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Rigid Unit Modes in disordered nepheline: a study of a displacive incommensurate phase transition

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Abstract Calculations of the Rigid Unit Modes (RUMs) allowed in the nepheline structure are used to explain the diffuse scattering previously seen in electron diffraction experiments. The RUM calculations also show that the modulation wavelength for incommensurate nephelines is essentially determined by the framework topology. X-ray diffraction is used to measure the intensity of the diffuse scattering as a function of temperature. The diffuse intensity increases sharply at 308 K. This effect is interpreted as being due to the softening of a phonon mode, indicating a phase transition. Measurements of this phase transition below the transition temperature are made using hard mode infrared spectroscopy.

Key words Nepheline · Incommensurate · Rigid unit mode

Introduction

Nepheline (stoichiometric composition $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$) is the most common member of the feldspathoid group of minerals. Geologically, feldspathoid minerals occur in alkali-rich, SiO_2 -poor rocks. Structurally, nepheline can be described as a stuffed tridymite. This subset of the feldspathoid group consists of minerals with the same framework structure as SiO_2 tridymite; sixfold rings of SiO_4 tetrahedra join to form sheets, which stack in an ABAB sequence to give a framework. Charge balance is maintained by alkali cations – usu-

ally Na and K – which occur in the large cavities in the framework. The aluminosilicate framework collapses around these stuffing cations to minimise the Coulombic energy. The majority of natural nephelines have a slight excess of Si over Al, balanced by vacancies on the K sites. The structural and chemical properties of stuffed tridymites are reviewed more fully in Palmer (1994).

One of the key questions concerning nepheline is the nature and stability of its incommensurate structure. In an electron diffraction study of a range of natural nephelines, McConnell (1962) found satellite diffraction maxima at $(1/3, 1/3, z^*)$, where z^* was slightly sample-dependent, varying between 0.205 and 0.214. In the majority of samples, these maxima were weak and diffuse, and were joined to the Bragg peaks by weak streaks, as shown schematically in Fig. 1. In certain nephelines, these maxima were sharp, but their intensity and sharpness were reduced irreversibly on heating. In no case was it possible to remove either the satellite peaks or the streaks by prolonged heating at high temperatures.

Subsequent analysis of the time-temperature dependence of the intensity of the satellite maxima (McConnell 1981) indicated that the transition was kinetically constrained by the diffusion of K along the $[0\ 0\ 1]$ channels in the nepheline structure. From this, McConnell concluded that the nephelines with sharp diffraction maxima had ordered vacancies on the K sites, which become disordered on heating. The equilibrium transition temperature for this process is 452 K.

In this study, we focus on the behaviour of disordered nepheline. The SiAlO_4 framework is relatively flexible, and we use the Rigid Unit Mode model of framework silicate phase transitions (Giddy et al. 1993; Dove et al. 1995; Hammonds et al. 1996) to investigate the dynamic properties of this framework. These results are then compared with data from X-ray diffraction and infrared spectroscopic studies.

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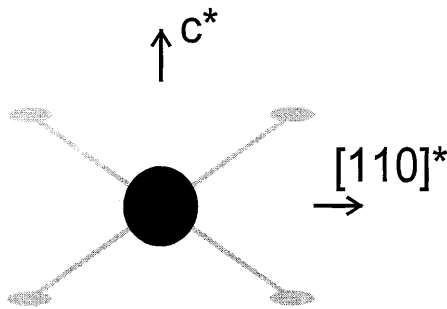


Fig. 1 Distribution of diffuse diffracted intensity around each Bragg maximum in the $c^*:[110]^*$ reciprocal lattice section of nepheline. (After McConnell 1962)

Rigid Unit Mode calculations

Nepheline was modelled using the Rigid Unit Mode model developed by Dove et al. (1993a, b), Hammonds et al. (1996), and coworkers. In this model, a framework crystal structure containing relatively stiff SiO_4 and AlO_4 units is modelled as an array of perfectly rigid tetrahedra.

To determine which distortions of the framework do not involve distortions of the tetrahedra, a computational technique known as the split atom method (Giddy et al. 1993) was used. In a split atom calculation, the vertices of these tetrahedra are joined by a strong harmonic force which allows them to separate by a small amount, but causes a high energy penalty to be incurred if they do. This represents, to a first approximation, the finite stiffness of the real SiO_4 and AlO_4 units. If a phonon mode may propagate through a framework aluminosilicate, such as nepheline, without requiring any of the vertices of the tetrahedra to separate, the energy associated with this mode will be very low. Such a mode is known as a Rigid Unit Mode (RUM) and their low energy makes them natural candidates for the soft modes which drive displacive phase transitions (Giddy

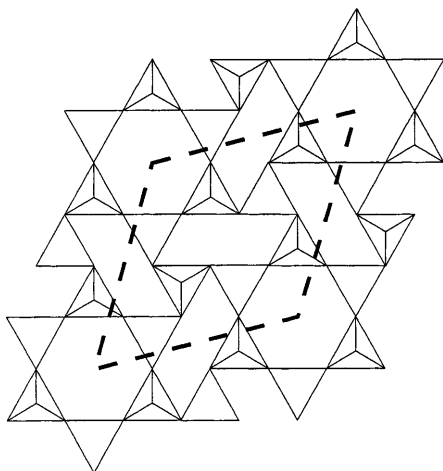


Fig. 2 Nepheline framework structure simulated in the RUM calculations

et al. 1993; Hammonds et al. 1996); more generally, they constitute low-energy excitations of the crystal lattice.

By performing lattice dynamic calculations on the tetrahedral framework representing the aluminosilicate crystal structure, the set of RUMs permitted by the crystal can be enumerated for any wave vector. This is achieved using the computer program CRUSH (Giddy et al. 1993; Hammonds et al. 1994). The crystal structure simulated in these calculations is illustrated in Fig. 2. The key feature of the nepheline framework is assumed to be the distribution of the hexagonal and oval cavities; this is preserved in the structure used for the RUM calculations. However, the exact shape of the oval cavities is somewhat stylised. The interstitial cations (Na and K in this case) are not included in the calculations because it is the vibrational properties of the framework which are of interest. These vibrations will be dominated by the stiff Si-O and Al-O bonds. In practice, these interstitial cations will tend to stiffen the framework slightly and reduce the oscillation amplitude of the RUMs. Determining the RUMs permitted by a crystal structure yields the set of possible displacive phase transitions which the lattice may undergo (Giddy et al. 1993). Moreover, the distribution of these RUMs in reciprocal space can be used to investigate the nature of the thermal diffuse scattering which may be seen in diffraction experiments on the crystal. The reason for this is that the intensity of the diffraction signal due to a single phonon varies with frequency as ω^{-2} (see, for example, Dove 1993).

A fine grid of wave vectors covering the symmetrically independent points in one Brillouin zone was generated. The spacing between adjacent points in reciprocal space was 0.001 \AA^{-1} , generating 10^9 points per \AA^{-3} . A pseudointensity was then calculated for each point on this grid, using the equation

$$I(\mathbf{k}) = \sum_j \frac{1}{\omega_{j,\mathbf{k}}^2 + \Omega} \quad (1)$$

where \mathbf{k} is the wave vector, $\omega_{j,\mathbf{k}}$ is the frequency of a phonon j at wave vector \mathbf{k} calculated by CRUSH, and the sum is over all the phonons at a given wave vector. Ω is an arbitrary small quantity chosen to prevent $I(\mathbf{k})$ from diverging to infinity when $\omega_{j,\mathbf{k}} = 0$. Therefore for a wave vector where there are n RUMs, $I = n\Omega^{-1}$.

The pseudointensity simulates the results of a thermal diffuse scattering experiment in the sense that it has the correct dependence on the phonon frequency, but it does not include the components associated with the structure factor or the phonon eigenvector. As a result, the pseudointensity model does not describe the different intensities of the diffuse diffraction in each Brillouin zone.

The dark lines in Fig. 3 show the loci of RUM wave vectors calculated for the $[110]^*:c^*$ section of reciprocal space for nepheline. The RUMs with wave vectors on the curved lines from (000) to $(1/3, 1/3, 0.27)$ correspond to the diffuse streaks seen by McConnell (1962). Very similar patterns of diffuse intensity are seen in tridymite (Withers et al. 1994; Dove et al. 1996) and

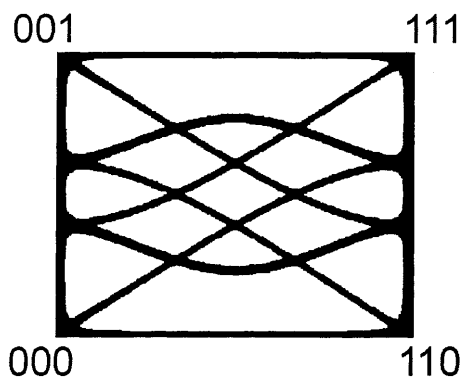


Fig. 3 Calculated RUM spectrum of nepheline. The *dark regions* correspond to the wave vectors where the pseudointensity $I(\mathbf{k})$ is low; that is, the values of \mathbf{k} for which RUMs exist

the stuffed tridymite kalsilite (Carpenter and Cellai 1996).

The intersection between the RUM surfaces at $(1/3, 1/3, 0.27)$ corresponds to the incommensurate structure of nepheline. There is a slight discrepancy between the position of this RUM and the observed modulation wavelength. The most likely reason for this is that the simulated structure is only an approximation to the real crystal structure of nepheline; the effect of (Al, Si) ordering and the precise shape of the oval rings in which Na sit were neglected.

The RUM analysis has shown that the modulated structure of nepheline and its wavelength are primarily properties of the framework. For nephelines with (K, □) order, the vacancy ordering scheme must adapt to fit the possible modulations of the framework. This explains why the modulation wavelength does not display a strong dependence on the fraction of vacant K sites.

X-ray diffraction

In order to confirm that the diffuse diffraction signals in disordered nepheline are due to dynamic effects, the temperature dependence of the diffuse intensity was analysed. The expected behaviour for $T > T_c$ is $I \propto T \omega^{-2}$, where the frequency of a soft mode varies as $\omega^2 \propto T - T_c$. Thus, the diffuse intensity varies with temperature as

$$I \propto \frac{T}{T - T_c} \quad (2)$$

Dynamic effects will be observed only above the transition temperature. As $T \rightarrow T_c$ from above, the dynamic intensity will tend to infinity. At high temperatures, I will tend to a finite limit. This behaviour contrasts with both convergent phase transitions ($I = 0$ for $T > T_c$) and nonconvergent transitions ($I \rightarrow 0$ as $T \rightarrow \infty$).

Experimental procedure

The nepheline used in this study was from a nepheline gneiss collected from near the Snipe river, Tambini,

Malawi (sample 65984 from the Harker collection, Cambridge University). McConnell (1962) observed sharp satellite reflections in the $c^*:[1\ 1\ 0]^*$ section of the diffraction pattern in a TEM study of this nepheline. This indicated that the Tambini nepheline has a well-ordered incommensurate structure. On heating, the satellites become weaker and more diffuse. The high degree of order measured in these experiments and the X-ray structure refinement of Parker and McConnell (1971) imply a reasonably low temperature of equilibration in nature.

For this study, a single crystal of nepheline was mounted on a four-circle X-ray diffractometer. The satellite reflection at $(1/3, 1/3, 5.79)$ was studied, this being the most intense. The sample was first disordered by heating to 923 K for several hours. This annealing should give full (K, □) disorder (McConnell 1981), without significantly affecting the (Al, Si) distribution. Intensity measurements were then made as the sample was cooled back to room temperature. The changes in the recorded intensity (Fig. 4) occurred instantaneously, indicating a displacive process.

The divergence of I_{sat} at 308 K implies the softening of a phonon mode at this temperature. From this, we can conclude that disordered nepheline undergoes a displacive phase transition to an incommensurate structure at 308 K.

Infrared spectroscopy

In order to obtain further data on this phase transition, it is necessary to study the behaviour of disordered nepheline below the transition temperature. In principle, this could be done using the X-ray method described above. If disordered nepheline undergoes a displacive phase transition, the diffuse satellite reflections (e.g. in Fig. 1) should sharpen at T_c , and the sharp satellite maxima should increase in intensity on cooling.

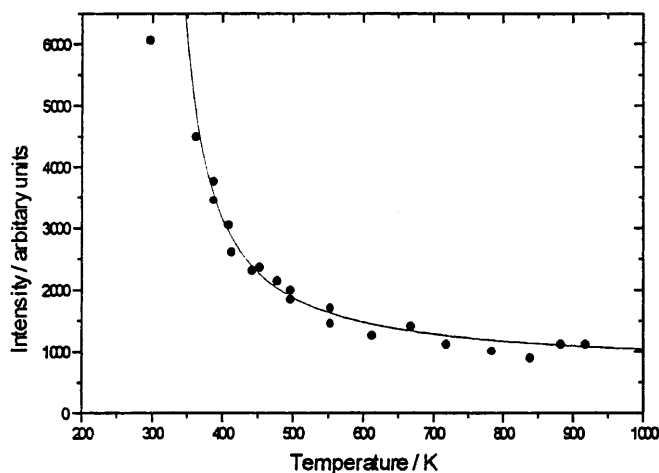


Fig. 4 Temperature dependence of the integrated satellite intensity at $(1/3, 1/3, 0.21)$ in a disordered nepheline. The fit is to the model in Eq. (1), with $T_c = 308$ K

The phase transition may also be studied using infrared spectroscopy. In the hard mode method reviewed by Bismayer (1990) and Salje (1992), small changes in the frequency, intensity and linewidth of phonon modes are found to correlate with the thermodynamic order parameter.

Sample preparation

Since IR spectroscopy is extremely sensitive to the presence of impurities in the sample, a quantity of the Tambani ordered nepheline was purified, principally to remove cancrinite. The resulting material was ground initially by hand, and then in a micromill.

Nepheline was then mixed with KBr to produce infrared pellets. A sample:matrix ratio of 1:300 was found to saturate the detector, so more dilute pellets, with a 1:1000 ratio were used. The resulting mixture was then pressed under vacuum at 0.75 MPa for 10 min, to produce optically transparent pellets.

Infrared spectroscopy experiments

Initially, ordered nepheline was heated from room temperature to 650 K, collecting spectra at 30-K intervals. No attempt was made to equilibrate the nepheline at these temperatures, even though it is known that the disordering behaviour of nepheline is time-dependent.

The sample was then cooled back to room temperature, during which time no measurements were taken. A second heating and cooling run was then performed on the now disordered nepheline. The maximum temperature reached during this cycle was 587 K. The sample was then transferred from a furnace to a cryostat. The pellet was then cooled to 50 K in 50-K steps, and finally heated back to room temperature.

Results

Figures 5 and 6 show the variation of the infrared absorption spectrum with temperature for ordered and disordered nepheline respectively. The broadness of the peaks at 700 and 1000 cm^{-1} is due to their each containing several vibrational modes (Matson et al. 1986). Useful data can be obtained by fitting each of these peaks to a single Gaussian function. The changes in peak position with temperature and (K, \square) order are shown in Figs. 7 and 8.

Both bands vary in the same way, though the effects are more marked in the 700- cm^{-1} band. The absorption frequency is reduced by disordering the material, and otherwise varies with temperature due to the effect of thermal expansion. At high temperatures, this effect is linear, but at low temperatures, the thermal expansion vanishes. To quantify this, X-ray powder diffraction was

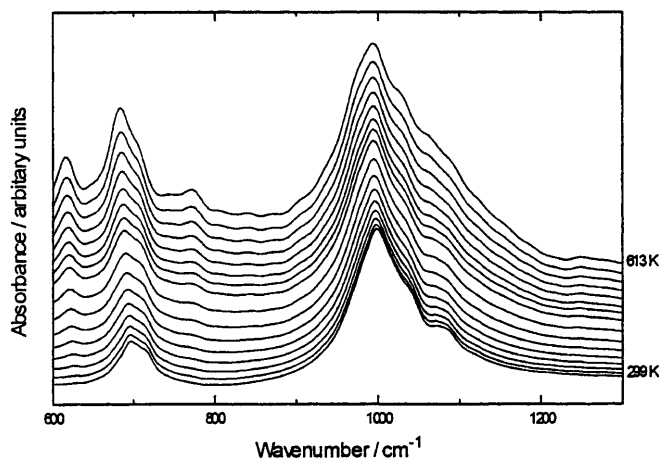


Fig. 5 Temperature dependence of the mid-infrared absorption spectrum of initially ordered nepheline between 299 K (where nepheline is fully ordered) and 643 K (where nepheline is fully disordered)

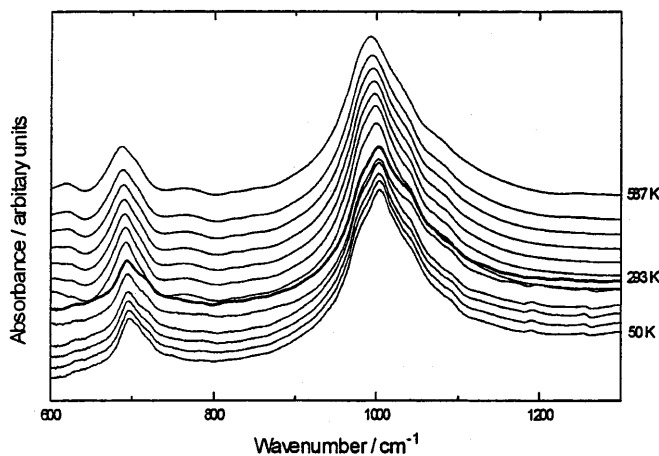


Fig. 6 Temperature dependence of the mid-infrared absorption spectrum of disordered nepheline between 303 and 587 K

used to determine the lattice parameters as a function of temperature (Table 1). The baseline shown in Fig. 7 is derived from the observed saturation of the lattice parameters below ca. 150 K.

The excess change in the position of the centre of the 700 cm^{-1} band below 300 K shown in Fig. 7 is consistent with the phase transition observed in the single-crystal X-ray data. The excess wavenumber $\Delta\omega$ is proportional to Q^2 , the square of the order parameter.

Discussion

A displacive phase transition in disordered nepheline

The changes in the infrared spectrum of nepheline support the idea that disordered nepheline undergoes a displacive phase transition at 308 K. Comparison with

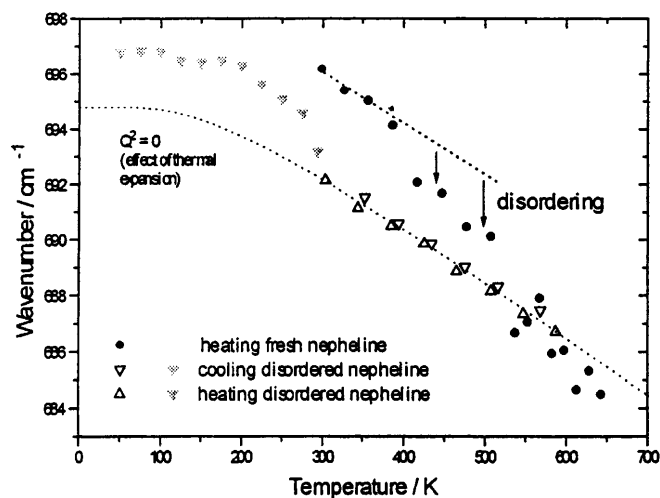


Fig. 7 Temperature dependence of the peak centre of the 700 cm^{-1} mode. The *broken lines* show the effect of thermal expansion in the absence of changes in the order parameters. The *lower line* is for disordered nepheline, based on changes in the lattice parameters in Table 1

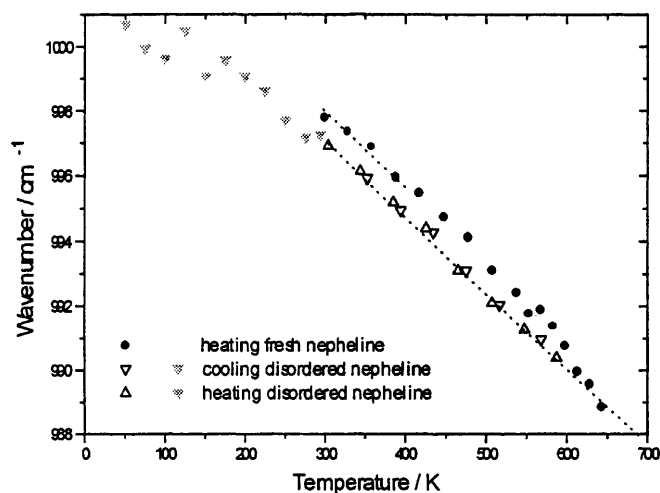


Fig. 8 Temperature dependence of the peak centre of the 1000-cm^{-1} mode. The *broken lines* show the effect of thermal expansion in the absence of changes in the order parameters

Table 1 Lattice parameters as a function of temperature in nepheline from 22 K to room temperature. Typical error is 3 in the last quoted decimal place

T/K	a/Å	c/Å
22	9.985	8.376
45	9.983	8.377
70	9.986	8.378
95	9.985	8.377
119	9.988	8.380
144	9.987	8.378
168	9.988	8.381
193	9.996	8.375
217	10.001	8.376
241	10.000	8.371
266	10.000	8.371
290	10.010	8.381

the X-ray diffraction data indicates that this transition involves the same distortion of the framework as seen in the (K, □) ordered phase.

This transition has strong parallels with the orthorhombic-monoclinic phase transition in tridymite ($T_c = 383\text{ K}$, Thompson and Wennemer 1979). The driving force of this transition is the energy of the Si-O-Si bond angle. In the ideal structures of both OC tridymite and disordered nepheline, the angle measured in an X-ray structure refinement is close to 180° . This bond angle is a high-energy structure; a T-O-T angle of approximately 135° is much more stable. (Gibbs et al. 1981).

At high temperatures, an apparent bond angle of 180° is achieved dynamically; the O1 oxygens precess around the triad axis, so that their time-averaged position is on the triad. At lower temperatures, this precession cannot occur, and so the structure becomes frozen in an off-centred position. Similar behaviour is seen in cristobalite (Swainson and Dove 1993, 1995; Hammonds et al. 1996; Dove et al. 1997). In tridymite, the wave vector of the phonon involved is at a commensurate point (Pryde and Dove 1998). In nepheline, on the other hand, the same phonon is at an irrational point, leading to an incommensurate structure.

The RUM calculations show that, for the crystal structure in Fig. 2, the appropriate soft mode is at an incommensurate point in reciprocal space. It is important to note that an incommensurate structure is obtained even without considering the bonding between the alkali cations and the O1 oxygens. The interactions between the framework and the stuffing cations will certainly affect the stability of the various phases. One example of this is that (K, □) order enhances the stability of the various incommensurate phase, as shown by the increase in T_c (452 K for ordered nepheline, 308 K for disordered nepheline). However, the underlying reason for the incommensurate structure of nepheline at low temperatures is the constraint that the structure is a framework of linked stiff SiO_4 and AlO_4 tetrahedra.

Estimation of the gradient energy

If the mechanism driving the commensurate-incommensurate phase transition in nepheline is the same as that for the orthorhombic-monoclinic transition in tridymite, we might expect a relationship between the thermodynamics of the two transitions. The difference in transition temperatures (383 K for tridymite, 308 K for nepheline) would then largely be due to the extra energy associated with the incommensurate structure which low nepheline is forced to adopt.

For a second-order transition where Q is nonuniform, the Landau potential is

$$G = \frac{A}{2}(T - T_c)Q^2 + \frac{B}{4}Q^4 + \frac{g}{2}(\nabla Q)^2, \quad (3)$$

where the modulated form of $Q(\mathbf{x})$ is

$$Q = Q_0 \exp(i\mathbf{k} \cdot \mathbf{x}) . \quad (4)$$

Substituting $Q(\mathbf{x})$ into the Landau potential,

$$G = \frac{A'}{2}(T - T_c)Q^2 + \frac{B'}{4}Q^4 + \frac{g}{2}Q_0^2|\mathbf{k}|^2 , \quad (5)$$

and so the actual transition temperature is reduced by the modulations,

$$T_c^* = T_c - \frac{g|\mathbf{k}|^2}{A'} . \quad (6)$$

If we make the rather drastic assumption that the only differences between the thermodynamics of nepheline and tridymite is the effect the modulated structure, then the observed change in T_c and the wavelength of the modulation allow g/A' to be determined.

The wave vector of the incommensurate structure in nepheline is (1/3, 1/3, 0.21), and so the modulations along the c^* axis have $|\mathbf{k}| = 0.16 \text{ \AA}^{-1}$. Given that the ΔT_c between nepheline and tridymite is 75 K,

$$\frac{g}{A'} = \frac{\Delta T_c}{|\mathbf{k}|^2} = 0.4 \times 10^{-16} \text{ K m}^2 .$$

An alternative method to determine g is based on kinetic analysis. Salje (1988) argues that modulations with a short wavelength will decay more rapidly, because they have higher free energy due to the term. Using this method, de Dombal (1992) found $g/A' = 2 \times 10^{-16} \text{ K m}^2$. For such a simplistic model, this degree of agreement is reasonable. Comparison of the two values of g shows that the incommensurate structure of nepheline is rather more stable than an equivalent modulated structure in nepheline-like SiO_2 (i.e the structure illustrated in Fig. 2). Possibly this is due to the interactions between the framework and the stuffing cations.

In this study we have shown that the static incommensurate structure in nepheline is defined by the need to bend the Si-O-Al angle without distorting the SiO_4 and AlO_4 tetrahedra. For nephelines which equilibrate at low temperatures, the (K, □) ordering scheme follows the framework modulation, which further stabilises the incommensurate phase.

The RUM model has been used to analyse the static distortion of the incommensurate phase and the dynamics of the high temperature structure. The intensity of the diffuse diffraction effects provides an insight into the frequency of the soft mode above the transition temperature. Similar effects have been observed for the α - β transition in quartz (Arnold 1965), though the experimental data in this case are less extensive.

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References

- Arnold H (1965) Diffuse Röntgenbeugung und Kooperation bei der α - β Umwandlung von Quarz. *Z Krist* 121: 145–157
- Bismayer U (1990) Hard mode Raman spectroscopy and its application to ferroelastic and ferroelectric phase transitions. *Phase Transitions* 27: 211–267
- Carpenter MA, Cellai D (1996) Microstructures and high temperature phase transitions in kalsilit. *Am Mineral* 81: 561–584
- de Dombal RF (1992) Phase transitions in nepheline and tridymite. PhD Thesis, University of Cambridge
- Dove MT (1993) Introduction to lattice dynamics. Cambridge University Press, Cambridge
- Dove MT, Heine V, Hammonds KD (1993a) Rigid Unit Modes in framework silicates. *Min Mag* 59: 629–639
- Dove MT, Giddy AP, Heine V (1993b) Rigid Unit Model of displacive phase transitions in silicates. *Trans Am Cryst Ass* 27: 65–74
- Dove MT, Hammonds KD, Heine V, Withers RL, Kirkpatrick RJ (1996) Rigid Unit Modes in the high temperature phase of SiO_2 tridymite: calculations and electron diffraction. *Phys Chem Miner* 23: 56–62
- Dove MT, Keen DA, Hannon AC, Swainson IP (1997) Direct measurement of the Si-O bond length and orientational disorder in β -cristobalite. *Phys Chem Miner* 24: 311–317
- Gibbs GV, Meagher EP, Newton MD, Swanson DK (1981) A comparison of experimental and theoretical bond length and angle variations for minerals, inorganic solids and molecules. In: Navrotsky A, O'Keefe M (eds) Structure and bonding in crystals. Academic Press, New York, pp 195–225
- Giddy AP, Dove MT, Pawley GS, Heine V (1993) The determination of Rigid Unit Modes as potential soft modes for displacive phase transitions in framework crystal structures. *Acta Crystallogr A* 49: 697–703
- Hammonds KD, Dove MT, Giddy AP, Heine V (1994) CRUSH – a FORTRAN program for the analysis of the rigid-unit mode spectrum of a framework silicate. *Am Mineral* 79: 1207–1209
- Hammonds KD, Dove MT, Giddy AP, Heine V, Winkler B (1996) Rigid-unit phonon modes and structural phase transitions in framework silicates. *Am Mineral* 81: 1057–1079
- Matson DW, Sharma SK, Philpotts JA (1986) Raman spectra of some tectosilicates and of glasses along the orthoclase-anorthite and nepheline-anorthite joins. *Am Mineral* 71: 694–704
- McConnell JDC (1962) Electron diffraction study of subsidiary maxima of scattered intensity in nepheline. *Min Mag* 33: 114–124
- McConnell JDC (1981) Time-temperature study of the intensity of satellite reflections in nepheline. *Am Mineral* 66: 990–996
- Palmer DC (1994) Stuffed derivatives of silica polymorphs. In: Heaney PJ, Prewitt CT, Gibbs GV (eds) Silica: physical behavior, geochemistry, and materials applications (Reviews in mineralogy, vol 29). Mineralogical Society of America, Washington, pp 83–122
- Parker JM, McConnell JDC (1971) Transformation behaviour in the mineral nepheline. *Nature Phys Sci* 234: 178–179
- Pryde AKA, Dove MT (1998) On the sequence of phase transitions in tridymite. *Phys Chem Miner* 26: 171–179
- Salje EKH (1988) Kinetic rate laws derived from order parameter theory I: theoretical concepts. *Phys Chem Miner* 15: 336–348
- Salje EKH (1992) Hard mode spectroscopy: experimental studies of structural phase transitions. *Phase Transitions* 37: 83–110
- Swainson IP, Dove MT (1993) Low frequency floppy modes in β -cristobalite. *Phys Rev Lett* 71: 193–196
- Swainson IP, Dove MT (1995) Molecular dynamics simulation of α - and β -cristobalite. *Phys Chem Miner* 22: 61–65
- Thompson AB, Wennemer M (1979) Heat capacities and inversions in tridymite, cristobalite and tridymite-cristobalite mixed phases. *Am Miner* 64: 1018–1026
- Withers RL, Thompson JG, Xiao Y, Kirkpatrick RJ (1994) An electron diffraction study of the polymorphs of SiO_2 -tridymite. *Phys Chem Miner* 21: 421–433