### ductivity.

R. D. LOWDE: I think it would be interesting to bring out the particular features of the "constant Q" method in the matter of intensity calculations, where it offers a special advantage.

A. D. B. Woods: In the standard method of taking energy distributions the expression for the integrated intensity of the neutron group corresponding to a phonon contains a factor 1/|J| which takes into account the fact that q is changing. (see references 3, 5 and 7). This factor 1/|J| depends on the gradient of the dispersion curve at each q-a term which we just do not know much about, particularly in off symmetry directions. When the experiment is done at constant Q the factor 1/|J|=1, and thus a very serious complication in the intensity analysis is removed.

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# Lattice Dynamics of the Ammonium Halides

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The cold neutron scattering technique has been applied to the study of the ammonium halides. The hindered rotation and "optical" vibrations are observed as single quantum transitions in contrast to the combination lines observed in optical measurements. In the high temperature phase (I) of  $NH_4I$  the motion of the ammonium ion may be described as a super position of a large amplitude hindered rotation and optical vibration.

The understanding of the nature of the phase transitions in the ammonium halides is a very old problem in chemical physics. As long ago as 1930, Pauling<sup>1)</sup> suggested that the transition in NH<sub>4</sub>Cl at  $-30^{\circ}$ C could be explained by the motion of the NH4<sup>+</sup> ions (in the field of the Cl<sup>-</sup> ions) changing from a hindered to a free rotation. Frenkel<sup>2)</sup> was the first to put forth the alternative scheme of an order-disorder transition of the equilibrium positions of the NH4+ ion relative to the chlorine lattice. Specific heat<sup>3)</sup> and infrared<sup>4)</sup> measurements established that the transition from phase III to phase II in the NH4 halides are of the order-disorder nature. Recent infra-red<sup>5)</sup> and neutron diffraction<sup>6)</sup> studies of the transition from phase II to phase I have again raised the possibility that in the high temperature phase I the ammonium ion can freely rotate in the halogen lattice.

The study of the motion of atoms in con-

densed matter by the scattering of cold neutrons has been utilized in the past to determine the phonon dispersion relations in solids<sup>7),8)</sup> and correlated motions of liquid molecules<sup>9),10)</sup>. When a cold neutron is scattered by a typical solid, the energy of single "phonon" or quantum of lattice vibration energy is usually gained by the neutron and the resulting change in energy and momentum of the neutron allows determination of the same quantities for the absorbed phonon<sup>9)</sup>. Since the interaction of the neutron and the atom (nucleus) is a point interaction the selection rules governing the types of motions which may be observed are much less restrictive than the selection rules governing the optical (infra-red and Raman) experiments. In principle, the neutron measurements can sample all the motions whereas the optical measurements are restricted to those associated with some dipolar distribuion of charge.

The results of our neutron scattering measurements of the ammonium halides provide a good example of the usefulness of this new technique for investigating motions of molecular solids. Fig. 1 shows the spectrum obtained for NH4Br at 20°C. The peak at the right hand side of the figure at an energy of  $5 \times 10^{-3}$  ev represents the energy spectrum of the incoming neutrons. The two peaks at approximately 25 and  $45 \times 10^{-3}$  ev result from the interaction of the incoming neutron with the hindered rotation, and the vibration of the NH<sub>4</sub><sup>+</sup> ion in the Br lattice. The energies of these transitions expressed in wave numbers is  $307\pm8$  and  $148\pm6$  cm<sup>-1</sup> respectively. The 148 cm "restsrahlen line" has never been amenable to infra-red or Raman measurements presumably because of selection



rule restrictions. The hindered rotation line at 307 cm<sup>-1</sup> has heretofore never been observed directly but only in combination with one of the bending modes of the NH<sub>4</sub> ion. We have measured the spectra of neutrons scattered from NH4F, NH4Cl, NH4Br and NH4I and have obtained the hindered rotation and restsrahlen frequencies for these materials as well as the changes in these frequencies for the different phases. The neutron measurements for NH<sub>4</sub>I in phase I are of great interest because they indicate that the ammonium ion is not freely rotating but that the motion of NH<sub>4</sub><sup>+</sup> may be described as a super-position of very large amplitude torsional plus vibrational modes.

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#### DISCUSSION

J. A. IBERS: The NMR results of Gutowsky and others on the ammonium halides indicate that at  $100^{\circ}-150^{\circ}$ K there is restricted rotation of the ammonium ion around one or more non-random axes and that the barrier restricting rotation is  $1\sim2$  kcal/mol. Above these temperatures the axis about which restricted rotation is occurring must be changing at faster than  $10^{\circ}$  cycles/sec. Do your results, with a time scale of about  $10^{13}$  cycles/sec, yield any additional information on the motion and, if so, are they compatible with the NMR results?

H. PALEVSKY: I don't think that the NMR data is in the same class as the neutron data in terms of the interpretation of molecular frequencies. For example with neutrons we directly measure the frequency of the torsional oscillation of the NH<sub>4</sub> ion in the bromine lattice at room temperature to be  $8.5 \times 10^{12}$  cycles/sec. From NMR data one learns something about the change in orientation of the axis of rotation, but does not obtain the fundamental torsional frequency.

P. P. EWALD: Would it be possible to distinguish by neutron diffraction between

the independent hindered rotation and one in which the phase of rotation is correlated in successive cells (rotation or oscillation wave-states of the crystal)?

H. PALEVSKY: I do not believe that in the case of an incoherent scatterer such as hydrogen one can distinguish between the hindered rotations in a single unit cell and that of a rotation wave of the type that would give a correlation between the successive cells.

It might be possible to see this difference in the case of a coherent scatterer, in fact I think such an experiment is indeed possible for coherent scattering substances.

S. W. PETERSON: As you are undoubtedly aware, the Raman measurements of Mathieu and the infra-red measurements of Hornig both indicated the existence of single axis rotation in phase I of the ammonium halides. Neutron diffraction measurements have given some supports to this finding. Have you tried to rationalize your results with these findings?

H. PALEVSKY: The NH<sub>4</sub>I-KI solid solution studied by Stephenson and which are believed to contain a freely rotating ammonium ion would be interesting to study by the cold neutron technique. The single axis rotation is ruled out by our inelastic neutron data. The interpretation of the infrared results are on rather shaky grounds because one observes the motion through combination lines, which disappear when free rotation sets in. The interpretation of the neutron diffraction data of Levy and Peterson seems to be fairly straightforward and the inconsistency between their conclusion and ours did at first puzzle me. I think that the two sets of measurements may be reconciled if the ammonium ion is vibrating at the same time it is undergoing a large amplitude torsional oscillation. If the optical vibration is in a particular direction relative to the turning points of the torsional oscillation, diffraction data of limited experimental accuracy could easily be interpreted as a free rotation. Inelastic neutron measurements are particularly sensitive to rotational motions, and any free rotations must be ruled out on the basis of our results.

W. C. HAMILTON: Recent infrared work by Hornig on these systems has shown, as Dr. Palevsky has suggested, that the motion of the NH<sub>4</sub><sup>+</sup> ion is extremely complicated, rotating about first one axis, then moving to another, perhaps in one vibrational period. Simple calculations of the potential surface by one of Dr. Hornig's students indicate that there are many low saddle points which may give rise to a very sloppery motion of the ammonium ion which cannot be described simply in such terms as hindered or free rotation. I am afraid that I cannot share the confidence of Dr. Palevsky in the unambiguity of the neutron scattering experiment nor of Dr. Ibers in the NMR results. I feel it is important to look at the neutron, IR, and NMR results together in an attempt to understand what must be an extemely complex situation. It should be noted also that Hornig believes that his present model is just as consistent with the neutron diffraction data of Levy and Peterson as the single axis rotation previously proposed.

R. D. Lowde: What are the angular speeds of rotation of the ammonia molecules?

J. A. IBERS: In reply to Lowde's question you can get a reasonable estimate of the frequency as a function of temperature by assuming a normal frequency factor and using the barrier determined in the NMR experiment.