

Rotational excitations of NH_4^+ in $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$

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Abstract. We propose a gaussian model for the distribution of rotational tunneling lines which constitute the experimentally observed inelastic neutron scattering spectra in the range 0 to 0.6 meV from the mixed system $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$. The intensity profiles generated by this model are in remarkable agreement with the experimentally observed ones.

Keywords. Neutron scattering; orientational glass; tunneling.

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A variety of molecular solids are known [1] to transform to orientational glassy phase at sufficiently low temperatures, due to the interplay of frustrated intermolecular interactions and site disorder in the system. At very low temperatures an almost-isolated molecule such as CH_4 , NH_3 or NH_4^+ in high symmetry solid state environments, is known to have low energy rotational excitations which are comparable to those of a quantum mechanical free rotor. As the rotational states are well characterized to begin with, it is possible to undertake a systematic study of how they change with the onset of disorder and frustration in the system, as concentration of such ions increases.

The room temperature NaCl-type structure (α -phase) of pure NH_4I transforms [2] at 255 K into CsCl-type structure (β -phase). In order to study the reorientational motion of NH_4^+ ions in the high symmetry α -phase at very low temperature, the transition $\alpha \rightarrow \beta$ has to be suppressed. It is known [3] that NH_4I and KI are completely miscible over the entire concentration range and the mixed salt retains the α -phase of pure NH_4I down to very low temperatures. All other ammonium-potassium halides also exist in α -phase over certain concentration ranges.

For small concentrations, x , of NH_4^+ ions ($x \rightarrow 0$), the NH_4^+ ions are more or less isolated from each other; at very low temperature ($T \cong 2\text{ K}$), the transition energy ($\approx 0.6\text{ meV}$) between the ground state and the first excited state ($J = 0 \rightarrow 1$) is very close to that of a uniaxial quantum mechanical free rotor (0.717 meV), as seen in the inelastic neutron scattering data [4] from $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$. As concentration of NH_4^+ ions increases, it leads to a build-up of the effective potential for the reorienting NH_4^+ ion and consequently to its rotational tunneling behaviour. For $x > 0.2$, their motions must be so hindered that a feature similar to quasielastic scattering is observed. Similar behaviour has been observed in subsequent experiments [5] in all other halides.

Inelastic neutron scattering experiments to study the rotational excitations of NH_4^+ ions in $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$ over a wide range of x from 0.02 to 0.44 at temperatures less

than 5 K were reported by Bostoen *et al* [4]. They invoked a nearest neighbour binomial model which is based on the concept of locally perturbed crystal field to explain the observed data and to generate a theoretical neutron scattering profile. However this model failed to yield profiles even qualitatively similar to those observed at concentration $x > 0.02$.

Here, we demonstrate that a model which takes into account the glassy behaviour [6] of these systems at low temperatures, is capable of generating intensity profiles which agree with the observed ones over a wide concentration range (0.02 to 0.17) except at the lowest one. For the sake of completeness and also for focusing attention on the assumptions involved in our model approach, we begin by discussing salient features of the binomial model used by Bostoen *et al* [4].

Binomial model

The total potential, V , experienced by an NH_4^+ ion in a solid is made up of a background uniform crystal field potential, V_c , and a small perturbative potential, V_x due to interaction of NH_4^+ ion with all the other NH_4^+ ions in the system. At very low temperatures, $T \rightarrow 0$, thermal fluctuations in V can be neglected and the NH_4^+ ions can be considered to be in their ground states.

However, there will be a site-to-site variation in the magnitude of V due to changes in 'local' environment. Consequently, different NH_4^+ ions will require different values of energy to make transitions between their ground states and their first excited states. To find the transition energy, E , for a given potential V , the ansatz [4]

$$E = E_0 \exp[-(V/V_k)^2] \quad (1)$$

is employed. Here, E_0 (≈ 16 K) is the free rotor transition energy between states with $J = 0$ and 1; $V_k \approx 305$ K is the barrier [7] of NH_4^+ in KBr matrix.

If one were to assume that an NH_4^+ ion is likely to experience one of the N possible values of V_x , then it would mean that the observed inelastic neutron intensity profiles are assumed to be made up of N transition lines. By further assuming that these values are simply multiples of some average value, V_1 , which is yet to be determined, an NH_4^+ ion is likely to experience a potential

$$V_n = V_c + nV_1; \quad n = 0 \text{ to } N - 1. \quad (2)$$

Since the energy states of an NH_4^+ ion are only defined in some average sense, the transition lines are assumed to have the gaussian shapes,

$$I_n(V; V_c, V_1, \delta_n) \cong \exp(-[V - V_n]^2/2\delta_n^2) \quad (3)$$

where the widths, δ_n , may weakly depend on the concentration. These transition lines, of course, have to be weighted by the probability, $P_n(x)$, that an NH_4^+ ion experiences the potential V_n .

The observed intensity profile is then given by

$$I(E) = R(E) * \sum_{k=0}^n P_k(x) J(E) I_k(E; V_c, V_1, \delta_n) \quad (4)$$

where $*$ represents the convolution of a gaussian instrumental resolution, $R(E)$, with

the rest of the expression, $J(E)$ is the Jacobian obtained from eq. (1) namely

$$J(E) = 2E \ln(E_0/E). \quad (5)$$

The detailed balance factor can be taken into account appropriately.

As the interaction between two NH_4^+ ions is, a priori, expected to be of the short-ranged octopolar type, only the nearest neighbour interaction need to be included in the calculation of V_n . This is equivalent to assuming that n is the number of NH_4^+ ions at the nearest neighbour sites. As the NH_4^+/K^+ ions in these systems occupy the sites of an fcc lattice, the maximum value of n is obviously 12, implying thereby that the intensity profiles are made up of 13 sublines. NH_4I is known to mix homogeneously with and form continuous solid solutions in KI in the range $x = 0$ to 1. Therefore, the nearest neighbour occupancy probability, $P_n(x)$, with which the various transition lines are to be weighted, is taken to be the binomial distribution given by,

$$P_n(x) = \binom{12}{n} x^n (1-x)^{12-n}; \quad n = 0 \text{ to } 12. \quad (6)$$

By assuming that the values of δ_n for all $n > 0$ are identical for any specific concentration, a set of four parameters, V_c , V_1 , δ_0 , δ_1 have to be estimated.

This model could not explain the data for $x > 0.02$. In fact, the values of the parameters (285, 35, 0.015 and 0.036 K respectively) obtained by fitting the model profile to the experimental data for $x = 0.02$ already suggest that V_1 has a much higher value than if $NH_4^+ - NH_4^+$ interactions were octopolar (≈ 7 K). In addition, on the basis of dielectric measurements [6], this system has been demonstrated to be a dipolar glass.

With the $NH_4^+ - NH_4^+$ interactions being long-ranged, n in eq. (2) cannot be taken to represent the number of NH_4^+ ions at the nearest neighbour sites. Moreover, the distribution, $P_n(x)$, cannot be binomial, as noted also by Bostoen *et al* [4].

If one were to insist on working within the framework of the binomial model, then it should be recognized that the only way for the long-ranged nature of the $NH_4^+ - NH_4^+$ interaction to manifest itself is in the form of a higher value for the effective number of NH_4^+ ions at the nearest neighbour sites. Numerically, this can be achieved by renormalizing the concentration x with the help of the parameter $c(x)\{x \rightarrow y = c(x)x\}$ —to be appropriately determined— so that the various sublines will now be weighted with $P_n(y)$. Moreover, the maximum number of lines in the spectra need not be equal to 13. With this interpretation, we have demonstrated [8] that with $N = 10$ it is possible to obtain inelastic neutron scattering profiles which are in reasonable agreement with the observed ones. However, it should be noted that in the presence of long range interaction, this model is unphysical and arbitrary.

Gaussian model

As the binomial model cannot be invoked when long-ranged interactions are present in the system, we have investigated alternative approaches based on heuristic arguments as explained in this section.

As already stated, this system is known to freeze into a dipolar glass state at low temperature [6]. It is then analogous to a vector spin glass system. Palmer and Pond [9] have numerically computed the zero-temperature distribution, $q(h)$, of

internal fields in the Sherrington–Kirkpatrick random Ising spin model of a spin glass and shown that it is of the form

$$q(h) \cong \frac{h}{\sigma^2} \exp(-h^2/2\sigma^2). \quad (7)$$

In the classical vector spin model also, they have shown that $q(h)$ is bell-shaped with a linear behaviour for small values of h , even though they could not fit either an exponential or a gaussian for large values of h .

Analogously, we assume that the internal field distribution in $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$ systems is also of the form eq. (6). However, to explain the observed inelastic spectra, we look for a distribution for barrier heights, V_α , which must exist for a given distribution of internal fields. To a first approximation we assume that it is a gaussian given by,

$$q(V_\alpha) = \frac{1}{\sqrt{2\pi}\sigma_v} \exp(-(v_\alpha - \bar{v}_\alpha)^2/2\sigma_v^2) \quad (8)$$

The barrier heights, V_α , are parametrized in terms of the sublines, labelled by a number $n (= 0 \text{ to } N - 1)$ where N is the total number of sublines in the neutron inelastic spectra. We therefore, have the gaussian form

$$P_n(x) = \frac{1}{\sqrt{2\pi}\sigma(x)} \exp(-(n - n_0)^2/2\sigma^2(x)) \quad (9)$$

for the probability distribution, after absorbing the factor V_1 into the width $\sigma(x)$. Here, n_0 refers to that subline in the spectra to which an NH_4^+ is most likely to contribute.

Results

Inelastic neutron scattering profiles given by eq. (4) as a function of four parameters V_c , V_1 , δ_0 , δ_1 were calculated as follows:

- (i) The width, ΔE , of the gaussian instrumental resolution, $R(E)$, has been taken to be $72 \mu\text{eV}$ [4].
- (ii) The value of V_c has been kept at 285 K, the same as that reported by Bostoen *et al*, so that the observed position of the $J = 0 \rightarrow 1$ line is maintained.
- (iii) The total number of sublines in the inelastic spectra was set equal to 8. This value of N has been arrived at by a trial and error process. We could not obtain reasonable looking intensity profiles with $N < 8$ for any combination of the parameter values. In other words, eight gaussian sublines are necessary and sufficient to generate the inelastic spectra for the concentrations reported.
- (iv) V_1 was found to acquire a value ($\cong 55 \text{ K}$) which is much closer to the value obtained for an interacting pair of NH_4^+ ions, when they are treated as dipoles of moment 1.4 D [6] and are separated by the nearest $\text{NH}_4^+ - \text{NH}_4^+$ distance in the lattice. This value is larger than even that ($= 35 \text{ K}$) of Bostoen *et al* [4].
- (v) Starting with the value of Bostoen *et al* [4] for $\delta_0 = 0.015 \text{ K}$, we observed that a slightly higher value ($\cong 0.02 \text{ K}$) is needed.
- (vi) The parameter δ_1 has been found to depend on concentration and is found to

Rotational excitations of NH_4^+ in $(NH_4)_xK_{1-x}I$

Table 1. List of values of the parameters δ_1 and σ at different concentrations x .

x	δ_1	σ
0.02	0.07	0.80
0.06	0.08	0.32
0.11	0.09	0.19
0.14	0.11	0.15
0.17	0.12	0.14

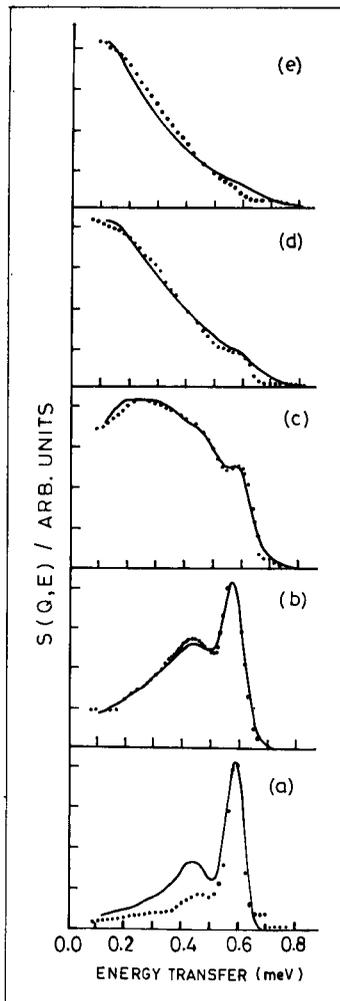


Figure 1. Inelastic neutron scattering profiles from $(NH_4)_xK_{1-x}I$. Points represent the data read off from [4]. Solid lines are obtained from the gaussian model, explained in the text. (a) $x = 0.02$; (b) $x = 0.06$; (c) $x = 0.11$; (d) $x = 0.14$; and (e) $x = 0.17$.

have the values given in table 1. These values are much higher than those of Bostoan *et al* [4].

(vii) We have observed a very weak concentration dependence of n_0 ; however, for preliminary calculations, we have set it at its average value $n_0 = (N - 1)/2$.

(viii) Regarding the parameter $\sigma(x)$, we found that it is the most crucial and sensitive parameter that depends on concentration. Even slight variation of $\sigma(x)$, especially at higher x , changes the nature of the profile drastically. The values of σ used for generating the intensity profiles are given in table 1. These values, however, should not be taken to suggest a functional behaviour of $\sigma(x)$ because in this preliminary analysis, our aim has only been to demonstrate that a gaussian model is more physical and works for all concentrations $x > 0.02$. A careful study of this model for the purpose of establishing the functional behaviour of $\sigma(x)$, and possibly of $n_0(x)$ also, is in progress.

The profiles arrived on this basis are compared with experimental data in figure 1. Here, the data read off from reported intensity profiles [4] for the concentrations, $x = 0.02, 0.06, 0.11, 0.14$ and 0.17 respectively, are represented by points in figure 1. Solid lines are results calculated on the basis of the model discussed in this section. It is observed that, but for the lowest concentration of $x = 0.02$, agreement between the calculated and the experimental profiles is remarkably good.

Conclusion

We have demonstrated that the inelastic spectra from $(\text{NH}_4)_x\text{K}_{1-x}\text{I}$ for the concentrations $x = 0.02, 0.06, 0.11, 0.14$ and 0.17 are all made up of a minimum of eight transition lines. We have shown that a gaussian distribution of rotational barriers for NH_4^+ ions can be used for weighting these lines. Calculated intensity profiles agree extremely well with the observed spectra over a wide concentration range.

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