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LETTER TO THE EDITOR

Anomalous dynamical effects in calcite CaCO_3 M J Harris[†], M T Dove[‡], I P Swainson[§] and M E Hagen^{||}[†] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK[‡] Mineral Physics Group, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK[§] Neutron Program for Materials Research, Steacie Institute for Molecular Sciences, National Research Council, Chalk River Laboratories, Chalk River, Ontario K0J 1P0, Canada^{||} Department of Physics, Keele University, Keele, Staffordshire ST5 5BG, UK

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Abstract. We present the results of an inelastic neutron scattering study of calcite. A continuum of excitations is observed, coupled with a soft phonon mode. Similar excitation spectra have been found in a number of other materials, due to electronic effects. However, calcite is an insulator, and we suggest that our results can instead be explained by a rather unexpected solution of the conventional picture that arises from coupling between phonon and relaxation modes.

One of the most significant improvements in our understanding of structural phase transitions was provided by the development of the soft mode model in the 1960s (e.g. [1, 2]). In this model, a displacive phase transition is driven by a dynamic instability in which a phonon mode softens to zero frequency at the critical temperature. The eigenvector of the soft mode gives the distortion that breaks the symmetry of the high-temperature paraphase and forms the low-temperature phase. These ideas have been extended to systems that have order–disorder phase transitions in which there is a coupling to the phonons. In short, there is a coupling between relaxational ordering modes and vibrational modes, which can lead to a softening of the phonons in a manner similar to that given in the soft mode model. This model can be derived from a number of analogous approaches, such as the pseudospin–phonon coupling model of Yamada *et al* [3], and the translation–rotation coupling model of Michel and Naudts [4]. These authors give an expression for the coherent neutron scattering cross section, which shows qualitatively different behaviour depending on the relative frequencies of the relaxational and vibrational phonons. In this letter, we show how a rather unexpected solution to these models explains anomalous dynamical effects previously observed in calcite (CaCO_3) [5]. In particular, calcite exhibits a soft mode and an extended continuum of excited states that are sharply localized at the F-point of reciprocal space. The main features of the inelastic spectrum are displayed schematically in figure 1.

A number of other materials show similar features in their inelastic spectra: magnetite (Fe_3O_4) [6], KCP [7], blue bronze [8], β -Ti [9] and β -Zr [10]. The soft mode and continuum of scattering in these materials is due to strongly one-dimensional electronic correlations which couple with a lattice distortion [11]. For example, in the bcc metals β -Ti and β -Zr the phonon softening occurs at the usual bcc phonon minimum point $(\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$, and the continuum represents dynamic domains of a phase with the structure given by the eigenvector of this phonon. Linear electronic coupling provides a strong enhancement of the effect [12]. On the other hand, calcite is an insulator, and electronic effects cannot be directly involved.

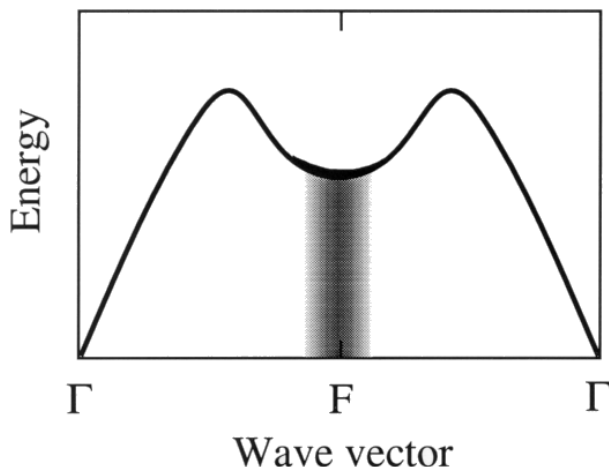


Figure 1. A schematic plot showing the transverse acoustic branch in calcite softening around the F -point, with the continuum of excitations shown as the shaded feature.

Calcite undergoes an orientational order–disorder phase transition on heating above 1260 K, with the symmetry change $R\bar{3}c \rightarrow R\bar{3}m$ [13]. This phase transition involves disordering of the orientations of the molecular carbonate groups about their three-fold axes. What is perhaps most unusual of all about the inelastic continuum in calcite is that there is no direct connection with this phase transition. Instead, the soft mode is more likely to be connected with the high-pressure I–II phase transition (see below), but the important point is that the anomalous effects observed at the F -point in calcite have a dramatic temperature dependence.

In this letter we present new inelastic neutron scattering measurements of the continuum and soft phonon branch in calcite. We have greatly extended the range of temperature over which the continuum is observed, and have studied it with much greater resolution than was previously obtained, allowing for a full quantitative analysis. Our data were obtained using the N5 triple-axis spectrometer at the NRU reactor at Chalk River Laboratories. A Si(113) monochromator and a pyrolytic graphite (002) analyser were used. The analyser energy was kept fixed at 3.05 THz, and the in-plane collimation was $30'-20'-30'-150'$, which provided an energy width of about 0.13 THz (FWHM) for the elastic scattering from a standard vanadium sample. The sample was a single crystal of calcite (of iceland spar quality) with an approximate volume of 14 cm^3 , mounted with the a^*-c^* plane of reciprocal space in the scattering plane of the spectrometer. The soft mode and continuum of inelastic scattering were characterized by a series of constant- Q and constant- E scans at the following temperatures: 295, 500, 600, 700, 800, 900, 1000 and 1100 K. Calcite decomposes into CaO and CO_2 on heating, and despite taking measures to avoid this [13], we were not able to retain the sample when attempting to heat beyond 1100 K.

In figure 2 we illustrate the anomalous dynamical behaviour of calcite with a series of constant- Q scans taken at the F -point, $Q = \left(\frac{\sqrt{5}}{2} 0 2\right)$, with sample temperatures 295, 600, 800 and 1100 K. At 295 K, the phonon can be seen as a sharp peak at an energy transfer of about 1.1 THz, and the inelastic continuum can be seen as a raised level of scattering slightly above the background level for energy transfers between zero and the phonon energy. As the temperature is raised, the frequency of the phonon peak decreases rapidly and the scattering

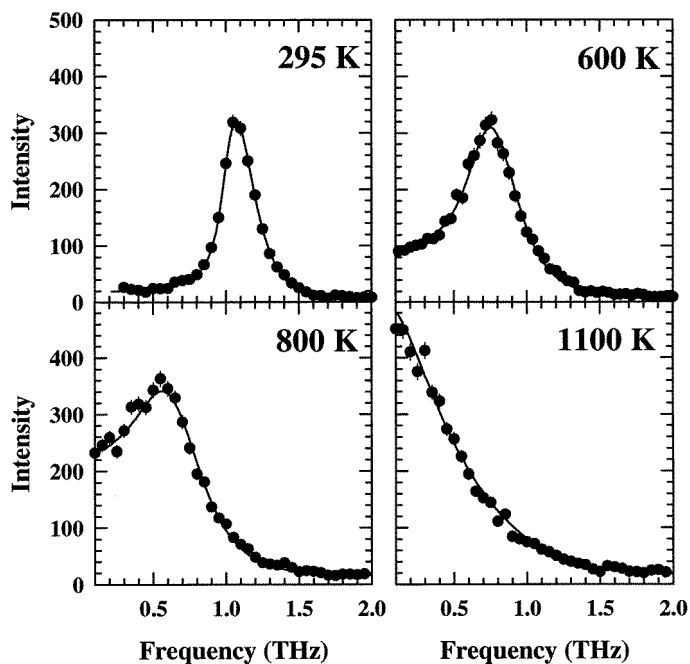


Figure 2. Constant- Q scans through the $\left(\frac{\sqrt{3}}{2}, 0, 2\right)$ F -point in calcite at sample temperatures of 295, 600, 800 and 1100 K, illustrating the softening of the phonon as the temperature is increased. The continuum is evident as the continuous distribution of scattering between the phonon peak and zero frequency. The curves show fits to the data of equation (1) convoluted with the experimental resolution function.

becomes overdamped, so that at 1100 K it cannot be distinguished from purely quasielastic scattering. At the same time, the intensity of the inelastic continuum can be seen to increase rapidly with temperature, and as the phonon softens and dampens, the continuum and the phonon merge into a single feature. In fact the intensity of this continuum increases much more rapidly upon heating than does the phonon peak, as is clear by comparing the 295, 600 and 800 K scans. In figure 3 we show constant- E scans across the inelastic continuum at several different energies and temperatures. In all of these scans, the sharp peak is the inelastic continuum centred on the F -point. No significant change was observed in the width in wavevector of the continuum as the sample was heated from 295 to 1100 K, indicating that the length scales of the fluctuations responsible for it are not critical, in spite of the pronounced softening of the phonon frequency at the F -point. The continuum has width 0.16 \AA^{-1} in the direction Γ - F and 0.09 \AA^{-1} in the orthogonal direction in the scattering plane, which translate to correlation lengths of 40 and 70 \AA respectively.

Additional measurements made in a number of different Brillouin zones clearly showed that the wavevector dependence of the intensities of the continuum and phonon peak scale together, which implies that they share the same structure factor and hence are given by the same atomic motions. Accordingly, both features must be treated within a single picture rather than as separate features.

We have analysed the inelastic neutron scattering data presented in figures 2 and 3 using the idea of a coupling between a relaxational mode and a phonon mode noted above, following the formalism of Michel and Naudts [4, 14]. The inelastic neutron scattering is

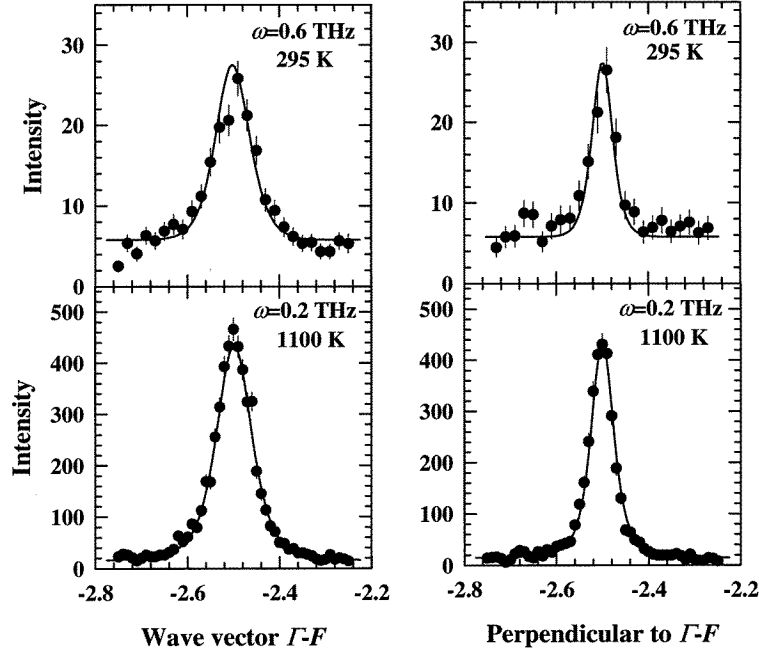


Figure 3. Constant- E scans through the continuum of excitations at the $\left(\frac{5}{2}02\right)$ F -point in calcite at sample temperatures of 295 and 1100 K. The scans were taken along the Γ - F direction and the perpendicular direction to it, which is close to the $[\bar{1}04]$ direction. The curves show fits to the data of equation (1) convoluted with the experimental resolution. Note that no significant change in the width in wavevector of the continuum occurs with temperature.

given as

$$S(\mathbf{Q}, \omega) \propto \frac{\omega \Phi''}{1 - \exp(-\hbar\omega/k_B T)} \quad (1)$$

where $\hbar\omega$ is the neutron energy transfer, T is the temperature and

$$\Phi'' = \frac{\beta^2 f(\omega)}{[\omega^2 - \Omega(\mathbf{Q})^2 - \omega^2 \beta^2 f(\omega)/\lambda]^2 + \omega^2 \beta^4 f(\omega)^2}. \quad (2)$$

$\beta^2 = \Omega(\mathbf{Q})^2 c(\mathbf{Q})^2 / (1 - c(\mathbf{Q})^2)$, $\Omega(\mathbf{Q})$ is the frequency of the phonon branch, λ is the relaxation frequency and $f(\omega) = \lambda / (\omega^2 + \lambda^2)$. $c(\mathbf{Q})$ gives the coupling between the phonon and relaxation modes. Representing the phonon variable as $\mathcal{Q}(\mathbf{Q})$ and the relaxational variable as $\mathcal{R}(\mathbf{Q})$, $c(\mathbf{Q})$ can be described as the correlation function [15]

$$c(\mathbf{Q}) = \frac{\langle \mathcal{Q}(\mathbf{Q}) \mathcal{R}(-\mathbf{Q}) \rangle}{\langle \mathcal{Q}(\mathbf{Q}) \mathcal{Q}(-\mathbf{Q}) \rangle^{1/2} \langle \mathcal{R}(\mathbf{Q}) \mathcal{R}(-\mathbf{Q}) \rangle^{1/2}}. \quad (3)$$

If $c(\mathbf{Q}) = 1$, the coupling is so strong that the phonon branch softens to zero frequency at wavevector \mathbf{Q} , and a phase transition occurs.

In using this model we have assumed that $c(\mathbf{Q})$ has a maximum, and $\Omega(\mathbf{Q})$ a minimum, at the F -point, and for computational convenience we represented the \mathbf{Q} -dependence of both as a Gaussian function of the variable $\mathbf{q} = \mathbf{F} - \mathbf{Q}$, where \mathbf{F} is the wavevector of the F -point. We also assumed that λ has a much slower \mathbf{Q} -dependence and could be treated as a constant. $c(\mathbf{Q})$, $\Omega(\mathbf{Q})$ and λ are temperature dependent.

We found that at every temperature $\lambda > \Omega$, for all wavevectors Q . In this case, the model predicts a continuum of scattering that spans the frequency range below the frequency of the soft phonon. In particular, there is no central elastic peak corresponding to very slow or static correlations, which would be the main result of the opposite solution to the model, where $\lambda < \Omega$. The latter condition is the case for many molecular compounds, such as ND_4Br [16]. In some cases, such as KCN [14], where the molecular relaxations couple to the acoustic modes, at small wavevectors there must be a cross-over between two regimes as the acoustic mode frequency falls to zero. This gives a continuum for wavevectors close to the zone centre, which merges continuously into the opposite situation of overdamped modes and a central peak for larger wavevectors. Thus calcite appears to be unique in that $\lambda > \Omega$ for all wavevectors, and all temperatures studied. What is perhaps more interesting is that the form of $c(Q)$ has a very tight maximum about the F -point (figure 4), resulting in the sharp width of the continuum scattering. In direct space, this is due to relatively long-ranged dynamic correlations. By contrast, in molecular crystals $c(Q)$ appears to vary more gradually across the whole Brillouin zone [15], thus representing a more localized effect in direct space.

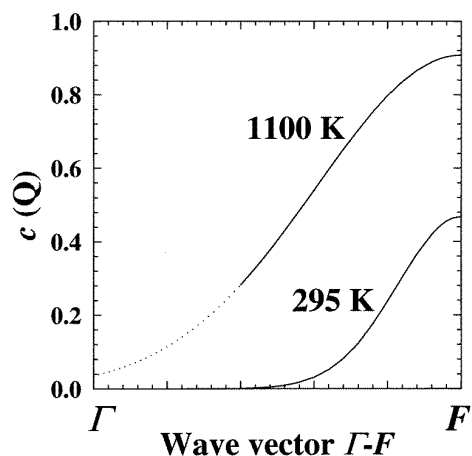


Figure 4. The dependence of the coupling parameter $c(Q)$ on wavevector for the temperatures 295 and 1100 K, determined by fitting equation (1) to the inelastic neutron scattering data.

The values of Ω , λ and c were obtained for each temperature by fitting expression (1) (convoluted with the experimental resolution function) to the constant- Q and constant- E scans simultaneously. The fitted values of these quantities at the F -point are shown in figure 5. First, Ω softens on heating as though a phase transition was due to occur at the F -point at high temperatures. However, as the orientational order-disorder phase transition is approached, the rate of softening gradually decreases and Ω never softens to zero frequency. Second, λ increases steadily on heating in a roughly linear fashion. Third, c increases on heating, eventually saturating at a value of about 0.9. As with Ω , it appears as if a phase transition might occur, but is somehow prevented.

We now proceed to discuss a possible interpretation of the model of coupled relaxational and phonon modes. As we have noted, in the bcc metals β -Ti and β -Zr the existence of the continuum of inelastic neutron scattering and the soft point on the phonon branch have been interpreted in terms of the phase transition that could arise from a condensation of the soft phonon [9, 10]. It has been suggested that the continuum could reflect dynamic fluctuations

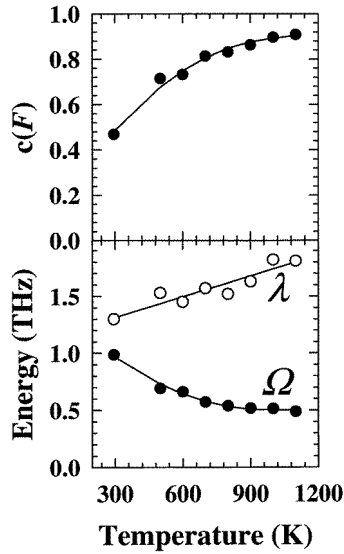


Figure 5. The temperature dependence of the soft mode frequency, Ω , the relaxation frequency, λ , and the coupling parameter, c , at the F -point. The lines are guides to the eye.

into a new phase that does not actually have any equilibrium stability. It is tempting to propose a similar mechanism for the continuum of inelastic neutron scattering in calcite, in which case the dynamic domains would have the structure of the phase given by the condensation of the soft mode at the F -point, namely the high-pressure phase II of calcite [17]. We have used a good empirical model of calcite [18] to show that this mode does indeed soften with increasing pressure until it precipitates a first-order displacive phase to the monoclinic phase II. Experimentally this phase transition occurs at a pressure of 1.6 GPa at ambient temperature. The main structural rearrangement that takes place on transforming to phase II is a planar rotation of the carbonate groups by 11° rotations about the molecular three-fold axes, in an alternately positive and negative sense [17]. By analogy with the behaviour of the bcc-metals, it may be that the continuum of inelastic scattering reflects dynamic fluctuations of regions of the crystal into the phase II structure. Certainly no electronic effects can be implicated in the anomalous dynamic behaviour of calcite at the F -point, and it must therefore have its origins purely in a structural relaxation mechanism, with a surprisingly large correlation length. The main difficulty with this simple explanation is that it would be natural to identify the relaxation process with that of the relaxation of domains fluctuating into and out of the calcite-II structure, but it is hard to reconcile the frequency of this fluctuation as being larger than the soft-mode frequency.

To summarize, we have observed a soft mode and an anomalous continuum of excitations in calcite at the zone boundary F -point, and have successfully modelled the data using a theory of phonon modes coupled to relaxational modes. We suggest that these features may be due to dynamical fluctuations into the high-pressure phase II, but there are difficulties in accounting for the relative magnitudes of the phonon and relaxation frequencies. In short, a number of clues to the origin of the anomalous inelastic neutron scattering results for calcite are given by the present work. Its importance lies in the fact we have shown that a relaxation mechanism can alter the traditional picture of a soft mode, and produce the dynamical spectrum generally associated with one-dimensional electronic materials.

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