

INELASTIC NEUTRON SCATTERING STUDY OF  $\text{NH}_4$  GROUND  
STATE TUNNELING SPLITTING IN SOLID  $\text{NH}_4\text{SnCl}_3$

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High resolution inelastic neutron scattering experiment on tunneling  $\text{NH}_4^+$  ion in polycrystalline  $\text{NH}_4\text{SnCl}_3$  sample is reported. Ground state splittings of  $1.52 \pm 0.06$   $\mu\text{eV}$  and  $3.00 \pm 0.03$   $\mu\text{eV}$  have been observed at  $T=5$  K and are interpreted as transitions between  $A \leftrightarrow T$  and  $T \leftrightarrow E$  spin symmetry states.

The rotational tunneling of the tetrahedral  $\text{NH}_4^+$  ion between its twelve equivalent orientations in a crystal field is the subject of an extensive experimental and theoretical investigation /1,2,3,4/. The librational ground state of  $\text{NH}_4$  ion around one of its 12 equilibrium orientations in the crystal is called the pocket state. For the finite orientational potentials for  $\text{NH}_4$  group in the crystal lattice, the tails of the pocket state wave function extend into the neighbouring pockets and there exists a finite probability for a tunneling process into a neighbouring pocket. The diagonalization of the  $\text{NH}_4$  Hamiltonian matrix evaluated for the pocket states leads to, in general, a singlet ground state (A), three triple (T), and one double (E) degenerate excited states /2/, but depending on a particular site symmetry the degeneracy of the levels may be increased /2,3/.

The 12 rotational wave functions which are linear combination of pocket states with A, T, and E type symmetry are combined with 16 spin wave functions to yield 16 eigenfunctions of the  $\text{NH}_4$  ion. In the limit of an infinitely strong rotational potential the libration ground state of the  $\text{NH}_4$

ion consists of 5A, 9T and 2E states and is thus 16-fold degenerate. If the orientational potential is finite, than the above ground state splits into separate spin isomer states and it is this splitting which is termed as the "tunnel splitting". The ground state splitting turns out to be extremely sensitive to the symmetry and strength of the crystal orientation potential at the site of an ammonium ion. A detailed knowledge of the ground state tunnel splitting in principle enables one to derive the correct shape and height of the crystal orientational, i.e. rotational, hindrance potential. With the help of the afore-mentioned 16 eigenfunctions the doubly differential scattering cross section of the tunneling system and the scattering intensity /1,2,3/, as a function of the neutron linear momentum transfer for the single crystal and powder experiments have been predicted.

A particular intensively studied example of the rotational excitations at low temperatures is the face centered cubic powder  $(\text{NH}_4)_2\text{SnCl}_6$  sample /2,4/, which represents a well known example of a tetrahedron in a potential with high (i.e. tetrahedral,  $T_d$  at the ammonium site) site symmetry. The low-temperature proton magnetic resonance study of the ammonium ion rotational dynamics as a function of temperature in powder samples  $(\text{NH}_4)_2\text{SnCl}_6$  and  $\text{NH}_4\text{SnCl}_3$  /4/, have revealed that both compounds exhibit extremely low second moments, small values of the proton spin-lattice relaxation times  $T_1$ , and almost identical low values of the activation energy for its thermally activated reorientation which is equal to  $E_a = 1.2$  kcal/mol. In view of these findings, it seems worthwhile to gain additional insight into the nature of the orientational crystal potential at the site of the ammonium ion in  $\text{NH}_4\text{SnCl}_3$  powder sample, in spite of the fact that its crystallographic structure is unknown. For this reason, the high resolution incoherent scattering experiment at  $T = 5$  K has been performed with the backscattering spectrometer IN10 at the ILL high flux reactor in Grenoble. Polished silicon crystals were employed both for the monochromator and analyser, with a resulting energy resolution of  $0.36 \mu\text{eV}$  (FWHM). The energy range of  $+15 \mu\text{eV}$  was covered, the incident neutron energy was  $2.08 \mu\text{eV}$  and the three values of momentum transfer,  $Q$ , were chosen:  $0.49 \text{ \AA}^{-1}$ ,  $1.49 \text{ \AA}^{-1}$ , and  $1.89 \text{ \AA}^{-1}$ . Only at  $Q = 1.89 \text{ \AA}^{-1}$  the two pairs of inelastic peaks in the scattering spectra were clearly visible and are presented in Fig. 1. As seen, the inelastic peaks measured in neutron energy gain and loss have equal intensities, thus indicating that the tunnel states are in thermal equilibrium with the phonon bath. The tunneling energies obtained are  $E_1 = (3.00 \pm 0.03) \mu\text{eV}$  for the

outer and  $E_2 = (1.52 + 0.06) \mu\text{eV}$  for the inner inelastic peaks. As their ratio is very nearly equal to 2 this serves as an indication that, for this compound also, the 180 degrees overlap matrix elements can be neglected, in comparison with 120 degrees overlap matrix elements. The intensity ratio of the outer to the inner inelastic peak is equal to  $1.40 + 0.04$ . Apart from the just quoted value the tunneling characteristics of both compounds are almost identical, however, even the intensity ratios lie within the same measurements interval. Consequently the strong similarity, as far as the ammonium ion orientational potential site symmetry is concerned, observed in NMR [4] experiments, exists also in the present case of high resolution inelastic scattering study. It is noted that the observed tunnel energies, which we interpret as transitions from  $A \leftrightarrow T$  and  $T \leftrightarrow E$  spin isomer states occur at almost precisely the same energies for both compounds. An additional search for a T splitting within the energy transfer range of  $\pm 4.23 \mu\text{eV}$  around the central peak, carried out at  $T = 5 \text{ K}$  on  $\text{NH}_4\text{SnCl}_3$  sample, has not presented evidence of separate inelastic peaks. Consequently the T splitting, if any is expected to be less than about  $0.2 \mu\text{eV}$ . On the basis of afore-mentioned arguments a hypothesis can be set forward according to which

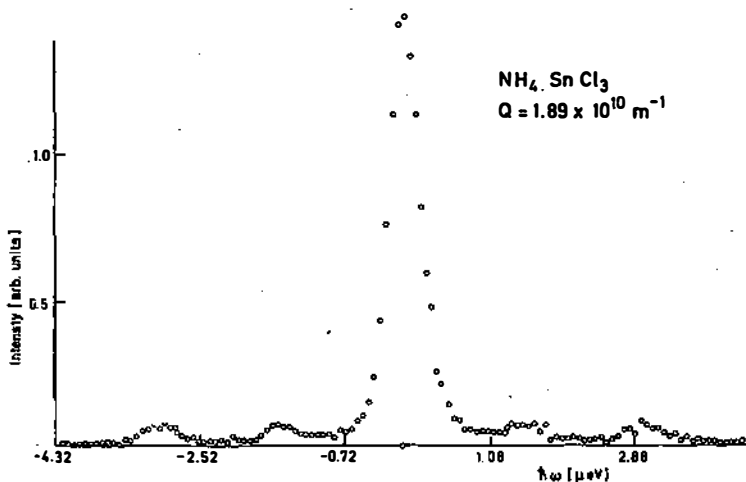


Fig. 1. Energy spectrum of neutrons scattered in polycrystalline sample of  $\text{NH}_4\text{SnCl}_3$  at  $T = 5 \text{ K}$ .

the  $\text{NH}_4$  ion in  $\text{NH}_4\text{SnCl}_3$  is likely to experience the orientational potential of the tetrahedral symmetry. The obtained intensity ratio indicates that the  $\delta$ -function approximation, or even the Gaussian function approximation for the pocket states wavefunctions, are no longer very good ones and the realistic rotational potential seems to be anharmonic.

An additional support for the hypotheses that the splitting of the torsional ground state - the tunnel splitting - of the tetrahedral ammonium ion in  $\text{NH}_4\text{SnCl}_3$  sample occurs due to the fact that it is situated in an orientational potential environment of tetrahedral symmetry. However, just for such cases the relationship between the orientational potential and the tunneling frequencies have been calculated /5/. On the basis of these calculations it is possible to predict that the energy of the first excited librational state for  $\text{NH}_4\text{SnCl}_3$  is expected to be at  $\hbar\omega = 17.2$  meV. Providing that orientational potential in this sample can be validly approximated with only the first term of the expansion in terms of a set of symmetry adapted orthonormal functions, than the coefficient of this first term, known as  $A_3$ , turns out to be  $A_3 = 66$  meV. The last two quoted values enable one to obtain an estimate for the activation energy,  $E_a$ , for rotational diffusion of  $\text{NH}_4$  ion in this sample at high temperatures which turns out to be:  $E_a = -8/9 A_3 - 1/2 \hbar\omega = 1.1$  kcal/mol. This value is surprisingly close to the measured value quoted in /4/, but nevertheless it ought to be taken with caution as it is very sensitive to the value of the first excited librational level. The latter, however, is amenable to an experimental verification. In addition, a thorough NMR T level splitting investigation is required before the hypothesis that the orientational crystal field at the site of  $\text{NH}_4$  ion in  $\text{NH}_4\text{SnCl}_3$  is of the tetrahedral symmetry can be accepted.

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