NMR study of ammonium reorientation motion in NH$_4$Br at high pressure

D P Kozlenko†§, S Lewicki‡, J Wąsicki‡, W Nawrocik‡ and B N Savenko†

† Frank Laboratory of Neutron Physics, JINR, 141980 Dubna Moscow Region, Russia
‡ Faculty of Physics, A Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

E-mail: denk@nf.jinr.ru (D P Kozlenko)

Abstract. Measurements of spin–lattice relaxation time T_1 have been performed for polycrystalline ammonium bromide as a function of hydrostatic pressure and temperature. Activation parameters for NH$_4^+$ ion reorientation as functions of pressure were obtained. A two-well potential model is proposed for description of ammonium reorientation motion. On the basis of the proposed model and obtained activation data the libration frequency of the ammonium ion as a function of pressure was calculated and good agreement between experiment and calculation was obtained.

1. Introduction

The ammonium halides are well known for a number of phase transitions they undergo with respect to the disorder and relative orientation of ammonium ions in the lattice [1]. At room temperature ammonium bromide NH$_4$Br has a CsCl type cubic structure in which ammonium ions are randomly distributed between two equivalent positions which correspond to two possible orientations of ammonium tetrahedra, space group $Pm3m$ [2], phase II (figure 1). Hydrogen atoms are directed essentially towards four of the eight surrounding halide ions. Thermal fluctuations of the lattice excite vibrations of ammonium ions around the equilibrium orientations—i.e. libration motion [3–5], and also jumps among some allowed orientations—i.e. reorientation motion. At pressure $P > 180$ MPa and low temperature in NH$_4$Br an order–disorder phase transition into the ordered CsCl type cubic phase IV occurs [6]. In this phase NH$_4^+$ ions are oriented in parallel.

Reorientation motion of ammonium ions in NH$_4$Br has been studied by quasielastic neutron scattering (QNS) [7, 8] and nuclear magnetic resonance (NMR) methods [9–11] in rather a wide range of temperatures. NMR results have clearly shown that the orientational disorder is dynamic. However this method is insensitive to the precise features of the reorientation mechanism. This can involve either 90° jumps around the twofold axes of NH$_4^+$ ions, or a combination of reorientations around twofold and threefold axes (120° jumps), although calculations [9] based upon interionic potentials derived from a point charge model [12] predict a barrier for rotations around threefold axes 80% higher than for twofold axes. In QNS experiments [7, 8] it was established that the ammonium ion reorientations by 90° jumps
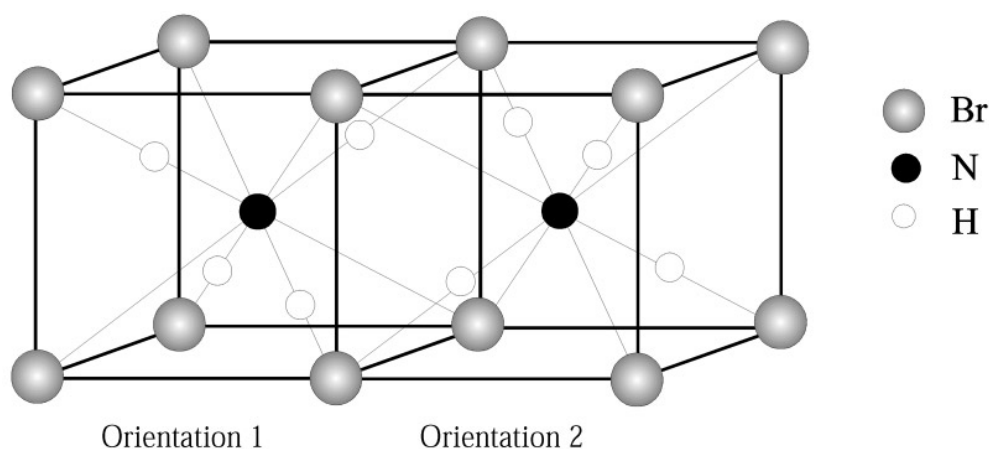
§ Corresponding author.

7175

Figure 1. Schematic structure of NH_4Br. The two possible orientations of ammonium ions are shown.

around twofold axes dominate, and the contribution from 120° jumps around threefold axes is negligible but cannot be excluded.

Effect of the pressure on the reorientation and libration motion of ammonium ions in the ammonium halides is not well studied yet. NMR experiments could bring information on the behaviour of correlation times and energy barriers hindering rotation under pressure.

To study the features of the ammonium reorientation motion in the phases II and IV of NH_4Br at high pressure, we have measured proton spin–lattice relaxation times T_1 at pressures up to 800 MPa.

2. Experiment

Spin–lattice relaxation time T_1 measurements were performed on a pulse NMR spectrometer working at frequency of 25 MHz by the saturation method using a special set-up for hydrostatic measurements [13]. To create the pressure, a gas compressor U-11 made by Unipress Warsaw producing pressure up to 1500 MPa and a pressure chamber made of beryllium bronze enabling measurements under pressures up to 800 MPa were used. All measurements were performed for polycrystalline samples. Measurements were performed at pressure values of 200, 400, 600 and 800 MPa in the temperature range of 100–295 K.

3. Results

Spin–lattice relaxation time curves measured at 200 and 800 MPa are shown in figure 2. They are shifted to the higher temperature region with pressure increase but the minimum value of the curve remains constant. Both curves have a discontinuity which corresponds to the II–IV phase transition. Experimental data were fitted by the Blombergen–Purcell–Pound formula [14]:

$$T_1^{-1} = \frac{2}{3}\gamma^2 \Delta M_2 \left[\frac{\tau}{1 + \omega^2\tau^2} + \frac{4\tau}{1 + 4\omega^2\tau^2} \right] \tag{1}$$

where γ is the gyromagnetic ratio of the proton, ω the angular resonance frequency $(2\pi \times 25 \times 10^6$ rad s$^{-1})$ and ΔM_2 the change of the second moment of the ^1H NMR line.
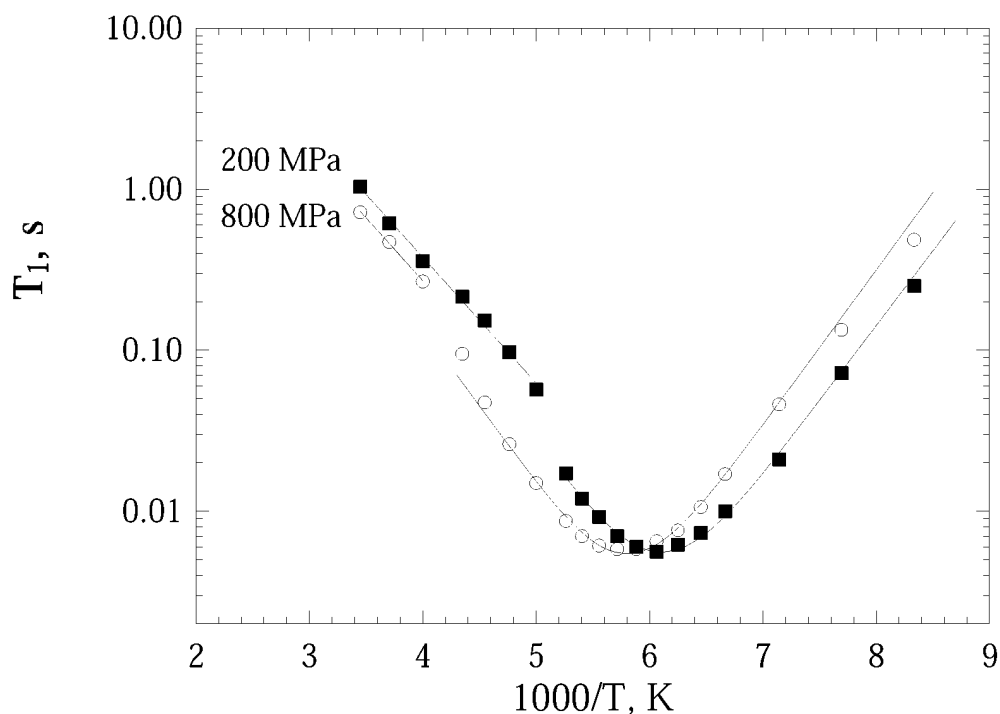
Figure 2. Spin–lattice relaxation time curves measured at 200 and 800 MPa as functions of temperature.

Table 1. Activation parameters obtained from NMR measurements.

	Phase II[a]		Phase IV		
P (MPa)	$\tau_0 \times 10^{-14}$ (s)	E_a (kJ mol^{-1})	ΔM_2 (G^2)	$\tau_0 \times 10^{-14}$ (s)	E_a (kJ mol^{-1})
200	2.00	14.98	41.35	0.83	17.78
400	1.88	15.31	42.38	0.87	17.99
600	2.04	15.44	42.39	0.99	18.20
800	1.96	15.77	42.28	1.03	18.41

[a] Parameters calculated with $\Delta M_2 = 42.41$ G^2.

Correlation time is defined by the Arrhenius equation:

$$\tau = \tau_0 \exp(E_a/RT) \tag{2}$$

where E_a is an activation energy. The obtained values of ΔM_2, τ_0 and E_a for the phases II and IV of NH₄Br are listed in table 1. Correlation times τ at different pressures for phases II and IV as functions of temperature are shown in figure 3.

Correlation time increases with pressure with a slightly different slope for phases II and IV (figure 4). Extrapolation of $\tau(P)$ data to $P = 0$ gives the value $\tau = 8.55 \times 10^{-12}$ s at $T = 290$ K which is in good agreement with the value $\tau = 8.92 \times 10^{-12}$ s obtained for the 90° rotational jump model of ammonium ion reorientations in QNS study [8]. Activation energies for phases II and IV as functions of pressure are shown in figure 5. E_a increases with pressure for both phases with nearly the same slope. From the extrapolation of $E_a(P)$ data for phase II to $P = 0$ the value $E_a = 14.73$ kJ mol^{-1} is obtained. This is in good agreement with the data [11]: $E_a = 14.56$ kJ mol^{-1}.
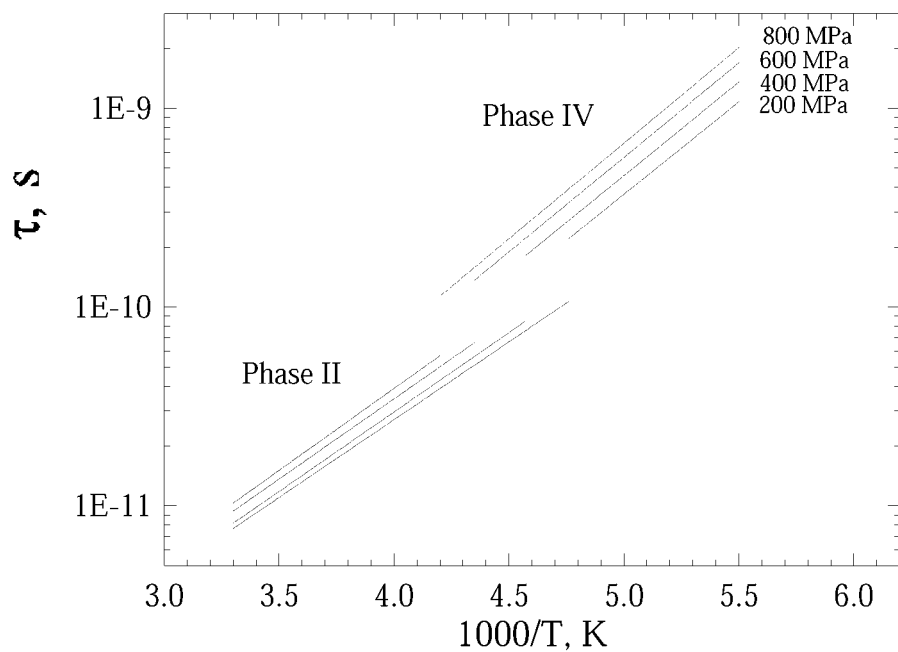
Figure 3. Correlation time for ammonium ion in NH$_4$Br for phases II and IV as a function of temperature at different pressures.
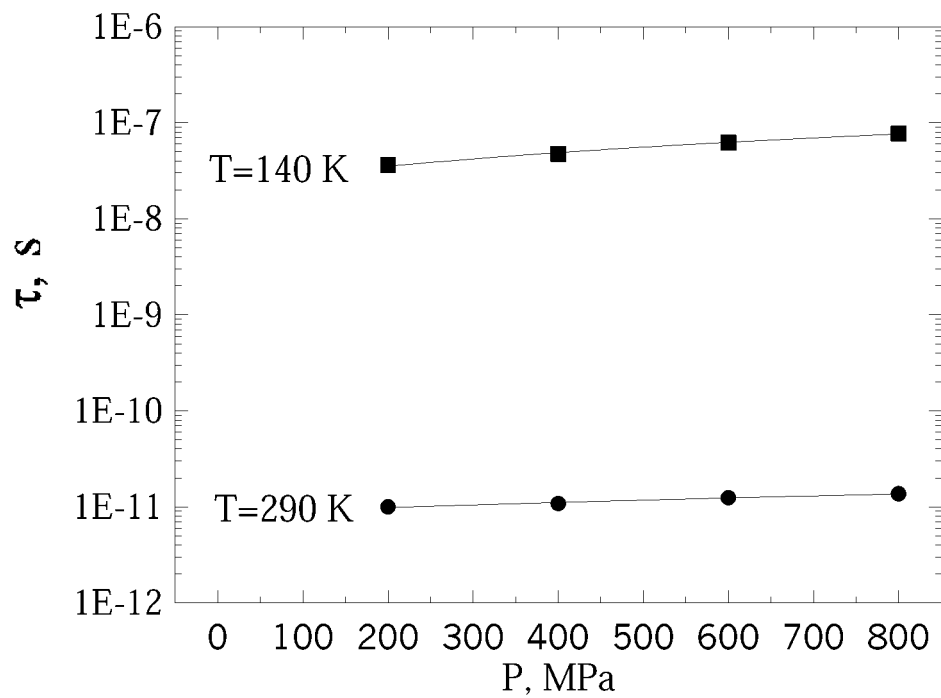

Figure 4. Correlation time for ammonium ion in NH$_4$Br as a function of pressure for $T = 290$ K (phase II) and $T = 140$ K (phase IV).
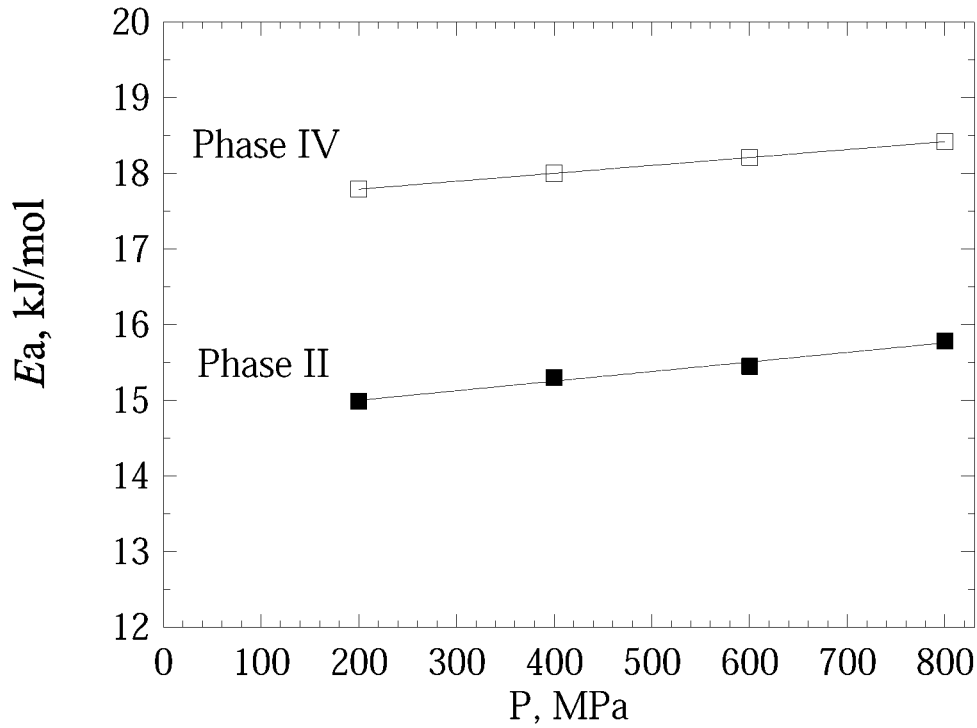
Figure 5. Activation energy for ammonium ion in phases II and IV of NH$_4$Br.

Table 2. Activation volumes for phases II and IV of NH$_4$Br.

NH$_4$Br	$RT\left[\dfrac{\partial(\ln T_1)}{\partial P}\right]_T$ (cm^3 mol^{-1})	$RT\left[\dfrac{\partial(\ln \nu)}{\partial P}\right]_T$ (cm^3 mol^{-1})	ΔV^* (cm^3 mol^{-1})	V_m * (cm^3 mol^{-1})	$\Delta V^*/V_m$
Phase II (at 290 K)	1.54 ± 0.17	0.09 ± 0.006	1.63 ± 0.23	40.3	0.04
Phase IV (at 140 K)	1.49 ± 0.15	0.04 ± 0.003	1.53 ± 0.18		0.038

The activation volume ΔV^* [15], which is usually defined as the difference between the critical volume (volume required for reorientation of the molecule or ion) and the molar volume, can be determined from the following expression:

$$\Delta V^* = RT\left[\frac{\partial(\ln \tau)}{\partial P} + \frac{\partial(\ln \nu)}{\partial P}\right]_T. \tag{3}$$

Here ν is a frequency of lattice vibrations. If we calculate ΔV^* for ammonium ion reorientations, it is reasonable to take as ν the libration frequency of ammonium ion. For a case of $\omega\tau \gg 1$ or $\omega\tau \ll 1$ we can write:

$$\Delta V^* = RT\left[\pm\frac{\partial(\ln T_1)}{\partial P} + \frac{\partial(\ln T_1)}{\partial P}\right]_T. \tag{4}$$

Values of ΔV^* and $\Delta V^*/V_m$ (V_m—molar volume) obtained for phases II and IV (neglecting the difference in libration frequency ν between these phases), and contributions from both terms in (4), are listed in table 2. Usually the second term in (4) is assumed to be much less than the first one and is omitted from the calculation. As can be seen from table 2, in the case

of NH_4Br the contribution of the second term is really much less in comparison with the first one and the error from neglecting it is only about 6%.

4. Discussion

In QNS study [7] it has been established that the main mechanism of the reorientation motion of ammonium ion is 90° jumps around the twofold (C_2) axes of the ammonium ion. For the description of such a motion, a two-well potential [16] with minima at $\theta = 0°$ and $\theta = 90°$, which correspond to two possible orientations of ammonium ion in the crystal lattice, is frequently used (figure 6). We can treat the height of potential barriers as activation energy E_a. In the disordered phase II two orientations of ammonium ion are equivalent and both potential wells have the same barrier height value E_a. In case of the ordered phase IV ammonium ions are oriented in parallel and the only one orientation is dominated. We can assume that, as a result of the II–IV phase transition, the potential becomes asymmetric with inequivalent potential barriers with the height defined by the values of E_a for the phases II (E_a^{II}) and IV (E_a^{IV}) (figure 5). The asymmetry parameter is $\Delta = E_a^{IV} - E_a^{II}$. With the pressure increase both potential barrier heights increase (figure 5), but the Δ value remains nearly constant (figure 7).
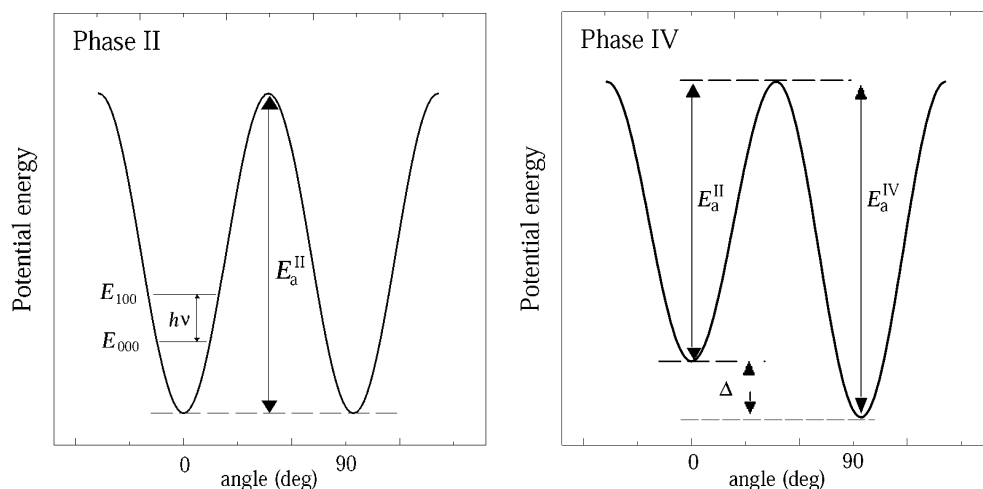

Figure 6. The shape of potential for ammonium ion reorientation in the disordered phase II and the ordered phase IV of NH_4Br.

There have been some attempts [9, 17] to establish the relation between the rotational potential barrier U and libration frequency ν of the ammonium ion. In [9] U is related to ν by

$$U = \frac{1}{16} \frac{(h\nu + 5h^2/2I)^2}{h^2/2I} \tag{5}$$

where I is the moment of inertia of the NH_4^+ ion, $I = 4.826 \times 10^{-40}$ g cm² [9]. This expression has been obtained for an anharmonic isotropic oscillator in the phenomenological potential [12] having the cubic symmetry of the lattice and tetrahedral symmetry of the ammonium ion. The observed libration frequency is determined by the values of the first and ground state energy levels (figure 6), $h\nu = E_{100} - E_{000}$.
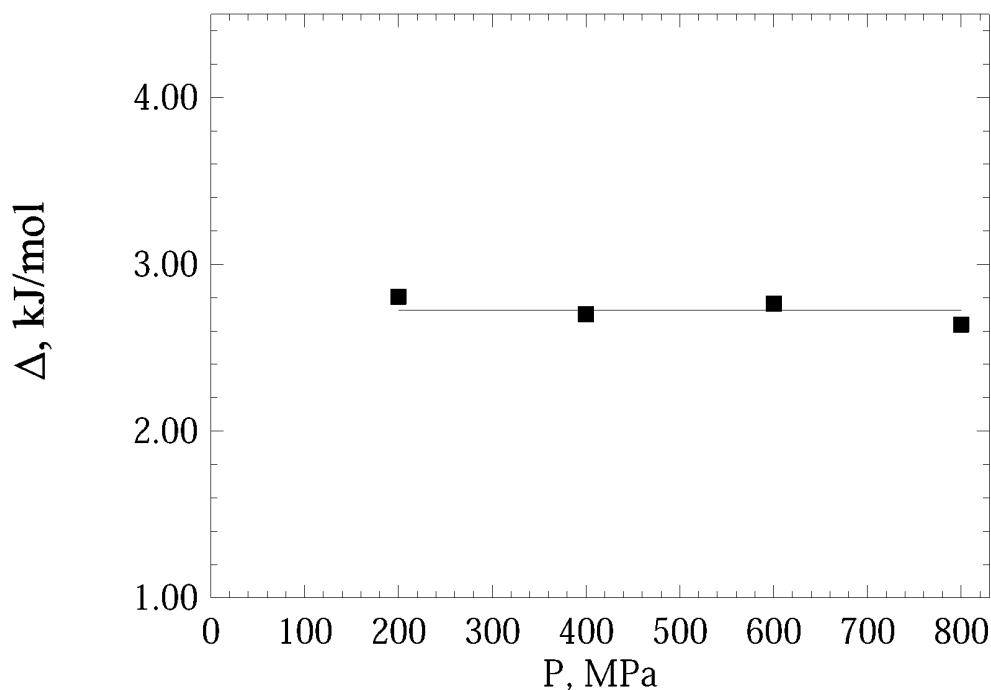
Figure 7. Pressure behaviour of asymmetry parameter, $\Delta = E_a^{IV} - E_a^{II}$.

We can now calculate the pressure behaviour of the libration frequency ν using the obtained pressure data of activation energy and expression (5). In [9] it is assumed that U and E_a are related by

$$U = E_a + \tfrac{3}{2}h\nu. \tag{6}$$

Here $\tfrac{3}{2}h\nu = E_{000}$ is the zero point libration energy of the ground state. Figure 8 shows the experimental $\nu(P)$ data for phase II of NH$_4$Br from Raman study [18] and the calculated with (5), (6) values. The value of libration frequency at normal pressure from [5] and $\nu(P)$ data [19] obtained by the inelastic neutron scattering (INS) method are also shown. Neutron data [19] seem to contain a systematic error in comparison with data [5, 18] which agree well.

The correspondence between theoretical and experimental curves is poor and difference between them is about $\tfrac{3}{2}h\nu$. If we take $U = E_a$ instead of (6), good agreement between theory and experimental data can be obtained (figure 8). This can be explained in the following way. Relation (6) defines the minimum energy which ammonium ion should have to perform the jump from one equilibrium position to another, in this case the NH$_4^+$ ion energy after the jump is assumed to be equal to zero. But after the jump its energy should be at least equal to or greater than the zero point libration energy of the ground state E_{000}, i.e. $E_a \geqslant U$.

5. Conclusions

Results of this work show that the reorientation motion of ammonium ions in NH$_4$Br can be described using the two-well potential corresponding to the model of ammonium ion reorientations by 90° jumps around twofold axes. The potential with equivalent barriers which corresponds to the disordered phase II is distorted after the order–disorder II–IV phase transition
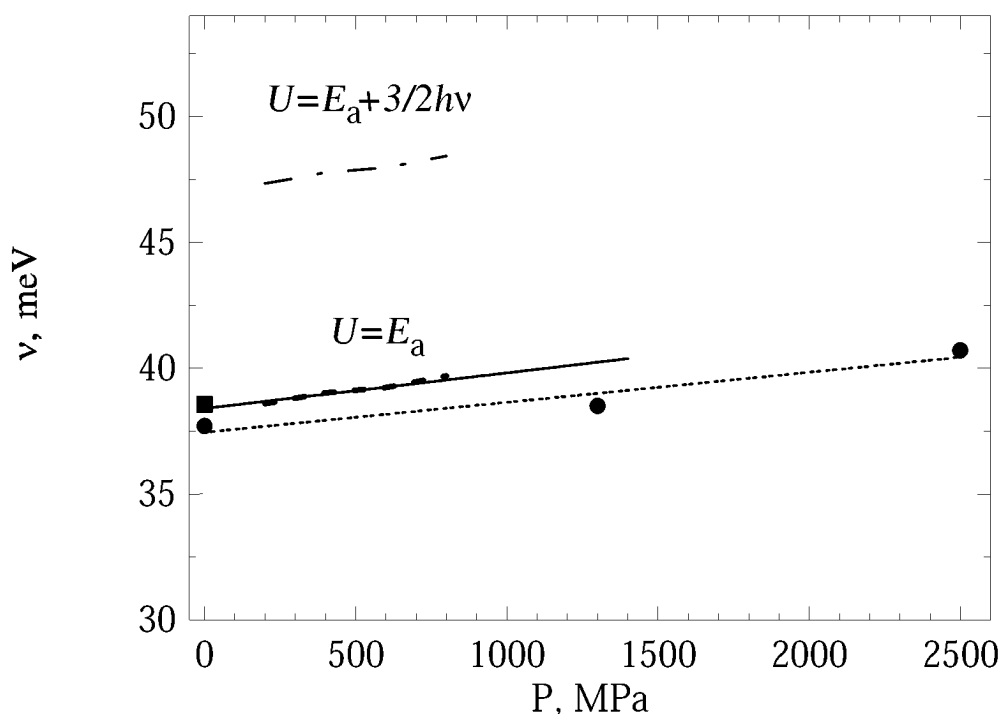
Figure 8. Libration frequency of ammonium ion in NH_4Br as a function of pressure. Solid line: experimental Raman data [18]; dashed-dotted line: result of calculation for $U = E_a + \frac{3}{2}h\nu$; dashed line: result of calculation for $U = E_a$. Black square: libration frequency at normal pressure from INS data [5]; black circles and dotted line: pressure behaviour of libration frequency from INS data [19].

has occurred and becomes asymmetric with different heights of potential barriers. The good agreement of experimental and calculated values of libration frequency of ammonium ion in phase II of NH_4Br proves that in the case of ammonium halides activation energy E_a can be considered in a good approximation as the height of the rotational potential barrier.

Acknowledgment

References

[1] Pistorius C W F T 1976 *Prog. Solid State Chem.* **11** 1
[2] Levy H A and Peterson S W 1952 *Phys. Rev.* **86** 766
[3] Schumaker N E and Garland C W 1970 *J. Chem. Phys.* **53** 392
[4] Wang C H and Wright R B 1972 *J. Chem. Phys.* **57** 4401
[5] Venkataraman G *et al* 1966 *J. Phys. Chem. Solids* **27** 1107
[6] Press W, Eckert J and Cox D E 1976 *Phys. Rev.* B **14** 1983
[7] Livingston R C, Rowe J M and Rush J J 1974 *J. Chem. Phys.* **60** 4541
[8] Lechner R E, Badurek G, Dianoux A J, Hervet H and Volino F 1980 *J. Chem. Phys.* **73** 934
[9] Gutowsky H S, Pake G E and Bersohn R 1954 *J. Chem. Phys.* **22** 643

[10] Woessner D E and Snowden B S Jr 1967 *J. Chem. Phys.* **47** 378
[11] Mandema W and Trappeniers N J 1976 *Physica* B **81** 285
[12] Nagamiya T 1942 *Proc. Phys. Math. Soc. Japan* **24** 137
     Nagamiya T 1943 *Proc. Phys. Math. Soc. Japan* **25** 540
[13] Lewicki S, Pająk Z, Porzuckowiak W and Wąsicki J 1995 *Proc. 28th NMR Seminar (Kraków)* Report 1717/PL
     p 190
[14] Blombergen N, Purcell E M and Pound R V 1948 *Phys. Rev.* **73** 679
[15] Anderson J W and Slichter W P 1966 *J. Chem. Phys.* **44** 1797
[16] Sorai M, Suga H and Seki S 1965 *Bull. Chem. Soc. Japan* **38** 1125
[17] Svare I, Thorkildsen G and Otnes K 1979 *J. Phys. C: Solid State Phys.* **12** 2177
[18] Ebisuzaki Y 1974 *J. Chem. Phys.* **61** 3170
[19] Balagurov A M *et al JINR Preprint* P13-97-312 (in Russian)