation, we obtain

$$C_{ij}^a(T) = C_{ij}^a(0) + \Gamma_{ij} \ln\left[\frac{r(T)}{r(0)}\right] \quad (13)$$

Here  $C_{ij}(0)$  and  $C_{ij}(T)$  are the elastic constants, at 0K and TK, respectively. Using a relationship given in [41,42] eqn (13) can also be expressed as :

$$C_{ij}^a(T) = C_{ij}^a(0) + \Gamma'_{ij} \ln\left[\frac{\alpha(T)}{\alpha(0)}\right] \quad (14)$$

where  $\Gamma'_{ij}$  is a constant.

### 3 RESULTS AND DISCUSSIONS

The methods of calculation developed above permit one to obtain the linear coefficient of thermal expansion and lattice constants as a function of temperature. The present calculated values of thermal expansion for temperature upto T = 300K for Li(H,D) and Na(H,D) systems from eqns (4-7) and the smooth experimental data of Li(H,D) are presented in Fig 1. The low-temperature thermal expansion calculations for Li(H,D) are also included in the figure in magnified scale. Fig. 1 shows that compared to LiH the thermal expansivity of LiD increases more rapidly with increasing temperature for T > 50K. This is borne out by experimental data. The same is true for the calculated values of  $\alpha$  for NaH and NaD. Experimental values of  $\alpha$  are available for upto T = 600K. We have plotted these data in Fig. 2. Our calculations and those due to Jex [24] have also been displayed in the Figure. As can be seen these calculated values start to differ at ~ 600K and the difference increases steadily right upto about melting temperature. It is

worth noting that the values of  $\alpha$  due to Jex [12] seem to level off after  $T \sim 600\text{K}$ . Similar type of deviation with experiment has also been observed in LiF, KCl by Namjoshi et al. [43]. They however pointed out that this is due to neglect of anharmonic effects at higher temperature. It may be mentioned here that Jex [24] calculated  $\alpha(T)$  in the framework of quasiharmonic approximations, and hence at high  $T$ ,  $\alpha(T)$  values will not be correct as has been discussed before. The above deviation at higher temperature has been compensated in our work by using the experimental rather than the calculated harmonic values of  $C_V$ . It is rather difficult to give an accurate value of vacancy contribution to expansion coefficient ( $\alpha_{vac}$ ) because defect formation volume and concentration are not known. But a rough estimate can be made as follows: From Fig 2 we note that  $\alpha T_m \sim 0.08$ . Assuming  $V_{vac}/V_m \sim 0.5$  and  $E_{vac}/k_B T_m \sim 20-25$  (typical values for alkali halides) and  $c_{vac} \sim 0.002$  (vacancy concentration is appreciable near the melting temperature), we obtain  $\alpha_m T_m \sim 0.004$ . Thus the vacancy contribution near melting temperature will be  $\sim 5\%$ . But it is certain that the correction is negligible at temperature as low as room temperature. Thus from what we have discussed it is certain that at higher temperatures the value of  $\alpha$  (if measured) will rise instead of levelling off.

The relative electronic contribution to the expansion has been discussed by Grimvall [38], and Barron et al. [36] for elements. The contribution is found to be negligible for  $T \sim (0.1-1)\Theta_D$ , i.e. for LiH,  $T \sim 100-1000\text{K}$ . The relative contribution should be noticeable below  $50\text{K}$  where the values of  $\alpha$  is already too small. No useful comparisons can be made for Na(H,D) due to the lack of experimental data or other theoretical calculations. But the success for Li(H,D) calculations gives an indication that Na(H,D) results are also valid. The crystals studied here have positive thermal expansivity. Some crystals, like RbI, have negative values of  $\alpha$  [43].

We evaluate  $r$  as a function of  $T$  by using eqns (8-11). Since the change of lattice constant at low temperature ( $T < 20\text{K}$ ) is extremely small,  $r$  values for the lowest available temperature can be used for  $T = 0\text{K}$  data for Li(H,D) systems [16]. Experimental lattice constant data are available for Na(H,D) systems only at room temperature. Here the lattice constants at  $40\text{K}$  are calculated from the experimental information of  $C_V$  [10,30,34] which are then used to calculate  $r(T)$ . The computed values of  $r(40)$  are found to be  $2.422\text{ \AA}$  and  $2.415\text{ \AA}$ , for NaH and NaD, respectively.

Figs. 3a and 3b show the interionic separation  $r(T)$  for Li(H,D) and Na(H,D) systems. The calculated results are compared with experimental data [14] for Li(H,D) in Fig. 3a. The comparison shows that our calculated values for LiH and LiD are in good agreement with experimental values. Fig. 3b show the calculations of  $r(T)$  for Na(H,D) systems. As a matter of interest the calculated  $r(T)$  between temperature  $T \approx 300-850\text{K}$  has been shown (along with the available experimental data) in the inset of Fig. 3a. No data on the temperature dependences of lattice constants are available for Na(H,D) systems except only those at room temperature (see [30]). The data show that the calculation for  $r(T)$  for Na(H,D) systems agree at room temperature. From the success of the techniques for Li(H,D) the present calculations should appear to be valid for Na(H,D).

The computation of the temperature variation of elastic constants needs  $\Gamma_{ij}$ . This is done by utilizing eqn (12) using our calculated lattice constants and the measured elastic constants [12]. In this way we obtain,  $\Gamma_{11} = 128.856 \times 10^{10} N.m^{-2}$ ,  $\Gamma_{12} = -18.82 \times 10^{10} N.m^{-2}$  and  $\Gamma_{44} = 44.945 \times 10^{10} N.m^{-2}$  for LiH. Similarly,  $\Gamma_{11} = 154.873 \times 10^{10} N.m^{-2}$ ,  $\Gamma_{12} = -16.164 \times 10^{10} N.m^{-2}$  and  $\Gamma_{44} = 36.275 \times 10^{10} N.m^{-2}$  for LiD. The temperature variation of the elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for Li(H,D) are shown in Figs. 4a,b,c,

respectively, over the temperature range  $0-320\text{K}$ . The temperature dependences of the elastic constants for Li(H,D) calculated by James and Kheyrandish [12] are also included in the Fig. 4 for comparison. It is seen that our calculated results for the elastic constants as a function of temperature show good agreement with the experimental values [12]. Overall slopes and magnitude are well represented. On the other hand the  $C_{ij}(T)$  values predicted by James and Keyrandish [12] are not as good as ours. The deviation is seen to be more near lower temperature.

$C_{11}$  is strongly temperature dependent while  $C_{12}$  and  $C_{12}$  depend weakly on temperature. The general pattern of behaviour is like alkali halides [44]. In our case  $\frac{1}{2}(C_{11} - C_{12}) < C_{44}$  for the entire temperature range whereas for alkali halides (exception, Li-halides) the inequality  $\frac{1}{2}(C_{11} - C_{12}) > C_{44}$  holds. The reason for this has been discussed by Huntington [45] as being due to the closed-shell repulsive potential between adjacent alkali and halide ions. The same can be applied here. Due to the small size of  $Li^+$  ion the most intimate contact is between  $H^-$  and  $D^-$  ions along [110] direction and not between  $Li^+$  and a  $H^-$  or  $D^-$  ion along the [100] directions. This results in a reversal in the sign of  $C_{44} - \frac{1}{2}(C_{11} - C_{12})$  through the entire temperature range.

The overall study suggests that the theory of anharmonic lattice applied in a manner as presented in the present study is useful for analysing the properties like thermal expansivity and temperature variation of elastic constants of Li(H,D) and Na(H,D) systems.

## 4 Acknowledgements

The authors would like to thank the Rajshahi University for support where a part of the work was done. AI thanks Professor Abdus Salam, the International Atomic Energy Agency and SAREC for hospitality at the International Centre for Theoretical Physics, Trieste, where the work was completed.

## References

- [1] Collins J. G. and White G. K., Progress in Low Temperature Physics. Vol. 4, p. 450, North-Holland, Amsterdam (1964).
- [2] Redmond A. D. and Yates B., J. Phys. C: Solid State. Phys. **5**, 1589 (1972).
- [3] Verble J.L., Warren J.L. and Yarnell J. L., Phys. Rev. **168**, 980 (1968).
- [4] Zemlianov M.G., Brocymann E.G., Chernopickov N.A. and Shitikov I.L., Inelastic Scattering of Neutrons, Vol. 2 (Vienna: IAEA) (1965).
- [5] Brodsky M.H. and Burstein E., J. Phys. Chem. Solids. **28**, 1655 (1967).
- [6] Laplaze D., J. Physique. **37**, 1051 (1976).
- [7] Guinan M.W. and Cline C.F., J. Nonmetals, **1**, 11 (1972).
- [8] Gerlich D. and Smith C.S., J. Phys. Chem. Solids, **35**, 1587 (1974).
- [9] Yates B., Wostenholm G.H. and Bingham J.L., J. Phys. C: Solid State Physics. **7**, 1769 (1974).

- [10] Sayre E.V. and Beaver J.J., *J. Chem. Phys.*, **18**(5), 584 (1950).
- [11] Pretzel F., Gritton G.V., Rushing C.C., Friauf R.J., Lewis W.B. and Waldstein P., *J. Phys. Chem. Solids*, **23**, 325 (1962).
- [12] James B.W. and Kheyrandish H., *J. Phys. C: Solid State Phys.* **15**, 6321 (1982).
- [13] Haüssühl S. and Skorczyk W.Z., *Kristallogr.* **130**, 340 (1969).
- [14] Zalkin A., Report US Atomic Energy Commission, Washington DC, UCRL. 4239 (1953)
- [15] Laquer H. L., USAEC Report AECD. 3706 (1952).
- [16] Smith D.K. and Leider H. R., *J. Appl. Cryst.* **1**, 246 (1968).
- [17] Brückner W., Kleinstück K. and Schulze G.R.E., *Phys. Stat. Sol.* **14**, 297 (1966)
- [18] Anderson J.L., Nasise J., Philipson K. and Pretzel F.E., *J. Phys. Chem. Solids*, **31**, 613 (1970).
- [19] Eash D.T., *J. Nucl. Matter.* **37**, 358 (1970).
- [20] Kheyrandish H., Ph. D Thesis, University of Salford (1977).
- [21] Bowman R.C., *J. Phys. Chem.* **75**, 1251 (1971).
- [22] Pandey R. and Stoneham A. M., *J. Phys.* **C18**, 5289 (1985).
- [23] Jaswal S.S., Sharma T.P. and Wolfram G., *Solid State Commun.* **11**, 1151 (1972).
- [24] Jex H., *J. Phys. Chem. Solids*, **35**, 1221 (1974).
- [25] Jaswal S.S. and Dilly V.D., *Phys. Rev.* **B15**, 2366 (1977).
- [26] Dyck W. and Jex H., *J. Phys.* **C14**, 4193 (1981).
- [27] Mel'nikova T.N., *High Temperature - High Pressures*, **13**, 675 (1981).
- [28] Mel'nikova T.N., *Phys. Stat. Sol.(b)* **181**, 3736 (1994).
- [29] Haque E. and Islam A.K.M.A., *Phys. Stat. Sol. (b)* **158**, 457 (1990).
- [30] Islam A.K.M.A., *Phys. Stat. Sol. (b)* **180**, 9 (1993).
- [31] Islam A.K.M.A., Haque E. and Azad A.S., *phys. stat. sol. (b)* **183**, 117 (1994).
- [32] Tyutyunnik V.I., *Phys. Stat. Sol.(b)* **172**, 539 (1992).
- [33] Islam A.K.M.A., *J. Phys. Chem. Solids*, **55**, 517 (1994).
- [34] Hoque M.T., M.Sc Thesis (unpublished), Rajshahi University (1994).
- [35] Grüneisen E., *Handbuch der Physik*, **10**, 1 (1926).
- [36] Barron T.K.H., *Adv. Phys.* **29**(4), 609 (1980).
- [37] Magee C.B., *Metal Hydrides*, Chapt. 6 (Edited by W.M. Mueller et al.) Academic Press, New York (1968).
- [38] Grimvall G., *Thermophysical Properties of Materials*, p. 197, North Holland, Amsterdam (1986).
- [39] Varotsos P.A. and Alexopoulos K.D., *Thermodynamics of Point defect and the Relation with Bulk Properties*.p. 65, North Holland, Amsterdam (1984).
- [40] Leibfried G. and Ludwig W., *Solid State Physics*, **275** (1961).
- [41] Anderson O.L. Chopelas A. and Boehler R., *Geophys. Res. Letters.* **17**, 685 (1990).
- [42] Kumar M. and Upadhyay S.P., *Phys. Stat. Sol.(b)* **184**, 113 (1994).
- [43] Namjoshi K.V., Mitra S.S. and Vetelino J. F., *Phys. Rev.* **B3**, 4398 (1971).
- [44] Lewis J.T., Lehoczky A. and Briscoe C.V., *Phys. Rev.* **161**, 877 (1967).
- [45] Huntington H.B., in *Solid State Physics* (Edited by F. Seitz and D. Turnbull) Vol. 7, p. 213-351, Academic Press Inc., New York (1958).

Figure Captions

1. Linear thermal expansion coefficient for Li(H,D) and Na(H,D) systems.  
 $\Delta$  exptl(LiD);  $\circ$  exptl(LiH); — this calc.  
 Inset: low temperature expansion for a) LiH, b) LiD.
2. Linear thermal expansion coefficient for LiH for temperature upto melting region.  
 Experimental data:  $\diamond$  (LiH) [12];  $\circ$  Zalkin [14];  $\bullet$  see [27].  
 Calculations: — this calc; + calc [24];  $\blacksquare$  calc.[27].
- 3(a). Variation of  $r$  as a function temperature for LiH and LiD crystals. The experimental data used are from [14,16,18].  
 $\bullet$  exptl(LiH);  $\circ$  exptl(LiD); — this calc.  
 Inset: Variation of  $r$  as a function of temperature for  $300 < T < 900K$ .  
 $\bullet$  exptl[18];  $\circ$  exptl[14]; — this calc;  $\diamond$  calc[27].
- 3(b). Variation of  $r$  as a function of temperature for Na(H,D) systems. For room temperature experimental data, see [30].  
 $\bullet$  exptl(NaH);  $\blacktriangle$  exptl(NaD); — this calc.  
 The extrapolated 0K values of interionic separation are:  
 $r_0(\text{NaH}) = 2.422 \text{ \AA}$ ;  $r_0(\text{NaD}) = 2.415 \text{ \AA}$ .
- 4(a). Variation of elastic constant  $C$  as a function of temperature.  
 $\bullet$ ,  $\circ$  exptl[12]; --- calc[12]; — this calc.
- 4(b,c). Variation of elastic constants  $C$  and  $C$  as a function of temperature.  
 $\bullet$ ,  $\circ$  exptl[12]; --- calc[12]; — this calc.

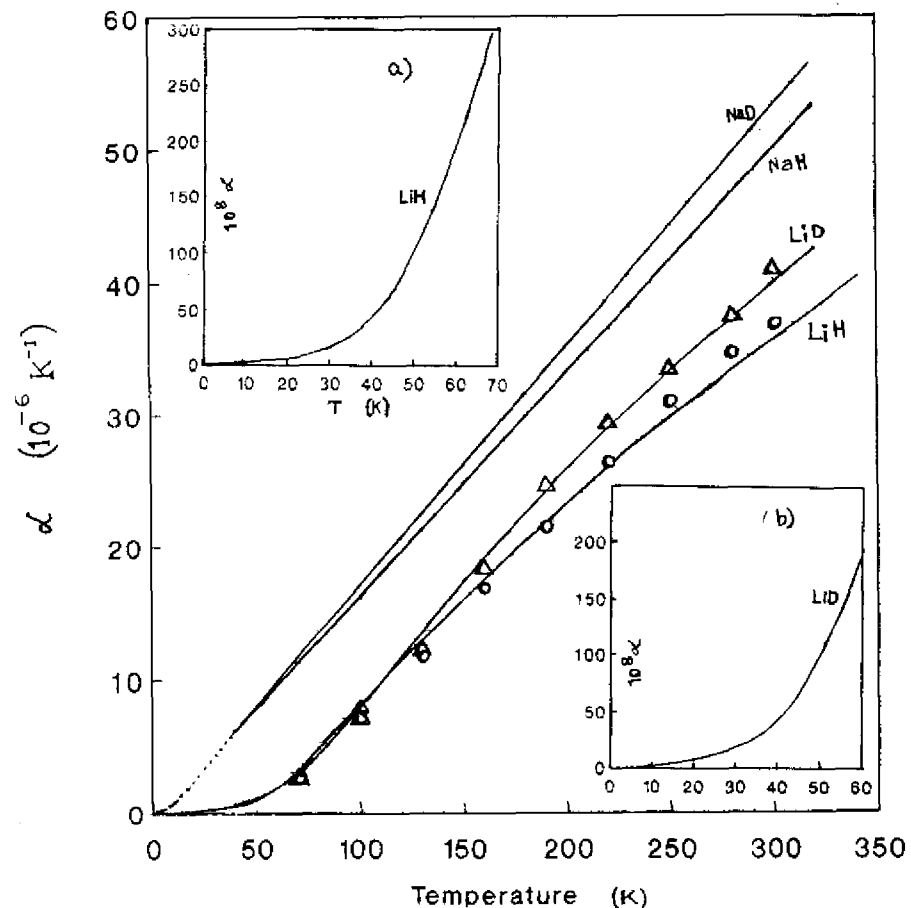


Fig.1



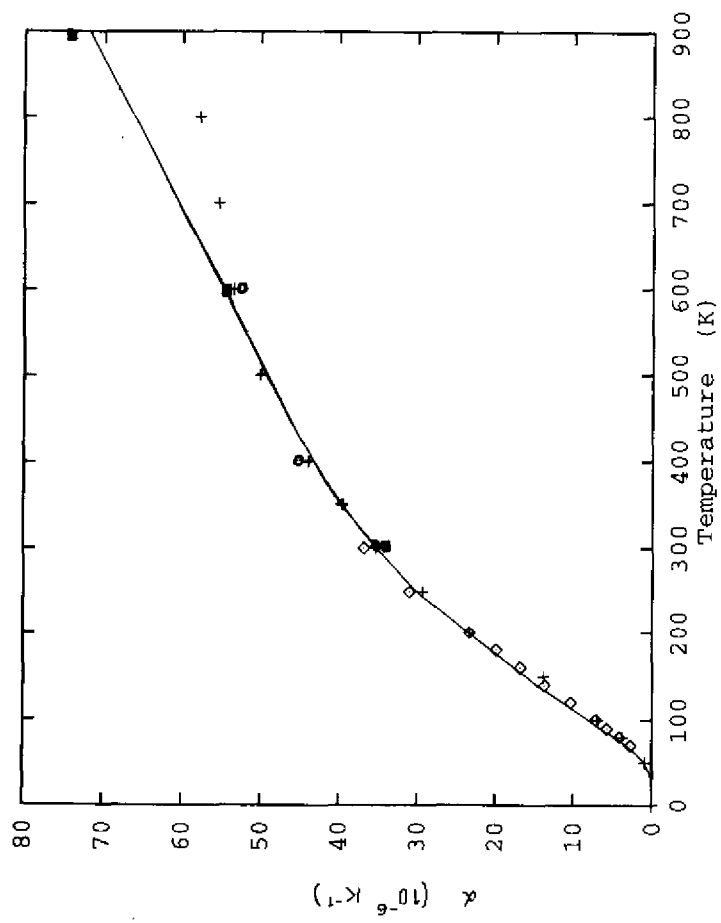


Fig.2

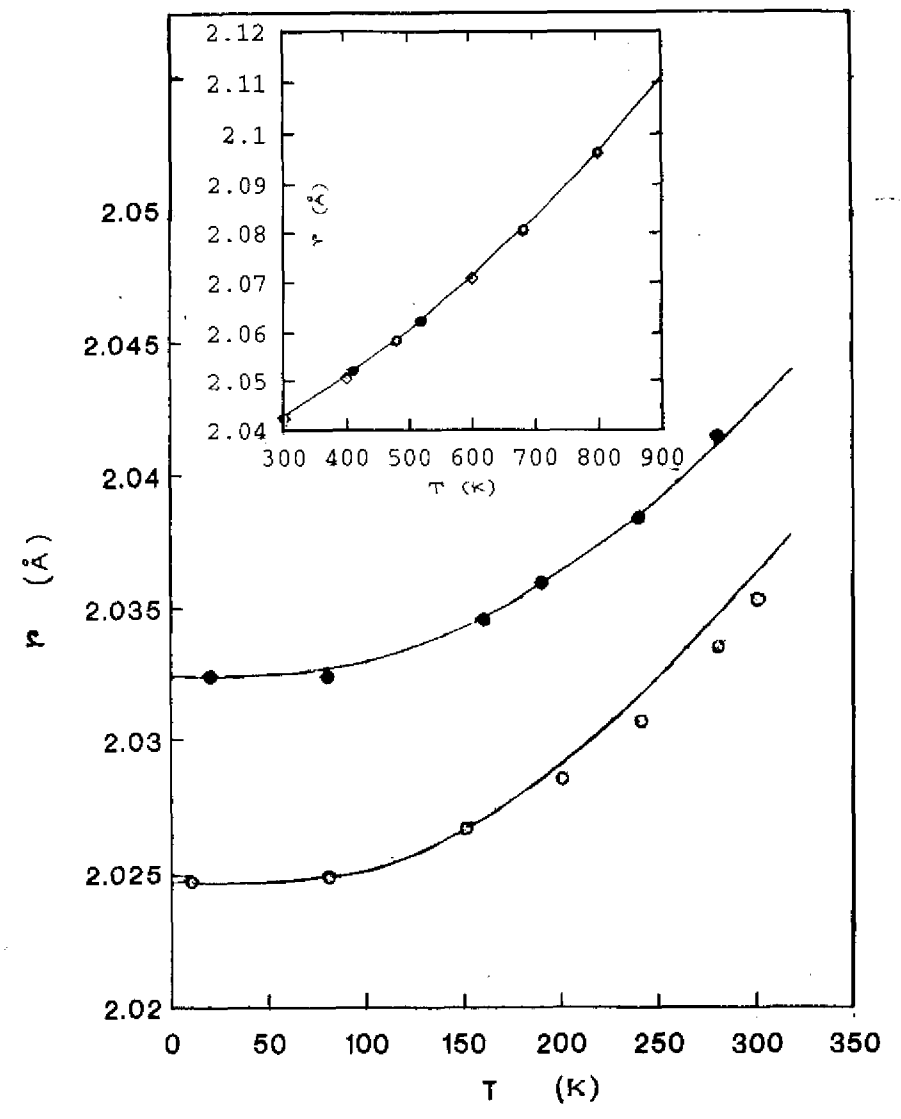


Fig.3a

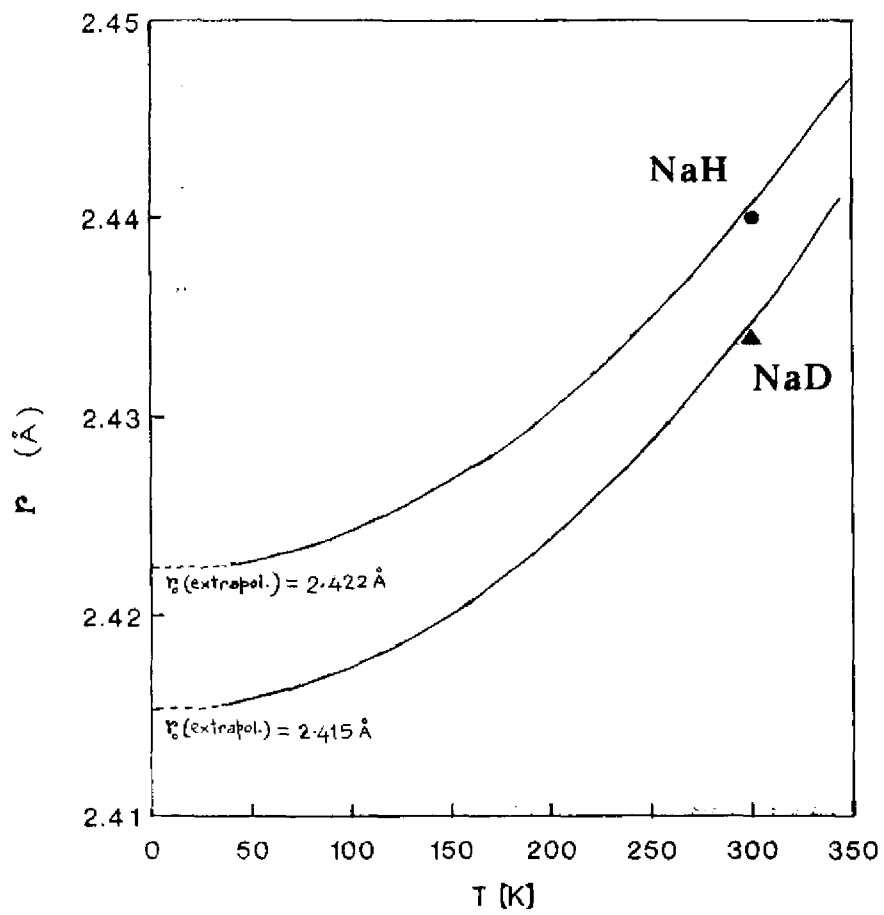


Fig. 3b

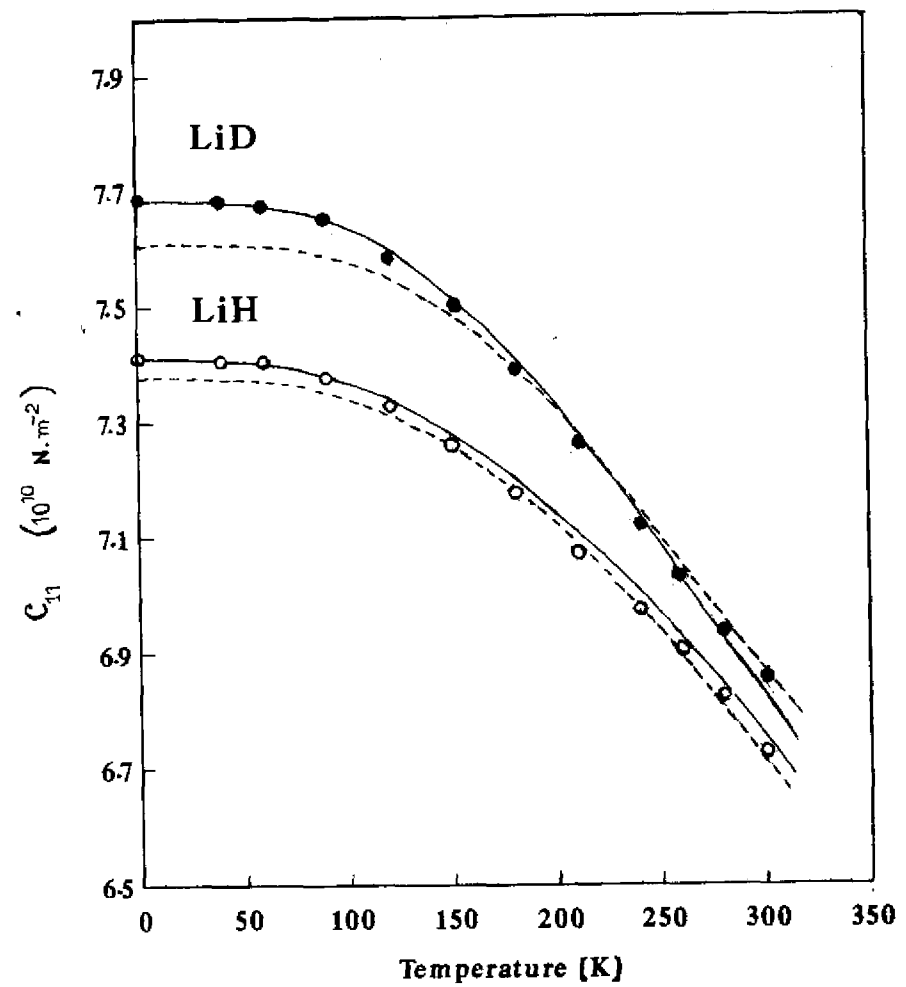


Fig. 4a

