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IN ITS HIGH TEMPERATURE PHASES

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†This work done while H. R. was on a Fulbright grant at the University of Helsinki Accelerator Laboratory
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Abstract

We have measured the temperature dependence of the low frequency
Raman spectrum of ammonium nitrate in its solid phases IV, II and I and
also in its melt. Librational modes are observed in phases IV and II
but disappear in both phase I and the melt. Our results indicate that the
NO₃ group is almost freely rotating in the solid phase I.

Zusammenfassung

Die Temperaturabhängigkeit des niederfrequenten Ramanpektrums
wurde für Ammoniumnitrat in der Schmelze und den festen Phasen I, II und
IV gemessen. In den Phasen II und IV wurden Librationsmoden beobachtet,
jedoch keine in Phase I und der Schmelze. Diese Resultate legen den
Schluss nahe, dass die NO₃-Gruppe in der festen Phase nahezu frei rotieren
cann.
The properties of ammonium nitrate through its various phase transi-
tions have been studied rather thoroughly by calorometric\textsuperscript{1,2} N.M.R.\textsuperscript{2,3,4,5} x ray\textsuperscript{2,6,7,8} and infra-red absorption\textsuperscript{9,10} techniques. Pure ammonium nitrate has four solid phases (V, IV, II, I) between \(-17^\circ\text{C}\) and \(169^\circ\text{C}\) where it melts. Particular interest has been generated in the high temperature phases II and I where x ray\textsuperscript{6,7} and N.M.R.\textsuperscript{2} investigations have suggested that both the \(\text{NH}_4\) and \(\text{NO}_3\) groups have considerable freedom of orientation in the solid state. Although Raman studies of the phases of several ammonium halides\textsuperscript{11,12} and nitrate salts\textsuperscript{13,14,15} have been quite successful, little effort has been expended on \(\text{NH}_4\text{NO}_3\).\textsuperscript{16,17} Penot, et al.,\textsuperscript{17} have made a study of the lattice modes of a single crystal in phase IV. They observed three intense modes at 85, 141 and 170 cm\(^{-1}\) which they assigned on the basis of their polarization measurements to either pure librations or to coupled librational-
translational modes. Since these modes depend sensitively on the orientational binding or freedom of orientation of the \(\text{NO}_3\) group, an extension of this investigation into the higher temperature phases should be quite informative. In this letter we shall present a Raman study of the lattice modes of a powdered sample of \(\text{NH}_4\text{NO}_3\) in phases IV, II, I and the melt.
The experimental set-up was similar to that described by Landon and Porto with a krypton laser operating at 6471 Å with 350 mW of power as the exciting source. The laser was focused on the powdered sample and the scattered radiation collected at 90° was analyzed with a Jarrell-Ash 25-107 double monochromator equipped with digital detection and recording. The slit and channel widths were respectively 2 and 1 cm\(^{-1}\). The sample was of reagent grade and was enclosed in a capillary tubing with an inside diameter of 3 mm. The tubing was inserted in a copper block which acted like a thermal reservoir and was temperature controlled to ±.01°C. It is well known that the presence of H\(_2\)O has a striking effect on the phases of NH\(_4\)NO\(_3\). For example, phase III occurs in a "wet" sample but does not occur in a "dry" sample. In this letter we shall only present spectra for "dry" samples. Measurements of both the lattice and internal modes for "wet" and "dry" samples are now in progress. The "dry" samples were prepared by heating the crystal to the melt and keeping it there under a vacuum of 80 mm for a few minutes. The sample was then cooled to the crystalline state and the capillary was sealed under a vacuum of .02 mm.
At room temperature a "dry" sample of NH$_4$NO$_3$ is in phase IV. As the temperature is raised it transforms into phase II at 50°C, phase I at 124°C and melts at 169°C. The structure of these phases as determined from x-ray studies are shown in fig. 1. Phase IV has a space group $V_h^{13}$ with two molecules in an orthorhombic unit cell of dimensions $a = 5.75 \text{ Å}$, $b = 5.45 \text{ Å}$ and $c = 4.96 \text{ Å}$. The nitrate groups have a fixed orientation in the unit cell while N.M.R. studies$^2$ of the ammonium groups indicate that they are randomly reorienting in this phase as well as in the higher temperature phases. Phase II has a space group $C_{4v}^2$ with two molecules in a tetragonal unit cell of dimensions $a = b = 5.74 \text{ Å}$ and $c = 4.95 \text{ Å}$. The transformation $\text{IV} \rightarrow \text{II}$ involves a small distortion of the lattice, a rotation of the planes of the NO$_3$ groups by 45° and a translation of one half of the NH$_4$ groups by $c/2$. Shinnaka$^6$ also suggests that the NO$_3$ group begin to rotate around on an axis perpendicular to their own planes. The rotation is, however, not free, the ions oscillating between two almost bound orientations in opposite directions. Phase I has CsCl-type structure with a single molecule in a cubic unit cell of dimensions $a = b = c = 4.40 \text{ Å}$. The transformation into this phase again involves a small distortion of the lattice and a translation of 1/2 of the NH$_4$ group by $c/2$. The most dramatic change, however, is in the orientational freedom of the NO$_3$ group. The x-ray studies of Hendricks, et al.,$^7$ suggest that in this phase the nitrate group is nearly freely rotating. It should be pointed out, however, that the x-ray data only measure the average symmetry of the lattice and cannot distinguish between
a model where the nitrate groups have fixed but random orientations and one where the NO$_3$ groups are randomly reorienting.

These structural changes can be sensitively probed by studying the Raman active lattice modes of this crystal in its various phases. These modes which involve motions of the molecules as a whole rather than relative motions of the atoms within a molecule can be conveniently divided into librations (rotations of the molecules) and translations. In general, the lattice eigenmodes can involve coupled rotational-translational motion. The symmetry and Raman activity of the $k = 0$ lattice modes can be determined from the space group of the crystal using the factor group analyses of Bhagavantam and Venkatarayudu.$^{20}$ For phase IV this analysis yields $2A_{1g} + 2B_{3g} + 2B_{2g}$ Raman active translational modes and $1B_{1g} + 1B_{2g} + 1B_{3g}$ Raman active librational modes. The libration of $B_{1g}$ and $B_{3g}$ character involve rotations about axis in the plane of the NO$_3$ group while the $B_{2g}$ libration involves a rotation about an axis perpendicular to the plane.

The Raman spectrum between 15 and 250 cm$^{-1}$ of phase IV at 25°C is shown at the top of fig. 2. Three intense modes are observed at 171, 138 and 89 cm$^{-1}$. Because of the large anisotropy in the polarizability of the NO$_3$ molecule parallel and perpendicular to its plane we would expect the $B_{1g}$ and $B_{3g}$ librational modes to contribute intensely to the Raman Scattering. On the other hand, the contribution from the $B_{2g}$ mode should be very weak since the polarizability does not change significantly for rotations of the NO$_3$ group about an axis perpendicular to its plane. On the basis of their polarization measurements Penot, et al. $^{17}$ have unambiguously assigned
the 171 cm\(^{-1}\) mode to the B\(_{1g}\) libration. They have also argued quite convincingly that the large intensity of the 139 and 89 cm\(^{-1}\) modes which have B\(_{3g}\) character indicates that they are coupled translational librational modes with a large contribution from the B\(_{3g}\) libration.

As the temperature is raised these modes gradually shift to slightly lower frequency and do not show any soft mode behavior as the phase IV-II transition temperature is approached in .5°C increments (see fig. 2). At the phase transition these three modes disappear in a temperature interval of less than 1°C and two modes of comparable intensity appear at 120 and 60 cm\(^{-1}\) (see fig. 1). The factor group analysis of phase II yields five Raman active translational modes and three Raman active librational modes. On the basis of the intensity arguments presented for phase IV, we suggest that the two observed modes are due to librations about the two principal axes in the plane of the nitrate group. These librations, of course, could be coupled to translational modes of the proper symmetry. As the temperature is raised these modes shift to lower frequencies and show no anomalous behavior as the II-I phase transition is approached in 1°C increments.

As the sample transforms into phase I these modes disappear in a temperature interval of less than 1°C and no new modes appear. The Raman spectrum of Phase I between 20 and 250 cm\(^{-1}\) is very similar to that of the melt of NH\(_4\)NO\(_3\) (see fig. 1) and appears to consist only of Rayleigh wing scattering with the intense elastic scattering from the powdered sample superimposed upon it. This spectrum is quite consistent with a freely rotating NO\(_3\) group. However, from a physical point of view we would expect that the NO\(_3\) group has at least in the statistical sense a preferred orientation. Our spectra in
phase I show that if a librational mode exists it must have a frequency less than 20 cm\(^{-1}\). Using a classical anharmonic oscillator model for the librations of the NO\(_3\) group one can show that this implies that the angular excursions of this group from its equilibrium position due to thermal agitation are greater than ±1 radian. Our data, therefore, clearly indicates that the NO\(_3\) group has considerable freedom of orientation in phase I. It is apparent, however, that an investigation of the inelastic scattering between 0 and 20 cm\(^{-1}\) could yield a more quantitative picture.

In conclusion, we have measured the temperature dependence of the librational modes of NH\(_4\)NO\(_3\) in its various phases. Our results indicate that the NO\(_3\) group is almost freely rotating in phase I.
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References


Figure Captions

1) The structure of ammonium nitrate in phases IV, II and I from Ref. 2.

2) Low Frequency Raman modes of ammonium nitrate in phases IV, II, I and its melt.

3) Temperature dependence of the low frequency modes in phases IV and II.
Figure Captions

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Fig. 1
Fig. 2

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Fig. 3 XBL 744-677
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