Observation of Lattice Melting at the Ferroelastic Phase Transition in Na_2CO_3

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A neutron powder diffraction study of the $m = 2$ ferroelastic phase transition at 755 K in Na_2CO_3 is presented, showing the first occurrence of ideal lattice melting. A detailed analysis of the profiles of the diffraction peaks shows a striking broadening which develops close to T_c, consistent with recent theoretical predictions for this type of transition.

The solid-liquid transition is generally thought to occur at a divergence of the mean-squared atomic displacements, which leads to a loss of the long-range and short-range order. Theoretical studies have shown that a similar divergence of the mean-squared atomic displacements will also occur at a ferroelastic phase transition, where there is a softening of the transverse acoustic modes over whole planes of wave vectors, the so-called $m = 2$ ferroelastic phase transition [1,2]. However, in contrast to conventional melting, long-range order is reestablished on cooling below T_c by a process of continuous recrystallization, and the short-range order is preserved. The transition state at T_c can be said to be "moltenlike," although the atomic displacements diverge only along one crystallographic direction, namely, that normal to the critical plane of the soft acoustic modes. Since this phenomenon possesses obvious similarities to the solid-liquid transition, we refer to it here as "lattice melting." Most ferroelastic materials have acoustic-mode softening only along critical directions in reciprocal space (they are therefore known as $m = 1$), and there is a conspicuous absence of crystals reported as having continuous $m = 2$ ferroelastic phase transitions [1,3]. In this Letter we show that the continuous ferroelastic phase transition in Na_2CO_3 belongs to this universality class. It is therefore the first example for ideal lattice melting, and in this Letter we describe neutron powder diffraction measurements that demonstrate this novel effect.

Previous work on this universality class has centered on the $(KBr)_{1-x}(KCN)_x$ mixed system [4], where a continuous $m = 2$ ferroelastic phase transition occurs for the compositions $0.6 \leq x \leq 0.7$. The decrease in the long-range order is revealed in a dramatic broadening of the diffraction peaks at Bragg positions. A theoretical analysis has shown that at T_c the Bragg peaks are replaced by power-law singularities that are analogous to the scattering from a two-dimensional system such as a smectic liquid crystal [5]. However, in practice the Bragg component never disappears entirely in the mixed cyanides, which suggests that the lattice melting is inhibited and long-range order is preserved. This behavior can be explained as the result of random shear stresses due to the disordered distribution of Br^- and CN^- ions which act as defects in these crystals [5]. Indeed, Knorr, Loidl, and Kjems [3] have raised the question of whether the theory for continuous $m = 2$ systems should really be valid at all for the mixed cyanides.

At ~ 755 K, Na_2CO_3 undergoes a hexagonal-monoclinic ($P6_3/mmc - C2/m$) ferroelastic phase transition that is driven by a planar elastic instability [6–8]. The order parameter is the ϵ_5 shear strain, which transforms as the E_{1g} representation of the hexagonal phase. As a third-order term in the sense of Landau theory is not allowed for this transition, it can be second order, and experimentally this appears to be the case [7,8]. Thus Na_2CO_3 shows a continuous $m = 2$ ferroelastic phase transition. Furthermore, since it is chemically a pure system, the type of random shear stresses which tend to preserve long-range order in the $(KBr)_{1-x}(KCN)_x$ system are absent. Consequently, the phase transition in Na_2CO_3 is the first example of an *ideal*, continuous $m = 2$ ferroelastic phase transition, and it is therefore expected to show the complete lattice melting predicted by theory.

The sample used in these experiments was high-purity anhydrous Na_2CO_3 which was obtained commercially as a powder. Neutron powder diffraction data were obtained using the high resolution powder diffractometer HRPD at the ISIS spallation neutron source (Rutherford Appleton Laboratory, U.K.) and the C2 DUALSPEC diffractometer at the N.R.U. reactor at Chalk River Laboratories (AECL Research, Canada). In the absence of any additional broadening, the width of a powder Bragg peak is controlled by two factors: the instrumental resolution and sample properties such as particle size and internal strains. These were all accounted for by determining an overall Rietveld-type resolution function for the experiment using Na_2CO_3 spectra with very sharp peaks measured several hundred degrees away from T_c. Full structure refinements from these data will be presented elsewhere [8].

The effect of lattice melting is apparent in Fig. 1. This figure shows three spectra around the hexagonal (2 0 2) peaks at temperatures above, just below, and well below T_c. In the middle spectrum, the diffraction peaks are highly broadened and are non-Gaussian in profile. Well above and below T_c they are significantly sharper (and are resolution-limited), which shows the subsequent recrystallization of the lattice after the transition has been passed. We will show below that there are two components to these peaks, a sharp Bragg component with a width that is determined by the resolution of the experiment, and a broad peak of diffuse scattering that is centered on the position of the Bragg peak. On approaching T_c the diffuse scattering component grows at the expense of the Bragg component. Numerous overlapping peaks occur in the monoclinic phase (especially close to T_c), and hence the line shape analysis presented in this Letter was largely performed on data obtained from the hexagonal phase.

The lattice melting shown by these data is very similar to the observations of Loidl, Knorr, Rowe, and McIntyre [9] for $(KBr)_{0.35}(KCN)_{0.65}$. In this case the diffraction peaks at temperatures close to the cubic-to-rhombohedral transition were found to be dominated by the broad peaks of diffuse scattering, which could be accurately described with an exponential line shape [10]. Owing to the remarkable similarity between these results and the results presented here for Na_2CO_3, it was decided

to perform the analysis of our data in a similar manner, with an exponential line shape for the broad peaks of diffuse scattering that arise from the lattice melting. Currently, no theoretical prediction exists for the exact form of the diffuse scattering line shape at temperatures away from the transition, but Mayer and Cowley [5] have developed a power-law line shape which is valid at T_c. Unfortunately, an analytical powder average of this line shape results in a complicated expression which cannot be usefully used to describe our profiles close to T_c. Furthermore, the use of Lorentzian or Lorentzian-squared profiles gives no improvement over an exponential line shape. We consider, therefore, that in the absence of a general theoretical model, the exponential line shape describes the powder-scattering profiles in Na_2CO_3 very effectively.

The critical modes which soften at the ferroelastic phase transition in Na_2CO_3 are the transverse acoustic modes with wave vectors in the critical planes $(0\,0\,l)$, and with eigenvectors parallel to $[0\,0\,1]$. The diffuse scattering from these modes takes the form of flat disks perpendicular to $[0\,0\,1]$ at reciprocal lattice vectors which have a component along c^*. In a powder diffraction experiment the resultant peaks are averaged over all orientations of the scattering vector in reciprocal space. Since the diffuse scattering produces a broadening of the $(0\,0\,l)$ peaks that is exactly perpendicular to the scattering vectors, it is not observed in our experiments. On the other hand, the broad components of diffuse scattering could clearly be seen under the strong Bragg peaks $(1\,0\,1)$, $(2\,0\,1)$, $(3\,0\,1)$, $(2\,0\,2)$, $(3\,1\,2)$, $(1\,0\,3)$, and $(2\,0\,3)$. These were analyzed by fitting two components to each peak: a sharp Bragg component given by the experimental resolution profile, and an exponential profile for the diffuse scattering component with an exponential profile of the form $I = I_0 \exp(-\left|Q - Q_{(h\,k\,l)}\right|/\kappa)$ convoluted with the resolution function, where $Q_{(h\,k\,l)}$ is the scattering vector for the Bragg peak, and κ gives the width of the peak of diffuse scattering in the powder diffraction spectrum. For each peak κ was determined close to T_c, and then left fixed in the analysis of the scattering at higher temperatures. The fits for all of the analyzed peaks were extremely good.

Results of the fitting procedure are shown in Fig. 2 for the $(1\,0\,1)$, $(2\,0\,2)$, and $(3\,1\,2)$ peaks at 756 K, which is one degree above T_c. At this temperature, no Bragg contribution was observable, and the fitted curve solely represents the exponential profile convoluted with the resolution function, above the background. The $(1\,0\,1)$ and $(3\,1\,2)$ peaks have the minimum and maximum values of the scattering vector Q which were analyzed. The widths of the three peaks shown in Fig. 2 are dependent on the resolution function and the changing effect of the powder average on the diffuse scattering component.

To illustrate the analysis procedure, in Fig. 3 we show the evolution of the scattered intensities above T_c for the $(2\,0\,2)$ peak. As the temperature is raised the exponential
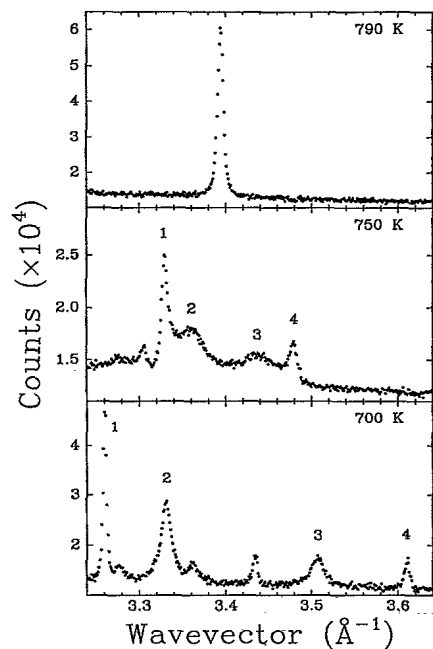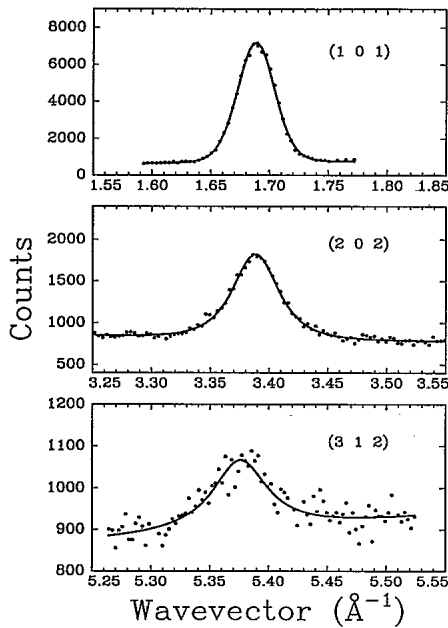

FIG. 1. Neutron powder diffraction spectra well above, close to, and well below T_c showing the splitting of the hexagonal (2 0 2) peak into the $(\bar{4}\,0\,2)$, $(\bar{2}\,2\,2)$, $(2\,2\,2)$, and $(4\,0\,2)$ peaks in the monoclinic phase (labeled 1–4, respectively). The lattice melting and subsequent recovery of the Bragg peaks through the transition are apparent.

FIG. 2. The (1 0 1), (2 0 2), and (3 1 2) peaks at 756 K, which is one degree above T_c. The fitted curves represent the pure diffuse scattering; no Bragg component is present.

component decreases rapidly in intensity as the width of the peak decreases towards the width of the resolution function.

The temperature dependences of the integrated intensities of the Bragg and diffuse scattering components for
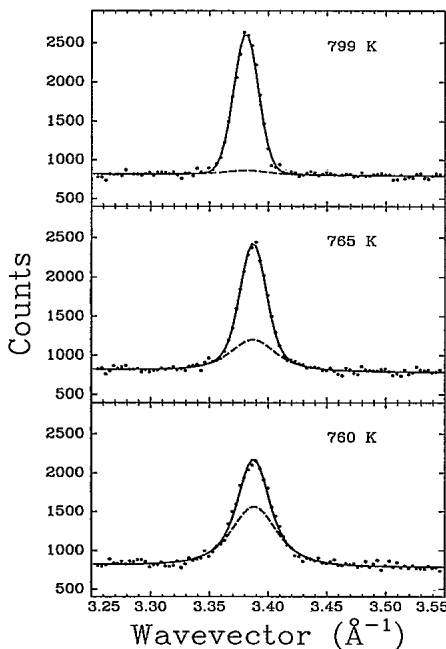
the (1 0 1), (2 0 2), and (1 0 3) peaks are shown in Fig. 4. The Bragg intensity for each analyzed peak falls to zero approaching T_c from above, while the intensity of the diffuse scattering component reaches its maximum at this point. Thus the total intensity associated with each Bragg peak remains approximately constant with temperature, even though the process which occurs is in effect that of a delta function being replaced by a broad peak. At 756 K, which is the closest temperature to T_c that could be analyzed, the data were fitted extremely well in all cases with just the exponential component (convoluted with the resolution function), as can be seen in Fig. 2. Inclusion of the Bragg component into the fitting procedure for this temperature always led to its having negligible intensity. This was found to be the case for all of the seven peaks that were analyzed. Hence, the Bragg intensity at this temperature must be extremely small or zero, indicating that within the resolution of the experiment the mean-squared atomic displacements diverge completely, and long-range order is absent in the critical planes. This effect signals the occurrence of complete lattice melting, which contrasts with the experimental observations of the mixed cyanides, where a small but significant Bragg component is always present at T_c [9]. Hence, the ferroelastic phase transition in Na_2CO_3 is the first example of ideal lattice melting. Because of the comparatively small number of overlapping peaks below T_c around the hexagonal (1 0 1) position in Na_2CO_3, a partial analysis of the diffuse scattering and Bragg intensities is possible. This shows that once the ferroelastic

FIG. 3. The temperature evolution of the line profile of the (2 0 2) peak above T_c. The broken line shows the exponential component, and the full line shows the complete analyzed profile with the Bragg component included.
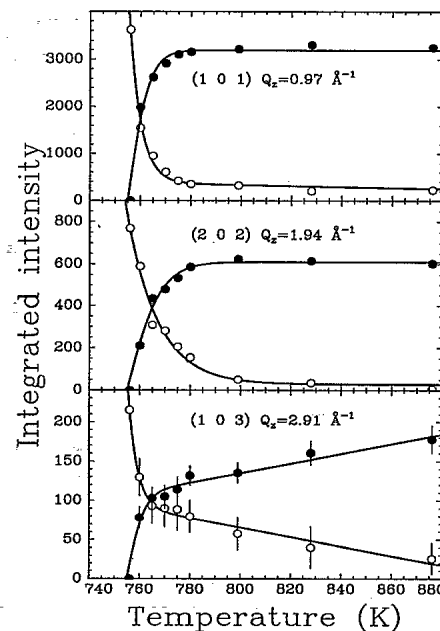

FIG. 4. Temperature dependence of the diffuse scattering (open circles) and Bragg (full circles) intensities for (1 0 1), (2 0 2), and (1 0 3) in the hexagonal phase. The curves represent guides to the eye, and error bars are shown where the error exceeds the size of the data point.
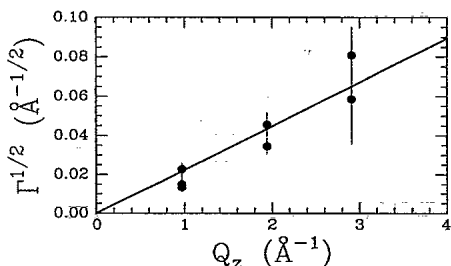
FIG. 5. The dependence of $\Gamma^{1/2}$ on Q_z determined at 756 K. The straight line is the result of a least-squares fit through the origin.

phase transition is passed, long-range order recovers continuously in the monoclinic phase.

It is apparent from Fig. 4 that the temperature dependences of the Bragg and diffuse scattering components depend on Q_z, the component of the scattering vector parallel to $\mathbf{c}^*$ (where $Q_z = 2\pi l/c$). The intensities of the Bragg and diffuse scattering components change more rapidly with temperature the lower the value of Q_z. This behavior simply reflects the conventional dependence of the Debye-Waller factors on the scattering vector: the intensities of the Bragg peaks with higher values of Q_z are more sensitive to the mean-squared atomic displacements, so that the onset of the divergence associated with the lattice melting is observed further from T_c.

The theoretical analysis of Mayer and Cowley [5] leads to the prediction that the width of the diffuse scattering peak at T_c (in this case the width of the diffuse scattering component in the $\mathbf{a}^*$-$\mathbf{b}^*$ plane, Γ) should, to a rough approximation, be proportional to Q_z^2. We show that this appears to be the case for Na_2CO_3 in Fig. 5, where we plot $\Gamma^{1/2}$ (obtained from the values of κ for the seven peaks analyzed from the 756 K spectrum) against Q_z. This result provides some validation for the theoretical Mayer-Cowley line shapes, even though we were unable to use these in the fitting procedure.

This Letter shows that Na_2CO_3 is the first example of a system which undergoes an ideal $m = 2$ ferroelastic phase transition, culminating in a "molten" state which recrystallizes once the transition has been passed. Clearly, a single crystal experiment is required to test fully the predictions of Mayer and Cowley [5] concerning the exact form of the scattering line profiles from this state, but we have shown that the dependence on temperature and scattering vector follows the expected theoretical predictions at least qualitatively. We anticipate that further study of this system will reveal a great deal about this intriguing and evidently very rare universality class.

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