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Observation of lattice melting in a single crystal: The ferroelastic phase transition in Na$_2$CO$_3$

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It was recently discovered that a continuous loss of long-range order occurs at the ferroelastic phase transition in Na$_2$CO$_3$. We present the results of a single-crystal neutron-diffraction study, and show that at $T_c$ the Bragg peaks are completely replaced by diffuse scattering with a power-law profile, consistent with theoretical predictions.

Nearly 20 years ago, theoretical predictions were made of a remarkable loss of long-range order that should occur at a structural phase transition where the elastic constant vanishes in sets of crystallographic planes, only for the order to recover once the transition is passed.$^{1,2}$ This effect has become known as “lattice melting,” and it was recently discovered to occur in Na$_2$CO$_3$, using neutron powder diffraction.$^3$ Currently, Na$_2$CO$_3$ is the only known example in nature. We present results of a single-crystal diffraction experiment and show that Na$_2$CO$_3$ corresponds to a special case of the theory, where long-range order is apparently preserved in one dimension at $T_c$, while being completely destroyed in the other two. The appearance of such a transition state is of particular interest because it results from the equilibrium behavior of a material that is fully crystalline at all other temperatures.

In Na$_2$CO$_3$, the lattice melting occurs at the hexagonal-monoclinic (P6$_3$/mmc–C2/m) ferroelastic transition at ca. 760 K.$^3$ On a microscopic scale the transition is driven by a complete softening of the transverse acoustic phonons that are polarized in the [0 0 1] direction and have wave vectors in the a*-b* plane. The softening leads to a complete divergence of the mean-squared atomic displacements along [0 0 1], which in turn results in the loss of long-range order as $T_c$ is approached.$^{1,2,4}$ Unlike a normal solid-liquid transition, this is a continuous process and the divergence only occurs along one direction. Also, once the transition is passed the long-range order recovers. There is no appreciable diffusion, and the melting is associated with the lattice rather than the atomic order. This is why it is known as “lattice melting.”

In the general case of a crystal undergoing lattice melting, Mayer and Cowley$^4$ predicted that the Bragg scattering is replaced completely by diffuse scattering with a power-law profile. However, calculations$^{3,5}$ suggest that Na$_2$CO$_3$ should correspond to a special case where the Bragg scattering is effectively preserved along c*, which is the perpendicular to the critical planes of wave vectors. At $T_c$, the scattering function may be approximated as

$$S(G+q) \sim \delta(q_\perp)|q_\perp|^{-\alpha},$$  \hspace{1cm} (1)

where $G$ is a reciprocal-lattice vector, $q$ is a wave vector with the components $q_\parallel$ and $q_\perp$ parallel and perpendicular to the c* axis, respectively, and $\delta$ is the Dirac delta function. The exponent $\alpha$ is given as

$$\alpha = 2 - KG^\parallel,$$  \hspace{1cm} (2)

where $G^\parallel$ is the component of $G$ parallel to c*, and $K$ is a constant. We can see from (1) that the scattering is sharp along c* but has the form of a power-law singularity within the a*-b* critical plane: it is an infinitely thin disk.

We have tested these predictions by performing a single-crystal neutron diffraction study of Na$_2$CO$_3$, and have found an excellent agreement. The experiment was performed using the PRISMA time-of-flight spectrometer configured in its diffraction mode,$^6$ at the ISIS spallation neutron facility, and a single crystal of Na$_2$CO$_3$ oriented so that the scattering plane was the a*-c* plane. Scans were performed at 27 different temperatures around the (0 0 2), (0 0 4), (0 0 6), and (0 0 8) Bragg positions.
FIG. 1. The scattering along the $\mathbf{q}_l$ direction through the (0 0 4) position, shown for the sample temperatures 893, 773, and 761 K. Note that $T_c = 760.6(3)$ K. The curves show fits to the data of the Mayer-Cowley scattering function (Ref. 4) convoluted with the experimental resolution function. The 761 K data have a clear cusp-shaped distribution, due to the loss of long-range order which results in a power-law singularity in the predicted scattering function. The 893 K data show very strong Bragg scattering with small wings of diffuse scattering due to the acoustic modes that are still soft, while the data taken at 773 K show an intermediate situation.

In Fig. 1, we show the temperature dependence of the scattering along $\mathbf{q}_l$ around the (0 0 4) position. Note that $T_c$ was determined to be 760.6(3) K. At the highest temperature shown (893 K) the scattering is predominantly sharp Bragg scattering with a line shape governed by the experimental resolution function. However, as the sample is cooled towards the transition, strong diffuse scattering appears along $\mathbf{q}_l$ while the Bragg scattering weakens. In the intermediate state at 773 K, the total scattering is divided about evenly between the diffuse and Bragg scattering. At 761 K the Bragg scattering is practically entirely replaced by broad diffuse scattering with a cusp-like distribution, reflecting the power-law singularity in (1). This signals the occurrence of lattice melting. Below the transition, sharp Bragg scattering reappears, showing that the long-range order recovers once the transition is passed.

The curves in the figure show fits to the Mayer-Cowley scattering function\(^6\) convoluted with the experimental resolution function.\(^6\) The exponent $\alpha$ was found to have the value 1.22(2) at $T_c$ for the scattering at the (0 0 4) position. For the $\mathbf{q}_l$ direction, the scattering was found to be described well for all temperatures by the convolution of a delta function with the resolution function, consistent with (1). Fits to the scattering along $\mathbf{q}_l$ of the experimental resolution function are shown in Fig. 2. A good agreement is also seen for the scattering at the (0 0 2) and (0 0 6) positions, with values of $\alpha$ obtained from the (0 0 4) value, using Eq. (2). Thus, for the (0 0 2) position, $\alpha = 1.80$, while at the (0 0 6) position $\alpha = 0.24$. Hence, the $\mathbf{q}_l$ scattering becomes increasingly broader as the $c^*$ component increases. At (0 0 8) it is so broad as to be indistinguishable from the background, and in fact, at this point and beyond $\alpha < 0$. Hence, (1) no longer holds, and the scattering should be finite for all $\mathbf{q}_l$, like a liquid structure factor.\(^7\)

A key parameter in the Mayer-Cowley model, $\kappa$, is proportional to $C_{44}^{1/2}$, the square root of the soft elastic constant. $\kappa$ controls the temperature dependence of the scattering function,\(^4\) and our fitted values show that it varies as $(T-T_c)^{1/2}$, fully consistent with the theoretical predictions,\(^1,2\) and with inelastic neutron scattering measurements of $C_{44}$.\(^8\) This result provides an additional check on our application of the Mayer-Cowley model.\(^4\)
In summary, we have made an observation of lattice melting in a single-crystal sample, allowing us to test the theoretical predictions of Mayer and Cowley. We find that our neutron scattering data are in excellent agreement with these predictions, and we show that Na$_2$CO$_3$ undergoes a special form of lattice melting where the long-range order is destroyed in a two-dimensional sense, but preserved parallel to the crystallographic c axis.

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