

## Orientalional order-disorder of $\text{N}(\text{D},\text{H})_4^+$ in tobelite

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### ABSTRACT

Orientalional order-disorder behavior of  $\text{NH}_4^+$  is a well-established phenomenon in certain ammonium halides and ammonium salts. Anticipating similar behavior of ammonium in the interlayer site of tobelite, synthetic  $\text{ND}_4/\text{NH}_4$  tobelite has been studied by infrared spectroscopy from room temperature down to 20 K. Both  $\text{ND}_4$  and  $\text{NH}_4$  are found to occupy the interlayer site in this mica structure. The spectra show noticeable changes on cooling. Autocorrelation analysis reveals distinct changes in the line width of the central autocorrelation peak. This is attributed to the transition of the  $\text{ND}_4^+$  group from an orientationaly disordered state at higher temperatures to a relatively ordered state below a critical temperature of 140 K. The order parameter for the transition follows classical second-order behavior as a function of temperature.

### INTRODUCTION

Ammonium silicate minerals occur in reducing environments where the degradation of proteins and amino acids in algal and other organic remains such as coal provides a means of delivering copious quantities of ammonium into those minerals capable of absorbing it (Loughman et al. 1983). Smith and Lee (1982) have proposed that environments which favor the formation of natural ammonium minerals are those where the de-amination of proteins is most favorable. For example, the concentration of ammonium is apparently high within organic-rich sediments that underlie a permanent body of anoxic water. Exceptions, of course, exist (e.g., Martin et al. 1999; Leggo and Ledesert 2001), but naturally occurring ammonium-bearing minerals (feldspar, mica, illite, alunite, zeolites) are therefore found most commonly in organic-rich shales (Gulbrandsen 1974; Juster et al. 1987; Crompton et al. 1992) and are thus often used as fingerprints in oil exploration. Whereas, in nature, biotite-phlogopite (tri-octahedral micas) can contain trace amounts of  $\text{NH}_4^+$  up to around 0.1 wt%, end member  $\text{NH}_4$ -analogues of phlogopite and/or biotite have yet to be described (Harlov et al. 2001b). In contrast,  $\text{NH}_4$ -analogues of K-feldspar, i.e., buddingtonite ( $\text{NH}_4\text{AlSi}_3\text{O}_8$ ; Erd et al. 1964), and of muscovite (di-octahedral mica), i.e., tobelite [ $\text{NH}_4\text{Al}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ; Higashi 1982], are found, generally as the product of low-grade hydrothermal alteration of K-feldspar and muscovite respectively in a reducing ammonia-rich environment.

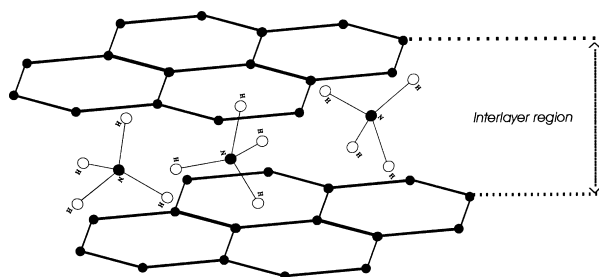
The present study concentrates principally on the dynamic behavior of the ammonium ion, as  $\text{ND}_4$ , within the mica structure (Fig. 1), specifically tobelite. The similarity between the size and charge of ammonium to those of  $\text{K}^+$ , which it usually

replaces isomorphically, has led to its classification as a “pseudo alkali ion.” Indeed, this similarity is underlined by the common isomorphism that exists between ammonium-bearing and potassium- or rubidium-bearing minerals. Detailed study, however, reveals that this superficial isomorphous relationship is limited in as far as the symmetry of the ammonium ion is concerned, especially when one takes account of its lack of spherical symmetry, i.e., the directional properties of the bonds from the ammonium ion to its surrounding coordination environment (Kearley and Oxtton 1983). Since it is similar in size to the alkali ion that it generally replaces, the ammonium ion finds itself in high co-ordination environments where only polyfurcated hydrogen bonds may be formed, if at all.

Many ammonium halides and other ammonium-bearing compounds are characterized by several solid-state phase transitions, which have been associated with rearrangements in hydrogen bonding (Kearley and Oxtton 1983). Pauling (1930) suggested the possibility of a transition from free rotation, or tumbling, of the ammonium ion to oscillatory motion on cooling. Pauling (1930) suggested that the equilibrium position is defined by a steep minimum in the potential energy and the barrier between minima in orientation space is greater than  $kT$ , then the molecule will tend to oscillate about this equilibrium. If, however, the minimum is shallow, the kinetic energy will be sufficient enough to induce non-uniform rotation. Frenkel (1935) however, has pointed out that such transformations are order-disorder transitions in the orientations. If the material undergoes an order-disorder transition, then the important energetic quantity is not the kinetic energy, but the correlated energy for ordering

A free ammonium ion has  $T_d$  point group symmetry. This may be related to four modes of internal vibration:  $\nu_1$  ( $A_1$ ): the symmetric N-H stretch;  $\nu_2$  ( $E$ ): the symmetric H-N-H deformation;  $\nu_3$  ( $T_2$ ): an anti-symmetric N-H stretch;  $\nu_4$  ( $T_2$ ): an anti-symmetric H-N-H deformation. External modes are usually

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**FIGURE 1.** A perspective view of the tobelite structure. Each tetrahedral site is represented by ( $\bullet$ ), forming two-dimensional quasi-hexagonal rings. The T-O-T sandwich is omitted for clarity. Only the interlayer region is shown, with the ammonium ion sitting within the cavities formed by two quasi-hexagonal rings. The ions are orientationally disordered.

denoted by  $\nu_5$  ( $T_2$ ): translation; and  $\nu_6$  ( $T_1$ ): rotation. Among the internal modes only  $\nu_3$  and  $\nu_4$  are infrared active though all four are Raman active.

The symmetry of the site occupied by an ion (with  $T_d$  symmetry in the case of  $\text{NH}_4^+$  or  $\text{ND}_4^+$ ) may be denoted  $S$ . Since the symmetry of the ion is  $T_d$  in the present case, the effective symmetry  $E$  is given by  $T_d \cap S$  (Oxton et al. 1976). In the present case the site symmetry of ammonium is  $C_{2v}$ , a subgroup of  $T_d$ , leading to peak splitting in infrared and Raman spectra. Information regarding the site symmetry obtained from infrared spectra is often difficult to interpret in case of  $\text{NH}_4$  and  $\text{ND}_4$  because of extensive Fermi-resonance between the stretching mode and a combination of two bending modes (Vedder 1965), both of which exist in the N-H (or N-D) stretching region. This problem has been successfully overcome by use of isotopically dilute  $\text{NH}_4\text{D}^+$  or  $\text{ND}_4\text{H}^+$  species (Oxton et al. 1976). However, if the ammonium ion is rotating, the average site symmetry is spherical. Upon orientational ordering this symmetry changes to that of the static surroundings, with a loss of degeneracy, peak splitting, as well as line narrowing. As such, infrared and Raman spectroscopy provide the possibility of acting as probes of the effective environment, and hence the degree of orientational order of the ammonium ion, even in complex natural silicates. For this reason infrared spectroscopy has been employed to investigate the orientational ordering behavior of ammonium within the mica host structure of tobelite, using low-temperature methods.

## EXPERIMENTAL PROCEDURE

### Sample preparation

$\text{ND}_4$ -tobelite was synthesized in 150 mg amounts using a stoichiometric mix of well-ground  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  powders and a 26%  $\text{ND}_3$  solution with  $\text{D}_2\text{O}$  in excess such that the amount of  $\text{ND}_4^+$  stoichiometrically available was 50% greater than needed for the actual synthesis (cf. Harlov et al. 2001a). Synthesis consisted of placing 150 mg of the dry  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  mix, an excess 5 wt% of  $\text{Al}_2\text{O}_3$ , and 100 mg of a 26%  $\text{ND}_3$  solution into a previously dried 5 mm wide, 4 cm long Au capsule with 0.2 mm thick walls. A new dry syringe was used for loading the 26%  $\text{ND}_3$  solution. Using an Ar plasma torch, the capsule

was welded shut while partially immersed in an ice water bath. The sealed capsule was then placed in a 6 mm bore, cold seal Rene' metal hydrothermal autoclave with a Ni-NiO filler rod and external thermocouple and left at 873 K and 500 MPa for seven days. This resulted in masses of euhedral to semi-euhedral flakes 1–2  $\mu\text{m}$  wide and less than 0.1  $\mu\text{m}$  thick of >99.9% pure tobelite with occasional minor corundum (Harlov et al. 2001a). The synthesis experiment was left running for only seven days to ensure minimal migration of  $\text{H}_2$  cations across the Au membrane into the Au capsule and minimal migration of  $\text{D}_2$  out in an attempt to limit contamination of the  $\text{ND}_4$ -tobelite with  $\text{H}_2$  as much as possible. Even so, IR evaluation indicates a definite tobelite component in each of the  $\text{ND}_4$ -tobelite synthesis runs (Harlov et al. 2001a).

### Infrared spectroscopy

Owing to the small size of the synthetic crystals obtainable (1–2  $\mu\text{m}$ ), powder methods were employed. Samples for IR absorption measurements were prepared by grinding 2 mg of  $\text{NH}_4^+/\text{ND}_4^+$ -tobelite and dispersing it into 600 mg of KBr. Approximately 200 mg of this homogenized mixture was then pressed into 13 mm diameter transparent pellets under vacuum, and then dried at 443 K.

The absorption spectra were recorded under vacuum using a Bruker 113v FTIR spectrometer at temperatures between 20 K and 300 K in the region of 500–5000  $\text{cm}^{-1}$ . A liquid nitrogen-cooled HgCdTe detector was coupled with a KBr beam splitter and a globar source. An instrumental resolution of 2  $\text{cm}^{-1}$  was used. A Leybold two-stage close-cycle helium cryostat with a working temperature range of 13–310 K was used for sample cooling. The sample holder was made from high thermal conductivity O-free copper. A gold-coated lattice made from O-free copper was installed at the sample position to improve the thermal contact between the sample and the sample holder. One temperature sensor, positioned near the heating unit, was used to control the temperature of the cryostat while another Si-diode temperature sensor (Lakeshore, DT-470-DI-13) calibrated by the manufacturer was glued on the center of the sample holder to measure the sample temperature. The temperature instability was found to be lower than 1 K.

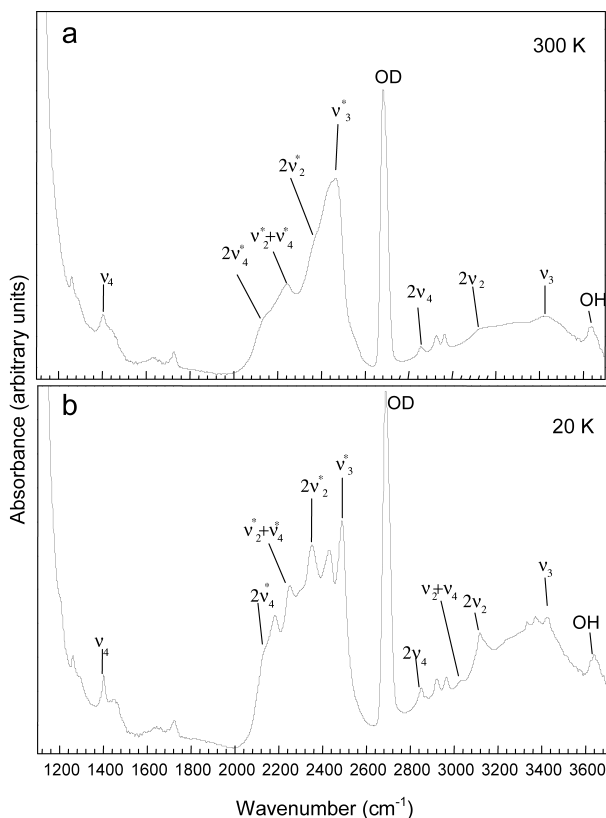
## RESULTS AND DISCUSSION

The infrared spectrum for  $\text{ND}_4$ -tobelite is shown in Figures 2a and 2b. The spectra are characterized by the presence of bands corresponding to  $\text{NH}_4$  and  $\text{ND}_4$ . These band positions are summarized in Table 1. The spectra show a system of complex overlapping bands in the region from 2000 to 2500  $\text{cm}^{-1}$  and from 2800 to 3500  $\text{cm}^{-1}$ , which are attributable to  $\text{ND}_4^+$  and  $\text{NH}_4^+$ , respectively. At 300 K, all the modes present can be assigned to those of a free molecule of  $\text{NH}_4^+$  and  $\text{ND}_4^+$ , whereas at 20 K additional peaks are found. There is a distinct peak at around 1402  $\text{cm}^{-1}$  ( $\nu_4$ ) and a system of overlapping bands from 2800 to 3600  $\text{cm}^{-1}$ , which are assigned to different combination modes of  $\text{NH}_4$  ( $2\nu_4 = 2855 \text{ cm}^{-1}$  and  $2\nu_2 = 3129 \text{ cm}^{-1}$ ). The  $\nu_4^*$  for  $\text{ND}_4$  is obscured by extremely strong Si-O stretching modes. The combination modes are represented by a system of complex bands from 2000 to 2600  $\text{cm}^{-1}$  ( $2\nu_3^* = 2131 \text{ cm}^{-1}$ ,  $\nu_2^* + \nu_3^* = 2246 \text{ cm}^{-1}$ ,  $2\nu_3^* = 2389 \text{ cm}^{-1}$ ). The presence of hydrogen

**TABLE 1.** Band assignment for vibrational modes with respect to the centers in  $\text{cm}^{-1}$  and relative intensities (*I*)

$\nu$ ( $\text{cm}^{-1}$ )	$\text{NH}_4^+$	$\text{NH}_4\text{Cl}$	N-H $\nu$ $\text{ND}_4$ -tobelite (300K)	N-H $\nu$ $\text{ND}_4$ -tobelite (20K)	N-D $\nu$ $\text{ND}_4$ -tobelite (300 K)	N-D $\nu$ $\text{ND}_4$ -tobelite (20 K)
	Center	Center	Center ( <i>I</i> )	Center ( <i>I</i> )	Center ( <i>I</i> )	Center ( <i>I</i> )
$\nu_4$	1400	1400	1402(w) 1428 (sh)	1399 (w) 1429 (sh)	x x	x x
$2\nu_4$		2810	2855(w)	2849(w)	2131(w)	2123 (w)
$\nu_2 + \nu_4$		3015		3027 (w)	2246 (m)	2249 (m)
$2\nu_2$		x	3129 (w)	3115 (w)	2389 (m)	2294 (m)
$\nu_3$	3145	3140	x x 3423 (w)	3334 (w) 3373 (w) 3434 (w)	2359 (s) 2431 (sh) 2492 (s)	2353 (s) 2433 (sh) 2481 (s)
$\nu_{\text{OH}}$			3640 (w)	3641 (w)		
$\nu_{\text{OD}}$					2681 (s)	2686 (s)

Note: The values for  $\text{NH}_4^+$  and  $\text{NH}_4\text{Cl}$  are from Harlov et al. (2001a); s = strong, sh = shoulder, m = medium, w = weak, x = not observed.



**FIGURE 2.** The IR spectrum of  $\text{ND}_4$ -tobelite at 300 K (a) and 20 K (b). Absorption bands due to  $\text{ND}_4^+$  are marked by asterisks. Bands due to  $\text{NH}_4^+$  are observed between  $2800 \text{ cm}^{-1}$  and  $3600 \text{ cm}^{-1}$  as well as at  $1400 \text{ cm}^{-1}$ . Normal modes for  $\text{NH}_4^+$  and  $\text{ND}_4^+$  are assigned on the basis of  $T_d$  symmetry. The corresponding deformation mode for  $\text{ND}_4^+$  ( $\nu_4$ ), which should occur at around  $1080 \text{ cm}^{-1}$ , is obscured by strong Si-O stretching modes. The presence of a protonated component is due to  $\text{H}_2$  transfer through the Au capsule membrane during synthesis as well as possible contamination from atmospheric  $\text{H}_2\text{O}$ . The relative intensity of the OH and OD peaks indicates the ratio of the two components.

bonding between the  $\text{ND}_4/\text{NH}_4$  and the surrounding O atoms (if any) may be estimated by comparison with other ammonium salts such as  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ , which generally have very weak N-H-X bonds giving an N-H stretching frequency of around  $3300 \text{ cm}^{-1}$ . The frequency  $\nu_4$  generally shifts to higher

energies upon the formation of hydrogen bonds (Plumb and Horing 1950). In tobelite it is around  $3334 \text{ cm}^{-1}$  (Fig. 2) suggesting potentially very weak hydrogen bonding between  $\text{ND}_4/\text{NH}_4$  and surrounding O atoms. The OH vector in di-octahedral layer silicates is inclined with respect to the (010) plane, and can be studied by spectroscopic methods (Vedder and McDonald 1963) and also by neutron diffraction methods (Rothbauer 1971; Pavese et al. 1999, 2000; Mookherjee et al. 2001). This inclination means that the OH vector can point toward two out of the six surrounding tetrahedral apical O atoms, with two possible configurations arising with respect to the cation occupying the tetrahedral site. The force field for the OH vector inclined toward these apical O atoms may be modified depending on whether both sites are occupied by Si (analogous to pyrophyllite), which gives a resulting OH stretching frequency of around  $3675 \text{ cm}^{-1}$ , or one tetrahedron is occupied by Si and the other by Al (analogous to margarite), resulting in an OH frequency of around  $3636 \text{ cm}^{-1}$  (Harlov et al. 2001a). The observed OH stretching frequency in the present synthetic tobelite is around  $3640 \text{ cm}^{-1}$  indicating one Si and one Al in the neighboring tetrahedra. At 300 K the isotopic relationship between the ammonium and deuterated ammonium molecules for the triply degenerate state is  $\nu_3\text{D}/\nu_3\text{H} = 0.728$ . This value is within the usual range of agreement for the isotopic relationship given by the harmonic approximation, i.e., 0.7303 (Wagner and Hornig 1950) and 0.7305 (Harlov et al. 2001a). The corresponding experimental ratio between the hydroxyl and deuterioxyl group absorption frequency is  $\nu_{\text{OD}}/\nu_{\text{OH}} = 0.7365$ . This is also in good agreement with the value of 0.7276 given by the harmonic approximation (Harlov et al. 2001a). All these frequency ratios serve to validate our band assignments.

The temperature evolution of the IR spectra of  $\text{ND}_4^+$ -tobelite between 2000 and  $2600 \text{ cm}^{-1}$  is shown in Figure 3. The mode  $\nu_3$  shows the greatest change in frequency with temperature compared to the other modes present in the complex band. Almost all the peaks become sharper (decrease in full width at half maximum) as the sample cools from 300 K to 20 K. This behavior provides the first indication of possible ordering. The autocorrelation analysis method was employed to analyze the temperature dependence of these spectra from 20 to 300 K.

#### Autocorrelation analysis

The autocorrelation method is a sensitive analytical tool for investigating the subtle effects of phase transitions and solid

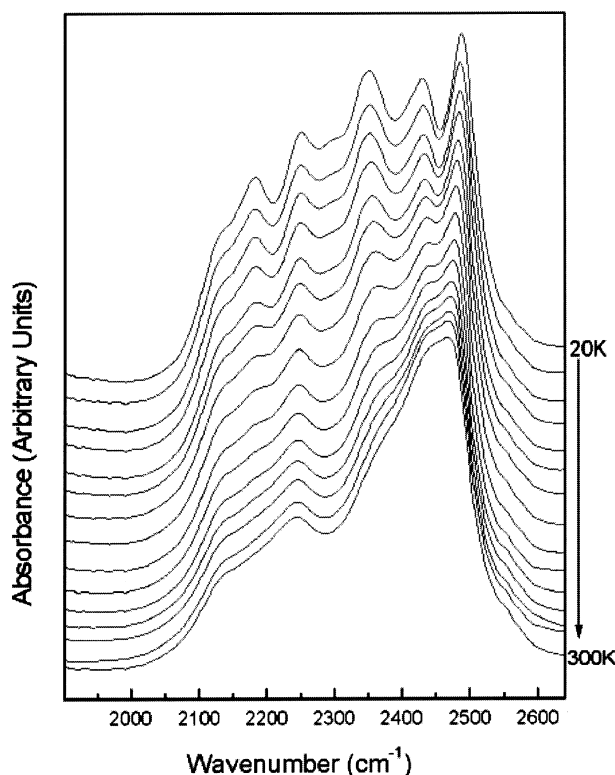


FIGURE 3. The thermal evolution of the  $\text{ND}_4^+$  peak between 20 K and room temperature. The width of each individual peak decreases with cooling.

solutions as seen in hard-mode spectroscopy. Its application in mineralogy is discussed by Salje et al. (2000), Ballaran et al. (2001), and Carpenter and Ballaran (2001). The principal idea is that if there is some kind of change in the crystal structure (such as a local strain heterogeneity due to cation substitution, or due to an orientational order-disorder or other type of phase transition) the resultant phonon absorption spectrum, which is made up of many absorption bands with different frequencies from phonons from different regions, will change. The method of autocorrelation is ideally employed for frequency intervals which contain only one phonon signal. However in most cases there are overlapping peaks in the infrared spectrum of a low symmetry large-unit cell mineral, hence this method can be extended to large spectral intervals provided the integration extends over a frequency region which is sufficiently wider than the typical width of any individual phonon signal. The primary spectrum is separated into segments, in such a way that the end points of each of the segments lie on a common base line. Each segment is correlated with itself, using the function

$$\text{Corr}(\alpha, \omega') = \int_{-\infty}^{+\infty} \alpha(\omega' + \omega) \alpha(\omega) d\omega \quad (1)$$

where,  $\alpha(\omega)$  is the IR spectrum and  $\alpha(\omega' + \omega)$  is the same spectrum offset in wavenumber by  $\omega'$ . The width of the central peak of the resulting  $\text{Corr}(\alpha, \omega')$  is the weighted average of the widths of the individual peaks and scales with the order parameter. In

general this provides a useful tool to determine the relative changes of the order parameter with respect to  $P$ ,  $T$ , chemical composition, or time. A Gaussian function of the form

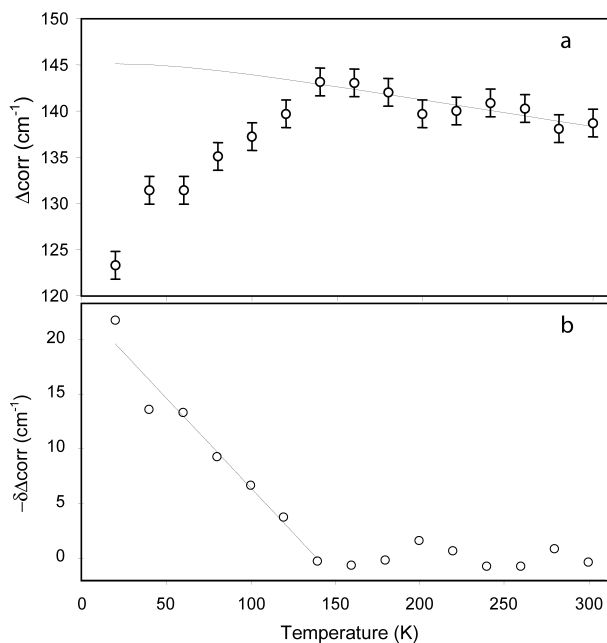
$$G = k_0 \exp\left[-\frac{(x - k_1)^2}{k_2}\right] \quad (2)$$

may be used to fit the central part of the  $\text{Corr}(\alpha, \omega')$ . Here, the coefficient  $k_2$  is related to the width  $\Gamma$  of the Gaussian peak by  $\Gamma = 2.354 \cdot k_2 / \sqrt{2}$ .

Fitting is carried out over progressively smaller limiting values of the offset,  $\pm\omega'$ , and the most reliable measure of changes in line width is given by extrapolation to zero offset ( $\pm\omega' = 0$ ). The resulting broadening parameter is usually referred to as  $\Delta\text{Corr}_\omega$  (with the symbol  $\omega$  as a label for the range of wave numbers used for autocorrelation analysis). This procedure was adopted for the region of our spectra between 2620  $\text{cm}^{-1}$  and 2000  $\text{cm}^{-1}$ . The resulting plot of  $\Delta\text{Corr}_{2620}$  for the  $\text{ND}_4^+$  group is shown in Figure 4a. Data scatter indicate an estimated standard deviation of around 1.5  $\text{cm}^{-1}$  in the determination of  $\Delta\text{Corr}$ . A change is observed in the effective characteristic line width of the band at around 140 K. This change is attributed to a transition of the ammonium ion, which undergoes free-rotation above this transition temperature, to hindered rotation or oscillation below this temperature. The increase in the effective absorption width on heating is similar to that expected for an order-disorder type transition. The ordered low-temperature phase displays a narrower effective line width and, upon disordering, the modes associated with the ammonium ion increase in width due to the effective entropy increase of the structure. The important quantity at a phase transition is the excess property. In this case, this is the excess line width associated with ordering, which is negative. This has been analyzed in terms of  $\delta\Delta\text{Corr}$ , which is the difference between the  $\Delta\text{Corr}$  values above the transition (in the paraphase) and the projected  $\Delta\text{Corr}$  values to the temperatures of the low symmetry phase assuming no transition. The saturation of the data points at around absolute zero ( $T = 0$  K) is tackled by extrapolating the  $\Delta\text{Corr}$  values above the transition temperatures by a hyperbolic cotangent function (Hayward and Salje 1998) yielding a saturation temperature around  $\sim 83$  K.  $\delta\Delta\text{Corr}$  is observed to vary linearly from a maximum at the lowest temperature of measurement (the state of assumed complete or near-complete orientational order of the ammonium ions) to 0 (the state of assumed complete disorder, i.e., free rotation of the ammonium ions) at the transition temperature and above (Fig. 4b). The quantity  $\delta\Delta\text{Corr}$  may be considered as the short-range order-parameter  $q$  for the transition. As such it is seen to scale linearly with temperature below  $T_c$ . Assuming that this order parameter scales with the square of the long-range order parameter (as is generally observed at such transitions), this implies an orientational order-disorder transition at  $T_c = 140 \pm 5$  K which is second order in thermodynamic character ( $q \propto Q^2 \propto [T_c - T]$ ).

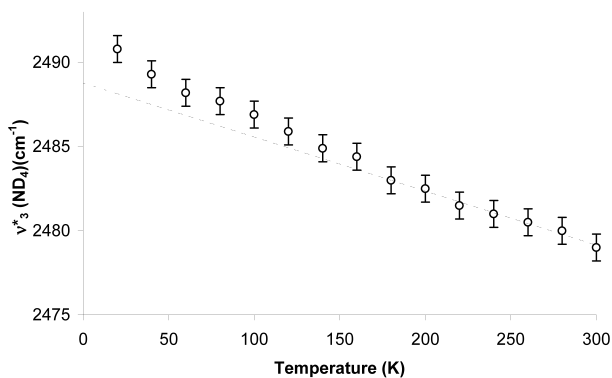
#### Peak position and integrated intensity results

The typical thermal variation of the peak position of isolated peaks, such as that of the  $\nu_3(\text{D})$  mode, is shown in Figure

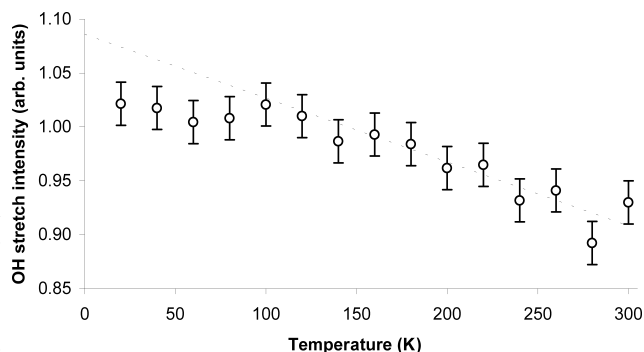


**FIGURE 4.** (a) The temperature dependence of  $\Delta Corr_{2620}$  for the  $ND_4^+$  group. There is a distinct change in the temperature-dependent trend of the  $\Delta Corr_{2620}$  values at around 140 K, which may be ascribed to the orientational order-disorder transition. The use of the hyperbolic cotangent base-line yields a saturation temperature of  $\sim 83$  K. (b) The temperature dependence of the negative excess line width,  $-\delta\Delta Corr_{2620}$ , for the  $ND_4^+$  group. The linear nature of this excess is indicative of a second-order phase transition at around 140 K.

5. This thermal evolution reflects changes in both the structure (and hence the dynamic matrix) and (for the intensities) the phonon population levels. Very weak changes in slope are found at temperatures close to those suggested by the autocorrelation analysis of the  $ND_4$  group. It is well known that the orientation of the hydroxyl and deuterioxyl group (and hence their vibrational character) is influenced by  $K^+-H^+$  interactions in an alkali mica. We anticipate that it will be similarly affected by  $NH_4^+-H^+$  interactions in tobelite. To check the effect of the orientational ordering of the ammonium ion (within the interlayer site) on the hydroxyl and deuterioxyl groups, we plotted the thermal dependence of the integrated intensities of OH stretching peaks, which indeed shows slight changes at a temperature corresponding to the ordering of ammonium ion (Fig. 6), indicating that the environment of OH vector is indeed sensitive to the orientational ordering of the  $NH_4$  ions. The plot of the temperature-dependence of the integral absorption intensity between 2761 and 3736  $cm^{-1}$  (corresponding to the  $NH_4$  complex band) also reveals a slight change around  $T_c$  (Fig. 7). These results indicate that there are changes in the force fields due to the ordering of the ammonium group and the corresponding response of the hydroxyl group, and show that the ordering processes are coupled via the lattice, revealed through the weak influence on the hydroxyl group. The freezing of the ammo-



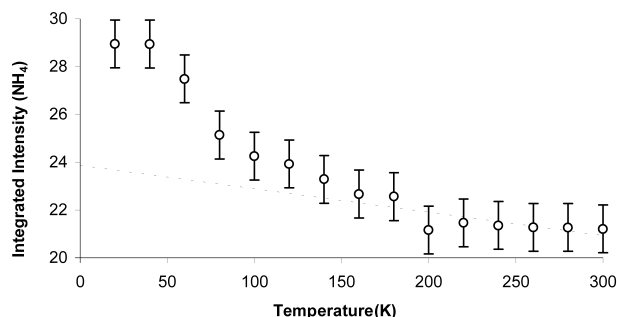
**FIGURE 5.** Temperature-dependence of  $\nu_3^*(ND_4)$ . The dashed line shows a fit to the data above 150 K.



**FIGURE 6.** Temperature-dependence of the integrated intensity of OH stretching. The dashed line shows the fit to the data above  $T_c$ , the transition temperature.

nium rotation on cooling thus appears to be a correlated phenomenon, corresponding to an orientational order-disorder phase transition. The distinct change of the trend in  $\Delta Corr$  at 140 K is attributed to the orientational order-disorder behavior of the  $ND_4$  ions. In addition, the peak position, integral intensity and correlation among various infrared bands also show distinct changes around  $T_c$ . The change in effective line width at a transition temperature of  $T_c = 140$  K can be understood in terms of a short-range order parameter with second-order behavior.

The transition of orientationally disordered to an ordered state of the ammonium ion in tobelite is very similar to that observed in synthetic ammonium phlogopite (Mookherjee et al. 2000). However, there are some slight differences, which can be ascribed to the differences in the character of the interlayer region. The OD vectors in di-octahedral layer silicates are inclined with respect to the [001] direction, whereas in tri-octahedral layer silicates they are parallel to the [001]\* direction, thus creating quite different force fields in the interlayer region. However, both the transition for synthetic tobelite and that for ammonium phlogopite are grossly similar, when compared to the orientational ordering of ammonium in the framework silicate  $ND_4$ -buddingtonite. Here the ammonium ion is caged within much tighter eightfold-coordinated M-site and shows a transition around 245 K (Mookherjee and Redfern 2001).



**FIGURE 7.** Temperature-dependence of the integrated intensity of the  $\text{NH}_4^+$  region. The dashed line shows the fit to the data from 150 K upward.

### ACKNOWLEDGMENTS

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### REFERENCES CITED

- Ballaran, T.B., Carpenter, M.A., and Ross, N.L. (2001) Infrared powder-absorption spectroscopy of Ca-free  $\text{P2}_1/\text{c}$  clinopyroxenes. *Mineralogical Magazine*, 65, 339–350.
- Carpenter, M. and Ballaran, T. B. (2001) The influence of elastic heterogeneities in silicate solid solutions. Solid solutions and silicate and oxide systems. C.A. Geiger, Ed., *EMU Notes in Mineralogy*, 3, 155–178. Eotvos University Press, Budapest.
- Crompton, J.S., Williams, L.B., and Ferrell, R.E. (1992) Mineralisation of organogenic ammonium in the Monterey formation, Santa Maria and San Joaquin basins, California, U.S.A. *Geochimica et Cosmochimica Acta*, 56, 1979–1991.
- Erd, R.C., White, D.E., Fahey, J.J., and Lee, D.E. (1964) Buddingtonite: an ammonium feldspar with zeolitic water. *American Mineralogist*, 49, 831–850.
- Frenkel, V.J. (1935) Über die Derhung von Dipolmolekulen in festen Korpen. *Acta Physicochimica U.R.S.S.*, 3, 23–36.
- Gulbrandsen, R.A. (1974) Buddingtonite, ammonium feldspar, in the Phosphoria Formation, southeastern Idaho. U.S. Geological Survey Journal of Research, 2, 693–697.
- Harlov, D.E., Andrut, M., and Peter, B. (2001a) Characterization of tobelite  $(\text{NH}_4)(\text{Al}_2)[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$  and  $\text{ND}_4$ -tobelite  $(\text{ND}_4)(\text{Al}_2)[\text{AlSi}_3\text{O}_{10}](\text{OD})_2$  using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, 28, 268–276.
- (2001b) Characterization of phlogopite  $(\text{NH}_4)(\text{Mg}_3)[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$  and  $\text{ND}_4$ -phlogopite  $(\text{NH}_4)(\text{Mg}_3)[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$  using IR spectroscopy and Rietveld refinement of XRD spectra. *Physics and Chemistry of Minerals*, 28, 77–866.
- Hayward, S.A. and Salje, E.K.H. (1998) Low-temperature phase transition: nonlinearities due to quantum mechanical saturation of order parameter. *Journal of Physics: Condensed Matter*, 10, 1421–1430.
- Higashi, S. (1982) Tobelite, a new ammonium dioctahedral mica. *Mineralogical Journal*, 113, 138–146.
- Juster, T.C., Browns, P.E., and Bailey, S.W. (1987)  $\text{NH}_4$ -bearing illite in very low-grade metamorphic rocks associated with coal, northeastern Pennsylvania. *American Mineralogist*, 72, 555–565.
- Kearley, G.J. and Oxtton, L.A. (1983) Recent advances in the vibrational spectroscopy of ammonium ion in crystal. In R.J.H. Clark and R.E. Hester, Eds., *Advances in Infrared and Raman Spectroscopy*, 10, p. 111–143, John Wiley and Sons, New York.
- Leggo, P.J. and Ledesert, B. (2001) Use of organo-zeolitic fertilizer to sustain plant growth and stabilize metallurgical and mine-waste sites. *Mineralogical Magazine*, 65, 563–570.
- Loughman, F.C., Roberts, F.I., and Lindner, A.W. (1983) Buddingtonite ( $\text{NH}_4$ -feldspar) in Condor oilshale deposit, Queensland, Australia. *Mineralogical Magazine*, 47, 327–334.
- Martin, R., Rodgers, K.A., and Browne, P.R.L. (1999) The nature and significance of sulphate-rich, aluminous efflorescences from the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand. *Mineralogical Magazine*, 63, 413–419.
- Mookherjee, M. and Redfern, S.A.T. (2001) Orientational order-disorder phase transition in buddingtonite  $(\text{NH}_4\text{AlSi}_3\text{O}_8)$ . *EOS*, 82, V51A-0987.
- Mookherjee, M., Redfern, S.A.T., Zhang, M., Harlov, D. (2000) Orientational ordering of  $\text{ND}_4^+$  in synthetic  $\text{ND}_4$ -phlogopite: an in situ low temperature X-ray diffraction and FTIR study. *Advances in Micras (Problems, Methods, Application in Geodynamics)*, 2-3 November 2000, 217–220. Academia Nazionale dei Lincei, Rome.
- Mookherjee, M., Redfern, S.A.T., and Zhang, M. (2001) Thermal response of structure and hydroxyl ion of phengite  $2\text{M}_1$ : an in situ neutron diffraction and FTIR study. *European Journal of Mineralogy*, 13, 545–555.
- Oxtton, I.A., Knop, O., and Falk, M. (1976) Determination of the symmetry of ammonium ion in crystal from the infrared spectra of the isotopically dilute  $\text{NH}_4\text{D}^+$  species. *Journal of Physical Chemistry*, 80, 1212–1217.
- Pauling, L. (1930) Rotational motion of molecules in crystals. *Physical Review*, 36, 430–443.
- Pavese, A., Ferraris, G., Pischedda, V., and Ibberson, R. (1999) Tetrahedral order in phengite  $2\text{M}$ , upon heating, from powder neutron diffraction, and thermodynamic consequences. *European Journal of Mineralogy*, 11, 309–320.
- Pavese, A., Ferraris, G., Pischedda, V., and Radaelli, P. (2000) Further study of the cation ordering in phengite  $3\text{T}$  by neutron powder diffraction. *Mineralogical Magazine*, 64, 11–18.
- Plumb, R.C. and Hornig, D.F. (1950) Infrared spectrum, X-ray diffraction pattern, and structure of ammonium fluoride. *Journal of Chemical Physics*, 23, 947–953.
- Rothbauer, R. (1971) Study of  $2\text{M}_1$ -muscovite by neutron diffraction. *Neues Jahrbuch für Mineralogie Monatshefte*, 4, 143–159.
- Salje, E.K.H., Carpenter, M.A., Malcherek, T., and Ballaran, T.B. (2000) Autocorrelation analysis of infrared spectra from minerals. *European Journal of Mineralogy*, 12, 503–519.
- Smith, J.W. and Lee, K.K. (1982) 15th Oil and Shale Symposium. Proceedings. Golden, Colorado, 101–14.
- Wagner, E.L. and Horing, D.F. (1950) The vibrational spectra of molecules and complex ion in crystal III. Ammonium chloride and deuterio-ammonium chloride. *Journal of Chemical Physics*, 18, 296–304.
- Vedder, W. (1965) Ammonium in muscovite. *Geochimica et Cosmochimica Acta*, 29, 221–228.
- Vedder, W. and McDonald, R.S. (1963) Vibrations of  $\text{OH}^-$  ions in muscovite. *Journal of Chemical Physics*, 38, 1583–1590.

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