

## Orientalional order–disorder phase transition in calcite

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We have performed inelastic neutron scattering experiments on calcite in the ordered phase, focusing on a zone boundary F-point that shows X-ray diffuse scattering. At this position we have observed an incipient soft mode along with a column of inelastic scattering ranging in energy between the soft mode energy and zero energy. The intensity of this scattering varies dramatically with temperature, and is described by an Arrhenius relation with an activation energy of 1035 K.

### 1. Introduction

Both calcite ( $\text{CaCO}_3$ ) and sodium nitrate ( $\text{NaNO}_3$ ) have the  $R\bar{3}m$  structure at high temperature and undergo an order–disorder phase transition to the  $R\bar{3}c$  structure at low temperature. This corresponds to an instability at the wave vector corresponding to the Z-point on the high temperature Brillouin zone boundary, and we therefore refer to the low temperature phase as the Z-phase. In calcite this transition occurs at 1260 K [1] and in  $\text{NaNO}_3$  at 530 K [2]. The second order nature of these transitions is unusual since most orientational order–disorder phase transitions are first order. The order parameter exponent  $\beta$  for both calcite [1] and  $\text{NaNO}_3$  [2] has been found to have a value of  $\beta = 0.25$  which is consistent with a tri-critical phase transition. Other unusual features have also been found in both experimental and theoretical studies of  $\text{NaNO}_3$ . X-Ray precession photographs of calcite and  $\text{NaNO}_3$  taken at room temperature [3] and molecular dynamics simulations [4] on  $\text{NaNO}_3$  have shown the existence of diffuse scattering at points in reciprocal space corresponding to the F-points of the high temperature Brillouin zone. A different, but related, phenomenon has also been observed in the high resolution infrared absorption measurements of Harris et al. on  $\text{NaNO}_3$  [5]. At temperatures close to  $T_c$  extra lines appear in the infrared spectrum which cannot be indexed by the  $R\bar{3}c$  structure.

Initially we had thought that the diffuse scattering peak at the F-points could be explained as an anomalous dip in the phonon dispersion relations, an incipient soft mode. This idea was supported by triple-axis measurements on calcite performed at room temperature, which indeed showed a substantial fall in energy of the lowest energy TA phonon at the F-point. Subsequent to this we embarked on a series of measurements using the PRISMA spectrometer at ISIS

which were aimed at determining the temperature dependence of the lowest energy phonon in calcite. However in the course of these measurements we discovered an extra feature, a column of inelastic scattering, which had not been prominent in our earlier triple-axis constant  $Q$  measurements. In this paper we only briefly describe our results, a more detailed account is given elsewhere [6].

### 2. Experimental

The PRISMA spectrometer is an indirect geometry multi-analyser time of flight spectrometer. A detailed description of the spectrometer and the measuring technique has recently been given by Steigenberger et al. [7]. The crystal of calcite used had a volume of  $6 \text{ cm}^3$  and was oriented with the  $[010]$  axis vertical. For measurements above room temperature the sample was mounted in a vacuum furnace which had an upper limit of 773 K, while for low temperatures it was mounted in a closed cycle refrigerator.

### 3. Results

In fig. 1 the results of three scans using PRISMA to measure phonons along the  $[10\bar{4}]$  direction ( $\Gamma$ –F) through the  $(300)$  Bragg peak are shown at room temperature (wave vectors are given with respect to the hexagonal unit cell of the high temperature phase). Each scan on PRISMA, which consisted of 11 spectra measured along this direction in reciprocal space, took about 8–12 h to perform. Figure 1 was constructed by plotting the positions of the peaks found in the 33 spectra. As an example the short dashed line shows the path taken by one of the spectra and the spectrum itself is shown in fig. 2 by the circles. The unusual and striking feature in fig. 1 is that at the  $(2.502)$  position, which is an F-point of the Brillouin zone boundary of the high temperature phase, the

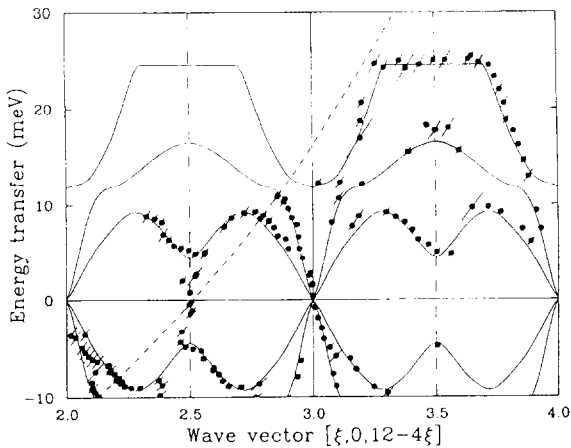


Fig. 1. The phonon dispersion relations measured on PRISMA along the  $[10\bar{4}]$  direction through the  $(300)$  Bragg peak at room temperature.

phonon energies appear to drop to zero. There was no equivalent scattering at the  $(3.50\bar{2})$  F-point, and furthermore there was no elastic central peak at  $(2.50\bar{2})$ . Moreover, the intensity of the scattering from zero energy up until the energy of the acoustic branch is reached was approximately constant. In fig. 3 we show a constant  $Q$  section at the  $(2.50\bar{2})$  point at room temperature, taken from our spectra, which shows this intensity variation. As can be seen from a comparison of figs. 1-3 the phonon energies do not drop to zero but instead there is a column of scattering extending

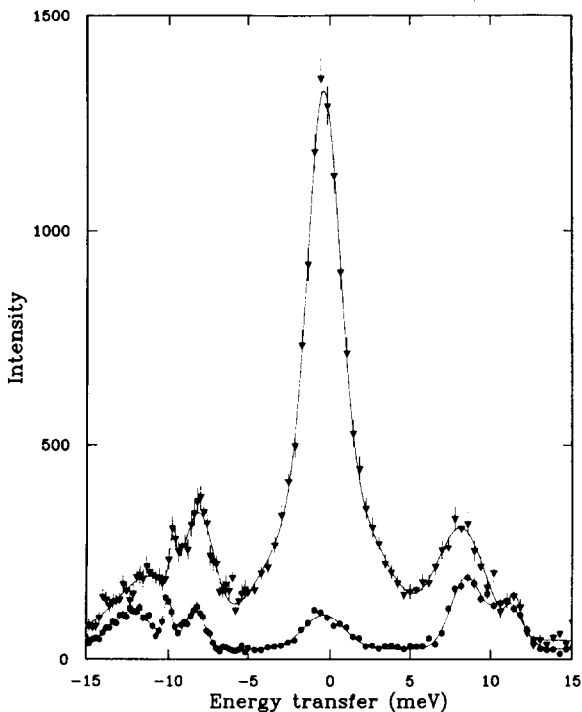


Fig. 2. The spectra measured along the path shown by the dashed line in fig. 1 at room temperature (circles) and at 773 K (triangles).

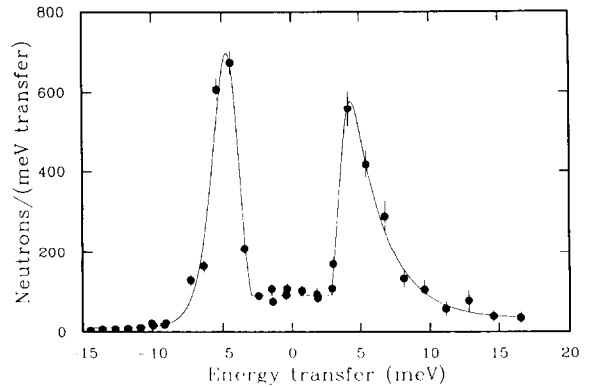


Fig. 3. A constant  $Q$  section at the  $(2.50\bar{2})$  F-point at room temperature, taken from the time of flight spectra.

up from zero energy to the TA mode at the F-point. The width of this column in reciprocal space is approximately  $0.01 \text{ \AA}^{-1}$ .

We have been unable to find a spurious scattering process to account for this column of scattering and confirmation that it is a real effect has been obtained from measurements of its temperature dependence. In fig. 2 the spectra corresponding to the short dashed line in fig. 1 are shown at room temperature (293 K) by the circles and at 773 K by the triangles. The scattering at the F-point has increased dramatically, by a factor of 14, while the thermal population factor  $\approx k_B T$  has only risen by 2.5 over this temperature range. In fig. 4 we show the integrated intensity of the F-point scattering as a function of temperature. The solid line is a fit to an Arrhenius law of the form

$$I = I_0 k_B T \exp\left(-\frac{T^*}{T}\right), \quad (1)$$

where  $T^* = 1035 \text{ K}$ .

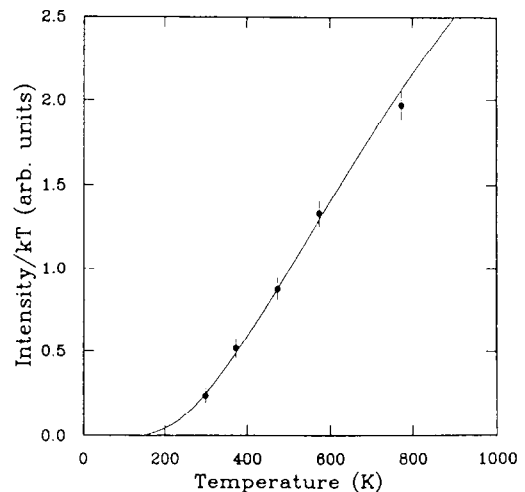


Fig. 4. The intensity of the F-point scattering divided by  $k_B T$  is shown against temperature. The solid line is the fit to the Arrhenius law as described in the text.

Following the discovery of this effect on PRISMA we repeated our earlier triple axis measurements this time carrying out constant  $E$  scans through the F-point. This was done for various energy transfers from zero up to the energy of the acoustic branch and confirmed the existence of this column of scattering at room temperature.

#### 4. Discussion

A possible origin for this scattering may be given by the following model which can also account for some of the anomalous infrared lines. At 1260 K calcite undergoes an order-disorder phase transition with the instability at the Z-point. We postulate that there is another possible structure with an energy lower than that of the disordered phase but higher than that of the Z-phase corresponding to an F-point instability. Lattice energy calculations of this structure using the model of calcite determined by Dove et al. [8] have found that its energy above the Z-phase is  $\approx 1000$  K. This is less than  $T_c$  and comparable to the activation temperature of the Arrhenius law. The effect observed in the PRISMA measurements at  $(2.502)$  is then related to fluctuations into this alternative structure.

No effect was observed at  $(3.50\bar{2})$  because the structure factor is weak at this point. A calculation of the infrared spectrum of the F-point structure for  $\text{NaNO}_3$  shows some, but not all, of the extra lines observed by Harris et al. [5]. We therefore anticipate the possibility that there are further, as yet undiscovered, structures in calcite with energies lower than the disordered phase but higher than the Z-phase.

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