American Mineralogist, Volume 84, pages 1632–1640, 1999

A new explanation for the unusual critical behavior of calcite and sodium nitrate, $NaNO_3$

M.J. HARRIS*

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, U.K.

ABSTRACT

The phase-transition behavior of both calcite and the isostructural compound $NaNO_3$ have long been thought to be anomalous. In particular, the β critical exponent for the orientational order-disorder transitions takes on a value close to tricritical behavior ($\beta = 0.25$) in both materials, and in $NaNO_3$ two crossovers to regimes where $\beta = 0.22$ and then $\beta = 0.41$ have been reported as T_c is approached. The most significant puzzle was why both materials should appear to be tricritical under ambient conditions of both pressure and the conjugate field. The experimental work on these materials is re-analyzed in the light of recent progress in understanding two-dimensional magnetic ordering. It is shown that the experimental results are fully consistent with the two-dimensional XY model. Unlike the tricritical model, this gives a simple physical explanation for the disordering process and observed critical exponents. In particular, it supports other recent experimental findings from calcite and $NaNO_3$ that the orientational order-disorder occurs through continuous planar rotations of the carbonate and nitrate groups, rather than discrete jumps.

INTRODUCTION

Over the past 90 years, an astonishing number of papers have been written on the order-disorder phase transitions in calcite ($CaCO_3$), and the closely related material $NaNO_3$ (with mineral name nitratine); a conservative count puts the number at around 80! There are several reasons for the abiding interest in these phase transitions: (1) geologically speaking, calcite is an important material, and the order-disorder phase transition has a marked influence on the calcite-aragonite transition that is widely used as a geobarometer and geothermometer (Salje and Viswanathan 1976; Redfern et al. 1989); (2) both calcite and $NaNO_3$ represent some of the simplest compounds containing both ionic and covalent interactions and so are interesting from the point of view of developing simulation techniques; and (3) attempts to assign the phase transitions to standard models have been largely unsuccessful, thus revealing a degree of complexity that is surprising in such chemically simple materials.

This paper aims to review recent experimental work on the problem and to provide a simple and transparent re-interpretation of it, in view of recent progress in understanding magnetic phase transitions.

The phase transitions in both calcite and $NaNO_3$ involve an orientational ordering of the carbonate and nitrate groups, respectively, on cooling. The symmetry change is $R\bar{3}m \rightarrow R\bar{3}c$ in both cases, which is marked by the appearance of superlattice Bragg reflections at the *Z*-points of reciprocal space, i.e., the (0,0,3/2) point indexed using the hexagonal setting of $R\bar{3}m$. In the high-temperature phases the nitrate and carbonate molecular ions are orientationally disordered about their threefold axes, which are parallel to the crystallographic *c* axis. One significant difference between the two materials is the phase-transition temperatures: for $NaNO_3$, $T_c = 549$ K, whereas for calcite, $T_c = 1260$ K. Experimental studies of calcite are made difficult by the fact that it decomposes into CaO and CO_2 at about 1100 K under normal conditions, so that the phase transition may only be observed if the sample is kept in a partial pressure of CO_2. For this reason, there have been many more experimental studies of the phase transition in $NaNO_3$, which I will therefore concentrate on.

PREVIOUS WORK

One obvious possibility for the mechanism is a continuous increase with temperature of the angular oscillation of the groups about the *c* axis, leading eventually to a cooperative free rotation above T_c. This so-called "free-rotation" model was first suggested by Kracek et al. (1931) and initially received a large amount of support, until an alternative model was proposed, the "two-position disorder" model. Here, the nitrate groups become progressively more disordered between the two possible orientations of the low form, which are achieved by 60° flips of the groups about the *c* axis. At T_c the space-averaged correlation function along *c* tends to zero, and the nitrate groups flip randomly between the two positions. This model was first put forward by Ketalaar and Strijk (1945), and until very recently was the generally accepted model. The two models are illustrated schematically in Figure 1.

Thus, the free-rotation model is analogous to the XY model, where a magnetic dipole can take any orientation in the *x*-*y* plane perpendicular to the *z* axis, while the two-position disorder model is analogous to the standard Ising model. However, the nitrate and carbonate groups are not dipoles, and so the free-rotation

---

*E-mail: mark.harris@rl.ac.uk

0003-004X/99/0010–1632$05.00

and two-position disorder models are not formally equivalent to these two spin models in terms of their microscopic Hamiltonians. Instead, the equivalence comes through the nature of the critical fluctuations, which drive the phase transitions in both the structural and spin models, as discussed below.

Experimental studies of the disordering mechanism

Recent work has cast doubt on the validity of the two-position disorder model as an accurate description of the phase transitions in calcite and NaNO$_3$. Data from X-ray structure refinements of NaNO$_3$ for $T < T_c - 26$ can be described equally well by both the two-position disorder model and a model invoking orientational disorder in the manner of the free-rotation model (Lefebvre et al. 1984). However, close to the phase transition, for $T > T_c - 26$, the free-rotation model provided a better description of the data. Gonshorek et al. (1995) performed a high precision structure refinement of NaNO$_3$ at room temperature ($T \approx T_c - 250$), and found absolutely no evidence for nitrate groups flipped by 60° from the ordered positions; instead, a significant degree of librational motion of the nitrate groups was detected. Because Schmahl and Salje (1989) observed that the order parameter appears still to be evolving even at temperatures as low as that of the Gonshorek et al. experiment, the disordering mechanism is probably not associated with 60° flips of the nitrate groups, in the manner of the two-position disorder model. For calcite, Markgraf and Reeder (1985), Dove et al. (1998), and Swainson et al. (1998) have all made similar observations: instead of statistical disorder, only large-amplitude planar librations of the carbonate groups seem to occur. Therefore, the orientational disorder in both calcite and NaNO$_3$ is driven primarily by large-scale planar rotations of the carbonate and nitrate groups. The phase transitions are then precipitated by the librational amplitude of the carbonate and nitrate groups exceeding a critical threshold, rather than as a result of a statistical number of "wrong" orientations.

Experimental work on the β critical exponent

Studies of the birefringence (Poon 1988), lattice parameters (Reeder et al. 1988), and X-ray superlattice peaks (Schmahl and Salje 1989) of NaNO$_3$ have all concluded that for temperatures below about $T_c - 50$, the order parameter for the phase transition, Q, may be expressed as

$$Q \propto t^{\beta} \tag{1}$$

where t is the reduced temperature $t = (T_c - T)/T_c$, and $\beta \approx 0.25$ (Table 1). In calcite, a neutron diffraction experiment has also observed a value of $\beta = 0.25$ (Dove and Powell 1989). This is

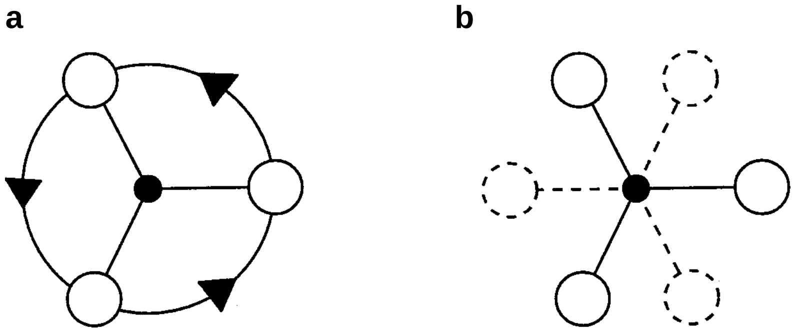

FIGURE 1. Schematic representations of a carbonate/nitrate group looking down the *c* axis for the orientational order-disorder transitions in calcite and NaNO$_3$. (**a**) The free-rotation model. (**b**) The two-position disorder model.

TABLE 1. Values for the β critical exponents for calcite and NaNO$_3$

	β	α
Tricritical mean-field (Landau) theory	0.25	0.5
3d 3-state Potts model	0.21	0.54
3d Ising model	0.326	0.106
3d XY model	0.345	–0.01
2d XY model	$3\pi^2/128 \approx 0.231$	0.36
Calcite (neutron diffraction)	0.240(8)	–
NaNO$_3$ (X-ray and neutron diffraction)	0.228(2) for $t > 10^{-2}$	–
	0.34(2) for $t < 10^{-2}$	–
NaNO$_3$ (spontaneous strain)	0.22(1)	–
NaNO$_3$ (birefringence)	0.22(1)	–
NaNO$_3$ (heat capacity)	–	0.40(6)*, 0.35(6)†
NaNO$_3$ (thermal expansion)	–	0.34(1)

Notes: The exponents are for various theoretical models and also extracted from previously published experimental data. See text.
* Reinsborough and Whetmore.
† Jriri et al.

the value for a tricritical phase transition described within the framework of mean-field (or Landau) theory. Tricritical behavior conventionally results at a point in the *T-P-H* phase diagram (where *P* is the pressure, and *H* can be any conjugate variable parameter such as the magnetic field, or the concentration of a chemical species) where lines of first and second order phase transitions meet so that three phases coexist (Griffiths 1970). Finding the tricritical value $\beta = 0.25$ thus suggests that the transitions in both calcite and $NaNO_3$ are intermediate between first order (discontinuous) and second order (continuous) behavior, and that both materials contain a tricritical point in their phase diagrams at conditions of ambient *P* and *H*.

What is perhaps more interesting is that as the transition in $NaNO_3$ is approached, the value of β appears to be reduced from 0.25 to 0.22, which happens at a temperature of approximately $T_c - 30$. There is currently no indication that a similar effect happens in calcite. In addition, a recent neutron diffraction study of the critical scattering from $NaNO_3$ has shown that an additional crossover occurs at about $T_c - 5$, where the order parameter changes again, this time to a value determined as $\beta = 0.41$ (Payne et al. 1997).

The outstanding questions

The experimental work has thus highlighted two principle questions: (1) why does the β exponent change in $NaNO_3$ and (2) why is β close to being tricritical in both calcite and $NaNO_3$? This latter question is at first sight the most puzzling, because it is extremely unlikely that a tricritical point should occur at conditions of ambient *P* and *H*, in both calcite and $NaNO_3$. In case one is inclined to doubt whether it is really so unlikely, consider the case of the alkali halides NX_4Cl and NX_4Br, where X is either H or D (Seeck et al. 1998). These compounds are chemically and structurally very similar under ambient conditions, and all contain well-attested tricritical points in their (*P*,*T*)-phase diagrams. However, the positions of the tricritical points are very different. For instance, the tricritical point in NH_4Cl occurs at a pressure of 1500 bar, while in ND_4Cl it is an order of magnitude lower, at 150 bar. In NH_4Br it is at a very different pressure again: 3250 bar. Clearly, changes in the chemistry have a profound influence on the positions of the tricritical points, and we would expect exactly the same argument to hold for calcite and $NaNO_3$, if indeed they were truly tricritical. Because no explanation for this problem has been put forward until now, I will discuss it later, after discussing previous attempts to answer question 1.

The most plausible explanation for the apparent change in the value of β from 0.25 to 0.22 in $NaNO_3$ is that strong critical fluctuations are present at temperatures close to T_c. These result in a breakdown of mean-field theory over a temperature interval known as the critical region, where the tricritical value for β is expected not to hold. The problem with this explanation is that the effect of critical fluctuations at a tricritical transition in a three-dimensional material is only to add a logarithmic correction to the temperature dependence of *Q* (Bruce 1980). Equation 1 then becomes

$$Q \propto t^{1/4} \, |\log t|^{1/4} \, . \qquad (2)$$

Whereas this logarithmic correction can be mis-identified as a slowly varying β exponent (Fig. 2), it would only result in an effective value of $\beta = 0.22$ between reduced temperatures $10^{-4} < t < 10^{-3}$, i.e., within about 0.5 K of the phase transition in $NaNO_3$. Experimental observation places the crossover to $\beta = 0.22$ much further from the transition, at about $T_c - 30$. Hence we can discount the possibility that the crossover is due to the breakdown of tricritical behavior in the critical region. Lynden-Bell et al. (1989) and Schmahl and Salje (1989) instead suggested that the change in the value of β from 0.25 to 0.22 is due to the existence of non-critical fluctuations into a further ordered phase, associated with the *F*-point of reciprocal space, which corresponds to the (1/2,0,2) point in the hexagonal setting. The unusual critical behavior might then be explained as the effect of strongly competing order parameters, one associated with the *Z*-point, the other with the *F*-point, with the *Z*-point order parameter winning. In support, a large body of experimental and computational work now exists for both calcite and $NaNO_3$, pointing toward the existence of such a non-critical phase associated with the *F*-point (see in particular: Lynden-Bell et al. 1989; Dove et al. 1992; Hagen et al. 1992; Harris 1993; Ferrario et al. 1994; Harris et al. 1998a, 1998b). However, it still does not answer the question of why the transitions in both materials are close to being tricritical in the first place. In addition, the suggestion that competing interactions

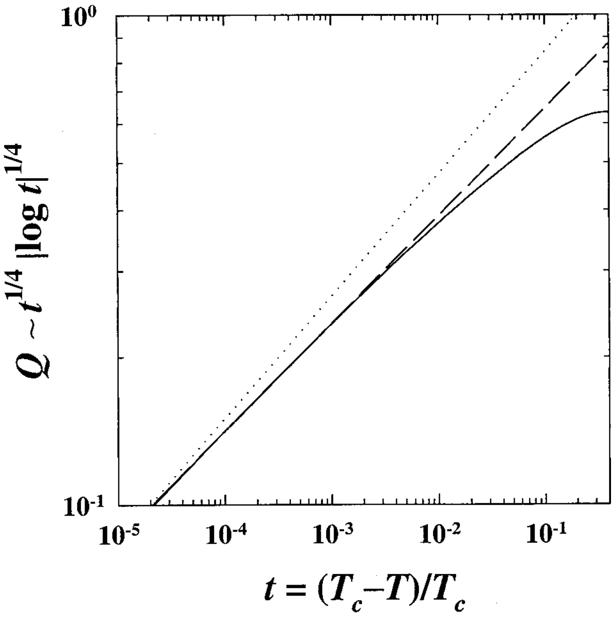

FIGURE 2. The order parameter for a tricritical phase transition with critical fluctuations—Equation 2—is shown as the solid line. Dashed line is the best fit to this line of Equation 1 with $\beta = 0.22$. Dotted line, $\beta = 0.25$. This illustrates that an effective exponent of $\beta = 0.22$ is only valid for very small reduced temperatures, $10^{-4} < t < 10^{-3}$. Both axes are shown on logarithmic scales, so that pure power-law behavior would be linear.

can modify critical exponents is a highly contentious one and is not in general supported by work on magnetic systems, where the microscopic interactions are better understood. The proposal below will answer both questions 1 and 2 without the need to invoke competing order parameters. It will also be argued that, interesting as they are, the *F*-point fluctuations are a "red herring" in terms of explaining the properties of the phase transitions.

One further suggestion has been made to explain the crossover in the value of β from 0.25 to 0.22 in $NaNO_3$. This suggestion was made by Schmahl and Salje (1989), who noticed that the three-dimensional 3-state Potts model has a theoretical value of $\beta \approx 0.21$ (Table 1). This model is appropriate for systems where the order parameter can have a choice of three values when the symmetry is broken, whereas for instance the 2-state Potts model is essentially the Ising model. Schmahl and Salje proposed that the 3-state order parameter is related to a type of wetting phenomenon where domains of the *F*-point structure form as interfaces between anti-ordered domains of the conventional *Z*-point structure. The interface thus corresponds to a pseudo-spin 0 between areas with pseudo-spins +1 and −1. However, there are two problems with this proposal: (1) more recent work shows that the suggested *F*-point structure is not energetically degenerate with the *Z*-point structure (Dove et al. 1992) and (2) fluctuations into the *F*-point phase are not critical fluctuations, while fluctuations into the *Z*-point structure are. Therefore, the *F*-point structure cannot now be considered to represent the third state of a 3-state order parameter, and so there is no clear physical basis for how the 3-state Potts model might apply to calcite and $NaNO_3$.

UNIVERSALITY AND SPIN MODELS

The universality principle

The universality principle is fundamental to the current understanding of phase-transition behavior inside the critical region. Put simply, it says that the values of the critical exponents of any system undergoing a phase transition are determined solely by the dimensionality (d) of the system, the dimensionality (m) of the order parameter, and the relative length scales of the microscopic interactions. Each different (d,m) case then corresponds to a different "universality class." Experimental tests have shown universality to hold in many cases, whether the phase transition is magnetic, superconducting, liquid-to-gas, or structural. Mean-field theory ignores the dimensionality and is appropriate for any system that contains long-range interactions, because the microscopic details of the Hamiltonian become less important. For instance, some materials undergoing ferroelastic phase transitions such as Na_2CO_3 (Swainson et al. 1995; Harris et al. 1996, 1997) are dominated by long-range forces to such an extent that no departure is observed from mean-field-type theory even extremely close to T_c. On the other hand, magnetic systems generally contain much shorter-ranged interactions (frequently as short as only a single nearest-neighbor bond length), and the critical region is then very large. Non-classical (i.e., non mean-field) critical exponents are observed up to large reduced temperatures, typically up to $t \approx 0.2$ or more (e.g., see Table 1 of Bramwell and Holdsworth 1993a). This is especially true of two-dimensional systems, which have significantly stronger critical fluctuations than three-dimensional systems (Als-Nielsen and Birgeneau 1977). An extreme example is that of the layered antiferromagnet Rb_2CoF_4, whose order parameter has been observed to follow the theoretical prediction for the two-dimensional Ising model (which is, of course, a non-mean field model) over a huge range of reduced temperature: $10^{-3} < t < 0.7$ (Collins 1989). Strictly speaking though, the critical region is asymptotic, in the sense that the "true" critical exponents will only be found at vanishingly small reduced temperatures. But whatever the size of the true critical region, it is a very frequent empirical observation that the non-mean field power law behavior extends out to reduced temperatures $t > 0.1$ in magnetic materials, particularly when the interactions are strongly two dimensional.

We might then consider whether we can apply the universality principle to calcite and $NaNO_3$. First, we need to determine qualitatively the length scale of the critical interactions. Most magnetic and structural order-disorder phase transitions (with the possible exception of ferroelectrics) are driven by short-range forces. In the case of molecular orientational ordering transitions this is due to the fact that, although relatively long-range dipolar and multipolar interactions are always present, the transitions are controlled on a very short-range scale by the steric constraints of molecules impinging against each other as they are reorganized. Whereas there is a displacive component to the phase transitions in both calcite and $NaNO_3$ (because c changes quite markedly), even this is a result of these steric considerations. Hence, to a first approximation, calcite and $NaNO_3$ are driven mostly by short-range forces, and so will have large critical regions like magnetic phase transitions. In that case, mean-field theory should not apply except for temperatures far from T_c, implying that we can assign the transitions to a universality class and compare their behavior with spin models.

A possible universality class for calcite and NaNO$_3$

At first sight, assignment of calcite and $NaNO_3$ to the relevant universality class appears trivial. The low-temperature ordered phases of both materials involve three-dimensional orientational ordering of the carbonate and nitrate groups, so we might expect that $d = 3$. Also, because there is a very strong degree of alignment (or "anisotropy") for the orientations of the groups in the low temperature phases, we might assume that the groups behave effectively as Ising spins, so that $m = 1$. This is the situation essentially favored by the two-position disorder model, where 60° flips of the groups about their threefold axes are equivalent to either "up" or "down" orientations of an Ising spin. So we might then expect the universality class to be that of the three-dimensional Ising model.

However, to be more precise, it is the dimensionalities of the critical fluctuations that determine the character of the phase transition. As discussed above, recent high precision structure refinements suggest that the phase transitions are driven by planar rotations of individual carbonate and nitrate groups rather than 60° flips, and so the fluctuations are more correctly described by the XY model, where $m = 2$. Furthermore, the calcite crystal structure is very two dimensional with respect to the carbonate groups, which lie in planes perpendicular to the *c* axis. Calculations (Dove, unpublished calculations) show that the forces between carbonate groups in the planes are considerably stronger than the forces between planes, by a factor of approximately 20. This means that we would expect the critical fluctuations in both calcite and $NaNO_3$ to be predominantly two dimensional in extent. This argument suggests that the expected universality class is the two-dimensional XY model. As we will see, this is borne out by the published experimental data. However, calcite and $NaNO_3$ are not perfect two-dimensional systems, so we might expect that at temperatures very close to the phase transition, the three-dimensional nature of the ordering will come into play, as will the effective anisotropy. This means that we expect a crossover to three-dimensional XY or three-dimensional Ising behavior to occur close to T_c. Again, this will be shown as consistent with the experimental data. This type of crossover from to two-dimensional to three-dimensional behavior is frequently observed in layered magnetic compounds (Collins 1989) and is simply due to the fact that three-dimensional correlations become important very close to a phase transition, once the much stronger two-dimensional correlations have diverged. Another way of looking at it is to say that the weak three-dimensional interactions modify T_c slightly from the purely two-dimensional ordering temperature, which means that they are then observed over this modified temperature range close to T_c.

The two-dimensional XY model

Until recently, it had always been assumed that the two-dimensional XY model does not exhibit a phase transition to a conventional magnetically ordered phase. Instead, theoretical calculations showed that a transition occurs on cooling to a state characterized by a spatial ordering of topological defects called vortices. This is known as a “Kosterlitz-Thouless-Berezinskii” (KTB) transition. The η and δ critical exponents may be quantified, but the exponents β, γ, and ν (which are those most easily accessible to experiment) are undefined. What was then surprising was that there exist several magnetic compounds that have microscopic Hamiltonians corresponding to the two-dimensional XY model, but which undergo conventional phase transitions, with a quantifiable order parameter and well-defined critical exponents. In particular, the β exponent is commonly found to be 0.23, which is close to the tricritical value of 0.25.

Bramwell and Holdsworth (1993a, 1993b) solved this apparent contradiction, and in doing so provided one of the few rigorous results that have been discovered in the theory of phase transitions in experimentally realizable systems, ranking alongside Onsager’s solution of the two-dimensional Ising model. Although there is no true ordered phase in the two-dimensional XY model for an infinite system, the correlation function has power-law decay, which means that a system of finite size should exhibit a finite order parameter. An estimate of the order parameter at the KTB transition is

$$Q = (2N)^{-1/16} \tag{3}$$

where N is the number of spins in the system. Bramwell and Holdsworth demonstrated this surprising effect with the following amusing illustration: a typical Monte Carlo simulation might contain $N = 10^5$ spins, which would give $Q \approx 0.47$, while a sample which was the size of a page of the average-sized journal might contain $N \approx 10^{16}$–10^{17} spins, which would still give $Q \approx 0.1$. Consequently, all experimental samples are expected to exhibit a conventional ordered phase and a finite order parameter at low temperatures, despite the findings of the original KTB work, which is valid only in the limit of infinite system size. As an aside, it should be noted that finite size can be equivalent to a whole series of related perturbations, including three-dimensional coupling. Significantly, Bramwell and Holdsworth found that the critical exponent for the order parameter of a finite-sized two-dimensional XY system can be determined exactly as

$$\beta = 3\pi^2/128 \approx 0.231 \tag{4}$$

which explained the previously mysterious experimental results.

RE-ANALYSIS OF EXPERIMENTAL DATA

Superlattice Bragg peaks

For calcite, the superlattice peak intensity data of Dove and Powell (1989) was analyzed by simultaneous least-squares fitting of Equation 1. One point from the original data set was eliminated from the fit, which is the intensity of the (1,1,3) peak at a temperature of 1258 K (where $t = 0.0016$). This point is so close to the phase transition that it is almost certainly contaminated heavily with critical scattering, and so will not represent an accurate measure of the order parameter. The value of the critical exponent obtained with this fitting procedure is $\beta = 0.240(8)$ (Fig. 3). Within the experimental error, this value is consistent with the original tricritical interpretation of Dove and Powell (1989), but also with the value (Table 1) expected for the two-dimensional XY model (Eq. 4).

For $NaNO_3$ (Fig. 4), data of Schmahl and Salje (1989) and of Payne et al. (1997) were scaled together to lie on a single curve. Combining the data greatly increases the precision of β, because we now have a measure of the order parameter over nearly three decades of reduced temperature. The clear change in slope at $t \approx 10^{-2}$ is the crossover. For $t > 10^{-2}$, the critical exponent is $\beta = 0.228(2)$, a value extremely close to the theoretical value for the two-dimensional XY model (Eq. 4). For $t < 10^{-2}$, $\beta = 0.34(2)$, which is consistent with three-dimensional Ising or three-dimensional XY behavior within the error. The generally accepted values for three-dimensional Ising and three-dimensional XY behavior are $\beta \approx 0.326$ and $\beta \approx 0.345$, respectively (Table 1).

Only the Schmahl and Salje data taken above 400 K ($t < 0.3$) were fitted. This is because for $t > 0.3$, the experimental data deviate slightly from the power law behavior. This could be due to the fact that the critical region extends out no further than $t \approx 0.3$. However, as shown in the next section, the spontaneous strain and birefringence data follow a power law behavior with $\beta = 0.22$ out to $t \approx 0.5$. The size of the critical region is thus large, and similar to that of many two-dimensional mag-

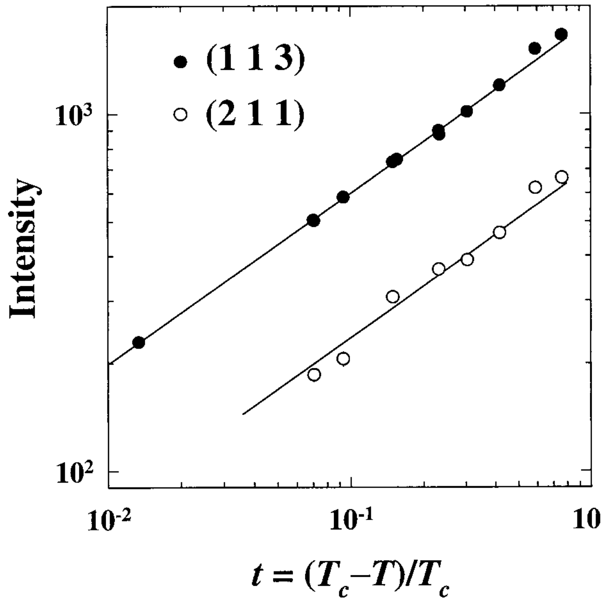

FIGURE 3. The intensities of the (1,1,3) and (2,1,1) superlattice Bragg peaks in calcite, measured using neutron diffraction by Dove and Powell (1989). Note that the data are plotted with both axes on logarithmic scales to bring out the power law behavior. The fitted lines show the results of a fit to both data sets simultaneously, with the critical exponent determined as $\beta = 0.240(8)$.

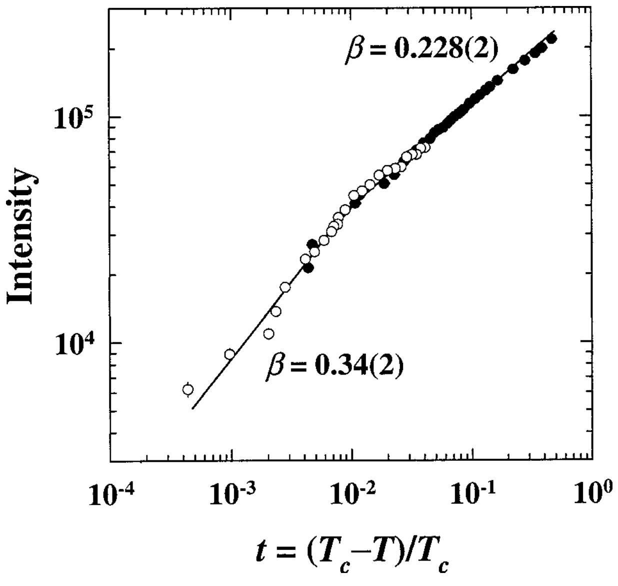

FIGURE 4. The intensities of superlattice Bragg peaks of NaNO$_3$. Filled circles = (123) measured using X-ray scattering (Schmahl and Salje 1989). Open circles = (113) measured using neutron scattering (Payne et al. 1997). The fitted line shows a regime of $\beta = 0.228(2)$ crossing over to a regime of $\beta = 0.34(2)$ at $t \approx 10^{-2}$. The temperature scale is again shown in units of reduced temperature, t, with $T_c = 553.7$ K for the Schmahl et al. data and $T_c = 548.5$ K for the Payne et al. data.

netic systems (Collins 1989). Such a large critical region is a signature of two-dimensional XY behavior (Bramwell and Holdsworth 1994). This suggests that the most likely explanation for the deviation of the superlattice intensity from a power law for $t > 0.3$ is extinction, which is always a serious concern with measurements of superlattice intensities (Cowley 1987). Schmahl and Salje (1989) disregarded the effect of extinction, and treated the data for $t > 0.3$ on an equal footing with the much more reliable data taken closer to T_c. This is probably the cause of their observation of a crossover from $\beta = 0.22$ close to T_c, to the tricritical value of $\beta = 0.25$ further from T_c (where $t > 0.1$): extinction always has the effect of increasing β anomalously.

Payne et al. (1997) also studied the critical scattering in NaNO$_3$ above T_c, and were able to determine the critical exponents for the correlation length and the susceptibility to be $\nu = 0.65(5)$ and $\gamma = 1.27(4)$, respectively. These are inconsistent with mean-field behavior ($\nu = 0.5$, $\gamma = 1$), but close to three-dimensional Ising ($\nu = 0.63$, $\gamma = 1.24$) and three-dimensional XY behavior ($\nu = 0.67$, $\gamma = 1.32$). Payne et al. noticed that the scaling relation

$$2\beta = d\nu - \gamma \tag{5}$$

is only just satisfied within the experimental errors with $\beta = 0.41$, which is the value they determined close to T_c. Using our newly determined value of $\beta = 0.34(2)$, we find that the scaling relation (Eq. 5) is satisfied exactly, which provides further support for this approach. Hence, above T_c we find the same three-dimensional behavior as for below T_c, for reduced temperatures $|\, t \,| < 10^{-2}$. Presumably, if we were able to measure the critical scattering above T_c for $|\, t \,| > 10^{-2}$, we would find a crossover back to two-dimensional XY behavior, matching the crossover below T_c. Unfortunately, NaNO$_3$ melts at a temperature corresponding to $|t|$ ◡0.04, making this experiment practically impossible.

Birefringence and spontaneous strain

Additional studies investigated the supposed tricritical nature in NaNO$_3$ (due to the experimental difficulties there are no additional data for calcite). Poon and Salje (1988) presented birefringence data to illustrate their interpretation that the transition is tricritical for $T < 500$ K, with a crossover to a region with $\beta = 0.22$ for 500 K $< T < T_c$. However, as an aside they noted that their data could equally well be fitted with the single exponent $\beta = 0.22(1)$. Because this involves fitting fewer parameters to the data, this must be the more reasonable value, and is also consistent with the two-dimensional XY model.

Reeder et al. (1988) measured the temperature dependence of the lattice parameters in NaNO$_3$. From this they determined the spontaneous strain, and like Poon and Salje (1988) presented an interpretation in terms of a crossover from tricritical behavior at low temperatures to $\beta = 0.22$ closer to T_c. During the data analysis, each of the two regions was allowed to have a different value of T_c, so that the tricritical region had an effective $T_c = 597$ K, and the $\beta = 0.22$ region had the "real" observed value of $T_c = 553$ K, some 10% lower. An equally satisfactory fit (Fig. 5) can be obtained using a single value of

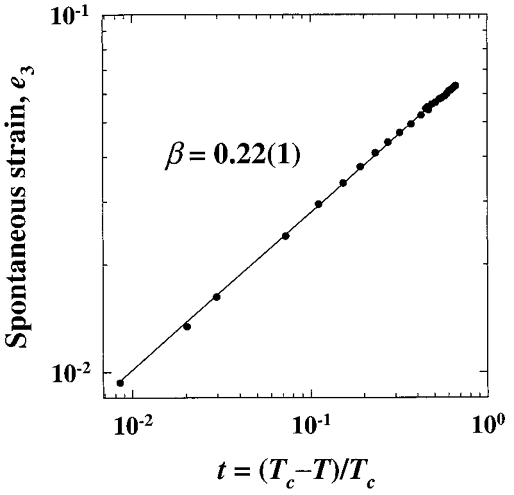

FIGURE 5. The spontaneous strain data of Reeder et al. (1988) with a fitted line where the critical exponent was determined as β = 0.22(1).

β over the entire temperature range they analyzed (200 to 550 K), and with T_c = 553 K. The exponent is determined as β = 0.22(1), again consistent with the two-dimensional XY model. Therefore no convincing evidence exists for a crossover from β = 0.25 to β = 0.22 in NaNO$_3$, and instead it is more likely that β = 0.22 holds over the whole two-dimensional critical range.

Heat capacity and thermal expansion

A large lambda anomaly in the heat capacity of NaNO$_3$ is seen at T_c [e.g., Reinsborough and Whetmore (1967) and Jriri et al. (1995)], similar to that which occurs at a conventional magnetic phase transition. In Figure 6, the above data sets were fits to the following power-law:

$$\Delta C \propto t^{-\alpha}, \quad (6)$$

where Δ*C* is the excess heat capacity due to the phase transition, and α is the critical exponent. The experimental values of α (Table 1) are in good agreement with each other, and with the expectations of the two-dimensional XY model, see below.

In 1987, in an unpublished heat capacity study, B. Wruck apparently determined α = 0.56(1), which is somewhat higher than my values listed in Table 1. Poon and Salje (1988) point out that Wruck's value of α is roughly consistent with that for the three-dimensional 3-state Potts model (for which the theoretical prediction is α ≈ 0.54). Obtaining accurate critical exponents from heat capacity data is notoriously difficult though, due to problems with ascertaining the "baseline" underneath the lambda anomaly, which comes from the non-critical lattice vibrations. Poon (1988) explains that Wruck used a lattice dynamical model to obtain his baseline, rather than the more common ad hoc method of extrapolating from temperatures far from T_c. Problems can certainly arise with this latter method, particularly when the lambda anomaly extends over a large range of temperature, as in NaNO$_3$, but the more recent very high-resolution data of Jriri et al. (1995) make it clear that there is a significant pre-melting effect in NaNO$_3$. This means that the baseline must have a convex shape underneath the lambda anomaly; note that the fits shown in Figure 6 include such a baseline. However, conventional lattice dynamics can only predict a concave shape to the baseline of the heat capacity as it asymptotes to the Dulong-Petit value at high temperatures. Hence, an incorrect baseline could be the origin of Wruck's anomalously high determination of α. In any case, Wruck's data and analysis have unfortunately never been published, and so we must treat this reported value of α = 0.56(1) with caution.

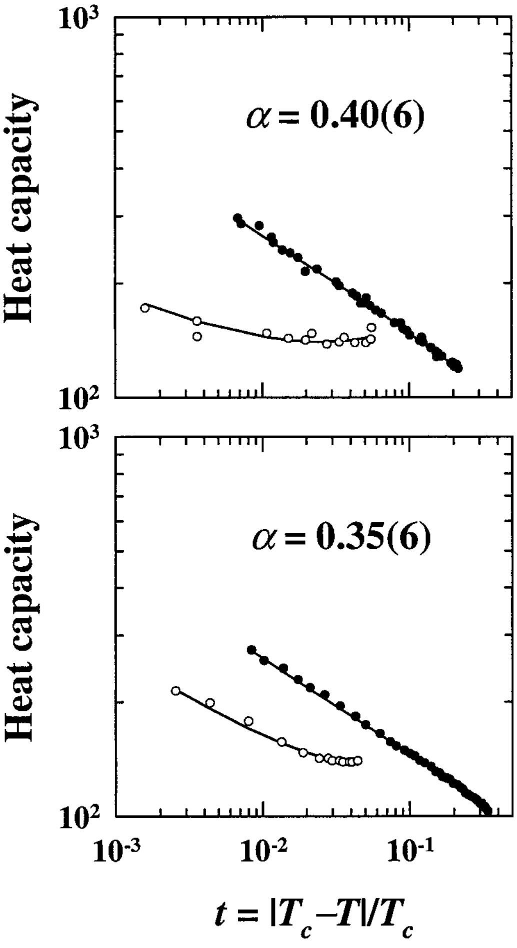

FIGURE 6. Heat capacity of NaNO$_3$. Top, data of Reinsborough and Whetmore (1967). Bottom, data of Jriri et al. (1995), fits are to Equation 6. Filled circles represent data taken below T_c. Open circles data above T_c. The data are not linear, even on double logarithmic axes, because the non-critical background is included.

The temperature dependence of the relative thermal expansion coefficients is expected to be roughly proportional to Δ*C*/*T*, which means that a further determination of the α critical exponent can be made for comparison with the heat capacity. In Figure 7, the thermal expansion data of Takeuchi and Sasaki (1992) give α = 0.34(1), in excellent agreement with the values determined from the heat capacity data. No baseline has been used in obtaining these fits.

There are no exact calculations of the heat capacity of the two-dimensional XY model, and so evidence from Monte Carlo calculations (e.g., Tobochnik and Chester 1979; Harris et al., manuscript in preparation) and experimental work is relied on. A truly two-dimensional XY system will have no three-dimensional ordering at T_c. Using Monte Carlo simulations, a peak is observed in the heat capacity which has a very similar shape to a conventional lambda anomaly, but with a slightly rounded top for small reduced temperatures ($t < 10^{-2}$). The peak temperature is weakly dependent on the system size, but is always slightly higher than T_c. Nevertheless, an effective critical exponent can be determined over a range of reduced temperature similar to that over which $\beta = 0.23$ holds. This effective exponent turns out to be $\alpha = 0.36(3)$ (Harris et al., manuscript in preparation). In experiment, there will always be a crossover to three-dimensional ordering very close to T_c, and the end result is to produce a sharp spike to the rounded two-dimensional XY anomaly. There are numerous magnetic examples of this behavior, such as BaNi$_2$(PO$_4$)$_2$, whose behavior corresponds very closely to the two-dimensional XY model, and has a well-defined lambda anomaly in the heat capacity (Regnault et al. 1980).

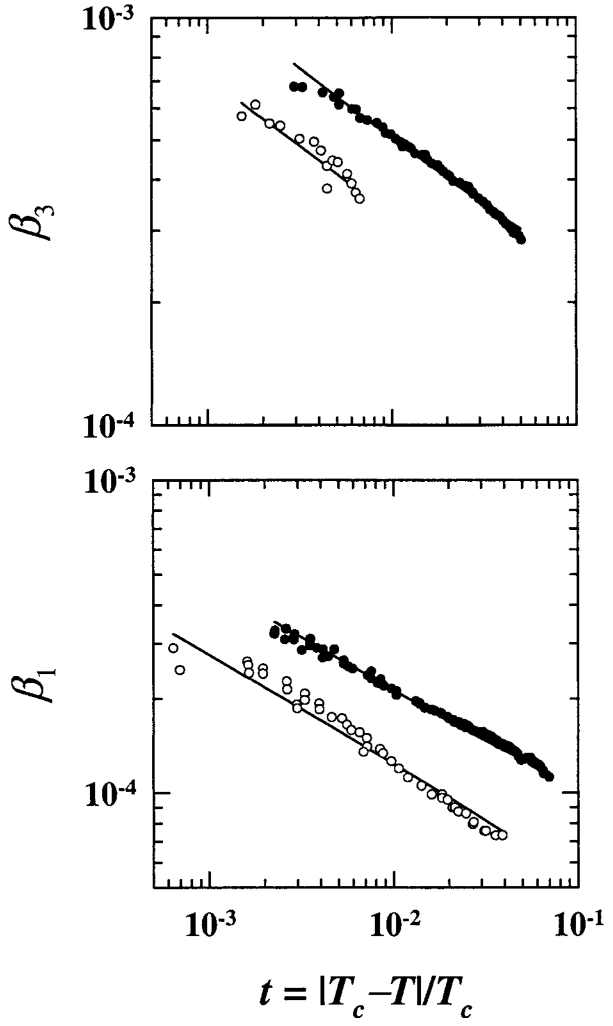

FIGURE 7. The relative thermal expansion data of Takeuchi and Sasaki (1992) with fits to the data of the relation $\beta_n \propto t^{-\alpha}/T$. (**Top**) The β_3 component of the relative thermal expansion. (**Bottom**) The β_1 component. Both data sets were fitted simultaneously, with the result $\alpha = 0.34(1)$. Filled circles represent the data taken below T_c. Open circles above T_c.

DISCUSSION

The various experimental results and predictions for the values of the critical exponents determined here are summarized in Table 1. Agreement between the experimental determinations of both α and β with the two-dimensional XY model are excellent. Althought there is a clear crossover to three-dimensional behavior in the superlattice intensity data of NaNO$_3$ (Fig. 4), no such crossover is apparent in the heat capacity. This is perhaps due to insufficient experimental resolution.

The above analysis shows that there is little reason to believe that the phase transitions in calcite and NaNO$_3$ are tricritical from the basis of any of the published experimental data, which instead are all at least as consistent with two-dimensional XY behavior. The two-dimensional XY model has the distinct advantage that it is readily identifiable with the physical properties of both calcite and NaNO$_3$, namely that the orientational order-disorder is driven by continuous planar rotations of the carbonate and nitrate groups, and that the interactions are strongly two dimensional in nature. Furthermore, the tricritical model has a distinct disadvantage, because it is highly unlikely to apply simultaneously to both calcite and NaNO$_3$, and has no obvious physical origin.

We can also refute the suggestion that competing interactions are responsible for the critical behavior of these materials. Whereas recent work has shown that characteristic fluctuations into a non-critical phase occur at the *F*-point of reciprocal space for both calcite and NaNO$_3$ (Lynden-Bell et al. 1989; Dove et al. 1992; Hagen et al. 1992; Harris 1993; Ferrario et al. 1994; Harris et al. 1998a, 1998b), they clearly have no significant effect on the observed critical exponents, which instead correspond simply to the universality classes (two-dimensional XY and three-dimensional Ising/XY) derived above. The crossover previously claimed to occur between $\beta = 0.25$ to $\beta = 0.22$ in NaNO$_3$ is not supported by the experimental evidence, but a clear crossover to three-dimensional behavior (where $\beta = 0.34$) does appear to occur in the superlattice intensities close to T_c. No evidence of a similar crossover to three-dimensional behavior has yet been observed in calcite, but this is probably due to the experimental difficulties associated with preserving calcite intact close to T_c.

ACKNOWLEDGMENTS

It is a great pleasure to thank my collaborators Martin Dove, Mark Hagen, and Ian Swainson for many invaluable discussions about calcite and NaNO$_3$ over the years. I am especially grateful to Steve Bramwell and Peter Holdsworth for introducing me to the two-dimensional XY model and for providing welcome insight. The financial support of the Engineering and Physical Sciences Research Council (U.K.) is acknowledged.

REFERENCES CITED

Als-Nielsen, J. and Birgeneau, R.J. (1977) Mean field theory, the Ginzburg criterion, and marginal dimensionality of phase transitions. American Journal of Physics, 45, 554–560.

Bramwell, S.T. and Holdsworth, P.C.W. (1993a) Magnetization and universal subcritical behavior in two-dimensional XY magnets. Journal of Physics: Condensed Matter, 5, L53-L59.

———(1993b) Universality in two-dimensional magnetic systems. Journal of Applied Physics, 73, 6096–6098.

———(1994) Magnetization: a characteristic of the Kosterlitz-Thouless-Berezinskii transition. Physical Review B, 49, 8811–8814.

Bruce, A.D. (1980) Structural phase transitions. II. Static critical behavior. Advances in Physics, 29, 111–217.

Collins, M.F. (1989) Magnetic Critical Scattering. Oxford University Press, New York.

Cowley, R.A. (1987) Phase transitions. In K. Sköld and D.L. Price, Methods of Experimental Physics, Vol. 23C, 1–67. Academic Press, New York.

Dove, M.T. and Powell, B.M. (1989) Neutron diffraction study of the tricritical orientational order-disorder phase transition in calcite at 1260 K. Physics and Chemistry of Minerals, 16, 503–507.

Dove, M.T., Hagen, M.E., Harris, M.J., Powell, B.M., Steigenberger, U., and Winkler, B. (1992) Anomalous inelastic neutron scattering from calcite. Journal of Physics: Condensed Matter, 4, 2761–2774.

Dove, M.T., Swainson, I.P., Powell, B.M., and Tennant, D.C. (1998) Neutron powder diffraction study of the tricritical orientational order-disorder phase transition in calcite, $CaCO_3$. Physics and Chemistry of Minerals, in press.

Ferrario, M., Lynden-Bell, R.M., and McDonald, I.R. (1994) Structural fluctuations and the order-disorder phase transition in calcite. Journal of Physics: Condensed Matter, 6, 1345–1358.

Gonshorek, W., Schmahl, W.W., Weitzel, H., Miehe, G., and Fuess, H. (1995) Anharmonic motion and multipolar expansion of the electron density in $NaNO_3$. Zeitschrift für Kristallographie, 210, 843–849.

Griffiths, R.B. (1970) Thermodynamics near the two-fluid critical mixing point in He^3-He^4. Physical Review Letters, 24, 715–717.

Hagen, M., Dove, M.T., Harris, M.J., Steigenberger, U., and Powell, B.M. (1992) Orientational order-disorder phase transition in calcite. Physica B, 180&181, 276–278.

Harris, M.J. (1993) Diffuse X-ray scattering and the anomalous soft mode in $NaNO_3$. Journal of Physics: Condensed Matter, 5, 5773–5782.

Harris, M.J., Dove, M.T., and Godfrey, K.W. (1996) A single crystal neutron scattering study of lattice melting in ferroelastic Na_2CO_3. Journal of Physics: Condensed Matter, 8, 7073–7084.

Harris, M.J., McMorrow, D.F., and Godfrey, K.W. (1997) Phonon softening at a continuous melting transition: lattice melting in ferroelastic Na_2CO_3. Physical Review Letters, 79, 4846–4849 (1997).

Harris, M.J., Dove, M.T., Swainson, I.P., and Hagen, M.E. (1998a) Anomalous dynamical effects in calcite. Journal of Physics: Condensed Matter, 10, L423–L429.

Harris, M.J., Hagen, M.E., Dove, M.T., and Swainson, I.P. (1998b) Inelastic neutron scattering, phonon softening, and the phase transition in $NaNO_3$. Journal of Physics: Condensed Matter, 10, 6851–6861.

Jriri, T., Rogez, J., Bergman, C., and Mathieu, J.C. (1995) Thermodynamic study of the condensed phases of $NaNO_3$, KNO_3 and $CsNO_3$ and their transitions. Thermochimica Acta, 266, 147–161.

Ketalaar, J.A.A. and Strijk, B. (1945) The atomic arrangement in solid sodium nitrate at high temperatures. Recueil des Travaux Chimiques des Pays-Bas et de la Belgique, 64, 174.

Kracek, F.C., Posnjak, E., and Hendricks, S.B. (1931) Gradual transition in sodium nitrate II. The structure at various temperatures and its bearing on molecular rotation. Journal of the American Chemical Society, 53, 3339–3348.

Lefebvre, J., Fouret, R., and Zeyen, C.M.E. (1984) Structure determination of sodium nitrate near the order-disorder phase transition. Journal de Physique, 45, 1317–1327.

Lynden-Bell, R.M., Ferrario, M., McDonald, I.R., and Salje, E. (1989) A molecular dynamics study of orientational disordering in crystalline sodium nitrate. Journal of Physics: Condensed Matter, 1, 6523–6542.

Markgraf, S.A. and Reeder, R.J. (1985) High-temperature structure refinements of calcite and magnesite. American Mineralogist, 70, 590–600.

Payne, S.J., Harris, M.J., Hagen, M.E., and Dove, M.T. (1997) A neutron diffraction study of the order-disorder phase transition in sodium nitrate. Journal of Physics: Condensed Matter, 9, 2423–2432.

Poon, W.C.-K. (1988) Raman and birefringence studies of phase transitions. Ph.D. thesis, University of Cambridge, U.K.

Poon, W.C.-K. and Salje, E. (1988) The excess optical birefringence and phase transition in sodium nitrate. Journal of Physics C: Solid State Physics, 21, 715–729.

Redfern, S.A.T., Salje, E., and Navrotsky, A. (1989) High-temperature enthalpy at the orientational order-disorder transition in calcite: implications for the calcite/aragonite phase equilibrium. Contributions to Mineralogy and Petrology, 101, 479–484.

Reeder, R.J., Redfern, S.A.T., and Salje, E. (1988) Spontaneous strain at the structural phase transition in $NaNO_3$. Physics and Chemistry of Minerals, 15, 605–611.

Regnault, L.P., Henry, J.Y., Rossat-Mignod, J., and de Combarieu, A. (1980) Magnetic properties of the layered nickel compounds $BaNi_2(PO_4)_2$ and $BaNi_2(AsO_4)_2$. Journal of Magnetism and Magnetic Materials, 15–18, 1021–1022.

Reinsborough, V.C. and Wetmore, F.E.W. (1967) Specific heat of sodium nitrate and silver nitrate by medium high temperature adiabatic calorimetry. Australian Journal of Chemistry, 20, 1–8.

Salje, E. and Viswanathan, K. (1976) The phase diagram calcite-aragonite as derived from the crystallographic properties. Contributions of Mineralogy and Petrology, 55, 55–67.

Schmahl, W.W. and Salje, E. (1989) X-ray diffraction study of the orientational order-disorder transition in $NaNO_3$: evidence for order parameter coupling. Physics and Chemistry of Minerals, 16, 790–798.

Seeck, O.H., Hupfeld, D., Krull, H., Tolan, M., and Press, W. (1998) Order-disorder transition of ND_4Cl and NH_4Cl. Physical Review B, 58, 623–632.

Swainson, I.P., Dove, M.T., and Harris, M.J. (1995) Neutron powder diffraction study of the ferroelastic phase transition and lattice melting in sodium carbonate, Na_2CO_3. Journal of Physics: Condensed Matter, 7, 4395–4417.

Swainson, I.P., Dove, M.T., and Harris, M.J. (1998) The phase transitions in calcite and sodium nitrate. Physica B, 241, 397–399.

Takeuchi, Y. and Sasaki, Y. (1992) Elastic properties and thermal expansion of $NaNO_3$ single crystal. Journal of the Physical Society, Japan, 61, 587–595.

Tobochnik, J. and Chester, G.V. (1979) Monte Carlo study of the planar spin model. Physical Review B, 20, 3761–3769.

MANUSCRIPT RECEIVED OCTOBER 22, 1998
MANUSCRIPT ACCEPTED JUNE 1, 1999
PAPER HANDLED BY SIMON A.T. REDFERN