Quantum molecular tunneling of NH_4^+ ions in mixed ammonium–alkali halide systems

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Abstract. The rotational excitations of NH_4^+ ions in dilute solution in metal alkali halide lattices have been studied at 4K by inelastic neutron scattering technique. It is found that the ions exist in matrix isolation at very low ammonium ion concentration, c ($c \rightarrow 0$), and it transforms to orientational glass phase on increase of c . It is shown that the onset of the orientational glass phase is moderated through the strain field generated by the substituted impurity in the lattice. The variation of the intensity profiles with increase of c have been successfully explained by a phenomenological model based on gaussian distributed heights.

Keywords. Quantum tunneling; neutron scattering; NH_4^+ ion.

1. Introduction

Molecular dynamics in the solid state are solely governed by the potential which the molecules experience in the field of their neighbours. This potential can be divided into two parts: static and fluctuating. Fluctuating part is proportional to the temperature. At low temperatures this part of the potential dies out and quantum mechanical aspects determine the molecular dynamics (Press 1981). In such a situation the quantum mechanical rotational states of a molecule can be obtained by solving the Schrödinger equation. For vanishing V the molecule is a free rotor and the magnitude of the level spacing is determined by the rotational constant $B = \hbar^2/2I$, where I is the moment of inertia. For strong potentials the molecule sits in one of the equilibrium positions and performs small oscillations and the excitation spectrum corresponds to a harmonic oscillator with equally spaced energy levels. In the intermediate regime, called the tunneling regime, the splitting is observed. The tunnel split spectra can be studied experimentally with the help of high resolution inelastic spectrometer.

Ammonium halides, NH_4X ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) and the mixed salt of ammonium metal–alkali halides, $(\text{NH}_4)_c\text{M}_{1-c}\text{X}$ ($\text{M} = \text{K}, \text{Rb}$), provide interesting systems for studying the dynamics of ammonium ions in different configurations and environments (Venkataraman *et al* 1966; Gardener *et al* 1977; Goyal and Dasannacharya 1978). Pure ammonium halides undergo a number of structural modifications at well defined transition temperatures (Perry and Lowndes 1969). Mixed salts of ammonium halides and alkali halides can be prepared up to fairly large concentrations of the ammonium ions. The ammonium ion can be present as an impurity in the alkali halide lattice; the host lattice maintains its high symmetry (α -phase) structure even at very low temperatures (Stephenson *et al* 1952). The miscibility of the different halides depends on the differences in their molar volumes and the temperature range over which the high symmetry α -phase is preserved depends on the ammonium concentration (Havighurst *et al* 1925; Barret *et al* 1992). In so far as the rotational dynamics of the NH_4^+ ion is determined mostly by the first neighbour halide interaction, it may be expected to be similar in both the mixed and pure salts.

2. Experimental

The mixed salts $(\text{NH}_4)_c\text{M}_{1-c}\text{X}$, $\text{M} = \text{K}, \text{Rb}$ and $\text{X} = \text{I}, \text{Br}, \text{Cl}$ were prepared by evaporation of an aqueous solution of the pure salts of stoichiometric proportions in vacuum. The recovered samples were dried in a furnace at about 60°C . The dried samples were then characterized by neutron diffraction. The diffraction patterns showed that the samples consisted of a single phase material.

Absence of diffraction lines from the pure salts confirmed the successful formation of the required mixed salt. 7–8 g of the dry samples were encapsulated in flat aluminium foil sachets about 3 mm thick and mounted in a variable temperature liquid–helium cryostat. Data were collected at 4 K and 20 K from all the samples.

Inelastic neutron scattering spectra were recorded on the IRIS time of flight spectrometer (Carlile and Adams 1992) at the ISIS pulsed neutron facility, UK. IRIS is an inverted geometry inelastic neutron spectrometer. The long incident flight path, and the array of backscattering-graphite-analysers provides an elastic resolution of $\sim 15 \mu\text{eV}$, at a final energy of 1.82 meV. From the diffraction detectors present inside the analyser tank, structural information was obtained simultaneously with the spectral information. Figure 1 shows the shift of the (200) reflection as the ammonium concentration c is varied from 0.0 to 0.11 in $(\text{NH}_4)_c\text{K}_{1-c}\text{Br}$. The line shifts to longer d-spacing by 0.5% and broadens as the concentration increases revealing the effects of disorder. The area under the line remains approximately constant. Interestingly, in case of the rubidium salts as distinct from the potassium salts the lattice parameter changes only slightly with ammonium concentration. It may be noted that the ionic radius of ammonium ions ($1.43 \text{ \AA}$) is close to that of rubidium ($1.44 \text{ \AA}$) than it is to potassium ($1.37 \text{ \AA}$).

3. Results and discussion

3.1 Mixed ammonium potassium halides, $(\text{NH}_4)_c\text{K}_{1-c}\text{X}$

The background corrected data (Mukhopadhyay *et al* 1992) from dilute solutions of NH_4^+ ions in potassium halides at 4 K are shown in figure 2. As can be seen from the

Figure 1. A portion of the diffraction pattern showing the shift of the (200) reflection of $(\text{NH}_4)_c\text{K}_{1-c}\text{Br}$ for (a) $c = 0.0$, (b) $c = 0.032$, (c) $c = 0.085$ and (d) $c = 0.11$.

Figure 2. Inelastic neutron spectra from: (a) $(\text{NH}_4)_c \text{K}_{1-c} \text{I}$ for $c = 0.045$ and (b) for $c = 0.09$, (c) $(\text{NH}_4)_c \text{K}_{1-c} \text{Br}$ for $c = 0.032$ and (d) for $c = 0.085$, (e) $(\text{NH}_4)_c \text{K}_{1-c} \text{Cl}$ for $c = 0.031$ and (f) $c = 0.075$. Solid lines are guide to the eye. Arrow shows the transition energy for a free rotor.

figure, at low ammonium concentrations ($\approx 3\text{--}4\%$), the spectra show sharp features. However, as concentration of NH_4^+ ion is increased, the intensity of the sharp line decreases and a broad distribution develops at lower energy transfers. These observations are common for all the potassium halides. The energy corresponding to the sharp line depends on the halide and the occurrence of the broad feature depends on the concentration of the NH_4^+ ion in a given halide lattice. We recall that the broad feature in case of mixed iodide salt was attributed due to the onset of orientational glassy state based on the dielectric data from the mixed iodide salt (Fehst *et al* 1990). Our data indicate that the broad feature is common to all the three mixed halides at large concentration of NH_4^+ ions.

It is obvious that the spectra from the three mixed halide salts show remarkable similarity. At low concentrations of ammonium ions, all the halide salts show a sharp tunneling line. The observed transition energy of this tunneling line varies systematically from lattice to lattice. As the lattice constant increases the transition energy increases, approaching more closely the J ($0 \rightarrow 1$) value of a uniaxial free rotor (Press 1981). When c is increased, the sharp tunneling line is accompanied by a broad distribution at lower energy transfers. The intensity of the accompanying band grows with increasing c , whilst the sharp tunneling transition line weakens rapidly. In $(\text{NH}_4)_c \text{K}_{1-c} \text{I}$ the spectrum gets completely degraded at $c = 0.15$. That is, above this concentration the sharp features disappear and the broad distribution grows towards the lower energy transfer region. This is in confirmation of the earlier work (Bostoen *et al* 1989). This effect may be associated with the onset of the orientational glassy state (OGS) (Fehst *et al* 1990). The onset of the OGS occurs sooner (i.e. at lower ammonium concentration) in the chloride salts than it does in the bromide salts which in turn occurs sooner than that in the iodide salts. The same order follows for the tunneling energies which may be explained in the following manner. Clearly lower transition energies occur for smaller ground state splitting which is linked to stronger rotational potentials. If the crystal field increases as the interatomic distances decrease the occurrence of the OGS will be at lower ammonium concentrations in those crystals with the smallest lattice parameters.

3.2 Mixed ammonium rubidium halides, $(\text{NH}_4)_c\text{Rb}_{1-c}\text{X}$

The ionic radius of ammonium ion is closer to that of rubidium ion than to that of potassium ion; so it is of interest to study the nature of rotational states of the ammonium ions in rubidium salts. Rubidium being a larger ion compared to potassium ion, the lattice constants of the rubidium salts are larger compared to the potassium ones.

The spectra (figure 3) from the rubidium salts (Mukhopadhyay *et al* 1994a, b) have remarkable semblance to the results obtained with potassium salts (Mukhopadhyay *et al* 1992). Comparison of the $J = 0 \rightarrow 1$ transition energies in both K and Rb salts is displayed in figure 4. Transition energies from Rb salts should have been higher than in the corresponding K salts. However, results contrary to this expectation suggest, that the local rotational potential well is in fact deeper in the rubidium salts than in the potassium salts. It may also be possible that, the octahedral field in rubidium lattice modifies the transition scheme differently than that in the potassium lattice.

We have seen earlier that for NH_4/K halides the spectral shape changes on increase of ammonium concentration; the sharp tunneling line decreases in intensity and a broad distribution develops at lower energy transfers. This is attributed to the onset of orientational glassy state. We have also seen that the occurrence of the OGS vary systematically in different halides. This is very apparent in figure 4 where spectra from NH_4/Rb halides are shown at constant ammonium ion concentration. The line in the iodide is sharp and unencumbered with any other signal, but this is not so in case of the bromide and chloride salts. Because the NH_4^+ ion concentration remains constant we

Figure 3. Inelastic neutron spectra from $(\text{NH}_4)_{0.03}\text{Rb}_{0.97}\text{X}$. (a) $\text{X} = \text{I}$, (b) Br and (c) $\text{X} = \text{Cl}$. Solid lines are guide to the eyes. Arrow shows the transition energy for a free rotor.

Figure 4. The variation of the $J=0 \rightarrow 1$ transition energy as a function of the lattice parameter of the respective matrices. Lines are guide to the eye.

are again observing a systematic tendency towards OGS among the rubidium halides. The concentration at which the onset of OGS occurs follows the same order as observed in the potassium salts: that is the onset of OGS in the chloride spectrum occurs sooner (i.e. at a lower ammonium concentration) than it does in the bromide spectrum which in turn occurs sooner than in the case of the iodide salt.

4. Phenomenological model

Inelastic neutron scattering experiments to study the rotational excitations of the NH_4^+ ions in $(\text{NH}_4)_c \text{K}_{1-c} \text{I}$, over a wide range of c from 0.02 to 0.44, were conducted by Bostoen *et al* (1989). For the lowest concentration ($c = 0.02$) studied, NH_4^+ ions are expected to be more or less isolated from each other. The observed transition energy (≈ 0.6 meV) from the ground state to their first excited state ($J = 0 \rightarrow 1$) is very close to that (≈ 0.72 meV) of a uniaxial quantum mechanical free rotor. As c increases, the observed intensity profiles carry the signature of the NH_4^+ ions rotational tunneling behaviour. For $c > 0.2$, their motion must be so hindered that the spectra seem to indicate a rotational diffusive behaviour. How to explain these spectra?

The INS spectra seem to be made up of a finite number, N , of transition lines. We do not have a theory that can fix the value of N and provide a physically motivated weighting scheme for these sublimes. Hence, model calculations have to choose a 'reasonable' weighting scheme, $P(c)$, with N as a fitting parameter.

The nearest neighbour binomial model— $P(c)$ is a binomial distribution—is not able to explain the spectra for concentrations, $c > 0.02$. This model can be shown to generate acceptable spectra, if the concentrations are artificially renormalized to higher values.

Intensity profiles agreeing with the observed ones over a wide range of concentrations can also be generated by assuming that $P(c)$ is obtainable from a gaussian

distribution of barrier heights: the total potential experienced by an ammonium ion can be written as

$$V = V_c + V_\alpha,$$

where V_α represents not only direct $\text{NH}_4^+ - \text{NH}_4^+$ interaction but also interactions mediated by the lattice and can be conveniently parametrized in terms of some average value V_1 to be estimated

$$V_\alpha = nV_1.$$

Because we are dealing with substitutionally disordered system, V_α is a random variable which can be assumed to be gaussian distributed. Support for this assumption comes from the following considerations.

The dielectric loss experiments (Birge *et al* 1984) from the quadrupolar glass, KBr-KCN, have been interpreted in terms of a Gaussian distribution of barrier heights. More recently, Grannan *et al* (1990) performed detailed simulation of these systems and presented convincing numerical support for the gaussian form of the barrier height distribution.

Against this background, we assume that the barrier heights, V_α , in $(\text{NH}_4)_c \text{K}_{1-c} \text{I}$ are also distributed in the form of a gaussian,

$$q(V_\alpha) = 1/(\sqrt{(2\pi)}\sigma_v) \exp\{-(V_\alpha - V_\alpha)^2/2\sigma_v\}. \quad (1)$$

Since the barrier heights, V_α , are parametrized in terms of V_1 , we have

$$P_n(c) = 1/[\sqrt{(2\pi)}\sigma(c)] \exp\{-(n - n_0)/2\sigma^2(c)\}, \quad (2)$$

Figure 5. Intensity profiles generated for different ammonium ion concentrations on the basis of the gaussian distributed barrier height.

where we have absorbed the factor V_1 into the width $\sigma(c)$ which should depend on concentration c . Here, n refers to that subline of the spectra to which an NH_4^+ ion is most likely to contribute.

We have demonstrated (Narasimhan and Mukhopadhyay 1993) that the intensity profiles, obtained by using the above distribution for $P_n(c)$, agree extremely well with the observed spectra over a wide range of concentrations. The profiles arrived at on this basis are compared with the experimental data in figure 5. Solid lines are results calculated on the basis of the gaussian model discussed above. Except for the lowest concentration, the agreement between the calculated and the experimental profiles is remarkably good.

In order to resolve the question of whether the observed tunneling behaviour of NH_4^+ ions is strain-field mediated, we have carried out the following experiment.

5. Ternary mixed salts $(\text{NH}_4)_{c-d} \text{Rb}_d \text{K}_{1-c} \text{X}$

We have also carried out inelastic neutron scattering measurements with ternary salts of ammonium-potassium halides: $(\text{NH}_4)_{c-d} \text{Rb}_d \text{K}_{1-c} \text{X}$; with $c = 0.08$ and $d = 0.06$. This system can be considered as the host salt KI containing two substitutional impurities NH_4 and Rb. The inelastic neutron spectrum of this salt shown in figure 6 has several surprises. A broad band is observed which cuts off sharply at $600 \mu\text{eV}$. This cut-off matches closely with the transition energy in $(\text{NH}_4)_{0.09} \text{K}_{0.91} \text{I}$ salt. However the ammonium ion concentration ($c = 0.02$) is not sufficient by itself to produce the broad distribution observed at low energy transfers. The spectrum is understandable only in terms of the total impurity concentration including both Rb and NH_4^+ , ($0.02 + 0.06 = 0.08$). This can be seen by comparison with the spectrum from $(\text{NH}_4)_{0.09} \text{K}_{0.91} \text{I}$ (figure 2b). The two spectra are almost identical. That is, the situation with small concentration of ammonium ion in the ternary salt is as if it were a higher concentration binary salt. This cannot be due to the ammonium ion responding to a random arrangement of dipoles at next neighbour sites. Rather the ammonium ion is responding to the strain field caused by the structural break-up of its neighbourhood. We believe that this is also true in the binary mixed salts. In this case the strain field is caused by other ammonium ions.

We now see that this orientational glass is very similar to other orientational glasses like KCl doped hydroxyl, alkali halide cyanide etc (Höchli 1990). Its dynamical properties are governed principally by its strained crystallographic environment. The onset of OGS is not directly due to pairs or higher multimer formations of ammonium ions. Instead it is a consequence of the ammonium site asymmetry. Onset of OGS is more rapid for the stronger crystal fields since strains in these crystals will provide larger field deformations. The relative size of any impurity will also be important.

Using the same phenomenological model outlined above we could successfully generate the intensity profile from the ternary salt also (figure 6) (Mukhopadhyay and Narasimhan 1995).

We should thus conclude that the gaussian strain fields experienced by the NH_4^+ ions play a dominant role in their observed tunneling behaviour.

6. Summary

Rotational excitations of NH_4^+ ions in potassium halide lattices or rubidium halide lattices show that the ion behaves as if it is in matrix isolation at very low ammonium

Figure 6. The inelastic neutron scattering spectra from the ternary salt $(\text{NH}_4)_{0.02} \text{Rb}_{0.06} \text{K}_{0.92} \text{I}$ at 4 K. Solid line represents the generated intensity profile.

concentration and then goes to orientationally disordered state at higher ammonium concentrations. Results are qualitatively similar for both the alkali halides; only a scaling with respect to the concentration of the ammonium ion is observed depending on the lattice constant of the matrix. This is attributed to the change of the potential as a function of lattice parameter. The transition energy between the two so-called almost free rotor levels ($J = 0 \rightarrow 1$) is found to be lower in case of rubidium salts than in the potassium salts. This suggests a deeper rotational potential well for the NH_4^+ ion in the rubidium salts, which is counter-intuitive since the lattice expands. The spectral degradation indicating transformation from an isolated rotor state to a orientational glassy state seems to be common in all the salts.

Inelastic neutron scattering data from $(\text{NH}_4)_{c-d} \text{Rb}_d \text{K}_{1-c} \text{I}$ show the direct interactions between NH_4^+ ions are not responsible for the dynamical behaviour. The detailed analysis of the data from the ternary salt has lead us to believe that the orientational glassy behaviour in these systems is mediated by the strain field caused by the substitutional impurity and not due to dipolar or higher multipolar interactions.

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