

Modified Pippard relationship describing the Raman frequency shifts of the rotatory lattice mode of ammonia solid II in the vicinity of its melting point

H KARACALI and H YURTSEVEN*

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey
e-mail: karacali@newton.physics.metu.edu.tr

MS received 30 September 2004; revised 14 July 2005

Abstract. We relate in this study the thermal expansivity, α_p , to the Raman frequency shift $(1/n)(\partial n/\partial P)_T$ for the rotatory lattice (librational) mode in ammonia solid II near its melting point. We have used our calculated Raman frequencies of this mode for pressures of 3.65, 5.02 and 6.57 kbars for this crystalline system. The values of the slope, dP_m/dT , which we deduced from our spectroscopic relation, are compared with those obtained experimentally. In particular, our computed slope value for the pressure of 5.02 kbar is in very good agreement with the empirical result.

Keywords. Thermal expansivity; librational mode; Raman frequency.

1. Introduction

Ammonia has been studied extensively and has a comprehensive body of literature, since it has various solid and liquid phases, and also a mixture of solid and liquid phases, as given in the $P-T$ ^{1,2} and $V-T$ ³ phase diagrams. There exist two triple points, where three phase lines intersect with one another; their coordinates are $T_{G-L-I} = 195.48$ K ($P = 0$ kbar)⁺ between the gaseous, liquid and solid I phases, and $T_{L-I-II} = 217.34$ K ($P = 3.07$ kbar) between the liquid, solid I and solid II phases in ammonia. Solid I melts into a liquid state at the melting temperature $T_m = 192.5$ K ($P = 0$ kbar). As the pressure increases to 3.07 kbar, solid II melts into a liquid state at the melting temperature $T_m = 222.4$ K. At this pressure, solid I phase transforms into the solid II phase. There exists another solid phase (solid III) at 35 kbar and 25°C, which has been observed experimentally.² We have considered these solid phases close to the melting point in ammonia; and using the mean field theory we have obtained $P-T$ phase diagrams for both solid I and solid II phases,⁴ and also for the solid I–II–III phases.⁵

Various experimental techniques have been used to study phase transitions in ammonia close to the melting point. Regarding the crystal structures of ammonia solids, X-rays⁶ and neutron scattering⁷

techniques have been used. By means of these techniques, it has been reported that solid I has a simple cubic (*sc*) structure with four molecules per unit cell^{6–8} and solid II has a hexagonal close-packed structure with two molecules per unit cell.⁹ Another solid phase of ammonia, solid III phase, has a face-centered cubic (*fcc*) structure and such a phase occurs in the solid II phase between 240 K and 300 K.^{2,9}

Another experimental technique which has been widely used to explain the mechanism of phase transformations in ammonia close to the melting point, is the Raman spectroscopic technique. For ammonia solid I, four translational and five rotatory lattice (librational) modes have been assigned in the Raman spectra. In particular, the frequencies of the translational modes of ~ 100 and ~ 130 cm⁻¹; and the librational mode of ~ 280 cm⁻¹, have been measured both at atmospheric pressure and at high pressures.³ Using the measured frequencies of the translational modes of ~ 100 and ~ 130 cm⁻¹, and the librational mode of ~ 280 cm⁻¹,³ we have calculated the Raman frequencies of these modes at various temperatures for pressures between 0 and 3.07 kbars in ammonia solid I.¹⁰ In this crystalline system, we have also calculated the Raman frequencies of these modes at various pressures, for fixed temperatures between 196 and 217 K.¹¹

For ammonia solid II, the Raman spectra have been obtained, and in particular, the frequencies of

*For correspondence

⁺1 bar = 0.1 MPa

the translational mode of $\sim 54 \text{ cm}^{-1}$, and the librational mode of $\sim 280 \text{ cm}^{-1}$, have been measured as functions of temperature for constant pressures of 3.65, 5.02 and 6.57 kbars respectively.^{12,13} Using the measured Raman frequencies of the librational mode of $\sim 280 \text{ cm}^{-1}$, we have calculated the Raman frequencies of this mode at various temperatures for those fixed pressures cited above,¹⁴ and as a function of pressure for the fixed temperatures of 230.4, 263.4 and 297.5 K¹⁵ respectively, in ammonia solid II.

The critical behaviour of ammonia near the melting point has been investigated experimentally and cited in the literature.^{16,17} For ammonia solids I and II, we have theoretically investigated the critical behaviour by calculating the thermodynamic quantities, such as the specific heat C_p , thermal expansivity \mathbf{a}_p , and the isothermal compressibility \mathbf{k}_T .¹⁸ By considering the divergence behaviour of these quantities in ammonia solids I and II near the melting point, we have established two Pippard relations for these crystals.¹⁹

In the current study, we examine our spectroscopic modification of the second Pippard relation in ammonia solid II, which relates the thermal expansivity, \mathbf{a}_p , to the frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$. For verifying this spectroscopic relationship, we have used our calculated frequencies of the rotatory lattice (librational) mode for fixed pressures of 3.65, 5.02 and 6.57 kbars in crystalline ammonia. The numerical values used in this study have been given as the SI equivalents.²⁰

In §2, we provide the theoretical basis for calculating the thermal expansivity \mathbf{a}_p and the frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$. In §3, our calculations and results are summarized; and we discuss our results in §4. Finally, our conclusions are given in §5.

2. Theory

The Pippard relation relates the thermal expansivity, \mathbf{a}_p , to the isothermal compressibility, \mathbf{k}_T , and can be written for ammonia solid II near the melting point as,

$$\mathbf{a}_p = (dP_m/dT)\mathbf{k}_T + T(dV/dT)_m. \quad (1)$$

Here dP_m/dT is the slope in the $P - T$ phase diagram of ammonia solid II and $(dV/dT)_m$ is the variation of the crystal volume with temperature at the melting point. The above relation can be modified spectroscopically by means of the \mathbf{g} -Grünesien relation defined as,

$$\mathbf{g}_T = (1/\mathbf{k}_T)(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T. \quad (2)$$

On the basis of the assumption that the isothermal mode Grünesien parameter, \mathbf{g}_T , remains constant across the region from the solid II phase to the liquid phase, the frequencies can be predicted from the volume, according to (2). By considering the definition of isothermal compressibility $\mathbf{k}_T = -(1/V)(\partial V/\partial P)_T$, the frequency can be evaluated from the volume by integrating (2), which yields

$$\mathbf{n}_T(P) = \Delta\mathbf{t} + A(T) + \mathbf{n}_m \exp[-\mathbf{g}_T \ln(V_T(P)/V_m)], \quad (3)$$

with additional terms $\Delta\mathbf{t}$ and $A(T)$. Here $\Delta\mathbf{t}$ is defined as the order-disorder contribution to the frequency. It is non-zero for $P > P_c$, and is zero for $P < P_c$, where P_c denotes the critical pressure for ammonia solid II close to the melting point. In (3) the temperature-dependent term $A(T)$ can be defined as,

$$A(T) = a_0 + a_1(T_m - T) + a_2(T_m - T)^2, \quad (4)$$

where a_0 , a_1 and a_2 are constants, and T_m is the temperature at the melting point. In (3) \mathbf{n}_m and V_m correspond to the values of the frequency and the crystal volume respectively at the melting point.

In order to predict the frequencies of different modes in ammonia solid II near the melting point, according to (3) we require the values of the volume obtained at various pressures for constant temperatures. These values can be obtained from the pressure dependence of the isothermal compressibility, \mathbf{k}_T , according to the power-law formula,

$$\mathbf{k}_T = k(P - P_m)^{-\mathbf{g}}, \quad (5)$$

due to Pruzan *et al.*¹⁶ In the above relation, \mathbf{g} is the critical exponent for the isothermal compressibility of ammonia solid II near the melting point and k is the amplitude. Such a power-law formula directly gives the pressure dependence of the solid volume,

$$V_s = V_c \exp[-k(1 - \mathbf{g})^{-1}(P - P_m)^{1-\mathbf{g}}], \quad (6)$$

where V_c is the critical volume that depends upon the temperature.

The temperature dependence of the crystal volume can also be obtained for ammonia solid II near the melting point by using the ratio,¹⁷

$$\frac{P - P_m(T)}{T_m(P) - T} = \frac{dP_m}{dT}. \quad (7)$$

By inserting (7) into (6), we obtain the temperature dependence of the volume for ammonia solid II close to the melting point,

$$V_s = V_c \exp[-k(1 - g)^{-1} (dP_m/dT)^{1-g} (T_m - T)^{1-g}]. \quad (8)$$

From this temperature-dependence of the solid volume, we can derive the temperature-dependence of the thermal expansivity, \mathbf{a}_p ,

$$\mathbf{a}_p = k(dP_m/dT)^{1-g} (T_m - T)^{-g} + (1/V_c)(dV_c/dT). \quad (9)$$

Thus, by inserting (2) into (1) the frequency shifts $(1/V)(\partial \mathbf{n}/\partial P)_T$ can be obtained as a function of temperature by means of (9). We then get,

$$\mathbf{a}_p = (1/g_T)(dP_m/dT)(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T + (1/V)(dV/dT)_m. \quad (10)$$

Equation (10) is our spectroscopically modified form of the second Pippard relation (1) for ammonia solid II in the vicinity of the melting point. According to (10), the thermal expansivity, \mathbf{a}_p , varies linearly with the frequency shift, $(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T$, close to the melting point in ammonia solid II. Thus, by plotting \mathbf{a}_p against $(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T$, we are able to predict the slope, dP_m/dT , and the intercept $(1/V)(\partial V/\partial T)_m$ at the melting point for ammonia solid II.

3. Calculations and results

In order to predict the frequencies as a function of pressure, at constant temperatures according to (3), we need to evaluate the solid volume $V_T(P)$. The calculation of $V_T(P)$ is done by means of (6), where V_S is used for $V_T(P)$. In (6), the temperature dependence of the critical volume V_c is taken as an empirical relation given by,

$$V_c(\text{II}) = V_{\text{II}} - d_{\text{II}}(T - T_{\text{L-I-II}}), \quad (11)$$

due to Pruzan *et al.*¹⁶ By using the experimental values of $V_{\text{II}} = 21.13 \text{ cm}^3/\text{mol}$, $d_{\text{II}} = 0.0146 \text{ cm}^3/\text{mol K}$ ¹⁶

with the triple temperature of $T_{\text{L-I-II}} = 217.34 \text{ K}$, the temperature dependence of the critical volume becomes,

$$V_c(\text{II}) = 24.30 - 0.0146T. \quad (12)$$

In order to obtain the temperature dependence of the thermal expansivity, \mathbf{a}_p , according to (9), we also need the temperature dependence of the slope dP_m/dT . For this dependence we use an empirical relation,¹⁶

$$P_m(\text{II}) = 11.156[(T/T_{\text{L-I-II}})^{1.516} - 1] + 3.07, \quad (13)$$

which gives us,

$$dP_m(\text{II})/dT = 4.854 \times 10^{-3} T^{0.516}. \quad (14)$$

This allows us to determine the temperature dependence of the thermal expansivity \mathbf{a}_p . By determining the frequency shift, $(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T$, and the thermal expansivity, \mathbf{a}_p , at various temperatures, we are able to examine the second Pippard relation in our modified version (10).

We have established here a linear variation of the thermal expansivity, \mathbf{a}_p , with the frequency shift $(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T$ for the librational mode of \mathbf{n} (270 cm^{-1}) in ammonia solid II. We obtained this linearity for three constant pressures, namely, 3.65, 5.02 and 6.57 kbars, in this solid system close to its melting point. By means of the linear relationship between \mathbf{a}_p and $(1/\mathbf{n})(\partial \mathbf{n}/\partial P)_T$, we are able to deduce the values of the slope dP_m/dT for the pressures indicated above in ammonia solid II.

For calculating the thermal expansivity, \mathbf{a}_p , according to (9), we use the values of the critical exponent $g = 0.60$ and amplitude $k = 0.0135$, which are deduced from the compressibility data according to (5) due to Pruzan *et al.*¹⁶ for ammonia solid II. For this calculation, we also need the variation of the critical volume with the temperature, dV_c/dT , which is obtained from the empirical relation (12) due to Pruzan *et al.*¹⁶ The values of $(1/V_c)(dV_c/dT)$ are obtained at the melting

Table 1. Values of coefficients $\Delta_T + a_0$, a_1 and a_2 , determined from (3), using Raman frequencies of the librational of \mathbf{n} (270 cm^{-1}) and volume data for ammonia solid II for the indicated pressures. Values of volume, V_m , and the Raman frequency, \mathbf{n}_m , for the librational mode at the melting temperatures, T_m , are taken from our previous study.¹⁴ Values of variation of the critical volume (V_c) with temperature, $(1/V_c)(dV_c/dT)$, are obtained from (2).

P (kbar)	T_m (K)	V_m (cm^3/mol)	\mathbf{n}_m (cm^{-1})	$(1/V_c)(dV_c/dT) \times$ 10^{-4} (K^{-1})	$\Delta_T + a_0$ (cm^{-1})	$-a_1$ ($\text{cm}^{-1} \text{ K}^{-1}$)	a_2 ($\text{cm}^{-1} \text{ K}^{-2}$)
3.65	225.0	20.82	267.4	6.95	0.6456	0.1695	-0.0107
5.02	242.0	20.56	265.0	7.03	13.0854	0.4450	0.0051
6.57	260.3	20.27	266.8	7.12	14.4053	0.2167	0.0016

temperatures of 225, 242 and 260.3 K for pressures of 3.65, 5.02 and 6.57 kbars respectively in ammonia solid II, as given in table 1. Thus, with these values, the thermal expansivity, α_p , is calculated as a function of temperature for fixed pressures of 3.65, 5.02 and 6.57 kbars, according to (9) in ammonia solid II.

The Raman frequency shifts $(1/n)(\partial n/\partial P)_T$ are also calculated at various temperatures, for the librational mode of n (270 cm^{-1}) for pressures 3.65, 5.02 and 6.57 kbars in ammonia solid II. For this, we first calculate the Raman frequencies as a function of temperature using observed data for the Raman frequencies of the librational mode of n (270 cm^{-1}) and for the volume as initial data (cf. (3)). These initial data were used to determine the coefficients $\Delta_T + a_0$, a_1 and a_2 in (4), with the values of the volume V_m and the Raman frequency n_m of the librational mode at the melting temperatures for pressures of 3.65, 5.02 and 6.57 kbars in ammonia solid II. Our calculated values of the coefficients $\Delta_T + a_0$, a_1 and a_2 are given in table 1, together with the V_m and n_m values at the melting temperatures T_m , for the pressures considered. The Raman frequencies of this librational mode are then calculated using (3), with these values of the coefficients $\Delta_T + a_0$, a_1 and a_2 and using the values of volume $V_T(P)$ for each pressure condition, namely 3.65, 5.02 and 6.57 kbars in ammonia solid II. In (3), we use $g_T = 0.9$ as the value of the mode Grüneisen parameter for the librational mode in ammonia solid II.¹³ By obtaining the values of the frequency shifts $(1/n)(\partial n/\partial P)_T$ for the librational mode, and using our calculated values of the thermal expansivity, α_p , at different temperatures, we are then able to establish linear plots for pressures of 3.65, 5.02 and 6.57 kbars. Figures 1–3 give the thermal expansivity, α_p , plotted against the Raman frequency shift $(1/n)(\partial n/\partial P)_T$ for the librational mode in ammonia solid II for pressures of 3.65, 5.02 and 6.57 kbars respectively. For pressures of 3.65 kbar (figure 1) and 5.02 kbars (figure 2), we calculate additional data points, apart from the calculated for temperatures at which the Raman frequencies of the n (270 cm^{-1})

mode are measured.¹³ Again, calculated values for the thermal expansivity, α_p , are obtained from (9) and values for the frequency shift, $(1/n)(\partial n/\partial P)_T$, are calculated by means of (3). Using all of the data for pressures of 3.65, 5.02 and 6.57 kbars, best-fit lines are obtained using (10). Based on these plots, we obtain the values of the slope, dP_m/dT , for the pressures studied, as given in table 2. The values of dP_m/dT , which are obtained from the empirical relation (14), are also given in table 2 for comparison. In addition, the intercept values of our plots, $(1/V_m)(dV/dT)_m$, are also given in table 2 for the pressures considered.

As given in figures 1–3 and in table 2, we also calculate the uncertainties in the slope, dP_m/dT , for the three pressures studied. Uncertainties in dP_m/dT vary from $\pm 0.4 \text{ bar/K}$ (3.65 kbar) to $\pm 0.2 \text{ bar/K}$ (5.02 and 6.57 kbars). In order to calculate these uncertainties in dP_m/dT according to (10), we first calculate uncertainties in the thermal expansivity, α_p , and in the frequency shift, $(1/n)(\partial n/\partial P)_T$, for the lattice mode studied for pressures of 3.65, 5.02 and 6.57 kbars in ammonia solid II.

Starting from uncertainties in the volume measurements $V_{II} = 21.13 \pm 0.02 \text{ cm}^3/\text{mol}$ and $d_{II} = 0.0146 \pm 0.0002 \text{ cm}^3/\text{mol K}$,¹⁶ we determine uncertainties in the critical volume, $V_c(\text{II})$, according to (11). Also, using the value of the critical exponent, $g = 0.60 \pm 0.01$, from (5), which is fitted to the experimental data for the isothermal compressibility, k_T , in ammonia solid II,¹⁶ we are able to calculate the uncertainty in α_p , according to (9) for pressures studied in this crystalline system.

In order to determine the uncertainty in the frequency shift $(1/n)(\partial n/\partial P)_T$, for pressures of 3.65, 5.02 and 6.57 kbars, we first determine the uncertainties in the Raman frequency $n_T(P)$ of the lattice mode in ammonia solid II using (3). For this determination, we calculate uncertainties in the crystal volume, V_s , by using uncertainties in V_c and g in (6). We then obtained uncertainty in the Raman frequencies (3) for the lattice mode in ammonia solid II. Once we determine the uncertainties in the Raman

Table 2. Values of slope dP_m/dT , deduced from the second Pippard relation (10) vs those obtained experimentally by (4) for indicated pressures. Intercept values of $(1/V_m)(dV/dT)_m$ from (10) are also tabulated here.

P (kbar)	T_m (K)	Calc. dP_m/dT (bar/K)	Obs. dP_m/dT (bar/K)	$(-1/V_m)(dV/dT)_m \times 10^{-4} (\text{K}^{-1})$
3.65	225.0	60.0 ± 0.4	79.4	2
5.02	242.0	84.0 ± 0.2	82.4	7
6.57	260.3	90.5 ± 0.2	85.6	8

frequencies $\mathbf{n}_T(P)$, we are able to calculate uncertainties in the frequency shift, $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, at different temperatures for constant pressures of 3.65, 5.02 and 6.57 kbars in ammonia solid II. We report these uncertainties in both \mathbf{a}_p and $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$ for each pressure condition, namely, 3.65, 5.02 and 6.57 kbars, in ammonia solid II as shown in figures 1–3 respectively.

4. Discussion

Our spectroscopic modification of the Pippard relation (10) proves that the thermal expansivity, \mathbf{a}_p , varies linearly with the Raman frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, for the rotatory lattice (librational) mode of \mathbf{n} (270 cm^{-1}) in ammonia solid II. As seen in figures 1–3, we obtain this linearity for the three pressures considered, namely, 3.65, 5.02 and 6.57 kbars respectively. As we noted earlier, the validity of our Pippard relation (10) is based on the fact that the thermal expansivity, \mathbf{a}_p , and the frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, exhibit similar critical behaviour near the melting point in ammonia solid II. In this study, we

have concentrated on the critical behaviour of the frequency shifts for the rotatory lattice mode of \mathbf{n} (270 cm^{-1}) in ammonia solid II. This leads us to establish (10), using our calculated Raman frequencies for this lattice mode, from which we extract the values of the slope dP_m/dT for the pressures considered, as given in table 2. Our value of 60 bar/K for $P = 3.65$ kbar is too low in comparison with the experimental value of 79.4 bar/K, which we obtain from the empirical relation (14). However, our values of 84 bar/K and 91 bar/K for pressures of 5.02 and 6.57 kbars respectively are close to the observed values (table 2). In particular, our value for $P = 5.02$ kbar is very close to the experimental value of 82.4 bar/K. Our calculated and observed values of dP_m/dT increases as the pressure increases, as expected (table 2).

In order to examine the range of variation in the slope, uncertainties in dP_m/dT are calculated, which are quite small, as given in table 2. This is due to the fact that uncertainties in the thermal expansivity, \mathbf{a}_p , and in the frequency shift, $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, are very small, as shown in figures 1–3. For $P = 3.65$ kbar

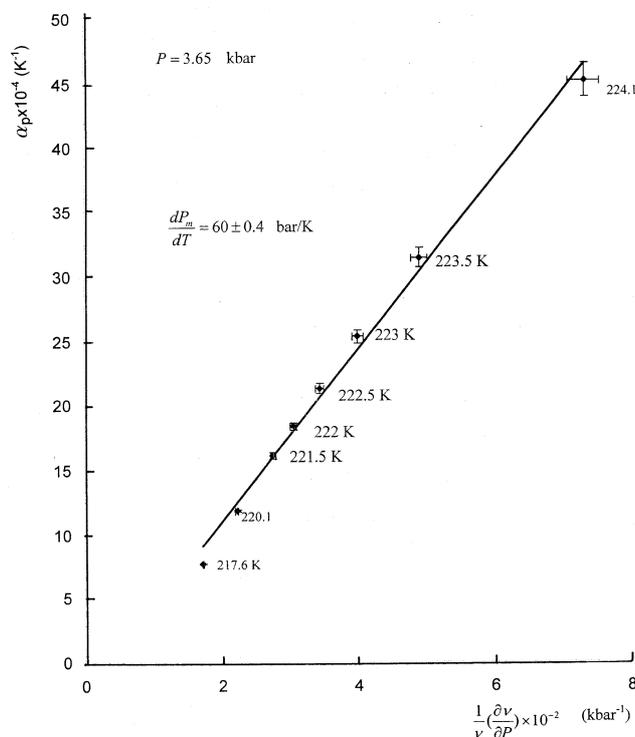


Figure 1. Thermal expansivity, \mathbf{a}_p , as a function of the Raman frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, for the librational mode ν (270 cm^{-1}) in ammonia solid II for a pressure of 3.65 kbar ($T_m = 225\text{ K}$), according to the second Pippard relation (10).

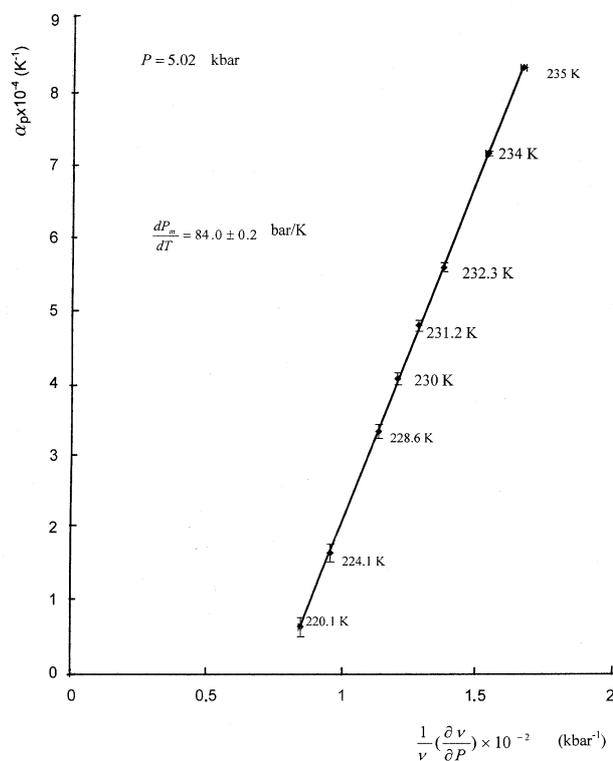


Figure 2. Thermal expansivity, \mathbf{a}_p , as a function of the Raman frequency shift $(1/\mathbf{n})(\partial\mathbf{n}/\partial P)_T$, for the librational mode ν (270 cm^{-1}) in ammonia solid II for a pressure of 5.02 kbar ($T_m = 242\text{ K}$), according to the second Pippard relation (10).

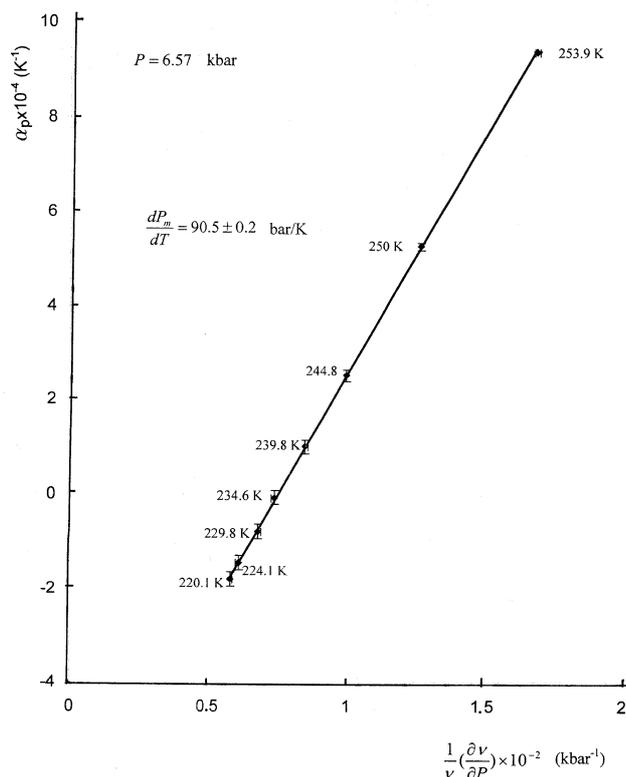


Figure 3. Thermal expansivity, α_p , as a function of the Raman frequency shift $(1/\nu)(\partial\nu/\partial P)_T$, for the librational mode ν (270 cm^{-1}) in ammonia solid II for a pressure of 6.57 kbar ($T_m = 260.3 \text{ K}$), according to the second Pippard relation (10).

(figure 1), uncertainties in α_p , and in $(1/\nu)(\partial\nu/\partial P)_T$, increase proportionately, as the temperature approaches the melting temperature ($T_m = 225 \text{ K}$). For example, this increase in uncertainty for both α_p and $(1/\nu)(\partial\nu/\partial P)_T$ is about twice as large close to T_m (at 224.1 K) in comparison with that at 223.5 K (figure 1). However, for pressures of 5.02 kbar (figure 2) and 6.57 kbar (figure 3), uncertainties in α_p and in $(1/\nu)(\partial\nu/\partial P)_T$ seem to increase as the temperature goes below the melting temperatures.

We also calculate uncertainties in $(1/V)(dV/dT)_m$ at the melting temperature, which is the intercept of (10). Our calculated values of $(1/V_m)(dV/dT)_m$ deviate from the values given in table 2 by about $0.5 \times 10^{-4} \text{ K}^{-1}$ for pressures of 3.65 kbar (figure 1) and 6.57 kbar (figure 3) and there is no deviation for 5.02 kbar (figure 2). These uncertainties in $(1/V_m)(dV/dT)_m$ are calculated from (10) by using uncertainties in α_p and $(1/\nu)(\partial\nu/\partial P)_T$, which we have already determined.

In our spectroscopic modification of the Pippard relation (10), we also assume a constant value for

the isothermal Grünesien parameter, g_T , for the rotatory lattice mode ($g_T = 0.9$) across the phase transition region. This indicates that the anharmonicity of the ammonia system does not change under various temperature and pressure conditions. In fact, in general, the mode Grünesien parameter is dependent upon the temperature and pressure. It has been reported in earlier studies^{2,16} that the compressibility, k_T , shows anomalous behaviour in ammonia solid II near the melting point. We have reported in our previous study¹⁴ that our calculated Raman frequencies for the rotatory lattice (librational) mode show no anomaly near the melting point in ammonia solid II, as has also been indicated using the measured Raman frequencies for this mode.¹³ Since we are concerned here with the derivative of the Raman frequency, the Raman frequency shift $(1/\nu)(\partial\nu/\partial P)_T$, does exhibit divergence behaviour close to the melting point. Alternatively, by considering the temperature and pressure dependence of the mode Grünesien parameter, g_T , the divergence behaviour of the Raman frequency shift, $(1/\nu)(\partial\nu/\partial P)_T$ can be modified to satisfy our spectroscopic relation (10), which might then yield improved values for the slope, dP_m/dT , and agree better with the empirical data (cf. table 2).

Conclusions

The thermal expansivity, α_p , varies linearly with the Raman frequency shift $(1/\nu)(\partial\nu/\partial P)_T$, in ammonia solid II near its melting point. Such linearity is obtained for the rotatory lattice mode of the crystal for pressures of 3.65, 5.02 and 6.57 kbars. This behaviour shows the validity of our spectroscopic modification of the Pippard relation applied to the librational mode studied in ammonia solid II for the cited pressures. By means of the relationship introduced here, we are able to explain the observed behaviour of ammonia solid II in the vicinity of its melting point.

References

1. Hanson R C and Jordan M 1980 *J. Phys. Chem.* **84** 1173
2. Mills R L, Liebenberg D H and Pruzan Ph 1982 *J. Phys. Chem.* **86** 5219
3. Nye C L and Medina F D 1985 *Phys. Rev.* **B32** 2510
4. Salihoglu S, Tari Ö and Yurtseven H 2000 *Phase Transitions* **72** 299
5. Enginer Y, Salihođlu and Yurtseven H 2002 *Mater. Chem. Phys.* **73** 57
6. Olovsson I and Templeton D H 1958 *Acta Crystallogr.* **12** 832

7. Reed J W and Harris P M 1961 *J. Chem. Phys.* **35** 1730
8. Hewat A W and Rickel C 1979 *Acta Crystallogr.* **A35** 569
9. Eckert J, Mills R and Satija S 1985 *J. Chem. Phys.* **81** 6034
10. Yurtseven H 1999 *J. Phys. Chem.* **A103** 5900
11. Yurtseven H 2001 *Acta Phys. Pol.* **A99** 557
12. Luo R K, Nye C and Medina F D 1986 *J. Chem. Phys.* **85** 4903
13. Luo R K and Medina F D 1990 *Phys. Rev.* **B42** 3190
14. Yurtseven H and Ugur S 2003 *Chinese J. Phys* **41** 140
15. Yurtseven H 2004 *Chinese J. Phys.* **42** 209
16. Pruzan Ph, Liebenberg D H and Mills R L 1982 *Phys. Rev. Lett.* **48** 1200.
17. Pruzan Ph, Liebenberg D H and Mills R L 1986 *J. Phys. Chem. Solids* **47** 949
18. Yurtseven H and Salihoglu S 2002 *Chinese J. Phys.* **40** 416
19. Yurtseven H 1999 *Int. J. Mod. Phys.* **B13** 2783