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Neutron powder diffraction study of the orientational order–disorder phase transition in calcite, CaCO$_3$

Abstract Neutron powder diffraction studies of calcite on heating towards the orientational order–disorder phase transition show that the phase transition is not a simple analogue of an Ising-like transition, but more similar to a rotational analogue of Lindemann melting. The transition is precipitated by the librational amplitude of the carbonate molecular ions exceeding a critical value rather than a result of a statistical entropy of 'wrong' orientations. Using tested interatomic potentials the single-particle orientational potential and nearest-neighbour orientational interactions have been calculated.

Introduction

The existence of a phase transition in calcite (CaCO$_3$) at high temperature has been suspected for a long time, but a detailed structural experimental investigation has not been possible because the carbonate group is chemically unstable at temperatures below the supposed transition temperature. Having an environment of CO$_2$ gas at a pressure of only a few atmospheres can retard the decomposition of the carbonate group. Because of the high penetrating power of neutrons compared to X-rays, it is possible to use standard furnaces to enclose the required environment. In a previous neutron diffraction study (Dove and Powell 1989), the temperature

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dependence of two superlattice Bragg peaks, 113 and 211, was monitored. It was observed that they both disappeared at $T_c \sim 1{,}260$ K, consistent with a halving of the c-lattice parameter and a change in the space group from $R\bar{3}c$ to $R\bar{3}m$. The intensity data were consistent with a temperature dependence of an order parameter Q, which was not characterized, of the form:

$$Q \propto I_{l=\text{odd}}^{1/2} \propto (T_c - T)^{1/4}, \tag{1}$$

where $I_{l=\text{odd}}$ is the intensity of a Bragg peak with an odd value of l.

The temperature dependence of the Bragg angles for the few reflections that were measured suggested the existence of a large spontaneous strain ε_3 that by symmetry should be proportional to Q^2. The strain data were accurately described by the function:

$$\varepsilon_3 \propto (T_c - T)^{1/2}. \tag{2}$$

Thus both the intensity data and the unit cell data appeared consistent with the temperature dependence of the order parameter of the form $Q \propto (T_c - T)^{1/4}$, which is for a classical tricritical phase transition (Bruce and Cowley 1981). Usually this follows from a Landau free energy function G_L of the form

$$G_L = \frac{1}{2}\eta_2 Q^2 + \frac{1}{6}\eta_6 Q^6, \tag{3}$$

which can arise "accidentally" from a Landau free energy with a strain-coupling term that in this case couples the large ε_3 strain to Q^2:

$$G_L = \frac{1}{2}\eta_2 Q^2 + \frac{1}{4}\eta_4 Q^4 + \frac{1}{6}\eta_6 Q^6 + \frac{1}{2}\alpha\varepsilon_3 Q^2 + \frac{1}{2}C_{33}\varepsilon_3^2, \tag{4}$$

where C_{33} is an elastic constant. Minimization with respect to ε_3 yields

$$\varepsilon_3 = \frac{-\alpha Q^2}{2C_{33}} \tag{5}$$

and

$$G_{\mathrm{L}} = \frac{1}{2}\eta_2 Q^2 + \frac{1}{4}\left(\eta_4 - \frac{\alpha^2}{2C_{33}}\right)Q^4 + \frac{1}{6}\eta_6 Q^6. \qquad (6)$$

Thus, (6) reduces to (3) when

$$\eta_4 \approx \frac{\alpha^2}{2C_{33}}. \qquad (7)$$

The experimental findings for calcite are similar to the behaviour observed in the analogous phase transition in sodium nitrate, $NaNO_3$ (Reeder et al. 1988; Schmahl and Salje 1990; Swainson et al. 1998). The latter is simpler to study as it has a lower T_{c} and does not require gas pressure to prevent decomposition, although the melting point lies not far above T_{c}.

It is unlikely that in the cases of both calcite and sodium nitrate $\beta \approx 1/4$ will be due to a cancellation of the fourth-order term in the Landau free energy expansion as expressed by (7). A tricritical point at ambient pressure would be an "accident" and the likelihood of both compounds having a tricritical point at the same pressure seems very small. In the case of $NaNO_3$ the exponent on the order parameter in (2) has been reported as dropping from 0.25 to 0.22 close to the transition temperature (Reeder et al. 1988; Schmahl and Salje 1990).

More recently, Harris (1999) argued strongly against tricriticality as an explanation of $\beta \approx 1/4$ in either transition. He proposed that both transitions could be modelled by a two-dimensional XY pseudospin model, which predicts values of β close to 0.23. Such a model implies that the disordering process is two-dimensional. This model appears to fit the static structure of calcite in the ordered phase, where the planar carbonate ions lie in 001 planes, and assumes insignificant coupling between layers. He also questioned the existence of a cross-over of β from 0.25 to 0.22 in $NaNO_3$, arguing that a value of 0.22 appeared to be valid over the entire temperature range until about 5.5 K of T_{c}, at which point the fluctuations were so large that the interactions become three-dimensional and β values of approximately 0.34 were more appropriate. We cannot settle the debate on the exact value of β from the data presented here, but we will comment on the validity of pseudospin models. In particular, our evidence suggests that there is a strong coupling of carbonate ions between the planes, revealed by large out-of-plane motion of these ions on heating.

There have been inelastic neutron scattering measurements (Dove et al. 1992a; Hagen et al. 1992; Harris et al. 1998) and computational studies on calcite (Dove et al. 1992b; Ferrario et al. 1994; Liu et al. 2001). The inelastic neutron scattering study showed the existence of an unexpected feature, namely strong inelastic scattering localized at a few points on the surface of the Brillouin zone (corresponding to the F-points on the surface of the Brillouin zone of the disordered phase) and which extended up to about 2 THz in energy. Due to the narrow width of this feature in reciprocal space, it has been described as a *column* of scattering. This col-

umn appears to be associated with a softening of one of the phonon branches at this point—a branch that is the transverse acoustic mode at small wave vectors. On heating, the intensity of the column increases dramatically, the frequency of the mode decreases and the mode becomes strongly damped. But within the resolution of the experiment, the width of the column does not broaden in Q on heating, reflecting some kind of long-range ordering (Harris et al. 1998). Conversely it disappears completely on cooling towards 0 K (Dove et al. 1992a).

In order to provide some insight into the inelastic behaviour a simple interatomic potential model has been developed for calcite (Dove et al. 1992b). This was used in static lattice energy relaxation calculations and in calculations of the harmonic lattice dynamics, which reproduced the softening of the transverse acoustic branch as described above. The model was used in an MD simulation of calcite (Ferrario et al. 1994), and many of the features of this simulation have been recently confirmed by more modern MD methods (Liu et al. 2001). The simulations reproduce many of the experimental observations remarkably well, e.g. the transition temperature, the large spontaneous strainε_3 and the results showing the growth of the librational amplitude, L_{33}, of the carbonate group that are presented in this paper.

The simulation of Ferrario et al. (1994) showed that the symmetry of the phonon branch that is the transverse acoustic branch at small k is of symmetry F^{2-}. F^{2-} is also the symmetry of the soft mode for the lowest high-pressure transition in calcite, to calcite II (Merrill and Bassett 1975; Hatch and Merrill 1981). On the other hand, the simulations have been unable to reproduce the columnar nature of the observed inelastic scattering. The narrow width of the column in reciprocal space suggests that the F-point ordering must involve correlations over distances that are much larger than the size of the sample used in molecular dynamics simulation.

The column is a rather unusual feature in a set of phonon dispersion curves. Its closest analogues appear to be β-Ti (Petry et al. 1988) and β-Zr (Heiming et al. 1991), where a "column" in the dispersion descends very steeply and whose eigenvectors also correspond to the ω-phase of these metals, related to the β-phase by a displacive transition at pressure. In the case of calcite, the behaviour could be fitted to an interaction between the phonon itself and a relaxational mode (Harris et al. 1998), using the model of Michel and Naudts (1978). This showed that the phonon frequency approaches zero as T_{c} is approached, and the value of c, a correlation function representing coupling between phonon and relaxational modes, appears to approach unity on heating towards T_{c}. A frequency mode approaching zero and a value of c tending to one are both signs of an imminent phase transition. It therefore appears that near the transition point for Z-point ordering (ca. 1,250 K) another nearly energetically degenerate ordering is competing at the F-point.

In order to shed further light on the features of this phase transition and the general mechanism of disordering, it is important to obtain good structural data at high temperatures, ideally to temperatures above T_c. Markgraf and Reeder (1985) have previously performed a single-crystal X-ray study up to 1,073 K, which is some 200 K short of T_c, but chemical decomposition prevented studies at higher temperatures. We have therefore attempted to extend the structural information to higher temperatures using neutron scattering.

Experimental details

Our present experiments were performed on the C2 DUALSPEC neutron powder diffractometer at the NRU reactor, Chalk River Laboratories. C2 has an 800-element detector covering an angular range of 80°. The wavelength selected was 1.50329(5) Å, calibrated via an external standard of NBS Si 640b. We collected data at each temperature for scattering angles between 5° and 117°. Two attempts were made to stabilize calcite into the disordered phase, resulting in two datasets.

Dataset 1. A sample of calcite powder was loaded into an open vanadium can of diameter 5 mm, which was then mounted in a furnace. In order to prevent chemical decomposition the sample was maintained in an overpressure of CO_2 gas. However, at high temperatures CO_2 is highly corrosive, and for this reason special furnace elements were required. The heating element was a cylinder of SiC, which surrounded the sample in the scattering plane. SiC is resistant to oxidation since the initial oxidation produces a silica surface layer that prevents further oxidation. The thermocouples, in direct contact with the sample, were sheathed with a coating of stainless steel to prevent oxidation. The inside of the furnace was evacuated and then filled with CO_2 to a pressure of 2 atm as measured by a gauge on the surface, which was held at ambient temperature. The pressure at the sample position is expected to be higher following ideal gas heating, but its value cannot be determined. Data were collected up to nominal temperatures of 1,155 K. Despite our careful preparations we found that we were unable to prevent decomposition on heating above 1,200 K. Pressurizing the entire furnace beyond 2 atm was not possible.

Dataset 2. The experiment was then repeated in a different furnace in which the calcite was placed into a vanadium foil, which in turn was inside a large vanadium tube. This tube can be pressurized up to 9 atm of CO_2 (as measured at room temperature) with the aid of a water-cooled seal, leaving the body of the furnace in vacuum. A full description of this equipment is found in Rollings et al. (1998). The only additional experimental difficulty with this setup up was that a sample thermocouple could not be placed in direct contact with the sample inside the pressure chamber. Therefore, the measured temperature was in error. We used the *c*-lattice

parameter as an internal calibrant over the range of temperatures that were measured in common. Using this we were able to reference the results from the latter furnace to those of the former furnace, which had a thermocouple in direct contact with the sample. A very linear temperature offset was found between 500 and 1,155 K ($R^2 = 0.9997$).

Data analysis

The diffraction data were analysed using two methods, Rietveld refinement and extraction of peak intensities. Rietveld refinement is not particularly suited for the study of orientational disorder, but we expect that the phases generated for the individual structure factors will be correct and therefore of use for producing Fourier maps with the observed structure factors. For reference we show the crystal structure of the ordered phase in Fig. 1. The structure consists of planar trigonal carbonate groups coordinated to Ca^{2+} ions in distorted octahedra. The carbonates lie in layers normal to [001]. The carbonate groups within a single layer have the same orientation. In the neighbouring layers the carbonate groups are rotated by 60° about [001]. Hence in
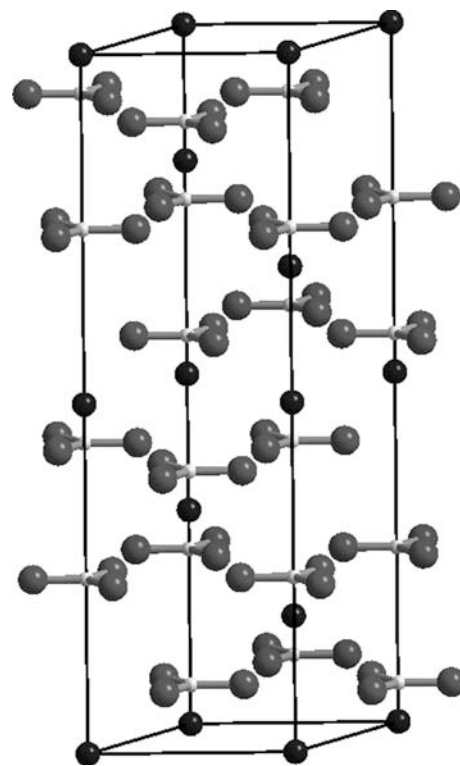
Fig. 1 The crystal structure of calcite in the hexagonal cell of the low-temperature ordered phase. The carbonate groups are the planar trigonal units and the calcium the isolated atoms. The carbonate groups lie in planes normal to *c*, which runs vertically. Within any plane all the carbonate groups point in the same direction. Neighbouring planes of carbonate groups have opposite orientations

Fig. 2 Temperature dependence of the unit cell parameters a and c for the two datasets, as numbered in the text. The a cell shows a small overall contraction on heating. The expansion of the c-lattice parameter is large. The esd's for the values of c are smaller than the points. The *line* represents a hypothetical extension of the c-parameter of the disordered phase, assuming the relationship given by (2) in the text
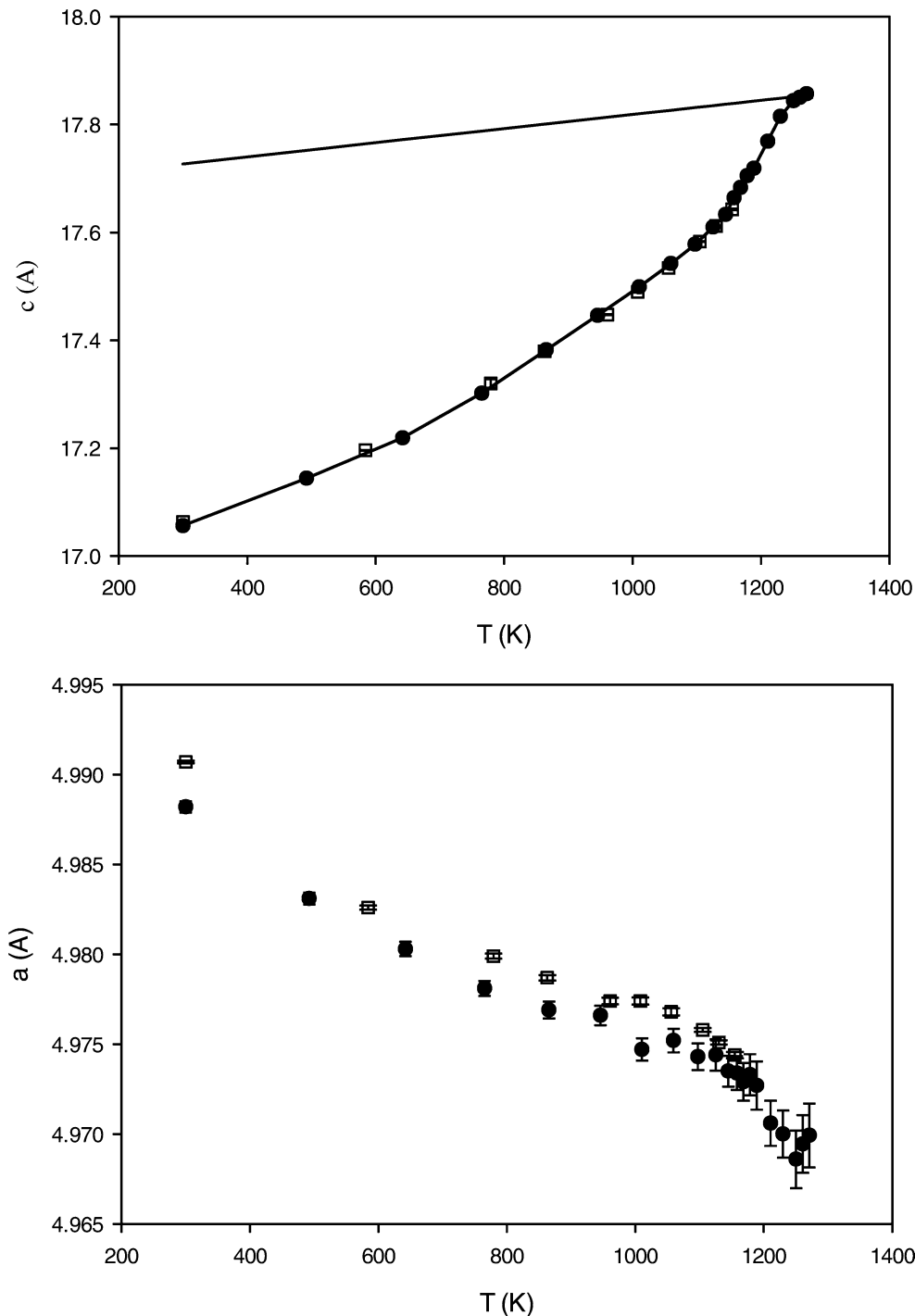

the ordered phase the layers of carbonate groups alternate in orientation. In the disordered phase there is no distinction between the neighbouring layers, and for any carbonate group both orientations ($\theta = 0°$ and $\theta = 60°$) are equally probable. This results in a halving of the c-axis in the disordered phase.

In Fig. 2 we show the temperature dependence of the unit cell parameters. These are consistent with our previous data and show the same small negative thermal expansion of a and the large thermal expansion of c associated with the spontaneous strain ε_3. The c-parameter of the ordered $R\bar{3}c$ cell is twice that of the $R\bar{3}m$ cell of the disordered phase, when expressed in the hexagonal setting. The large expansion of the c-lattice parameter is anomalous, since it is clearly coupled to the phase transition, yet is normal to the plane in which the main disordering process of the carbonate groups takes place. The origin of this effect is discussed below. Since we have used the complete diffraction pattern to obtain the cell parameters, rather than using only two
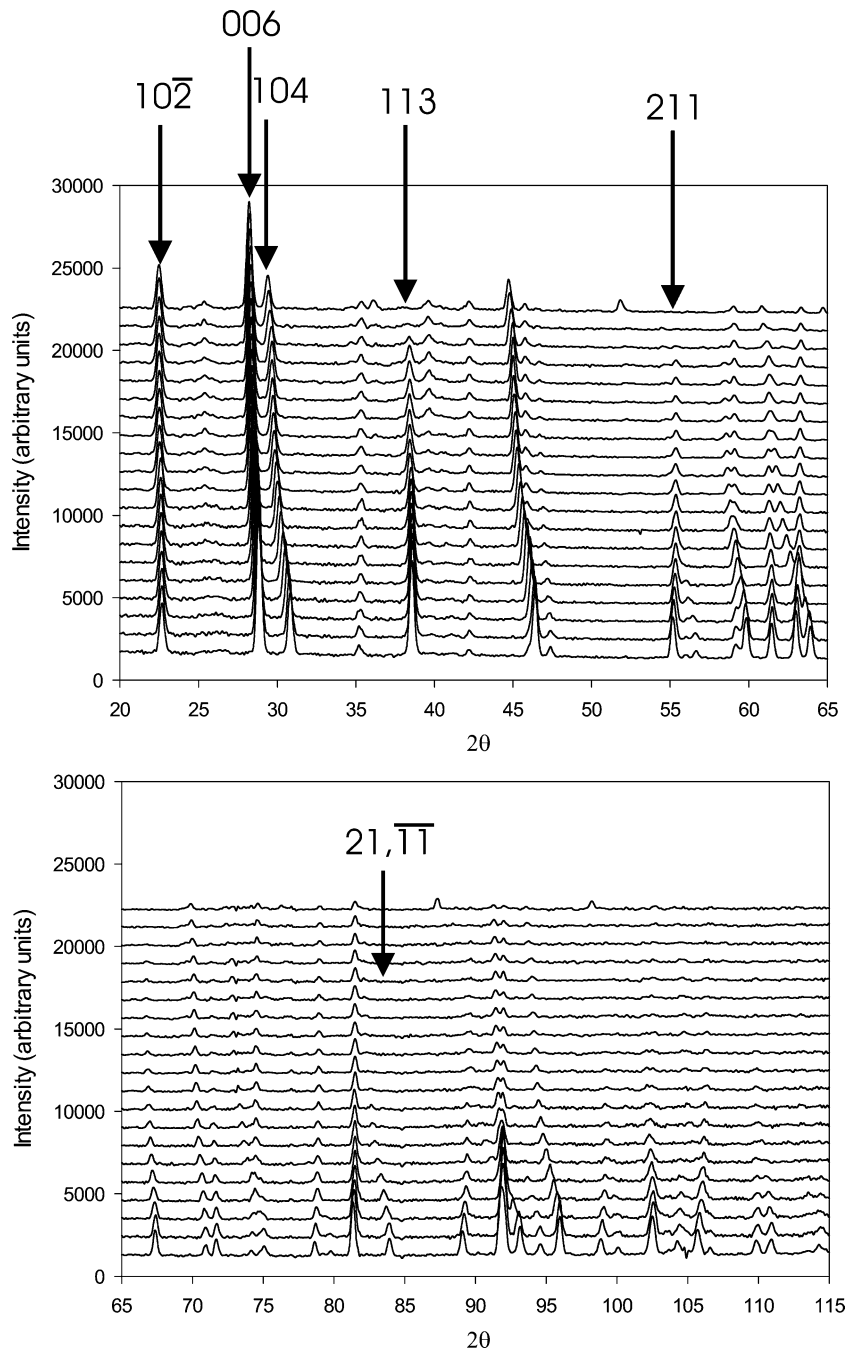
reflections as in the study of Dove and Powell (1989), we have significantly improved upon the precision of the measurements. The straight line in Fig. 2 represents the extrapolated value of twice the value of the c-lattice parameter of the disordered phase, using all the measured values of c and assuming that (2) holds, and that expansion in the disordered phase is reasonably approximately by a linear expansion. Our best estimate from these method yields $8.8438 + 6.5527 \times 10^{-3} T$Å, where T is in Kelvin. Due to the higher temperature reached in this study and the fact that we use all the Bragg peaks, we consider this to be a better estimate than that given earlier (Dove and Powell 1989).

The small plateau region in the expansion of the a cell parameter at around 1,000 K was also seen in the previous neutron powder diffraction study (Dove and Powell 1989). With the extension of the dataset to higher temperatures in this study it is shown that this plateau is followed by another region of contraction above ca. 1,050 K.

The remaining part of the analysis below deals with the more extensive second dataset. In the ordered phase, reflections hkl with l odd are superlattice reflections generated by the ordering of the carbonate groups. In Fig. 3 we show a stack plot of the diffraction patterns of calcite on heating up to 1,250 K. The lowest order

Fig. 4 Temperature dependence of the intensities of isolated reflections with both even and odd values of *l*. In descending order these are $10\bar{2}$, 104, 006, 113, 211 and 21,$\overline{11}$. Odd *l* reflections all show a strong decrease in intensity on heating, as these are superlattice peaks generated by the ordering of the carbonate groups below T_c. Even *l* reflections show a much smaller reduction in intensity and are only affected by the general increase in all Debye–Waller factors. All intensities have been normalized to unity at room temperature. *Inset* The square of the intensity of the lowest order superlattice peak, 113, as a function of temperature
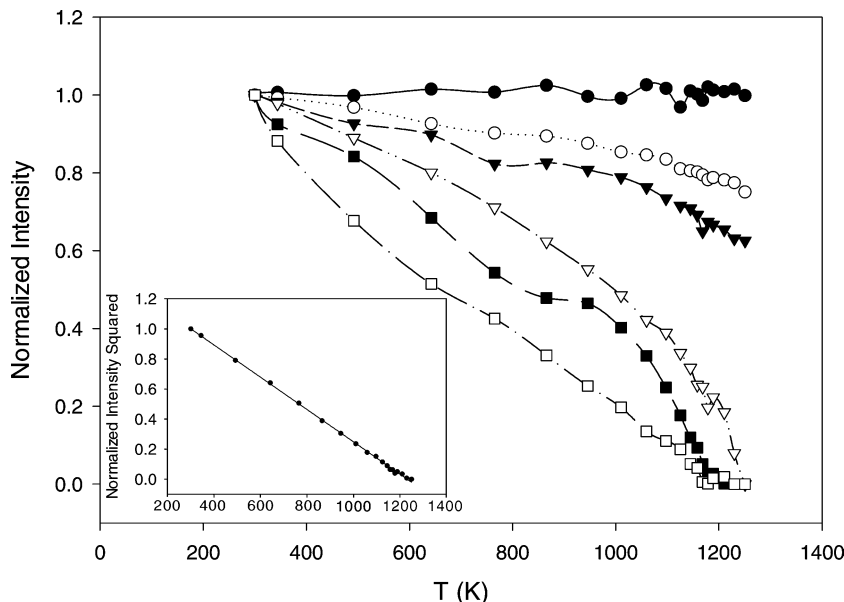
superlattice peak 113 at ~39° 2θ can be seen to disappear, at least to the level at which we could measure them. This would be a signal that we had entered the disordered phase, but it is always possible that we lack the signal-to-noise ratio sufficient to claim this. The new peaks that appear correspond to reflections from CaO, due to the onset of breakdown of the sample. Two additional diffraction patterns were taken at 1,260 and 1,270 K, but it is difficult to display them as CaO becomes increasingly dominant due to the serious breakdown of the sample near the disordered phase. It was still possible to determine lattice parameters, but little other information.

In Fig. 4 we show the temperature dependence of the intensities of a number of reflections from the data presented in Fig. 3. The reflections with even values of *l* are not expected to disappear on heating into the high-temperature phase, and these show a temperature dependence that is only determined by the general increase in temperature factors with temperature. Therefore the intensities of the lowest angle reflections with even *l* barely change with temperature. In contrast the reflections with odd values of *l* have intensities that decrease on heating towards the transition temperature. The lower angle reflections with odd values of *l* are consistent with (1) to within statistical uncertainty. The higher angle data deviate slightly from the form of (1) because they are more sensitive to the increase in temperature factors, whose effects are also clearly seen in the temperature dependence of the reflections with even values of *l*. The square of the intensity of the lowest order superlattice peak, 113, is shown as a function of temperature in Fig. 4, together with a best-fit straight line representing (1) in accordance with values of *β* near 1/4.

We attempted refinements of calcite using a classical "spin" model of disorder, but such refinements were not

stable at any temperature, as reported by previous workers in calcite and $NaNO_3$ (e.g. Markgraf and Reeder 1985; Gonschorek et al. 1995). The crystal
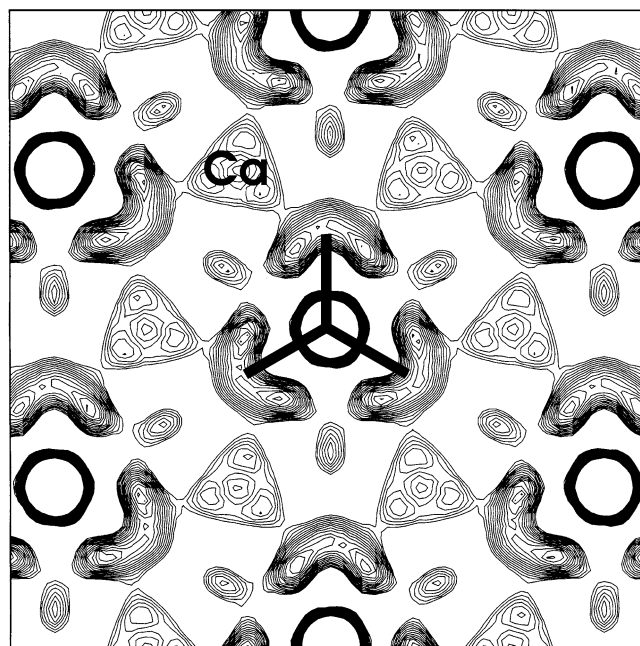

Fig. 5 Observed Fourier maps of calcite for a section viewed down [001] at 0 0 1/4 containing the carbonate ions, from the 1,189 K data. A schematic of a carbonate ion is placed on top of the major observed intensity group. The Ca ion is also labelled. The map shows that the centre of mass of carbon, as shown in the *centre* of the figure, is still well defined on approaching T_c. The scale has been deliberately strongly amplified. While this shows up some noise, it was done so in order to show the extent of the spread of orientations of the carbonate groups. However, it is clear that the distribution of orientations does not include a significant population of the anti-ordered orientations, i.e. those rotated by 60°

structure of calcite at high temperatures is best illustrated using Fourier maps. In Fig. 5 we show a Fourier map with an exaggerated scale, calculated using the observed structure factors and the calculated phase values from the data taken at 1,189 K. The most striking feature is the large librational amplitude of the carbonate groups for rotations about [001], which increases dramatically on heating. There is also an absence of any distinct nuclear density at positions that would correspond to oxygens being in the anti-ordered positions, i.e. with the carbonate ion having rotated by 60° about [001]. These observations follow the trends found by Markgraf and Reeder (1985) at lower temperatures. If

the transition were due to a classical pseudospin model, assuming a value of $\beta \approx 0.25$, we would expect approximately 1/4 of the carbonates to be in the anti-ordered orientation in Fig. 5. A similar absence of any "anti"-ordered groups was seen in the combined synchrotron and neutron single-crystal studies performed on $NaNO_3$ by Gonschorek et al. (1995) at room temperature.

In order to quantify these features we have analysed the atomic motions given by the atomic temperature factors associated with the carbonate groups in terms of the rigid body TLS tensors, the approach previously used by Markgraf and Reeder (1985) in the analysis of X-ray single-crystal diffraction data of calcite. We used

Fig. 6 Temperature dependence of the thermal parameters T_{11}, T_{33}, b^2L_{11} and b^2L_{33} (*top*), where b is the C–O bond length, and of the librational amplitudes $\sqrt{L_{11}}$ and $\sqrt{L_{33}}$ (*bottom*)
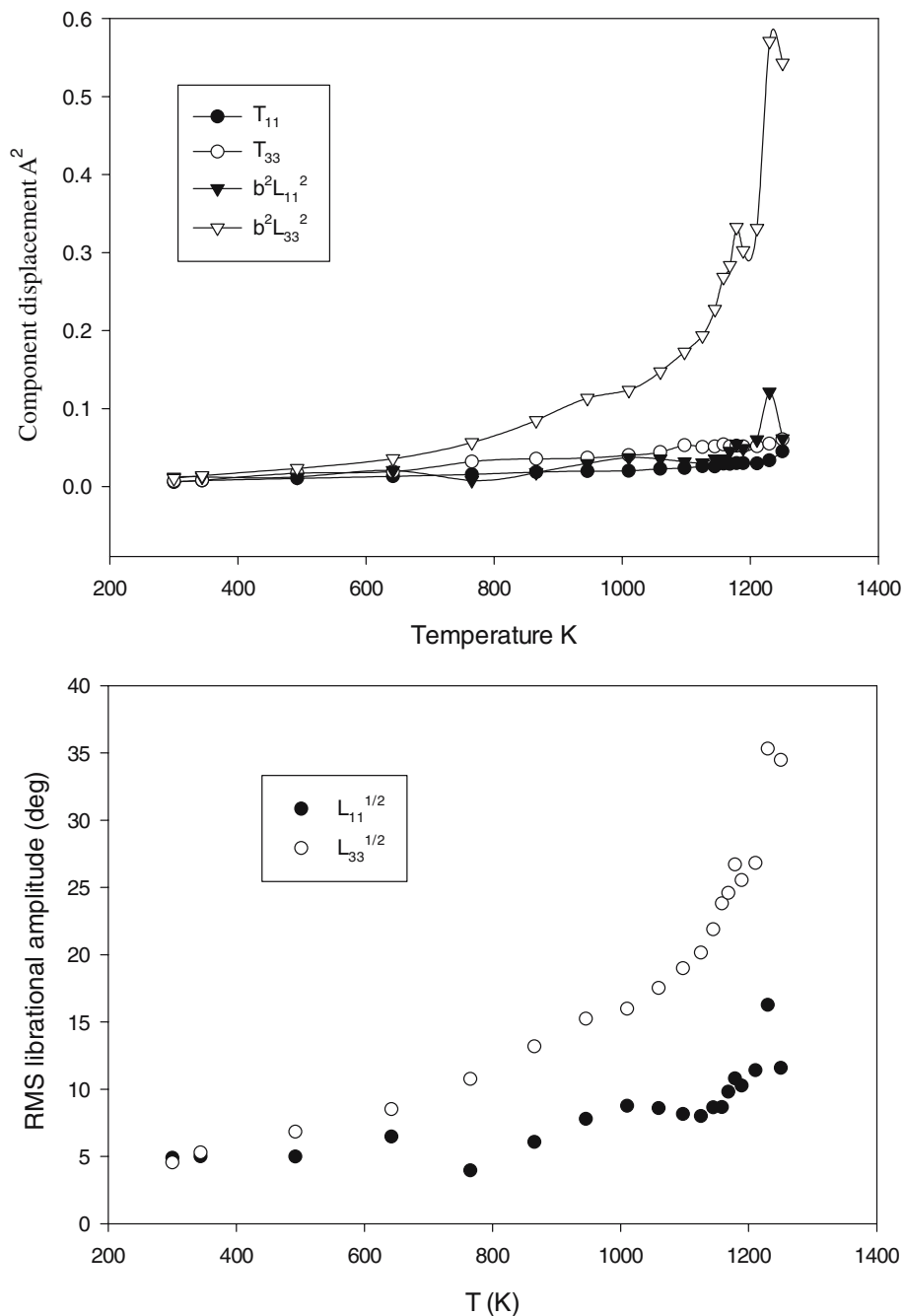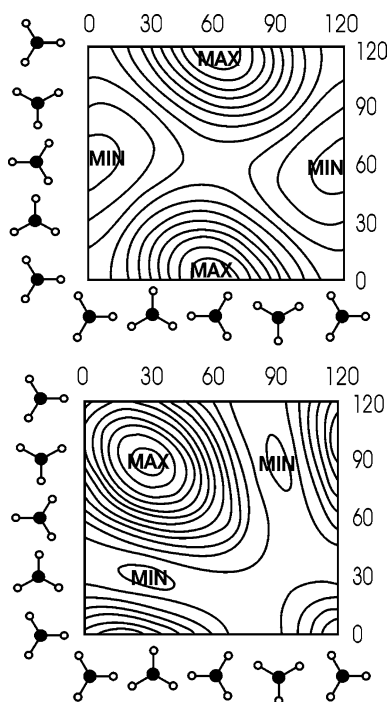
Fig. 7 a Interaction potential between two nearest-neighbour carbonate pairs in the same (001) plane as a function of the orientations of the two groups. The relative orientations for different points on the contour map are shown as symbolic axis labels, alongside the angular values. *Solid contours* are in increments of 1,000 K. The maximum at (60°, 0°) has a relative energy of 8,376 K; the saddle point at (60°, 60°) has a relative energy of 0 K; and the minimum at (0°, 60°) has a relative energy of $-2{,}848$ K. **b** Interaction potential between two nearest-neighbour carbonate pairs in neighbouring (001) planes (separated by $c/6$) as a function of the orientations of the two. *Dashed contours* are in intervals of 50 K. The maximum at (30°, 90°) has a relative energy of 348 K; the saddle point at (90°, 30°) has a relative energy of -236 K; and the minima at (30°, 30°) and (90°, 90°) have relative energies of -281 K

the TLS facility in both GSAS (Larson and VonDreele (1987) for the results presented here, although we have checked them with refinements using Fullprof (Rodriguez-Carvajal 1990) and no significant differences were found. These serve as an illustration of the main disordering processes, as at high librational amplitude the approximation that thermal motion is a small perturbation of a static structure becomes much poorer. We did not find the screw components to be stable under either of these programs, so we present only T and L. In Fig. 6 we show the temperature dependence of the thermal parameters T_{11}, T_{33}, $b^2 L_{11}$ and $b^2 L_{33}$, where b is the C–O bond length, T_{11} and T_{33} are rigid body translations of the carbonate group along axes parallel to [100] and [001], respectively, and L_{11} and L_{33} are librations of the carbonate group about the same axes. L_{11} and T_{33} rotate and translate the carbonate group out of the (001) plane, whereas L_{33} and T_{11} correspond to the in-plane motions. It is clear that the increase of the L_{33} librational components far exceeds that of all other components. However, there is a substantial growth of

L_{11} corresponding to the out-of-plane motion of the carbonate ions. This suggests that the spins are not decoupled between neighbouring planes. It may also be the origin of the large thermal expansion along c, since there is an increase in the effective size of the carbonate ion along [001] as the disorder increases.

In Fig. 6 we also show the temperature dependence of the librational amplitudes $\sqrt{L_{11}}$ and $\sqrt{L_{33}}$—the rapid increase of $\sqrt{L_{33}}$ on heating is clearly seen. The growth of $\sqrt{L_{33}}$ was also observed in the molecular dynamics simulations of Ferrario et al. (1994) and Liu et al. (2001). Once the amplitude for librations about [001] reaches 30° each carbonate group will be able to flip easily into the anti-ordered orientation. In the disordered phases for calcite and $NaNO_3$ both simulations suggest that there is some preferred occupation in anti-ordered sites, superimposed on a general background of orientational disorder. It appears that the large librational amplitudes near the disordered phase are responsible for the breakdown on heating of calcite and the relatively small temperature range of the disordered phase in $NaNO_3$ before the melting point. In this respect, it bears some resemblance to the hexahydrate, ikaite, in which hindered librations of the carbonate ion have also been suggested as the mechanism of decomposition of that metastable phase (Swainson and Hammond 2003).

Discussion

We have observed a rapid decrease in intensity of the reflections with odd values of l on heating, consistent with the change in space-group symmetry. The presence of distinct hkl, $l = 2n + 1$, superlattice peaks in the comparatively well-ordered state of calcite at room temperature which are lost at high temperature only gives information that there is an alternating order along the [100] direction, which is destroyed on heating. By directly examining the structure of calcite or by calculating explicitly the structure factors, it is clear that this ordering is orientational ordering of carbonate groups, as defined by oxygen atoms. Our structure analysis has shown the rapid growth of thermal motion, in particular in the librational amplitude on heating towards the phase transition.

The disorder we envisage for the high-temperature phase, and the only one that is consistent with the change in space-group symmetry, is that each carbonate group occupies a site of point symmetry $\bar{3}m$, so that there is an equal probability of locating an oxygen atom at intervals of 60°. The simplest way to view this is to think of each carbonate group as having two possible orientations related to each other by rotations of 60° (or equivalently 180°). Thus one might assign a pseudospin to each site, of value ± 1 depending on whether the orientation is 0° or 60°. We would then expect that at low temperature all the carbonate groups in any given plane will have the same orientations and on heating the number of carbonate groups in the same plane with the

opposite orientation will increase, similar to the behaviour found in any Ising-like phase transition. The order parameter would then be defined as the difference between the number of carbonate molecular ions in the 'correct' (ordered) and 'wrong' (anti-ordered) orientations, which are related by 60° rotations.

This pseudospin scenario, as we have seen in the previous section, is not borne out by our Fourier maps at high temperatures, which show no sign of any carbonate groups in opposite orientations. This observation was also previously reported from the X-ray results of Markgraf and Reeder (1985), for temperatures up to 1,073 K. Instead of a simple statistical disorder, we find only large-amplitude librations about [001], which on heating increase in size much more rapidly than the usual linear temperature dependence. This effect was also seen in the molecular dynamics simulation as a broadening of the single-molecule orientational distribution function for the carbonate groups (Ferrario et al. 1994; Liu et al 2001).

We are therefore forced to view the phase transition in a new way. We start by considering the local potential at the carbonate site due to the surrounding calcium atoms. In the disordered phase this has point symmetry $\bar{3}m$, so the potential is the same for rotations of 60° and can be described by a local single-particle potential $V_{\text{Local}}(\vartheta)$ of the form:

$$V_{\text{Local}}(\vartheta) = V_0 \sin^2(3\vartheta), \tag{8}$$

where θ describes the orientation of the carbonate ion about [001], and $\theta = 0°$ gives the average orientation in the layer shown in Fig. 5 (the values of θ alternate between 0 and 60° on going between the planes). The description in terms of pseudospins is equivalent to the approximation that $V_0 \to \infty$. Using the potential of Dove et al. (1992b), we have calculated a value for $V_0 \approx 4{,}500$ K, assuming that the most important contributions are the short-range interactions with the neighbouring Ca ions and the long-range Coulomb interactions. For the Coulomb interactions we have calculated the potential for a single carbonate ion in a field due to point charges and have assumed that at typical distances the neighbouring carbonate groups can be represented as point charges at the carbon position.

From the theory of phase transitions, as described in detail by Bruce and Cowley (1981), comes the ratio

$$s = \frac{V_0}{k_B T_c}, \tag{9}$$

which specifies the type of phase transition.

When $s \gg 1$ the phase transition is said to be of the order–disorder type. The local site potential is much stronger than the thermal energies, so that distribution of orientations is sharply clustered around the minima of the local potentials. In general it is assumed that orientational ordering over distinct sites will give a behaviour that is typical of order–disorder transitions, which is why analogies are often made to pseudospin systems. In

the other extreme, $s \ll 1$, the phase transition is of the displacive type. Thermal energies are comparable to, or greater than, the local site potential, so that there is a wide distribution of orientations rather than sharp distributions around the potential minima. In the present case we find that $s \approx 3.5$. Because of the relatively low value of s, we might expect that the phase transition in calcite would share many characteristics with a typical displacive phase transition, although it involves the disorder of the carbonate groups. This is consistent with the main features of the Fourier maps at high temperatures, which certainly resemble more closely the displacive type of phase transition rather than a simple order–disorder picture.

There is one feature that is special to the case of orientational ordering and which is not found in typical displacive phase transitions, namely that the local potential has rotational symmetry. This means that as the [001] librational amplitude ($\sqrt{L_{33}}$) increases, it will eventually become so large that the orientational probability distribution function for the carbonate ions will encompass both the ordered orientation ($\theta = 0°$) and the anti-ordered orientation ($\theta = 60°$). Then the carbonates ions will tend towards orientational disorder. In a way this mechanism is a rotational analogue of Lindemann melting. Unlike the pseudospin analogue, below T_c we would not expect, in this case, to see a growing fraction of carbonate groups in the anti-ordered orientation.

It may be that calcite provides a new type of orientational order–disorder phase transition. In most cases the transitions in these systems are so discontinuous that the ordered phase is almost fully ordered at all temperatures below the transition temperature. In such cases there is little scope for discussion of the mechanism of disorder closer to the critical region, so it has often been assumed that the transitions can be described within a pseudospin formalism. We are suggesting that calcite represents quite a different viewpoint. The observation that in calcite the carbonate ion only occupies the one orientational "state" in a manner becoming increasingly less defined on heating, rather than flipping between two distinct states, does make it difficult to see how any pseudospin model (e.g. Harris 1999) physically maps to calcite.

There are, however, some difficulties that must be considered. The first is that without a pseudospin formalism it is not immediately clear how to define the order parameter in microscopic terms. This is not to say though that a quantity that reflects an order parameter on a macroscopic scale cannot easily be measured—the example of using the spontaneous strain to determine the temperature dependence of the order parameter has been described earlier. We suggest that the simplest definition in the present case is

$$Q = 1 - \frac{1}{2} \langle \pm \cos 3\vartheta \rangle, \tag{10}$$

where the sign alternates between the layers along [001], since the carbonate groups in alternate layers are rotated

by 60°. In the limit $Q \rightarrow 1$, we can expand the cosine to give

$$Q = 1 - \frac{1}{2}\left\langle (3\vartheta)^2 \right\rangle = 1 - \frac{9}{2}L_{33}. \qquad (11)$$

However, $\left\langle (3\vartheta)^2 \right\rangle$ is a fairly crude guide to the ordering because the detailed shape of the orientational distribution function affects it. Also, because the temperature factors are the quantities that are determined with least accuracy in a powder diffraction experiment and the TLS model is only really valid for small amplitude motions, (11) is only at best approximated by our data. The macroscopic measurements of the temperature dependence of Q are to be preferred over estimates taken from the measurements of L_{33}. The main result, then, is not in the individual values of T and L tensors, but their relative magnitude as a function of temperature.

There are two important directions along which to consider orientational correlations: intraplanar and interplanar. The existence of the $R\bar{3}c$ to $R\bar{3}m$ transition signifies the loss of the latter, i.e. any average *anti*-correlation between carbonate layers. However, this disorder could be achieved in several ways with regard to the intraplanar correlations. The symmetry change has nothing to say about the disordering mechanism taking place within a layer: the limiting cases would be individual free carbonate rotors or large-amplitude fluctuations of orientations within entire sheets, but could lie anywhere in between. Furthermore, diffraction and the extracted values of the TLS tensors cannot distinguish between individual free carbonate rotors or correlated, large-amplitude reorientations of groups of carbonate anions.

The local orientational potential is given by $V_{Local}(\vartheta)$, but we must now add the interactions between neighbouring carbonate groups. We restrict our discussion to nearest-neighbour interactions, and for the present purposes we aim to present the qualitative picture. In Fig. 7a we show a contour plot of the intraplanar orientational interaction between nearest neighbours. In Fig. 7b we show a contour plot of the interplanar orientational interaction between nearest neighbours.

The most striking point from Fig. 7 is that the interactions within a single plane are much stronger than those between the carbonates in different planes. This may imply that the loss of orientational ordering between neighbouring 001 layers takes place by *correlated* L_{33} librations within each plane (i.e. each carbonate group is far from being a free rotor), but with perhaps little correlation between spins in neighbouring planes. Nevertheless, if each plane maintained absolute correlation of the orientations of all the carbonate ions, with the disordering process being just a loss of correlation between the layers, it seems difficult to explain why there would be an increasing amount of out-of-plane motion of ions, as revealed by the increase in the values of T_{33} and L_{11} with temperature.

It seems that even if individual orientations are not strongly coupled between layers, whole layers do interact strongly, yielding the large anomalous strains up the c-axis, normal to the principal disordering process occurring within 001. Lynden-Bell and Michel (1994) made the point that while in true molecular crystals, there are large interactions between molecular orientations, in ionic compounds a lattice of counterions separates the molecular ions, and the major interaction between orientations then becomes indirect. It is therefore possible that the rotations and displacements of the carbonates are coupled to those of the neighbouring layers by the translations of the Ca ions. It has also been suggested that translation–rotation coupling may be the mechanism by which Z and F-ordering are linked in calcite and sodium nitrate (Lynden-Bell et al. 1989; Lynden-Bell and Michel 1994).

Summary

We have presented new diffraction data for calcite on heating into the phase transition, which are consistent with, but more extensive than, our previous measurements. Analysis of the crystal structure from the diffraction data shows that there is appreciable in-plane thermal motion of the carbonate ions, which we model by the L_{33} librational amplitude, and that this increases rapidly on heating towards T_c. This suggests that the mechanism of disordering is closer to that of a continuous rotational melting than that of a pseudospin disordering. This agrees with the features observed in the orientational distribution functions of the simulations of Ferrario et al. (1994) and Liu et al. (2001). The anomalous expansion of the c-axis, occurring normal to the plane of the main disordering process, may be explained by the growth of the amplitude of the out-of-plane motion. We have shown that the local single-particle ordering potential is not significantly stronger than the nearest-neighbour orientational interactions. We suggest that the transition in calcite is representative of a new type of orientational order–disorder phase transition.

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