

Orientalional order-disorder of $\text{ND}_4^+/\text{NH}_4^+$ in synthetic ND_4/NH_4 -phlogopite: a low-temperature infrared study

MAINAK MOOKHERJEE^{1*}, SIMON A. T. REDFERN^{1,2}, MING ZHANG¹ and DANIEL E. HARLOV³

¹ Mineral Physics Group, Department of Earth Sciences, University of Cambridge,
Downing Street, Cambridge, CB2 3EQ, UK

* Corresponding author, e-mail: mm329@cam.ac.uk

² Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

³ GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

Abstract: The dynamic behaviour of the ammonium ion in synthetic ND_4/NH_4 -phlogopite has been studied as a function of temperature by infrared spectroscopy, from room temperature to 20 K. Ammonium occupies the interlayer site in phlogopite. Orientalional order-disorder of NH_4^+ is a well-established phenomenon in ammonium chloride (NH_4Cl) and other ammonium halides and ammonium salts. Although ammonium chloride has higher symmetry than ND_4/NH_4 -phlogopite, we anticipate similar dynamic behaviour of ammonium in the interlayer site of the phlogopite structure. Infrared spectra show noticeable changes on cooling. Using the autocorrelation analysis method we find distinct changes in the line width of the Gaussian profile fitted to the central autocorrelation peak. This is attributed to a transition of the ND_4^+ group, which is orientationaly disordered at higher temperatures and becomes relatively ordered at temperatures below the transition temperature of around 130 K. The order parameter for the transition appears to follow classical second-order behaviour as a function of temperature.

Key-words: ND_4 -phlogopite, ammonium, mica, orientational disorder, low-temperature FTIR, phase transition, autocorrelation analysis.

Introduction

Spectroscopic study of ammonium chloride and its variation with temperature has been of interest to the solid-state community from two points of view. First, it is well known that crystalline NH_4Cl displays a λ -type transition at 242 K in the vicinity of which various of its physical properties exhibit anomalous behaviour. Pauling (1930) suggested that the NH_4^+ ion is capable of free rotation above the transition temperature (T_c) and this changes to oscillation below T_c . The observed changes in ammonium chloride are just those expected to accompany the transition from rotation to oscillation of the NH_4^+ ion. On the other hand, Frenkel (1935) favoured the view that the NH_4^+ ion executed only torsional oscillations both above and below T_c .

Secondly, ammonium chloride crystallises in the cubic system, with a structure similar to that of caesium chloride below 450 K. Caesium chloride has six vibrational modes, none of which are active in light scattering. The same is to be expected for crystalline ammonium chloride if the NH_4^+ ion is freely rotating and thus is spherically symmetric. If, however, this is not the case (because of the specific orientation of the tetrahedral NH_4^+ ion in the lattice) some of the modes of oscillation in which the ion moves as a unit may

become active in light scattering. This has been observed previously in several Raman spectroscopic studies of ammonium chloride (Krishnan, 1947).

More recently, a series of studies of various ammonium salts have been undertaken using quasi-elastic neutron scattering to elucidate the dynamics of ammonium within them. Various models have been proposed for the rotational diffusion of H in the NH_4^+ molecule. Springer (1993) measured the elastic scattering intensity for different directions of the scattering vector (\mathbf{Q}). He interpreted his results in terms of two types of rotational jumps. One corresponds to 90° rotation about axes parallel to the inverse tetrads of the tetrahedral molecule, which switches the orientation of the NH_4^+ -group. The other corresponds to 120° rotation about axes parallel to the triads (the N-H vector), this is equivalent to the identity operation, interchanging only the H-positions but leaving the orientation of the entire molecule unaltered.

In the present study, we are interested in the behaviour of NH_4^+ or ND_4^+ in the interlayer region of the trioctahedral mica phlogopite. This mineral, with lower symmetry, poses a greater challenge than the higher-symmetry ammonium salts previously investigated. Here, we concentrate principally on the dynamic behaviour of the ammonium ion, as ND_4^+ , within the interlayer region. Although NH_4^+ or ND_4^+

is a simple polyatomic cation, it is of great interest by virtue of its unusual properties in the solid state. The similarity between its size and charge to that of K^+ , which it often replaces isomorphically, has led to its classification as a "pseudo alkali ion". Such ammonium-substituted minerals are found in a wide variety of crustal environments, and have recently been suggested as possible soil enhancers in mine-waste remediation activities (Leggo & Ledesert, 2001). It has been suggested that they may form an important part of the Martian regolith (Mancinelli, 1996), explaining the present day low nitrogen content of the Martian atmosphere.

The similarity between the alkali ion and ammonium ion is underlined by the common isomorphism that exists between NH_4 -bearing and K- or Rb-bearing minerals (*e.g.* the existence of a solid solution between muscovite and tobelite above 350 °C in very low-grade metapelites associated with coal (Juster *et al.*, 1987)). Detailed study, however, reveals that this superficial isomorphous relationship is limited in as far as the symmetry of the NH_4^+ ion is concerned, especially when one takes into account its lack of spherical symmetry and the directional properties of the bonds from the NH_4^+ ion to its surrounding co-ordination environment (Kearley & Oxtun, 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 characterised by several solid-state phase transitions, which have been associated with rearrangements in hydrogen bonding (Kearley & Oxtun, 1983).

Historically, these sorts of transitions have been considered in two ways. Pauling (1930) expressed orientational ordering of a tetrahedral molecule, such as the NH_4^+ ion, in terms of the orientation-dependent potential energy. If the barrier between orientations is greater than kT , the molecule will oscillate about the equilibrium position. If, however, the barrier is lower than kT , the thermal energy will be sufficient to induce non-uniform rotation. Frenkel (1935) however, initially developed a parallel theory by considering molecular dipoles in gas under the influence of an electric field. The field will be sufficient to orient those molecules possessing lower energies, whereas those with higher energies will remain unaffected by the field. Extending this to crystals, he added that each molecular dipole will no longer be free and will experience a field due to its neighbouring dipoles. Hence the effective field experienced will be different, which will prevent full rotation (contrary to Pauling's suggestion). He 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. However, the idea remains similar.

Experimental procedure

Sample preparation

ND_4^+ -phlogopite was synthesised in 150 mg amounts using a stoichiometric mix of well-ground Al_2O_3 and SiO_2 powders and a 26 % ND_3 solution in D_2O in excess such that the amount of ND_4^+ stoichiometrically available was 50 %

greater than needed for the actual synthesis (*cf.* Harlov *et al.*, 2001). Synthesis consisted of placing 150 mg of the dry SiO_2 - Al_2O_3 mix, an excess 5 wt % of Al_2O_3 and 100 mg of a 26 % 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 % 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 μm wide and less than 0.1 μm thick of > 99.9 % pure NH_4 -phlogopite with occasional minor corundum (Harlov *et al.*, 2001). The synthesis run was left up for only seven days in order to ensure minimal migration of H_2 cations across the Au membrane into the Au capsule and minimal migration of D_2 out in an attempt to limit contamination of the ND_4 -phlogopite with H_2 as much as possible. Even so, IR evaluation indicates a NH_4 -mica component in each of the ND_4 -phlogopite synthesis runs (Harlov *et al.*, 2001).

Infrared analysis

Owing to small size of the synthetic crystals obtainable (1–2 μm), powder methods have been employed rather than single-crystal measurements. Samples for IR absorption measurements were prepared by grinding 2 mg of NH_4^+/ND_4^+ mica and dispersing it into 600 mg of KBr. Approximately 200 mg of this homogenised mixture was then pressed into 13 mm diameter transparent pellets under vacuum, and then dried at 443 K. No recognisable difference was observed was seen between the IR spectrum of powdered sample taken using IR microscope as compared to a sample dispersed in a prepared KBr pellet (Harlov *et al.*, 2001), suggesting that matrix effects resulting from the use of KBr are not significant to our results. The absorption spectra were recorded under vacuum using a Bruker 113v FT-IR spectrometer at temperatures between 20 K and 300 K in the region of 500–5000 cm^{-1} using a liquid-nitrogen-cooled HgCdTe detector, a KBr beam splitter, and a globar source. An instrumental resolution of 2 cm^{-1} was used. A Leybold two-stage close-cycle helium cryostat with working temperature range of 13–310 K was used for sample cooling. The sample holder was made from high thermal conductivity oxygen-free copper. A gold-coated lattice made from oxygen-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 less than 1 K.

Results and discussion

From the point of view of symmetry, a free ND_4^+/NH_4^+ ion has T_d point group. This gives nine normal modes of internal

Table 1. Effective symmetries of NH₄⁺/ND₄⁺, NH₃D⁺/ND₃H⁺ and NH₂D₂⁺ ions in crystal sites of symmetry “S” (modified from Oxton *et al.*, 1975).

polytype	S	NH ₄ /ND ₄	NH ₃ D/ND ₃ H	NH ₂ D ₂
	T _d	T _d	C _{3v}	C _{2v}
1M	C _{2h}	C ₂	C _i (2), C _i (2)	C ₂
2M ₁	C ₂	C ₂	C _i (2), C _i (2)	C ₂

 Table 2. Normal modes of ND₄/NH₄ ion in different symmetry environments.

Symmetry	v ₁	v ₂	v ₃	v ₄
T _d	A ₁	E	T ₂	T ₂
C ₂	A	2A	A + 2B	A + 2B

vibration: v₁ (A₁), the symmetric N-H stretch; 2v₂ (E), the symmetric H-N-H deformation; 3v₃ (T₂), an anti-symmetric N-H stretch; and 3v₄ (T₂), an anti-symmetric H-N-H deformation. External modes are usually denoted by v₅ (T₂), translation; and v₆ (T₁), rotation. Using selection rules, among the internal modes only v₃ and v₄ are infrared active, although all four are Raman active.

If the symmetry of the site occupied by an ammonium (NH₄⁺ or ND₄⁺) ion with T_d symmetry is denoted as S, the effective symmetry E is then given by T_d ∩ S as outlined in Oxton *et al.* (1976). In the present case, however, we are dealing with two polytypes of (ND₄/NH₄)-phlogopite, 1M (C₂/m) and 2M₁ (C₂/c) as reported by Harlov *et al.* (2001). The site symmetry of NH₄ or ND₄ within the phlogopite structure is C_{2h} (2/m) for the 1M polytype and C₂ (2) for the 2M₁ polytype. Additional complexity arises because of the presence of the isotopic species of intermediate composition such as NDH₃⁺, NH₂D₂⁺, and NHD₃⁺. These have different symmetry compared to pure NH₄⁺ or ND₄⁺ [symmetry (T_d)]: NDH₃⁺ and NHD₃⁺ are C_{3v} (3m), NH₂D₂⁺ and ND₂H₂⁺ have C_{2v} (2mm) symmetry. It follows that the effective symmetry

E' will be different in each case (Table 1). The effective symmetry for the NH₄⁺ and ND₄⁺ ion turns out to be C₂, whether it sits on C_{2h} (2/m) or C₂ (2). This is subgroup of T_d, and leads to predictable extra peak splitting (Table 2) in infrared and Raman spectra (*e.g.* Nakamoto, 1986; Cotton, 1971). Similar splitting can be determined for the other isotopic species. Information obtained from infrared spectra regarding the site symmetry is often difficult to interpret in case of NH₄ and ND₄ because of extensive Fermi-resonance between the stretching mode and a combination of two bending modes (Vedder, 1965; Bastoul *et al.*, 1993), both of which exist in the N-H (or N-D) stretching region.

In a series of studies, Oxton *et al.* (1975, 1976) investigated the spectroscopic signature of NH₄⁺ (or ND₄⁺) and isotopically dilute NH₃D⁺ (or ND₃H⁺) as a probe ion of lower symmetry, to decipher information about the site symmetry. Not only do the isotopic species have different symmetries as discussed above, they also have different moments of inertia. In the present study, we cannot accurately determine the H:D ratio. One might quantify the H:D ratio from the absorbance of the OH and OD peak, as was done for (H,D)₂O and (H,D)₂O-NaCl systems by Wyss & Falk (1970). Our spectra, however, are more complex as the relevant region is not only dominated by Fermi resonance, but also by further perturbation and coupling (as explained by Oxton *et al.*, 1975; Sherman & Smulovitch, 1970). None the less, it can be seen that if the ammonium ion undergoes free tumbling on its site, the site symmetry that it sees is effectively spherical. Upon orientational freezing the site symmetry will change to that of the static surroundings, leading to peak splitting, as well as effective line narrowing. As such, infrared and Raman spectroscopy provide sensitive probes of the effective environment, and hence the degree of orientational order of the ammonium ion, even in complex natural silicates.

The infrared spectrum for synthetic ND₄/NH₄-phlogopite is shown in Fig. 1. The spectra are characterised by the presence of bands corresponding to NH₄ and ND₄. These band positions are summarised in Table 3.

 Table 3. Band assignment for vibrational modes with respect to the centres in cm⁻¹ and relative intensities (Int).

v(cm ⁻¹)	NH ₄ ⁺	NH ₄ Cl	N-H v	N-H v	N-D v	N-D v
	Centre	Centre	ND ₄ -phlogopite (280 K)	ND ₄ -phlogopite (20 K)	ND ₄ -phlogopite (280 K)	ND ₄ -phlogopite (20 K)
			Centre (Int)	Centre (Int)	Centre (Int)	Centre (Int)
v ₄	1400	1400	1430 (w)	1400 (w) 1433 (sh)	x x	x x
2v ₄		2810	2857 (w)	2856 (w)	2144 (w)	2133 (w)
v ₂ +v ₄		3015		3024 (w)	2250 (m)	2246 (m)
2v ₂		x	3128 (w)	3122 (w)	2356 (m)	2349 (m)
v ₃	3145	3140	3304 (w)	3330 (w)	2450 (s)	2470 (s)
			x	x	2431 (s)	2413 (sh)
v _{OH}			3678 (w)	3682 (w)		
			3706 (w)	3706 (w)		
v _{OD}					2735 (s)	2737 (s)
					2711 (s)	2712 (s)

s- strong, sh- shoulder, m- medium, w- weak, x- not observed. *Note:* The values for NH₄ and NH₄Cl are from Harlov *et al.* (2001).

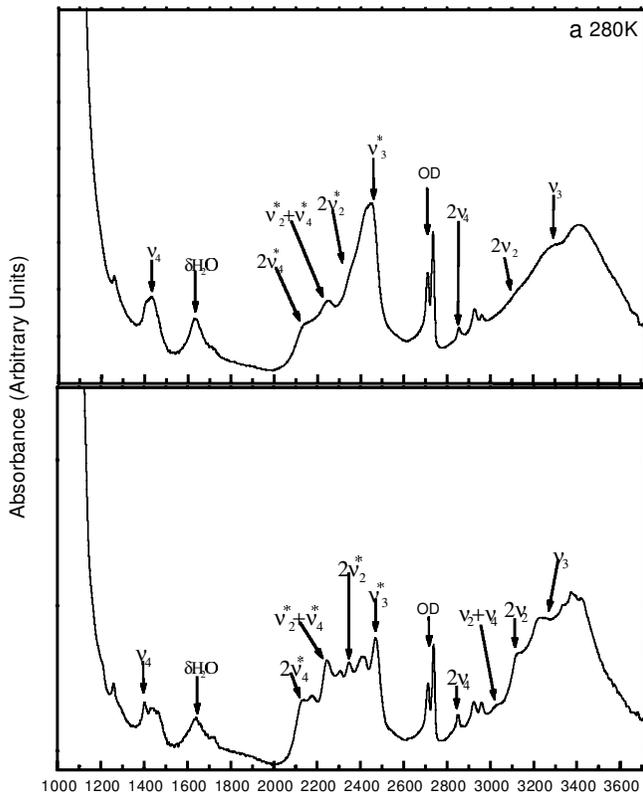


Fig. 1. The IR spectrum of ND_4 -phlogopite at 280 K (a) and 20 K (b). Absorption bands caused by ND_4^+ are denoted by asterisks. Bands due to NH_4^+ occur from 2800 cm^{-1} to 3600 cm^{-1} as well as at 1400 cm^{-1} (ν_4). The corresponding deformation mode for ND_4^+ (ν_4), which should occur at around 1080 cm^{-1} is obscured by strong Si-O stretching modes.

N-D and N-H stretching vibrations

The spectra show a system of complex overlapping bands in the region from 2000 to 2500 cm^{-1} and from 2800 to 3500 cm^{-1} , which are assigned to NH_4^+ and ND_4^+ , respectively. At 280 K, all the modes present can be assigned to NH_4^+ or ND_4^+ ions which are freely tumbling. At 20 K additional peaks are found, suggestive of a local symmetry change. These can perhaps be assigned after referring to the standard correlation tables. However, for the reasons outlined above, assignment of the bands in this region must be done carefully. The system of overlapping bands from 2800 to 3600 cm^{-1} may be assigned to combination modes of NH_4^+ ($2\nu_4 = 2857 \text{ cm}^{-1}$, overtone of the bending vibration, and $2\nu_2 = 3128 \text{ cm}^{-1}$ at 280 K). The combination modes for ND_4^+ are represented by a complex system of bands between 2000 and 2600 cm^{-1} ($2\nu_4^* = 2144 \text{ cm}^{-1}$, overtone of the bending vibration, $\nu_2^* + \nu_4^* = 2250 \text{ cm}^{-1}$, $2\nu_2^* = 2356 \text{ cm}^{-1}$ and $\nu_3^* = 2450 \text{ cm}^{-1}$ at 280 K). Since we are dealing with a system consisting of all possible isotopic species (NH_3D^+ , ND_3H^+ and NH_2D_2^+) in addition to ND_4^+ and NH_4^+ ions, we are likely to have N-D and N-H stretching modes from these species too.

In the N-D stretching complex band, ND_4/NH_4 -phlogopite spectrum shows additional unassigned resolvable bands at 2173 cm^{-1} , 2301 cm^{-1} , and one split band at 2407–2413

cm^{-1} (at 20 K) in the N-D stretching region. The intensity of the band at 2301 cm^{-1} diminishes noticeably upon heating. Oxtan *et al.* (1975) have characterised the N-D stretching modes in ammonium hexachloroplatinate (in which the site symmetry for ammonium is cubic), as a function of the percentage of D. For the probe ion NH_3D^+ , the ν_1^* (A_1) mode, which is infrared inactive in case of pure $\text{ND}_4^+/\text{NH}_4^+$, becomes IR active and lies around 2372 cm^{-1} . It is quite likely that our spectra contain similar modes. However, because of the lack of structural information, the low symmetry and structural complexity, and the inability to perform polarised studies owing to the sample size, they remain unassigned.

The presence of hydrogen bonding between the ammonium ions and the surrounding oxygen atoms (if any) may be estimated by comparison with other ammonium salts such as NH_4Cl and NH_4Br . The ammonium salts generally have very weak N-H-X bonds giving an N-H stretching frequency typically around 3300 cm^{-1} . The deformation of mode ν_4 , which can be used as a clear indicator for the formation of hydrogen bonds, generally shifts it to higher energies (Plumb & Hornig, 1950). In phlogopite the absorption frequencies are seen at around 3304 (ν_3) and 1430 cm^{-1} (ν_4) at 280 K (Fig. 1). Upon cooling, there is only a slight shift in the stretching and deformation modes, of the order of 30 cm^{-1} to higher energies. This would suggest the possibility of very weak hydrogen bonding between the ammonium ion and the surrounding oxygen atoms.

Bending vibrations

The bending modes of the $\text{NH}_{4-n}\text{D}_n^+$ species give rise to absorption in the region 1050 to 1600 cm^{-1} . However, since our sample is a silicate, many of these modes (e.g. ν_4^* for ND_4) are obscured by the extremely intense and broad Si-O stretching modes. There is a distinct peak at around 1430 cm^{-1} (ν_4) at 280 K and 1400 cm^{-1} at 20 K, which is the triply degenerate H-N-H deformation mode of the NH_4 ion. There is also an additional unassigned band with slightly higher energy than the (ν_4). The relative intensity of these two bands swaps at 280 K. At around 1240 cm^{-1} there is a distinct peak, which could be due to the deformation modes (H-N-D) of the isotopic species $\text{NH}_{4-n}\text{D}_n^+$ (Oxtan *et al.*, 1975).

OH/OD stretching region

The OH/OD vector in trioctahedral layer silicates is perpendicular to the (010) plane, and can be studied by spectroscopic methods (Vedder & McDonald, 1963). The two distinct OD peaks are found at around 2711 and 2735 cm^{-1} at 280 K and 2712 and 2737 cm^{-1} at 20 K (Fig. 2a). In the present case, the OH peaks are obscured by the large hump produced by the NH_4 ions. However, two OH peaks are seen at 3680 and 3700 cm^{-1} at 280 K and become more distinct at 20 K (Fig. 2b). The presence of two hydroxyl peaks indicates two distinct octahedral environments. Harlov *et al.* (2001) concluded that one of the OH groups in synthetic NH_4 or ND_4 -phlogopite could be assigned to a local configuration of three Mg cations in the M(1,2) triplet (Farmer, 1974) with the other one associated with a vacant site. The vacancy concentration of this site, based on the stretching frequen-

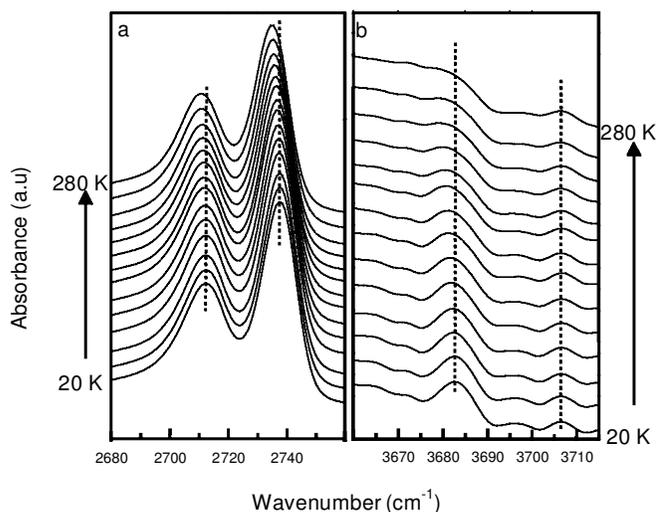


Fig. 2. Temperature-evolution of the infrared spectrum of synthetic ND₄-phlogopite in the regions *a*) 2680–2760 cm⁻¹, (corresponding to OD absorption) and *b*) 3660–3715 cm⁻¹ (corresponding to OH stretching vibrations).

cies of OH group has been calculated by Harlov *et al.* (2001) for ND₄/NH₄-phlogopite to be around 38 %. In this study, using the formula $X_{\text{vacancy}} (\%) = (3753 - 3678) / [(3753 - 3678) + 3 \times (3753 - 3706)]$ we obtain a value of 34.7 %, which is in reasonable agreement with Harlov *et al.* (2001) considering the fact that the OH peaks are obscured by the strong hump due to NH₄. At 280 K the ratio of frequencies for the ν_3 mode was found to be $\nu_3\text{D}/\nu_3\text{H} = 0.7415$. Assuming cubic symmetry, this value is within usual range of agreement for the isotopic relationship between the NH₄ and ND₄ molecules for the triply degenerate state given by the harmonic approximation, *i.e.* 0.7303 (Wagner & Hornig, 1950) and 0.7305 (Harlov *et al.*, 2001). The frequency ratios serve to validate our band assignments.

The temperature evolution of the IR spectra of ND₄⁺-phlogopite in the region from 2000 to 2600 cm⁻¹ is shown in Fig. 3. The triply degenerate stretching mode ν_3 shows the maximum change in frequency (~ 20 cm⁻¹) with temperature compared to the other modes present in the complex band. All the peaks gain in intensity as the sample cools down from 280 K to 20 K. An autocorrelation method was employed to analyse the temperature dependence of these spectra in the temperature range from 20 to 280 K.

Autocorrelation analysis

The autocorrelation method is a sensitive analytical tool for investigating the subtle effects of phase transitions and solid solutions as seen in hard-mode spectroscopy. Its application in mineralogy is discussed by Salje *et al.* (2000), Ballaran *et al.* (2001) and Carpenter & 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.

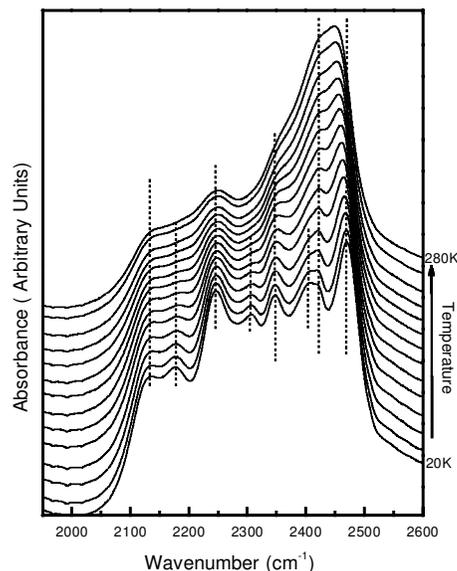


Fig. 3. The thermal evolution of the infrared spectra of synthetic ND₄-phlogopite from 2000 to 2600 cm⁻¹.

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

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

where, $\alpha(\omega)$ is the IR spectrum and $\alpha(\omega' + \omega)$ is the same spectrum offset in wave number by ω' . 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 state parameter. In general this provides a useful tool to determine the relative changes of the state parameter with respect to P , T , chemical composition or time. A Gaussian

function of the form $G = k_0 \exp\left[-\left(\frac{x - k_1}{k_2}\right)^2\right]$ may be used to fit

the central part of the $\text{Corr}(\alpha, \omega')$. Here, the coefficient k_2 is related to the width Γ , of the Gaussian peak by

$$\Gamma = \frac{2.354 \cdot k_2}{\sqrt{2}}$$

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 ΔCorr_ω (with the symbol ω as a label for the range of wave numbers used for autocorrelation analysis). This procedure has been adopted for the region of our spectra from 2600 cm⁻¹ to 2000 cm⁻¹. The resulting plot of ΔCorr_{2600} for the ND₄⁺ group is shown in Fig. 4.

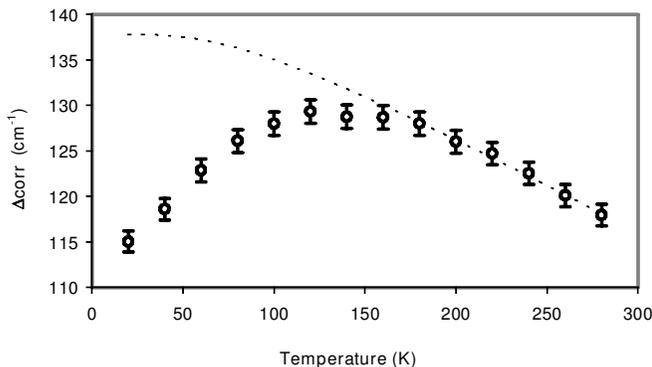


Fig. 4. Temperature dependences of ΔCorr_{2600} for the ND_4^+ absorption. There is a distinct change in the gradient of ΔCorr_{2600} at around 130 K, which may be ascribed to the orientational order-disorder transition. Note the curve fitted to the data points of the high symmetry phase is a hyperbolic cotangent, giving an estimate of the saturation temperature of around 115 K

A distinct change was observed in the effective characteristic line width of the absorption at around 130 K. This change is attributed to a transition of the ammonium ion, which changes from a fully disordered state above the transition temperature to a relatively ordered state 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 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 analysed in terms of $\delta\Delta\text{Corr}$, which is the difference between the fictive ΔCorr of the paraphase (projected to the temperatures of the low-symmetry phase) and those of the low-symmetry phase at those temperatures. The saturation of the ΔCorr just above absolute zero is tackled by fitting the paraphase data ($T > T_c$) by a hyperbolic cotangent function (Hayward & Salje, 1998) yielding a saturation temperature around 115 K. The negative excess quantity, $\delta\Delta\text{Corr}$, is observed to vary linearly from maximum magnitude at the lowest temperature of measurement (the state of assumed complete or near-complete orientational order of the ammonium ions) to zero (the state of assumed complete disorder, *i.e.* free rotation of the ammonium ions) at and above T_c (Fig. 5). 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. 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 $T_c = 130 \pm 5$ K which is second order in thermodynamic character ($q \propto Q^2 \propto [T_c - T]$).

Above T_c , ΔCorr shows a negative slope as a function of temperature. This is at variance with what one might at first expect, since it might be taken to imply decreasing line width with temperature. However, the probable explanation lies in the fact that at higher temperature some peaks within the area for which ΔCorr is computed (and whose individu-

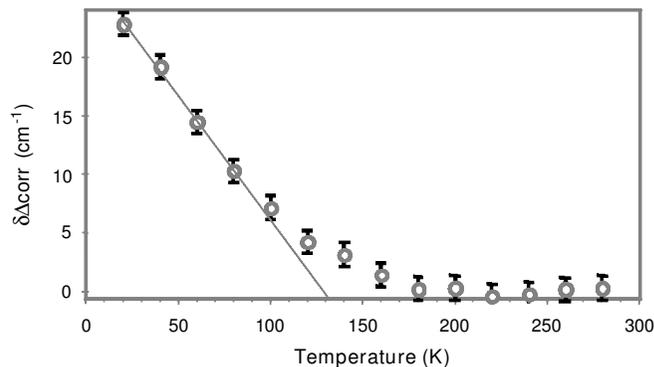


Fig. 5. The excess function, $\delta\Delta\text{Corr}_{2620}$, for the ND_4^+ absorption plotted as a function temperature.

al FWHM is not resolvable) may become absent owing to the transition to orientational disorder. Thus, although the remaining peaks can be expected to show increasing FWHM with temperature, the average may slightly decrease due to the disappearance of peaks.

It should be born in mind that the situation is likely more complicated than the results predicted by autocorrelation analysis. Although these are supported by a proven physical basis (Salje *et al.*, 2000) and scale reasonably with conventional order-parameters, the analysis does not provide a full insight of the operating dynamics. We do observe changes in relative intensities as the sample is cooled, in several instances, in the bending region at around 1430 cm^{-1} and also in the stretching region, an unidentified peak at around 2295 cm^{-1} . The causes of these observations remain unaccounted for, and await resolution with single crystal, polarised spectroscopic study aided with proper crystal structure data. We note, however, that Oxtan *et al.* (1976) demonstrated that temperature-dependent spectroscopic modifications arise simply from isotope effects in low-temperature spectra of ammonium nitrate (NH_4NO_3).

The T_c for the transition from the fully disordered state to the relatively ordered state of the ammonium ion in phlogopite (130 K) is very similar to the T_c (140 K) for the analogous transition in synthetic tobelite (a dioctahedral ammonium mica) reported by Mookherjee *et al.* (2002). However, there are some slight differences, which can be ascribed to the differences in the character of the interlayer region. The OD vectors in dioctahedral layer silicates are inclined with respect to the [001] direction, whereas in trioctahedral 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, certainly when compared to the framework silicate ND_4 -buddingtonite. Here the ammonium ion is caged within much tighter polyhedra at the feldspar M-site and shows a transition at around 245 K (Mookherjee & Redfern, 2001).

Conclusions

The low-temperature infrared study of synthetic ND_4 -phlogopite shows a distinct change in the line width of the

central peak of the autocorrelation function (fitted with a Gaussian profile) upon cooling below 130 K. This distinct change in the value of ΔCorr is attributed to the orientational order-disorder behaviour of the ND_4 ions. Assuming that the ions undergo free rotation at higher temperatures, our results indicate that there is a transition to hindered oscillation at low temperature. The change in effective line width at a transition temperature of $T_c = 130$ K is interpreted to represent a short-range order parameter with second-order behaviour. Future plans include supplementing this study with low-temperature X-ray diffraction and neutron diffraction investigations, in order to obtain a picture of the associated structural response to the dynamic disorder of the ND_4 ion above 130 K.

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