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Low-temperature behaviour of ammonium ion in buddingtonite [$N(D/H)_4AlSi_3O_8$] from neutron powder diffraction

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Abstract The structural response of buddingtonite [$N(D/H)_4AlSi_3O_8$] on cooling has been studied by neutron diffraction. Data have been collected from 280 K down to 11 K, and the crystal structure refined using the Rietveld method. Rigid-body constraints were applied to the ammonium ion to explore the structural properties of ammonium in the M-site cavities at low-temperature. Low-temperature saturation is observed for almost all the lattice parameters. From the present in situ low-temperature neutron diffraction studies, there is no strong evidence of orientational order–disorder of the ammonium ions in buddingtonite.

Keywords Ammonium · Buddingtonite · Neutron · Rigidbody

Introduction

Buddingtonite [$NH_4AlSi_3O_8$] is an ammonium-feldspar typically reported from andesitic rocks taken from ammonium-rich hot springs. It was first described by Erd et al. (1964) and Barker (1964). It is a natural analogue of K-feldspar and its near-surface formation and the enrichment of $NH_4{}^+$ in this feldspar may be the result of ion exchange between K-feldspar or possibly plagioclase and an ammonium-rich fluid under highly reducing conditions, generally at temperatures below 100 °C (~373 K). Erd et al. (1964) stated the mineral to be anhydrous above 430 °C (~703 K), otherwise it contains half a mole of structurally bound zeolitic water. Voncken et al. (1988), however, synthesized anhydrous ammonium feldspar ($NH_4AlSi_3O_8$).

The structure of buddingtonite is very similar to that of K-feldspar, except that K^+ ($r \approx 1.52$ Å) is replaced by $NH_4{}^+$ ($r \approx 1.69$ Å). Smith and Brown (1988) described buddingtonite as having a $P2_1/m$ or $P2_1$ space group, with $C2/m$ as the topochemical symmetry of the framework, corresponding to disordering of Al and Si in tetrahedral sites and a distorted M site (Fig. 1). Kimball and Megaw (1974) speculated about possible disorder of the $NH_4{}^+$ ion in buddingtonite. One possibility is that each NH_4^+ ion is in one of several orientations, at random (rather than rotating about its single ordered hydrogen bond N-H ... O). In this case, each ammonium is locked in orientation favouring the formation of additional hydrogen bonds (the positional disorder could be static and frozen in, or the NH_4^+ ions could make frequent jumps from one orientation to another under the influence of thermal fluctuations). An alternative description suggests that there is a perfectly regular alteration of $NH_4{}^+$ molecular orientations, with small domains bounded by randomly occurring faults. They concluded the structure was randomly disordered in time, or space or an average over regularly repeating sub-cells. There remains the possibility that the structure becomes ordered at low temperature.

This kind of orientational ordering was initially discussed by Pauling (1930), who 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,

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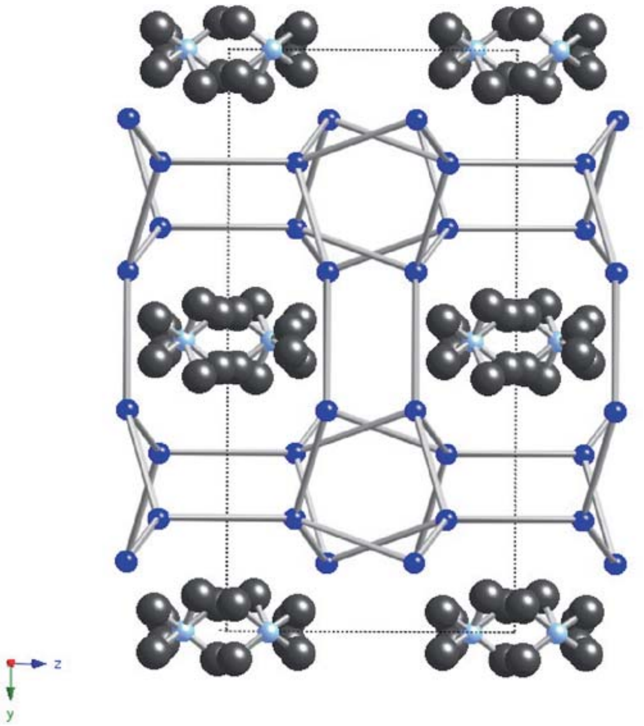

Fig. 1 Buddingtonite structure at 280 K, looking down the crankshafts. The *y* axis is perpendicular to the mirror plane in *C*2/*m*. The ammonium ions are disordered within the large M cavities. O atoms are omitted for clarity. *Black spheres* deuterium/ hydrogen atoms; *light blue spheres* nitrogen atoms; *deep blue spheres* silicon/ aluminium atoms

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 energy for correlated ordering. However, the idea remains similar.

As well as the possibility of a low-*T* orientational order–disorder transition, the introduction of the NH_4 within the feldspar structure, replacing K, can be expected to modify any *T*-dependent ferroelastic behaviour associated with transition from monoclinic to triclinic symmetry. We have therefore probed the low-temperature dependence of buddingtonite, using neutron diffraction, in order to gain insight of the behaviour of the ammonium and the response of the framework as a whole, with a view to identifying possible low-*T* phase transitions.

Experimental

Sample preparation

ND_4-buddingtonite was synthesized 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 previouslydried 5-mm-wide, 4-cm-long Au capsule with 0.2-mm-thick walls. A new dry syringe was used to load 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 an Ni–NiO filler rod and external thermocouple and left at 873 K and 500 MPa for 7 days. This resulted in masses of euhedral to semi-euhedral flakes 8–10 μm wide and less than 2 μm thick of > 99.9% pure ND_4-buddingtonite (Fig. 2) with occasional minor corundum (Harlov et al. 2001). The synthesis run was left up for only 7 days in order to ensure minimal migration of H_2 across the Au membrane into the capsule and minimal migration of D_2 out in an attempt to limit contamination of the ND_4-buddingtonite with H_2 as much as possible. Even so, IR evaluation indicates a NH_4-buddingtonite component in each of the ND_4-buddingtonite synthesis runs (Harlov et al. 2001).

Crystal structure and morphology

The structure of the feldspars is formed by tetrahedra of (Si, Al)O_4, linked to each other in three dimensions. Large cations fill the open spaces in the tetrahedral network. The crystal faces of high sanidine can be classified by the PBC (periodic bond chain) method (Woensdregt 1982). There are a limited number of PBCs i.e. uninterrupted chain of strong bonds, consisting exclusively of T(=Si, Al)–O bonds. These are parallel to $\langle 001\rangle, \langle \frac{1}{2}\frac{1}{2}0\rangle$,

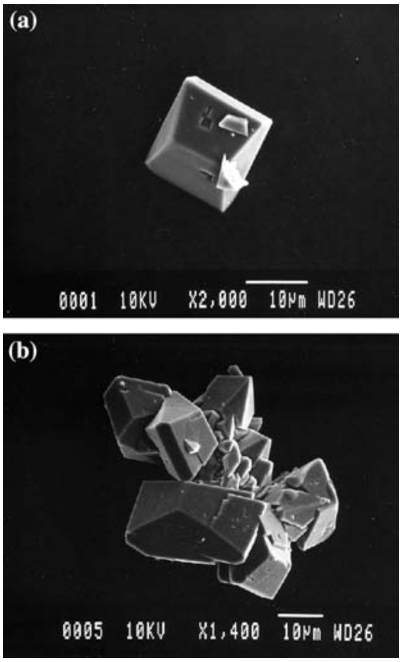

Fig. 2a, b SEM images of a single buddingtonite crystal, the *scale bar* represents 10 μm

$\langle 101\rangle, \langle 001\rangle, \langle \frac{1}{2}\frac{1}{2}1\rangle, \langle 010\rangle$ and $\langle 102\rangle$. Many other PBCs are present having both T–O and K–O bonds as strong bonds, e.g. $\langle \frac{1}{2}\frac{1}{2}1\rangle, \langle \frac{3}{2}\frac{1}{2}1\rangle, \langle \bar{1}01\rangle, \langle \frac{3}{2}\frac{1}{2}0\rangle, \langle \frac{1}{2}\frac{1}{2}2\rangle, \langle 201\rangle$ and $\langle 111\rangle$. The most important crystal faces may be classified as F_1 faces parallel to at least two PBCs having only T–O, or as F_2 faces parallel to at least two PBCs, one of which in addition has K–O bonds (Woensdregt 1982). The F_1 faces are $\{110\}$, $\{001\}$, $\{010\}$, $\{\bar{2}01\}$ and $\{\bar{1}11\}$. The F_2 faces are $\{130\}$, $\{021\}$, $\{\bar{2}21\}, \{\bar{1}12\}\{100\}$, and $\{\bar{1}01\}$. The remaining faces parallel to the various PBCs is S faces, the presence of which is induced by internal factors rather than crystal structure or by external factors such as impurities and supersaturation (Woensdregt 1982). The tiny euhedral crystals (Fig. 2), drawing analogy with the indexing of the crystal faces by Voncken et al. (1988), show the forms $\{110\}$, $\{010\}$, $\{100\}$, $\{010\}$ and $\{\bar{1}01\}$. The morphology of the synthetic ND_4-buddingtonite is similar to that of high-sanidine, indicating further that their crystal structures are strongly related.

Neutron diffraction

Our ND_4-buddingtonite sample was studied by low-temperature powder neutron diffraction at the C2 DUALSPEC diffractometer, Chalk River, Canada. C2 consists of an 800-wire BF_3 detector, which floats pneumatically over an epoxy "dance floor". Each wire has a nominal spacing of 0.1°, resulting in the ability to measure 80° 2θ simultaneously. The wavelength can be selected by altering the monochromator reflection and can be continuously varied by controlling $2\theta_m$ (the takeoff angle) of the drum. The wavelength selected for the experiments was 1.3286 Å, generated from a Si531 reflection at a $2\theta_m$ of 92.7°. The wavelength was calibrated with an external Si powder standard. The incident horizontal collimation on the monochromator was 0.6°. Data were taken over the range 10–80° 2θ counting for approximately 3 h per step. The temperature was varied in a closed-cycle He refrigerator, and measured using Si diodes. The diffraction patterns were refined by Rietveld analysis (Rietveld 1969) using the GSAS software package (Larson and Von Dreele 1986), using *C*2/*m* space group. Rigid-body constraints were invoked for the ammonium ion, which reduced the number of variables to only three rotations, three translations and one N–D bond length. Experimental details for the *C*2/*m* refinement scheme are enlisted in Table 1. In order to check whether there is a symmetry reduction at low temperature, data were also refined using *C*2 space group and we invoked the TLS tensors to study the behaviour of the ammonium rigid body. The diffraction pattern, refined with *C*2/*m* space group at 280 K, is shown in Fig. 3.

Table 1 Experimental and instrumental parameters pertaining to Rietveld refinement

Instrumental	
Diffractometer	*C*2 diffractometer, Chalk River, Canada
Wavelength	1.3288 Å
Temperature	280–20 K (20 K interval)
Refinement	
Space group	*C*2/*m*
Unit cell refinement	Whole pattern
Observations	
Refinement parameters	29
Structural	4
Profile	10
Background	4
Unit cell constraints	a) O atoms have equal U_{iso}'s and Si/Al atoms have equal U_{iso}'s. b) Al6 = Si7 (T1), Al8 = Si9(T2) c) Ammonium ion treated as rigid body, TLS tensors invoked only while refining with *C*2 space group
Thermal parameters	See Table 2
Agreement factors	See Table 2

Table 2a Low-temperature to 280K lattice parameters, fractional coordinates (*x*,*y*,*z*) and nitrogen and hydrogen U_{iso} for ND_4-buddingtonite refined with *C*2/*m* space-group symmetry

T/ K	*a* (Å)	σa	*b* (Å)	σb	*c* (Å)	σc	β(°)	$\sigma\beta$	Volume (Å^3)	σa	wR_p	R_p
11	8.79182	0.00113	13.11084	0.00148	7.20473	0.00079	116.097	0.009	745.811	0.127	5.15	4.03
30	8.79262	0.00158	13.11594	0.00222	7.20487	0.00109	116.092	0.01	746.211	0.234	6.85	4.86
45	8.78986	0.00131	13.11193	0.00186	7.20277	0.00095	116.083	0.009	745.588	0.196	5.86	4.64
60	8.79145	0.0013	13.11253	0.00185	7.20275	0.00095	116.091	0.009	745.706	0.196	5.85	4.63
80	8.79223	0.0013	13.1098	0.00185	7.20232	0.00095	116.091	0.009	745.571	0.194	5.88	4.64
100	8.79484	0.0015	13.10793	0.00214	7.20255	0.00109	116.095	0.01	745.689	0.225	6.61	5.29
120	8.79716	0.00135	13.10576	0.00192	7.20152	0.00097	116.099	0.009	745.626	0.203	5.8	4.61
140	8.80097	0.00143	13.10489	0.00202	7.20157	0.00101	116.104	0.01	745.872	0.212	5.98	4.69
160	8.80284	0.00142	13.10121	0.00202	7.20023	0.00101	116.099	0.01	745.719	0.212	5.98	4.72
180	8.80929	0.00147	13.1003	0.00209	7.20098	0.00103	116.116	0.01	746.18	0.218	5.97	4.71
200	8.81184	0.00149	13.0991	0.00211	7.20074	0.00104	116.122	0.01	746.264	0.221	5.92	4.69
210	8.81611	0.00154	13.09609	0.00216	7.20155	0.00106	116.121	0.01	746.547	0.225	5.97	4.7
220	8.81764	0.00153	13.09444	0.00215	7.20094	0.00106	116.125	0.01	746.494	0.225	5.97	4.73
230	8.81901	0.00155	13.0923	0.00219	7.20069	0.00108	116.126	0.01	746.453	0.229	6.03	4.73
240	8.82194	0.00159	13.09191	0.00222	7.20053	0.00109	116.133	0.01	746.616	0.233	6	4.76
250	8.82388	0.00159	13.08936	0.00225	7.20035	0.0011	116.144	0.01	746.549	0.235	6.03	4.75
260	8.82698	0.00164	13.0881	0.00226	7.20103	0.00111	116.14	0.011	746.831	0.24	5.95	4.7
280	8.83157	0.00158	13.08541	0.00222	7.20024	0.00109	116.147	0.01	746.94	0.234	5.87	4.63

Table 2b Low-temperature to 280-K fractional coordinates (x,y,z) and nitrogen and hydrogen U_{iso} for ND_4-buddingtonite refined with $C2/m$ space-group symmetry

T/K	11	σ	210	σ	280	σ
N(x,0,z)	0.2903	0.0008	0.2949	0.0008	0.2955	0.0008
	0.1424	0.0008	0.1473	0.0009	0.1486	0.0009
NU_{iso}	1.452	0.33	2.367	0.346	3.027	0.292
D1(x,y,z)	0.4147	0.0012	0.4155	0.0013	0.4170	0.0015
	0.0190	0.0013	0.0198	0.0014	0.0200	0.0021
	0.2066	0.0019	0.2159	0.0022	0.2186	0.0030
D2(x,y,z)	0.2614	0.0017	0.2629	0.0022	0.2647	0.0028
	−0.0311	0.0009	−0.0317	0.0011	−0.0360	0.0015
	0.2518	0.0017	0.2497	0.0020	0.2492	0.0028
D3(x,y,z)	0.2659	0.0021	0.2765	0.0023	0.2762	0.0032
	−0.0513	0.0008	−0.0495	0.0011	−0.0465	0.0012
	0.0275	0.0019	0.0354	0.0022	0.0303	0.0027
D4(x,y,z)	0.2191	0.0021	0.2247	0.0026	0.2244	0.0033
	0.0634	0.0008	0.0614	0.0011	0.0625	0.0012
	0.0838	0.0022	0.0879	0.0025	0.0961	0.0033
DU_{iso}	3.999	0.349	7.414	0.538	9.924	0.547
T1(x,y,z)	0.7070	0.0019	0.7062	0.0019	0.7065	0.0020
	0.1179	0.0009	0.1176	0.0010	0.1192	0.0010
	0.3447	0.0019	0.3456	0.0021	0.3474	0.0020
T2(x,y,z)	0.0167	0.0016	0.0213	0.0018	0.0222	0.0019
	0.1881	0.0011	0.1931	0.0012	0.1936	0.0012
	0.2347	0.0022	0.2373	0.0023	0.2365	0.0024
O1(0,y,0)	0.1580	0.0009	0.1584	0.0010	0.1584	0.0010
O2(x,0,z)	0.6607	0.0015	0.6625	0.0015	0.6652	0.0017
	0.2950	0.0018	0.2928	0.0021	0.2898	0.0020
O3(x,y,z)	0.8274	0.0011	0.8267	0.0013	0.8265	0.0013
	0.1587	0.0007	0.1583	0.0008	0.1580	0.0008
	0.2252	0.0013	0.2245	0.0014	0.2236	0.0015
O4(x,y,z)	0..0399	0.0010	0.04197	0.0010	0.0418	0.0011
	0.3123	0.0006	0.3120	0.0006	0.3123	0.0007
	0.2624	0.0012	0.2631	0.0016	0.2631	0.0016
O5(x,y,z)	0.1713	0.0012	0.1695	0.0013	0.1697	0.0012
	0.1260	0.0007	0.1264	0.0007	0.1270	0.0007
	0.4071	0.0013	0.4086	0.0011	0.4096	0.0015

The ammonium ions were treated as rigid bodies (Schomaker and Trueblood 1968; Downs 2000), which are defined as a geometric constraint applied to a molecule or a known fragment (e.g. ND_4). Since ND_4 has five atoms, there are $5 \times 3 = 15$ structural variables, whereas when treated as a rigid body, the ND_4 molecule has only six structural variables, three rotations (R_x, R_y, R_z) and three translations (T_x, T_y, T_z). Hence, there is a reduction of the number of variables (assuming ammonium to be a regular tetrahedron). The rigid body is defined in Cartesian coordinates XYZ, in comparison with the atoms defined by space group being listed as fractional coordinates of the axes a, b and c. The transformation between the two coordinate systems is expressed as $X \parallel a$, $Z \parallel a \otimes b$ and $Y \parallel (a \otimes b) \otimes a$.

Similar orientational ordering is also exhibited by other minerals, for, e.g. ammonium perrhenate, (ND_4ReO_4), (Swainson and Brown 1997). Powder neutron diffraction proved are effective means of studying such disordering processes and hence justifies our methodology.

Results and discussions

The room-temperature structure of buddingtonite has space group symmetry $C2/m$ and the ammonium ion sits on the Wykoff site at fractional coordinates (x, 0, z), on a mirror plane (C_s or m). In addition, there is a nominal presence of hydrogen (confirmed by infrared spectroscopy cf. Harlov et al. 2001) in the system due to H_2 migration across Au capsule. It is likely that we have not only ND_4^+ but also NDH_3^+, $NH_2D_2^+$, NHD_3^+ and NH_4^+ (our sample is dominated by ND_4^+, however). Although these species are likely to have different moment of inertia, they will have very little, if any effect on smearing reorientation dynamics.

There are several possible ways in which an ammonium ion of cubic symmetry could become compatible with the mirror site. Either it is orientated such that the mirror plane passes through two H/D and one N atom, with the remaining two H/D atoms form a mirror image of one another, or they are disordered over the mirror plane (only the N atom lies on the mirror, all the H/D atoms lie away from the mirror and for an individual ion

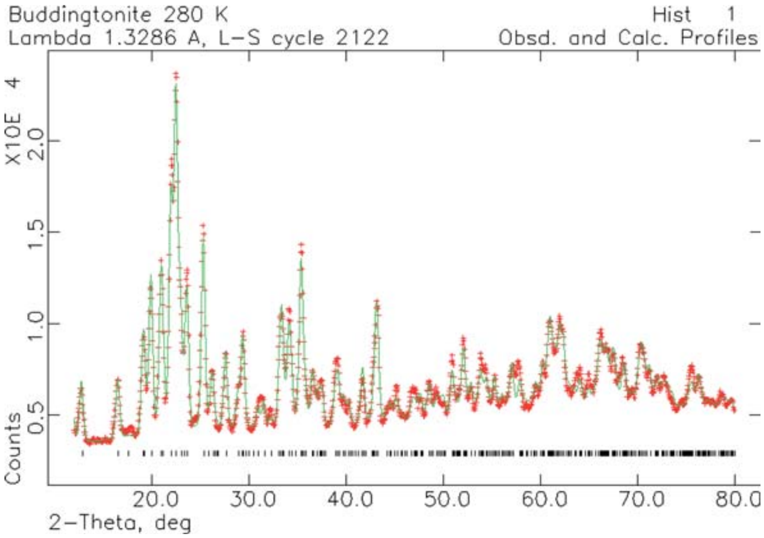

Fig. 3 Rietveld refinement of powder neutron diffraction data (280 K) for ND_4-buddingtonite with some NH_4-buddingtonite component. The refinement was done in accordance with space group symmetry $C2/m$. The (+) represents the measured data, the *line* through the (+) represents the fitted pattern, the *ticks* (|) represents the peaks

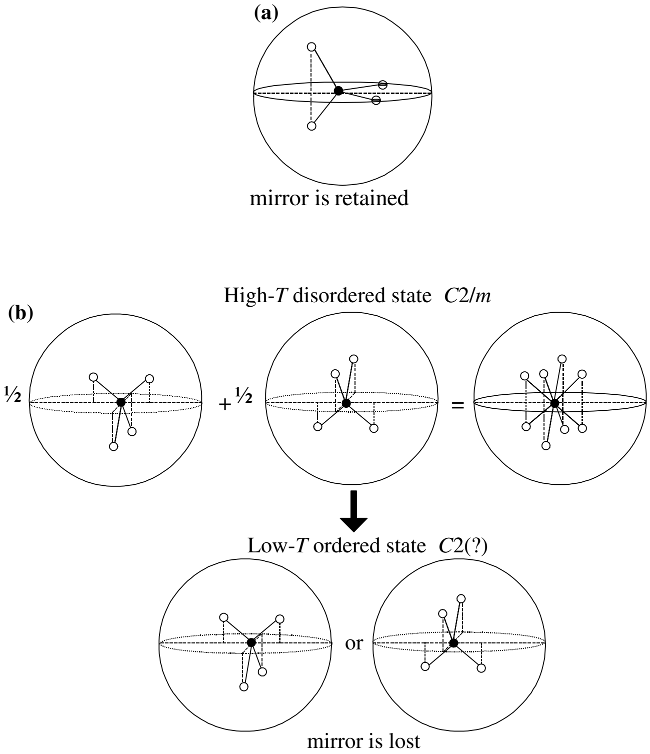

Fig. 4a, **b** A schematic diagram depicting the symmetry relation between the mirror site and the ammonium ion (T_d). **a** shows a special orientation of ammonium ion such that two of the H and the N atoms lie on the mirror plane and the remaining two H atoms are mirror images of each other, **b** shows end-member orientations of ammonium ions in which each is having no mirror symmetry, however on an average they seem to retain a mirror symmetry; mimicking a disordered ammonium ion, *arrow* shows one of the possible transitions ($C2/m \rightarrow C2$) caused by the reorientation of the ammonium group and thus losing the mirror symmetry

the mirror is not obeyed); however, the disordered average will obey the mirror symmetry (Fig. 4a,b). Lowering of symmetry to *Cm* (by losing the two fold axis) instead of *C*2 seems unlikely, since if any symmetry change is to be caused by ammonium ordering it would imply loss of mirror, as the ammonium sits on the mirror and not on the two fold. However, further lowering to *C*1 cannot be ruled out.

Lattice parameters

The lattice parameters obtained from refinement of the neutron diffraction data of the powdered buddingtonite are $a = 8.8301$ (12), $b = 13.075$ (2), $c = 7.1957$ (7) Å and $\beta = 116.7$ (1)° at 280 K (refined in $C2/m$ space group). The temperature dependence of the lattice parameter is as shown in Fig. 5(a–e). The topochemical (framework) symmetry of buddingtonite, as suggested by Smith and Brown (1988), is $C2/m$. In the present work, the refinement of the diffraction patterns for various temperatures were done according to $C2/m$ symmetry. Since the ammonium ion sits on the mirror plane and if the ammonium ion is to order, the mirror plane has to disappear, as shown in Fig. 4b, we have also refined the powder patterns with *C*2 symme-

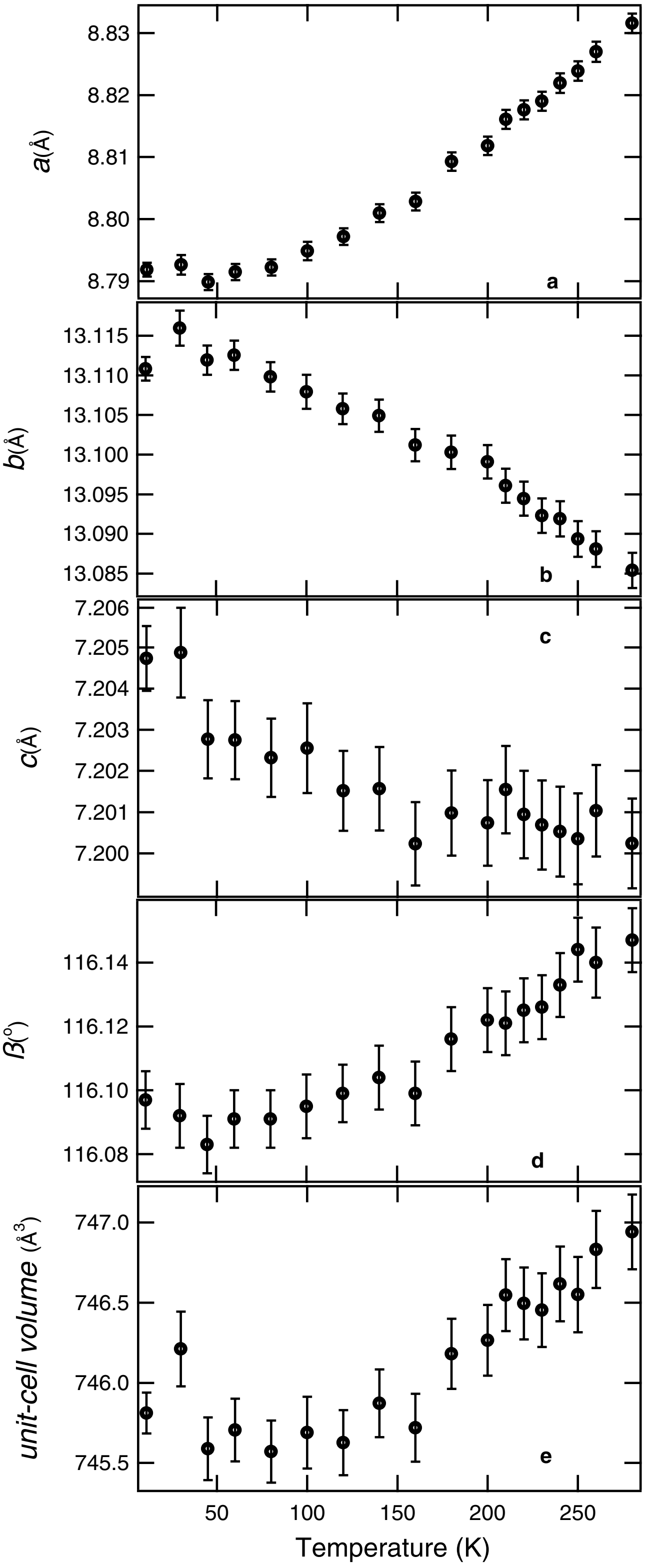

Fig. 5a–e Variation of **a** *a*; **b** *b*; **c** *c*; **d** *β* lattice parameters and **e** volume of ND_4-buddingtonite. Refinements were done with $C2/m$ space group. Note the low-temperature saturation

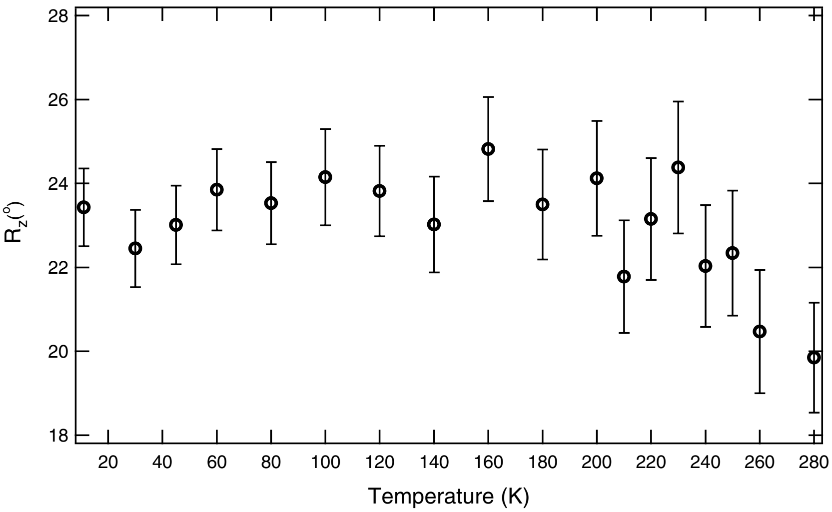

Fig. 6 Temperature variation of R_z rotational parameter of the ammonium rigid body in ND_4-buddingtonite. If there is any change in behaviour, it may occur around 210 K, as shown by the R_z rotational parameter, refined with *C*2/*m* space group

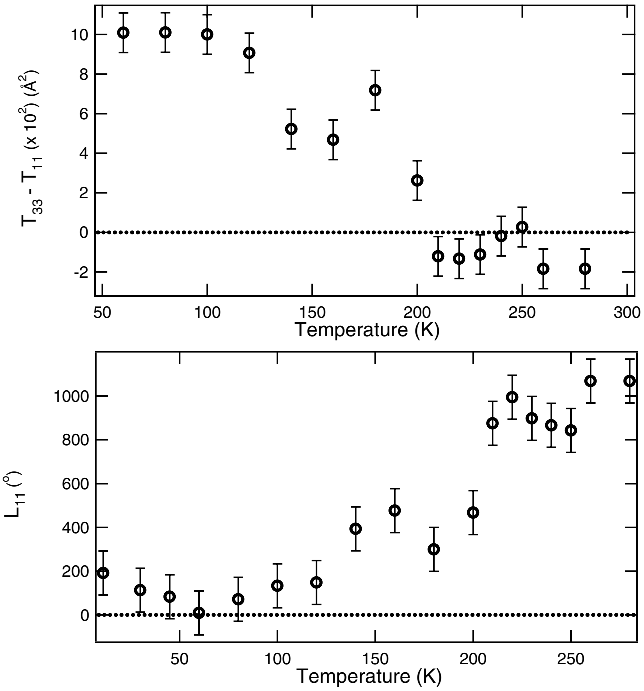

Fig. 7a, **b** Variation of the **a** translational elements T_{33}–T_{11} and **b** librational component L_{11} of the ammonium rigid body in ND_4-buddingtonite, with temperature

try and present the thermal dependence of the TLS tensors. Refinement of ammonium ion in *C*2/*m* would mean an N atom sitting on the mirror with a multiplicity factor of 4 and the D atoms with a multiplicity factor of 8, with occupancy of 0.5 in accordance with the stoichiometry. When refined in the *C*2 space group symmetry, the lattice parameter shows similar behaviour. At low temperature the lattice parameter tends to saturate towards a constant value due to effects related to quantum-mechanical saturation (Hayward and Salje 1998).

*C*2/*m* refinement scheme

The rotational parameters R_x, R_y and R_z of the ammonium ion, treated as a rigid body within the framework of *C*2/*m* space group symmetry, are shown in Fig. 6.

*C*2 refinement scheme

In buddingtonite at low temperature, if there is a transition as shown in Fig 4b, the ammonium ion is expected to sit on a one-fold site, since if reorientation is to occur the mirror symmetry is to be lost (corresponding to the *C*2 space group). With this assumption, and considering site-symmetry requirements imposed by the crystallographic point groups, all the T_{ij}, L_{ij} and S_{ij} (for *i* and $j = 1$ to 3) needs to be refined (for more information please refer to Downs, 2000). At higher temperatures, however, the presence of the mirror plane constrains components, leading to fewer free variables.

For the sake of simplicity, the components of screw tensors were not refined. The temperature dependence of T_{33} –T_{11} and L_{11} are as shown in Fig. 7a and b. These parameters, however, show strong correlations among themselves and are often unrealistic owing to the low resolution of the instrument and a low space-group symmetry and large unit-cell volume. The structural parameters corresponding to the rest of the framework did not converge while attempting a *C*2 refinement scheme. Care should be taken in their interpretation.

From the infrared measurements, especially far-infrared (H_4N–O stretching and lattice mode, Mookherjee et al. 2004) and the internal modes of the ammonium ion, it appeared that it is the ammonium ion which undergoes slight changes at low temperatures. However, it is also likely that the ammonium ion cage undergoes a change at around 210 K influencing the orientation of the ammonium ion, i.e. a symmetry-breaking lattice distortion leading to the ammonium reorientation, but from the present neutron diffraction study we do not find any such evidence.

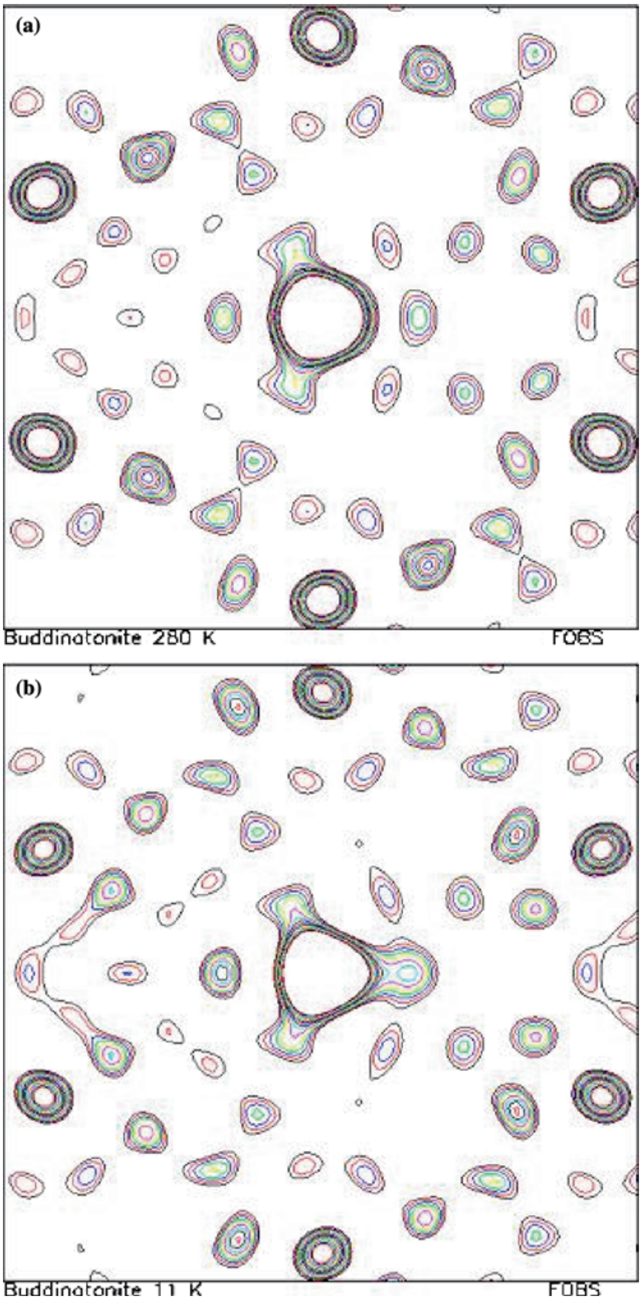

Fig. 8a,b Fourier maps of the ammonium ion **a** at 280 K and **b** at 11 K. Both the figures are with the center of reference, 0.29, 0.00, 0.14, which is the N atom fractional coordinate, which is located at the *center of the figure*. *Contours* are at 0.03 to 0.48 with an interval of 0.03 eV Å^{-3}. The map size is 10 Å

Moreover, ammonium orientation is also influenced by the local distribution of Al in the tetrahedral sites (Likhacheva et al. 2002) and hence might smear out the transition, if any. Also, the Fourier maps generated at the highest and lowest temperatures do not show any change in orientation of the ammonium ions (Fig. 8).

From this present diffraction study, we find no strong evidence of ammonium reorientation; however, there is weak evidence at around 210 K, which needs detailed spectroscopic studies. To conclude, the two main arguments against a true phase transition from these data are:

1. That we observe no radical changes in orientation of the ammonium ion as examined by rigid body methods, although, based on past experience, this should have been obtained if one were present.
2. There appears to be no spontaneous strain, which would be quite unusual for an ammonium ion ordering in such a crystal.

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