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Citation for published version:
Harris, M, DOVE, MT & Godfrey, KW 1995, 'Observation of lattice melting in a single crystal: the ferroelastic phase transition in Na_2CO_3', *Physical Review B (Condensed Matter)*, no. 51, pp. 6758-6760. https://doi.org/doi:10.1103/PhysRevB.51.6758

Digital Object Identifier (DOI):
doi:10.1103/PhysRevB.51.6758

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review B (Condensed Matter)

Publisher Rights Statement:
©Harris, M., DOVE, M. T., & Godfrey, K. W. (1995). Observation of lattice melting in a single crystal: the ferroelastic phase transition in Na2CO3. Physical Review B: Condensed Matter and Materials Physics, (51), 6758-6760doi: doi:10.1103/PhysRevB.51.6758

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Download date: 29. Nov. 2021

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 10 1 MARCH 1995-II

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Observation of lattice melting in a single crystal: The ferroelastic phase transition in Na_2CO_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_2CO_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_2CO_3, using neutron powder diffraction.[3] Currently, Na_2CO_3 is the only known example in nature. We present results of a single-crystal diffraction experiment and show that Na_2CO_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_2CO_3, the lattice melting occurs at the hexagonal-monoclinic ($P6_3/mmc$–$C2/m$) ferroelastic transition at ca. 760 K.[3] On a microsopic 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."[3]

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_2CO_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

$$S(\mathbf{G}+\mathbf{q}) \sim \delta(q_{\parallel}) q_{\perp}^{-\alpha}, \tag{1}$$

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 δ is the Dirac delta function. The exponent α is given as

$$\alpha = 2 - KG_{\parallel}^2, \tag{2}$$

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_2CO_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_2CO_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.

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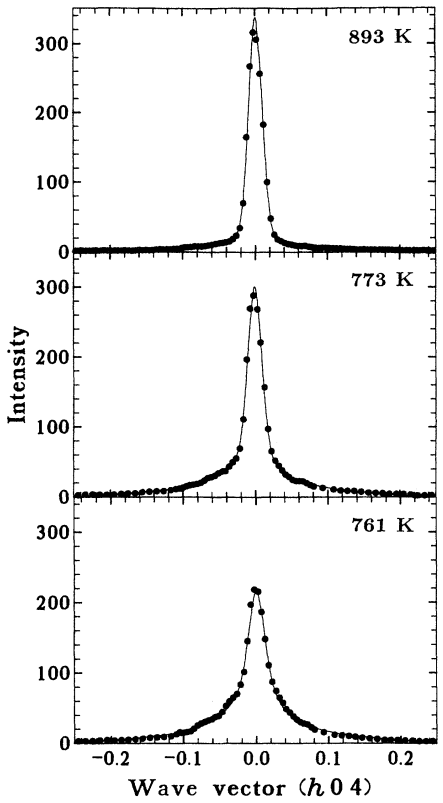

FIG. 1. The scattering along the $\mathbf{q}_\perp$ direction through the (0 0 4) position, shown for the sample temperatures 893, 773, and 761 K. Note that $T_c = 760.6(3)$ K. The curves show fits to the data of the Mayer-Cowley scattering function (Ref. 4) convoluted with the experimental resolution 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.

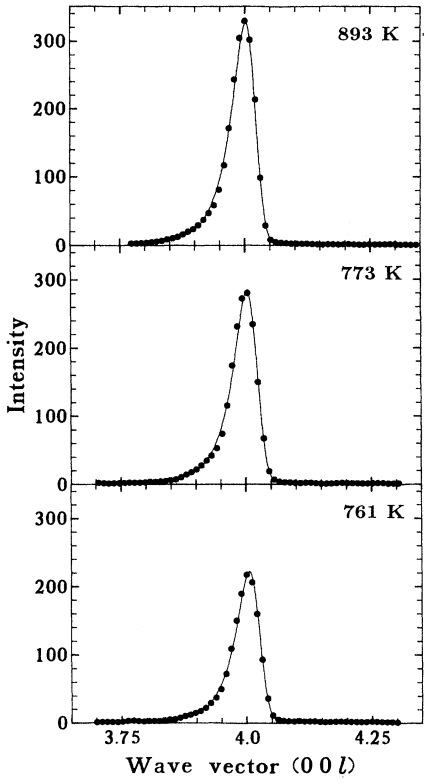

FIG. 2. The scattering along the $\mathbf{q}_\parallel$ direction through the (0 0 4) position, shown for the sample temperatures 893, 773, and 761 K. Note that $T_c = 760.6(3)$ K. The curves show fits to the data solely of the experimental resolution function; the asymmetry is due to the time structure of the incident neutron pulse.

In Fig. 1, we show the temperature dependence of the scattering along $\mathbf{q}_\perp$ 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 $\mathbf{q}_\perp$ 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 cusplike 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[4] convoluted with the experimental resolution function.[6] The exponent α was found to have the value 1.22(2) at T_c for the scattering at the (0 0 4) position. For the $\mathbf{q}_\parallel$ 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 $\mathbf{q}_\parallel$ 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 α 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 $\mathbf{q}_\perp$ scattering becomes increasingly broader as the $\mathbf{c}^*$ 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 $\mathbf{q}_\perp$, like a liquid structure factor.[7]

A key parameter in the Mayer-Cowley model, κ, is proportional to $C_{44}^{1/2}$, the square root of the soft elastic constant. κ 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.[4] We find that our neutron scattering data are in excellent agreement with these predictions, and we show that Na_2CO_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.

The authors wish to thank R. A. Cowley, M. Hagen, U. Steigenberger, and I. P. Swainson for many helpful discussions, and the EPSRC for financial support.

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