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Raman study of high-pressure phase transitions in dehydrated analcime

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ABSTRACT

The high-pressure behaviour (up to 30 kbar) of dehydrated analcime, Na[AlSi₂O₆], has been studied in detail using polarized microscopy and Raman micro-spectroscopy. Samples were compressed using a diamond anvil cell in a quasi-hydrostatic medium (glycerol or water-ice). Two transitions at 3.7 and 11 kbar were observed.

At the first transition, phase II is observed under cross polarized light as a contrasting black zone, moving from the edge to the centre of the sample. At this transition the strong Raman doublet at ~480 and 500 cm⁻¹ transforms discontinuously to a singlet, which is similar to that of quasi-cubic natural analcime. This transition, with an increase of effective symmetry, seems unusual on increasing pressure.

The analcime framework may be thought of as an array of four-, six-, or eight-membered interconnected rings. Phase transitions in the analcime group are considered in the literature in terms of deformations of the six-membered rings. However, the present work shows that these phase transitions should be associated with deformations of the four-membered rings (as the minimum size secondary building units) by rotation of rigid TO₄ units. The strongest Raman band frequency is correlated with the mean T-O-T angle inside the four-membered ring: a rate of 4.5 cm⁻¹/degree was found for analcimes and leucites. Using this correlation, one can estimate from Raman data the possible deformation of four-membered rings at the phase transitions.

KEY WORDS: phase transitions, high pressure, analcime, Raman spectra.

Introduction

THE high-pressure behaviour of aluminosilicates, especially zeolites, has been the subject of much interest recently. Using X-ray diffractometry (XRD) under high pressure (up to 30 kbar), Hazen and Finger (1979) observed four phase transitions in natural analcimes, including orthorhombic analcime from Golden (Colorado). The presence of H₂O molecules in the pores of natural analcime frameworks complicates the nature of phase transitions and increases their number, so it seems reasonable to study first the phase transitions in dehydrated analcime, observed earlier by Belitsky (pers. comm.), and then to compare these with those in natural hydrated analcime.

Phase transitions are related to the structural features of a particular crystal. Therefore the structural properties of analcime should be described in detail. Analcime NaAlSi₂O₆·H₂O is a high-pore framework aluminosilicate, of the ANA (analcime) structure type, which is the end-member zeolite with the smallest H₂O cage. Analcimes from different localities exhibit different (cubic, tetragonal and orthorhombic) symmetries, orthorhombic being shown in Fig. 1. In cubic analcime, all extra-framework cation sites, S, are equivalent. In tetragonal analcime, there are two cationic sites. In orthorhombic analcime, the S site splits into three: M2, M11 and M12 (Line *et al.*, 1996). The structural topology of analcime type zeolite is that of an interconnected array of tetrahedra, TO₄ (where T = Al,Si), as primary building units, which are linked to form four-, six- and eight-membered rings. These may be thought

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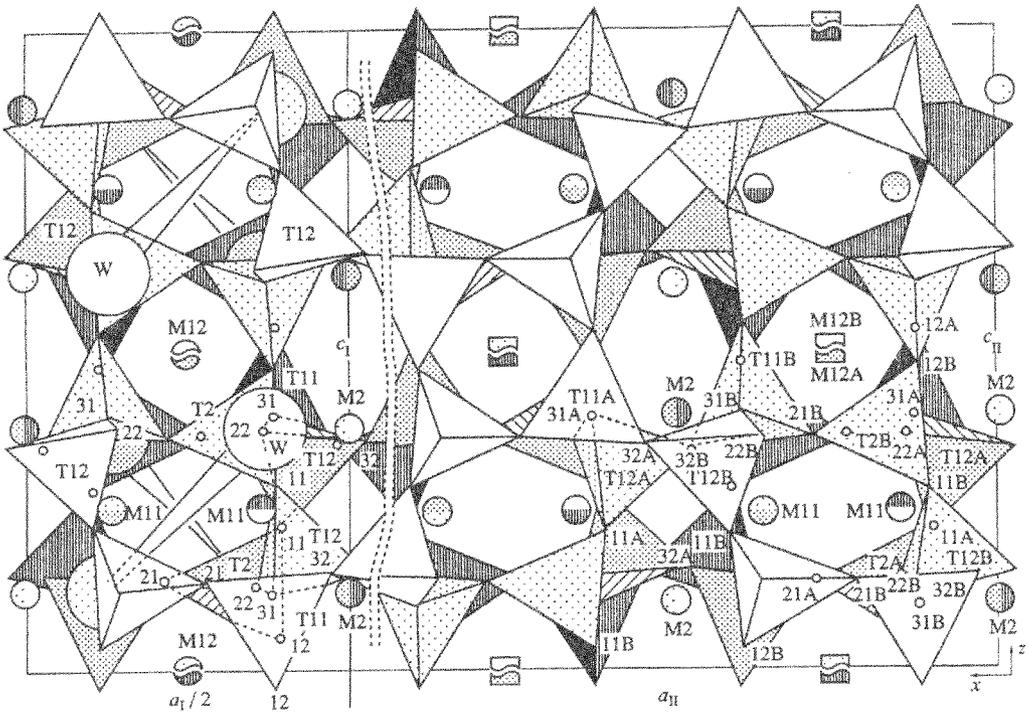


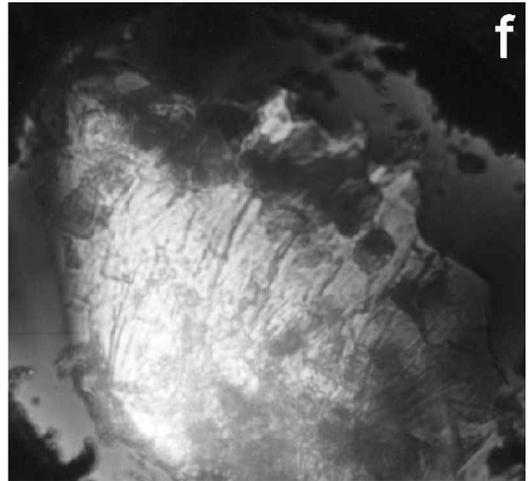
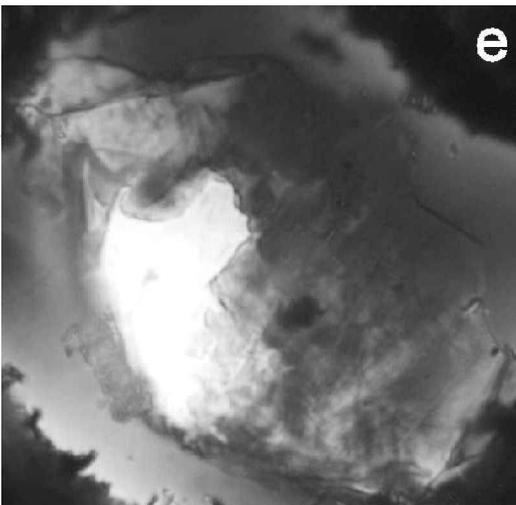
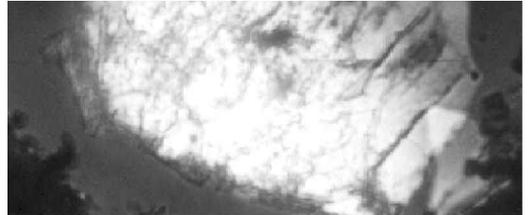
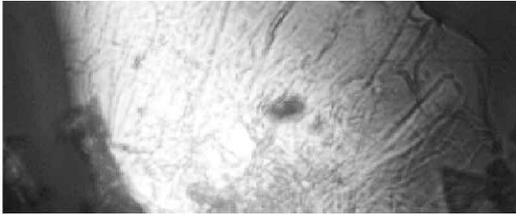
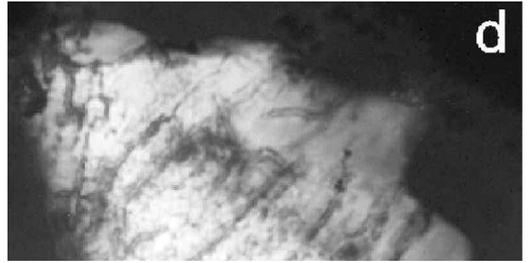
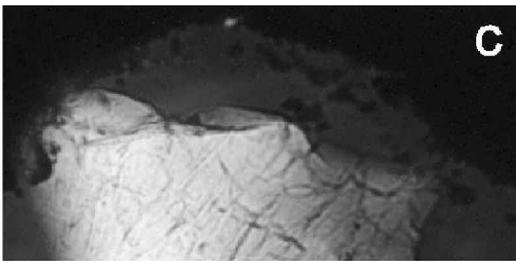
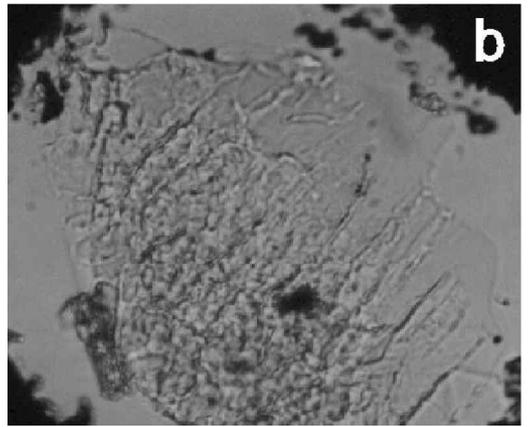
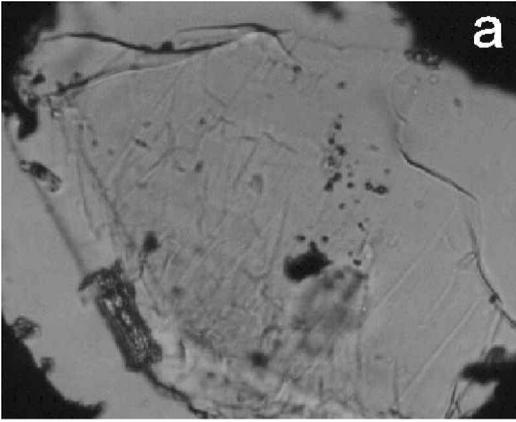
FIG. 1. Crystal structures, viewed parallel to [010], of natural hydrated analcime $\text{Na}[\text{AlSi}_2\text{O}_6]\cdot\text{H}_2\text{O}$ and dehydrated analcime at room conditions according to the X-ray data of Bakakin *et al.* (1994). To the left is natural orthorhombic *IbcA* analcime (from the Nidym River region). On the right is a dehydrated monoclinic *I2A* analcime. Channel cations are disposed in M_{ij} sites marked by medium circles, while empty cationic positions are indicated by squares. Water molecules lie in W sites marked by large circles. Tetrahedral cations are positioned in T sites marked by small circles.

of as secondary building units. Six-membered rings (of which there are two types) are highly distorted at ambient conditions.

In the structure of a natural orthorhombic analcime from the Nidym River (East Siberia), studied by Bakakin *et al.* (1994), Na cations

randomly occupy three S sites around one W position: 0.72 on M_{11} , 0.74 on M_2 , 0.45 on M_{12} . In monoclinic dehydrated analcime at room temperature, these site occupancies change to 0.93 on M_{11} , 0.91 on M_2 , and 0.0 on M_{12} , the last site being empty (Fig. 1).

FIG. 2. (Opposite page) Photomicrographs under polarized light of a dehydrated analcime single crystal under pressure in the diamond anvil cell (using glycerol as pressure transmitting medium). The field of view of each photograph is equal to $250 \times 220 \mu\text{m}$. (a) Initial phase I at $P = 1$ bar in transmitted plane-polarized light. (b) Complex 'zebra-like' microstructure of phase III and phase IIb lamellae at $P = 3$ kbar, obtained after decrease of pressure from 27 kbar. Plane polarized light is used. (c) Phase I at $P = 1$ bar in cross polarized light after release of pressure. This stressed twinned sample was obtained after decrease of pressure from 27 kbar. (d) Complex 'zebra-like' microstructure of phase III and phase IIb lamellae at $P = 3$ kbar, obtained after decrease of pressure from 27 kbar. Cross polarized light is used. (e) Phase transition at 3.7 kbar after 80 s at the first run through the transition. Phase I seems to be bright (transparent due to pressure-induced twinning), while phase IIa seems to be black and spotted in cross polarized light. (f) Repeated phase transition at 4 kbar after 30 s. Phase I seems to be brighter, while phase IIa appears as black spots in cross polarized light.



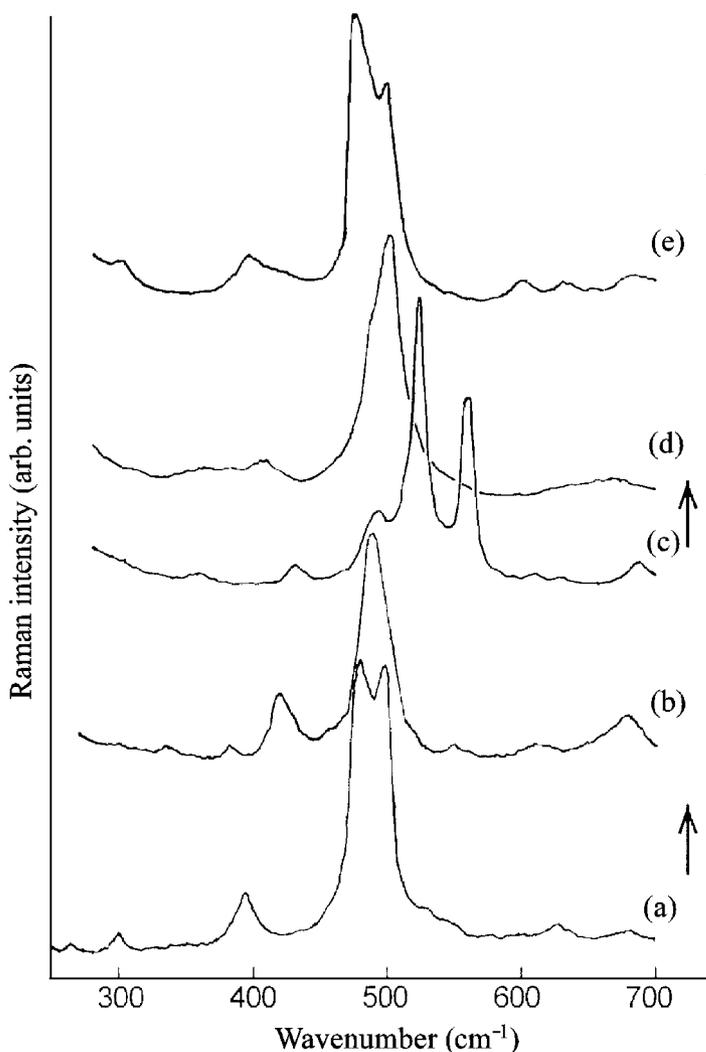


FIG. 3. Raman spectra of dehydrated analcime compressed in glycerol: (a) the original phase I at 1 bar; (b) phase IIa at 6.7 kbar after the first run through the 3.7 kbar transition; (c) phase III at 11 kbar after the second phase transition at 11 kbar; (d) phase IIb at 1.2 kbar after decreasing pressure from 27 kbar; (e) phase I at 1 bar after release of 27 kbar pressure. The arrows show the time sequence of spectra recorded on increasing pressure (a,b,c) and on decreasing pressure (d,e).

It would be interesting to find the relationship between structural changes and vibrational spectral changes in the ANA structure as a function of pressure, water content and cation composition. In the present polarized microscope and Raman study, the microscopic features of high-pressure phase transitions in dehydrated analcime are examined and compared with those in native hydrated analcime and its cation-

exchanged forms, and also with those in natural leucite.

Experimental

The high-pressure behaviour (up to 30 kbar) of dehydrated analcime (from Nidym) was studied in detail using polarized microscopy and a Raman spectrometer with an attached Olympus micro-

scope. Raman spectra were measured using a triple spectrometer (OMARS 89, Dilor) equipped with a high sensitivity charge-coupled-device (LN/CCD-1100 × 330 PB, Princeton Instr.). Samples were compressed in a diamond anvil cell (DAC) under quasi-hydrostatic conditions using glycerol or water-ice VI-ice VII as the pressure transmitting medium (Goryainov and Belitsky, 1995; Goryainov *et al.*, 1996). Single crystals of natural analcime $\text{Na}_{1.88}[\text{Al}_{1.88}\text{Si}_{4.12}\text{O}_{12}]\cdot 2\text{H}_2\text{O}$ from the Nidym River (East Siberia) were used to prepare dehydrated samples which had been dehydrated for at least two years at room temperature and pressure prior to experiment. Structure-vibrational correlations have been investigated by comparison of Raman data from dehydrated analcime with those from natural and cation exchanged (Li,K,Rb) forms of analcime and natural leucite (Orvieto, Italy). In addition, Raman measurements at varying pressures were carried out for these samples.

Results and discussion

We selected a single crystal of dehydrated analcime, defined as the initial phase I in Fig. 1, which was black (non-transmitting) in transmitted cross polarized light at room temperature and pressure. With increasing pressure, phase I becomes lighter in cross polarized light (the white zone in Fig. 2e). This effect is connected with the appearance of large twins, overlaid in the viewing plane and covering the larger part of crystal. The difference in twin angle reaches 24° at 3.7 kbar. At the first transition (3.7 kbar), phase IIa formation is observed in cross polarized light as a contrasting black zone, moving from the edge to the centre of the sample. At this transition the doublet of strong Raman bands at 478 and 499 cm^{-1} transforms discontinuously to a singlet at 493 cm^{-1} , which is similar to that of quasi-cubic natural analcime (Fig. 5). This suggests that at this transition the effective symmetry of the structure increases with increasing pressure, which is unusual in high pressure transitions. Ross (1998) has already shown, however, that the distortion of perovskites may either increase or decrease with pressure.

With further pressure increase, from 4 to 11 kbar, some lightening of sample is observed in cross-polarized light. At 11 kbar a weak darkening of the sample occurs. A 'zebra-like' twin microstructure appears (Fig. 2b,d), indi-

cating that the twin plane is orthogonal to the plane of view. A triplet of strong Raman bands at 500, 525 and 560 cm^{-1} appears in phase III, indicating a lowering of symmetry.

At both transitions, the weak darkening is observed in plane polarized light due to reflection from the domain boundaries. Both transitions exhibit a large hysteresis: ~ 2.5 kbar at the first transition and ~ 8 kbar at the second (Fig. 4). In addition, on release of pressure, an additional phase (IIb) is observed (Figs 3,4).

Comparison of the transitions in hydrated and dehydrated analcimes proves that these transitions are rather poorly correlated in both structures. In dehydrated analcime the transitions give contrast in cross-polarized light and are accompanied by strong discontinuities of Raman O-T-O band frequencies (up to ~ 60 cm^{-1} at the second transition). In hydrated analcime, however, two weak transitions were found from Raman spectra in the same pressure range: the first at 8 kbar with small discontinuities (< 3 cm^{-1}) in the positions of these bands and the second at 20 kbar with drop in the slope of the *P*-dependent curve of strongest band frequency (Goryainov *et al.*, 2000). These two transitions cannot be seen using polarized light microscopy. Large anomalies in the Raman O-T-O band frequencies (abrupt increases of up to 30 cm^{-1}) occur in natural analcime at higher pressure (~ 40 kbar). Comparison of the Raman spectra of hydrated and dehydrated Li-analcimes supports the suggestion that the transition pressure is greater in hydrated crystals.

The analcime framework may be regarded as an array of interconnected four-membered (R4) or six-membered (R6), or eight-membered (R8) rings. Usually, phase transitions in analcime-leucite structures are considered as a result of deformation of the R6 rings (e.g. Palmer *et al.*, 1990). However, it should be noted that the minimum-size secondary building unit is not a six-membered, but a four-membered ring. Therefore it seems more consistent to interpret structural changes with pressure and temperature in terms of R4 ring deformation by rotations of TO_4 tetrahedra as rigid units.

There are six degrees of freedom for distortions of isolated four-membered rings, occurring through rigid TO_4 rotations on six angles α , β , θ_1 , θ_2 , θ_3 , θ_4 . These angles, in the case of regular tetrahedra with alternating signs of $\theta_1 = -\theta_2 = \theta_3 = -\theta_4 = \theta$ are shown in Fig. 5: α is the acute angle between two projections of neighbouring O-O vectors inside the R4 ring on the R4 plane, which

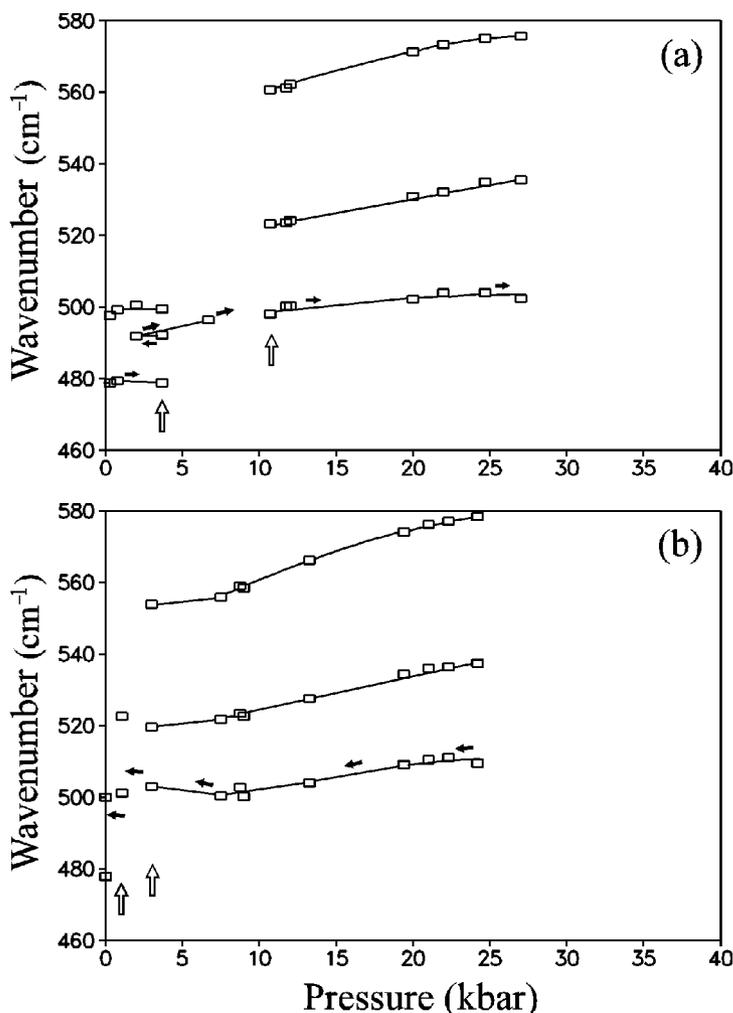


FIG. 4. Pressure dependence of strong Raman band frequencies of dehydrated analcime compressed in glycerol: (a) with increasing pressure; (b) with decreasing pressure. Black arrows show the time sequence of acquisition of the spectra. During the first run at the first transition, as indicated in (a), the pressure in the DAC decreased from 3.7 to 2 kbar. Empty arrows indicate the transitions at 3.7 and 11 kbar on increasing pressure (a) and those at 1.2 and 3 kbar on decreasing pressure (b).

is based on two crossed lines drawn through the mean points of opposing O-O edges inside R4; β is the angle between this O-O edge and the R4 plane; θ is the angle of rotation around the O-O edge, measured from the R4 plane to the tetrahedral axis, drawn through the mid-point of the O-O edge forming the R4 ring and the mid-point of the opposite O-O edge inside a given TO₄ tetrahedron.

Assignments of vibrational modes of A zeolite were carried out by Bartsch *et al.* (1994). Dutta *et al.* (1988) found a linear correlation between the strong Raman O-T-O band frequency at ~ 500 cm⁻¹ and the mean T-O-T angle inside the four-membered ring: the frequency increases with a decrease in the angle at a rate of 6 cm⁻¹/degree in synthetic zeolites. We obtained a similar linear dependence (with a rate of 4.5 cm⁻¹/degree) for

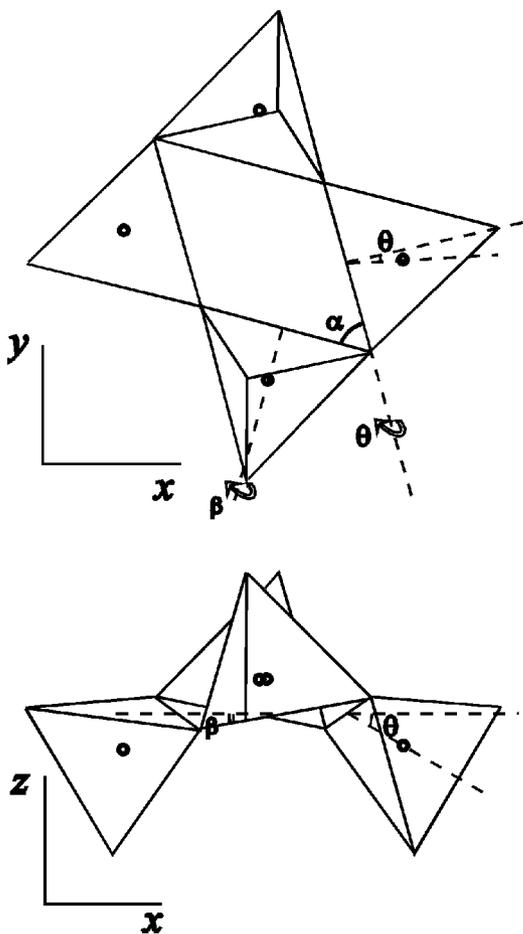


FIG. 5. The four-membered R4 ring of corner-linked tetrahedra shown in two projections. There are six degrees of freedom for rigid TO_4 rotations in R4: α , β , θ_1 , θ_2 , θ_3 , θ_4 . The angles of each tetrahedron rotation around its own O-O axis inside the ring are taken in analcime-type alternating sequence: $\theta_1 = -\theta_2 = \theta_3 = -\theta_4 = \theta$. To illustrate the distortions of the R4 ring, the angles have been chosen to be $\alpha = 30^\circ$, $\beta = 10^\circ$, $\theta = 60^\circ$.

the dependence Raman O-T-O band frequencies upon the noted angle, using available structural data (Bakakin *et al.*, 1994; Goryainov *et al.*, 2000) for hydrated and dehydrated analcimes and natural anhydrous leucite. The geometrical properties of the R4 ring were not determined by Dutta *et al.* (1988). Analysis of possible distortions of the R4 ring, suggested here, led to the conclusion that it is important to understand the relationship

between the O-T-O band frequency and each of the six angles α , β , θ_1 , θ_2 , θ_3 and θ_4 . However, we restrict the present work to a discussion of the correlation to the mean T-O-T angle inside R4.

The strong bands at about 500 cm^{-1} in analcimes (Fig. 3) and leucite are attributed to oxygen vibrations along a direction normal to the plane of the T-O-T bond in the R4 rings. The mean T-O-T angle at ambient conditions is $\sim 144.4^\circ$ in natural analcime and 143.1° in dehydrated analcime. The small decrease of mean T-O-T angle results in a small increase of the strong Raman band frequency from 485 cm^{-1} in natural analcime to a mean frequency 489 cm^{-1} in dehydrated analcime (two bands at 478 and 499 cm^{-1} in Fig. 3).

In the leucite unit cell there are six R4 rings of three types: one R4(1) and one R4(3) ring in the (001) plane, composed of the T1-T1-T1-T1 and T3-T3-T3-T3 tetrahedra, respectively, and four R4(2) rings, composed of T1-T2-T3-T2 tetrahedra. Mean T-O-T angles are equal to 144.3° in R4(1), 138.9° in R4(2), and 130.4° in R4(3). We relate the high-frequency peak 2(3) at 530 cm^{-1} to the R4(3) ring with the smallest mean T-O-T angle, the strongest peak 1(2) at 492 cm^{-1} to the R4(2) ring, and the weak shoulder (peak 3(1)) at 480 cm^{-1} to the R4(1) ring. If these rings give rise to the same intensity at a given scattering geometry, then the intensity ratio of the three peaks would be 4:1:1, whereas the observed ratio is 11:4:1. The mode related to the R4(3) ring (530 cm^{-1} at 1 bar), shows a parabolic pressure dependence above 23 kbar according to our measurements and the data of Palmer (1991), and may be considered as an additional order parameter of B_{1g} symmetry. Thus, we consider that the distinct transition in leucite at 23 kbar is related to structural changes in the framework, including the rotation and bending of TO_4 polyhedra first of all in the R4(3) ring on the (001) plane with its square-rhombic distortion controlled by angle α (3).

Leucite, tetragonal at room conditions, transforms on heating to a cubic structure (Palmer and Salje, 1990; Palmer *et al.*, 1989, 1990, 1997). Taking into account the above interpretation of Raman bands and experimental data (Palmer *et al.*, 1990), we can show that this transition may be associated with a square-rhombic distortion of the R4(2) ring, involving the α (2) angle as order parameter. This mechanism leads to a parabolic dependence of Raman peak 1(2) at 492 cm^{-1} , the strong intensity of which is determined by a

number of rings 4R4(2). The mean T-O-T angle in R4(2) is determined by the β and θ angles, and also essentially by the $\alpha(2)$ angle, which changes at the tetragonal-cubic transition, while the $\alpha(1)$ and $\alpha(3)$ angles in the two other rings remain at 90° . The mean T-O-T angles in R4(1) and R4(3) are determined by the corresponding $\beta(1)$, $\theta(1)$ and $\beta(3)$, $\theta(3)$ angles, which are non-zero in the cubic phase ($\beta \approx 12^\circ$ and $\theta \approx 30^\circ$) and show small linear changes in the tetragonal phase. Note that the present model of R4 ring distortions complements the description of the tetragonal-cubic structural transition in leucites given by Palmer *et al.* (1990, 1997) based on R6 ring distortions resulting from framework relaxation around displaced channel cations.

The splitting, $\Delta\nu$, of the strong O-T-O band at $\sim 500 \text{ cm}^{-1}$ is shown in Fig. 6 as a function of the tetragonal distortion parameter $d = lc - (a+b)/2l$. The experimental data of Bakakin *et al.* (1994) and Goryainov *et al.* (2000) were used. A linear dependence is found by least square methods. This correlation between $\Delta\nu$ and d proves that one mechanism dominates the tetragonal distortion of the primary cubic framework. Data for NH_4 -analcime deviate from this linear dependence, suggesting the contribution of another type of framework distortion.

Conclusions

Two transitions at 3.7 and 11 kbar have been observed in dehydrated analcime. Both transitions exhibit large hysteresis: 2.5 kbar at the first transition and 8 kbar at the second. Comparison of the present data with previous studies (Goryainov *et al.*, 2000) shows that, generally, the presence of H_2O molecules in the pores of the natural analcime framework shifts the phase transition to higher pressures, thus complicating the nature of the transitions and increases their number.

The transitions in ANA zeolitic structures are apparently connected with structural changes, in the first place with distortions of four-membered rings, and in the second place with displacement of channel cations from S to S' sites in S forms (hydrated and dehydrated analcimes) and from W to W' sites in W forms (leucite and K-, Rb-analcimes). Taking into account the correlation between the frequency of the strong Raman band and the mean T-O-T angle inside the R4 ring, one can estimate from Raman data possible deformations of R4 rings at phase transitions. The

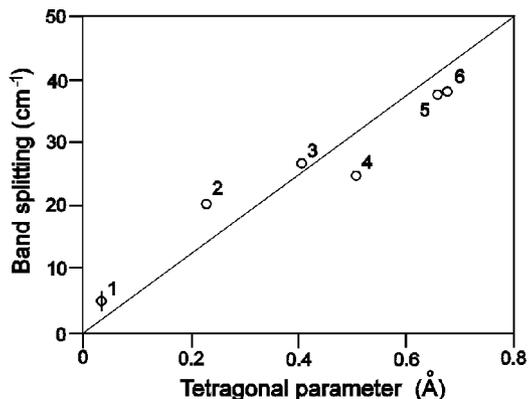


Fig. 6. Dependence of the O-T-O band splitting upon the tetragonal distortion parameter $d = lc - (a+b)/2l$. Experimental points (open circles) are data for: (1) natural Nidym analcime, the splitting of which was estimated from broadening of the O-T-O band; (2) dehydrated Na-analcime; (3) Rb-analcime; (4) NH_4 -analcime; (5) K-analcime; and (6) Orvieto leucite. The band splitting is measured with an accuracy of $\pm 1 \text{ cm}^{-1}$.

$18\text{--}35 \text{ cm}^{-1}$ splitting of the strong T-O-T band at the second phase transition in dehydrated analcime is connected with a suggested change of the mean T-O-T angle in the R4 rings of $3\text{--}7^\circ$. The rotation angles of TO_4 polyhedra and the displacements of channel cations may be considered as the order parameters of these transitions. Our suggested model of square-rhombic distortions of four-membered rings explains the origin of these dramatic transitions in analcimes and leucites. Further interpretation of experimental data in terms of a model of R4 ring distortions and vibrational characteristics seems appropriate.

A correlation between the mean tetragonal parameter $d = lc - (a+b)/2l$ and mean splitting of the strong Raman O-T-O band is found (Fig. 6). This shows linear dependence with a rate of 0.016 Å/cm^{-1} allowing one to predict the mean cell parameter difference in the high-pressure phases using Raman measurements.

Acknowledgements

We thank B.A. Fursenko, Yu.V. Seryotkin, I.A. Belitsky and G.P. Valueva for helpful discussions. This work was supported by the Russian Academy of Sciences, the Russian Foundation for Basic Researches (grants 98-05-65658, 98-05-64474, 96-15-98547), the 'Zeolites of Russia'

Program of the Russian Ministersvo Nauki and Educational Scientific Centre (NSU-UIIGGM).

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[Manuscript received 8 May 1999;
revised 30 September 1999]