Crystal Symmetry Lowering at an Order-Disorder Transition

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Neutron diffraction measurements in the high-temperature disordered phase of NaSn show that the transition to this phase from the ordered low-temperature phase is associated with a lowering of crystal symmetry which is unique among disordering transitions. The structure refinement reveals intimate correlations between the Na^+ cation positions and $Sn_4{}^{4-}$ polyanion orientations in the disordered phase, and indicates that the cation migration takes place along convoluted channels in the crystal.

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NaSn undergoes a polymorphic transition from a low-temperature (β) to a high-temperature (α) phase at $T_c = 484\,^\circ\mathrm{C}$. The entropy increase at the transition is similar in magnitude to the entropy of melting, which takes place at $T_m = 578\,^\circ\mathrm{C}$ [1]. The electrical conductivity, which has semiconducting behavior below T_c, shows a small drop at T_c and then rises rapidly to metallic values as T_m is approached [2]. Both quasielastic neutron scattering (QENS) [3,4] and NMR [5] measurements show that the α phase is dynamically disordered, with fast Na^+ cation migration and $Sn_4{}^{4-}$ polyanion reorientations taking place on a similar time scale. However, none of these measurements gives information about the structure and symmetry of the disordered phase, the pathways for the migration, or the spatial relationship between the migrating cations and the rotating polyanions. While such information could be obtained in principle from QENS measurements on a single crystal, the difficulties of growing large single crystals of this material (which would have to be done *in situ* on the spectrometer) make such studies unfeasible. We have therefore made use of powder neutron diffraction which, combined with Rietveld profile refinement, has proved to be a reliable technique for obtaining three-dimensional information.

In this Letter we report neutron diffraction results on α-NaSn which show that the disordering at T_c is associated with a change in crystal structure from tetragonal to orthorhombic, a unique example of symmetry *lowering* at a disordering transition. They also demonstrate that the Na^+ positions and $Sn_4{}^{4-}$ orientations are closely interlocked, consistent with strong coupling between cation migration and polyanion reorientation [3]. The cation migration takes place along convoluted pathways parallel to the orthorhombic c axis.

A sample of polycrystalline NaSn was loaded in a vanadium container, sealed under vacuum by e-beam welding and mounted in a vanadium vacuum furnace on the SEPD instrument at IPNS. A neutron diffraction run was made at room temperature to confirm the β-phase structure [6], after which the sample was heated through T_c (which occurred at a recorded temperature of 475 °C) and allowed to equilibrate at a temperature just above it. A run of 25 h was then made at 480 °C to determine the structure of the α phase. Representative sections of the diffraction patterns for the two phases are shown in Fig. 1. The α-phase pattern is dominated by the diffuse scattering arising from the dynamic disorder. Nevertheless, Bragg peaks can still be clearly identified. The lower symmetry of the α phase is immediately obvious from the higher density of these peaks relative to the β phase. The highest symmetry space group to which the peaks can be indexed is orthorhombic, *Fddd*, in contrast to the

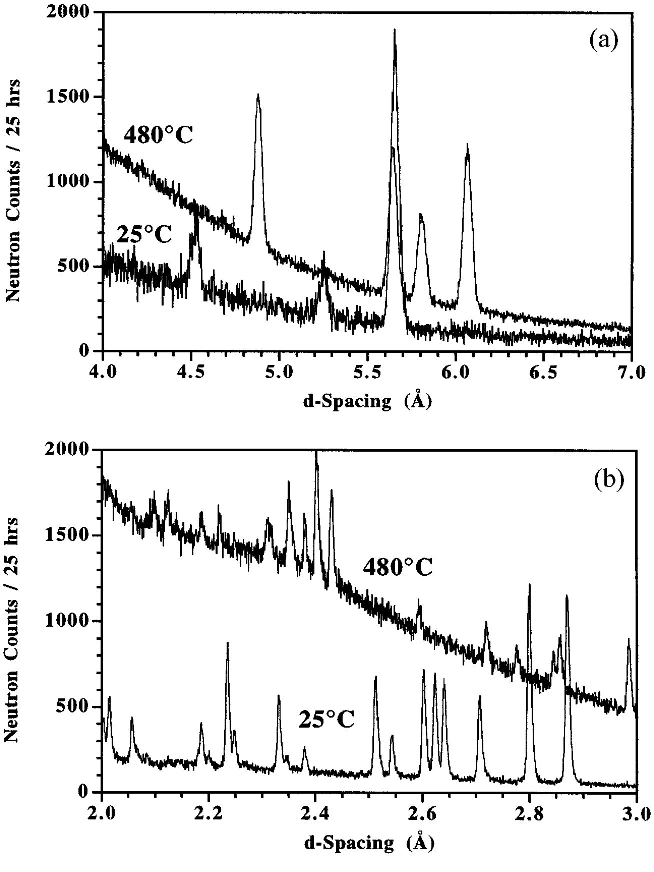

FIG. 1. Diffraction patterns for (a) $d = 4-7$ Å and (b) $d = 2-3$ Å for β-NaSn at 25 °C and α-NaSn at a recorded temperature of 480 °C.

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tetragonal $I4_1/acd$ structure of the β phase. The unit cell volume in the α phase just above T_c is 2151 Å^3, in contrast to the corresponding volume of the β phase at room temperature 1929 Å^3, and its value extrapolated to the temperature of the α-phase measurement 2020 Å^3.

The atomic positions were derived by Rietveld profile refinement [7]. The quality of the fit was satisfactory, with R factors $R_{wp} = 2.5\%$ and $R_{F^2} = 11.5\%$. We illustrate the structure in a sequence of two-dimensional real-space Fourier maps obtained from observed Bragg peak intensities. The section through the plane $x = 0$ is shown in Fig. 2. At this level only the $Sn_4{}^{4-}$ polyanions contribute to the scattering density. Surprisingly, the sites in each tetrahedral configuration have an occupancy of only one-quarter. From a given configuration, a second is obtained by inversion about the center of the tetrahedron, and the third and fourth by transformation of the $Sn_4{}^{4-}$ units to equivalent, but differently oriented, inversion sites. Thus, the $Sn_4{}^{4-}$ polyanions undergo translational as well as orientational disorder.

There are three types of Na^+ cation sites represented in this structure: (a) fixed, high symmetry sites which maintain the rigidity of the structure, (b) closely spaced sites along the direction of fast migration (the c axis of the orthorhombic cell), and (c) very weakly populated general sites. Shown in the section of the Fourier map through the plane $x = \frac{1}{8}$ (Fig. 3) are Na^+ ions of types (a) and (b). There are two crystallographically distinct fixed (a) sites, identified as Na(1) and Na(2), with a total occupancy of one. Interestingly, the migrating Na^+ ions (b sites) are not totally diffuse, appearing to jump between two characteristic sites: distinct Na(3) sites ($\frac{2}{3}$ occupation), and Na(4) sites (not shown) midway between them ($\frac{1}{3}$ occupation). The weakly occupied Na(5) atoms are situated in general positions, not shown in the figures.

The simple picture implied by Figs. 2 and 3 is complicated by unusual statistical populations and unacceptably close proximity of structural units. The one-quarter occupancy of $Sn_4{}^{4-}$ units is explained by the fact that the point symmetry and spacing of the 16 inversion sites in each unit cell are incompatible with fully ordered $Sn_4{}^{4-}$ units. Instead, about each of the inversion centers there must be only one of two equally probable orientations of $Sn_4{}^{4-}$ tetrahedral units occupied at a given time. In addition, neighboring inversion sites displaced from each other by $(\pm\frac{1}{4}, 0, \pm\frac{1}{4})$ are probably too close (3.7 Å) to be simultaneously occupied. Furthermore, it appears that the presence of Na(2) ions introduces new steric constraints on neighboring $Sn_4{}^{4-}$ units, allowing only certain orientations. Finally, because Na(1) and Na(4) are too close (2.7 Å) to be simultaneously occupied, there must be a correlation between the occupations of Na(3) and Na(4)

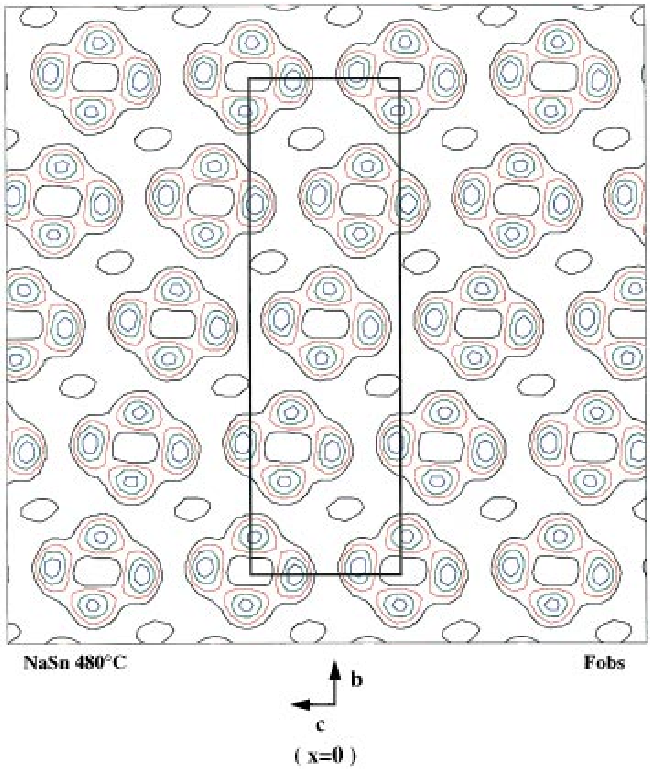

FIG. 2 (color). Fourier contour map of model for α-NaSn structure, $x = 0$ plane. The rectangular represents the boundary of the orthorhombic unit cell.

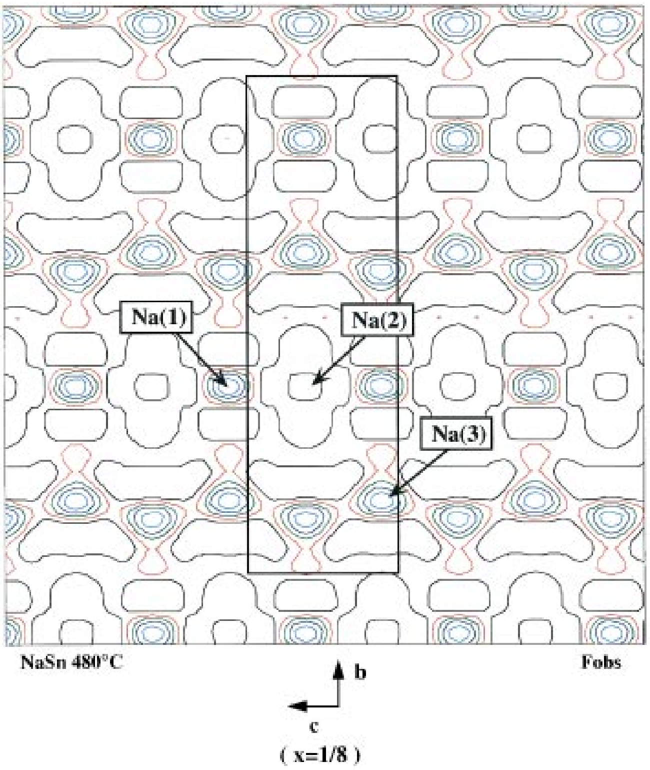

FIG. 3 (color). Fourier contour map of model for α-NaSn structure, $x = \frac{1}{8}$ plane. The rectangle represents the boundary of the orthorhombic unit cell. Na(1) and Na(2) are fixed sites and Na(3) sites along the direction of fast migration, as discussed in the text.

sites, and between those of Na(1) and Na(2) sites. It appears that, in a local sense, the structural units of α-NaSn are intimately interlocked in a manner not directly commensurate with the orthorhombic cell we have described. This suggests the possibility of a lower symmetry representation for the structure. A variety of alternatives was explored, without any indication that a longer period exists. We conclude, therefore, that local dynamical correlations are propagated through rapid reorientation.

The $\beta \rightarrow \alpha$ transition is fully reversible and strongly first-order, with a large increase in entropy ($\Delta S_c = 4.95\ \mathrm{J\,mol^{-1}\,K^{-1}}$, compared with $\Delta S_m = 8.48\ \mathrm{J\,mol^{-1}\,K^{-1}}$ [1]) and in volume $[\Delta V/V_\beta(T_c) = 0.065]$. The lowering in crystal symmetry on disordering, $I4_1/acd \rightarrow Fddd$, is to our knowledge the only known example of such behavior at a disordering transition. A number of ferroelastic phases exist [8] which are sandwiched between two paraelastic phases, but in these cases both low- and high-temperature disordered phases have higher symmetry than the ordered phase. Some other cases exist where the symmetry is lowered on heating through a phase transition, including NaOH [9], malonitrile [10], and $La_{2-x}Ba_xCuO_6$ [11], but these transitions have a displacive rather than order-disorder character. Tetracyanoethylene [12] has a sluggish irreversible transition from a cubic to a monoclinic structure on heating, probably also of a displacive type. We are not aware of any examples, besides the present case, of disordering transitions where the symmetry is lowered.

Finally, at $T_m = 578$ °C, the crystal melts. Since the α phase is stabilized by the Na(1) and Na(2) sites, melting must be associated with disordering of these sites. The fact that these two sites have a total occupancy of one suggests that this disordering may start to occur as the temperature is raised within the α phase. If so, the rapid increase in electronic conductivity with temperature in this phase may be related to this disordering. *Ab initio* molecular dynamics simulations of liquid NaSn [13] indicate that Sn_4 clusters are stable in the liquid but form a network structure rather than independent polyanions as suggested by Alblas *et al.* [14] on the basis of their neutron diffraction measurements and by Geertsma and Saboungi on the basis of thermodynamic data [15]. However, the present diffraction data show that Sn_4 clusters exist as independent, although strongly correlated, polyanions in both ordered and disordered phases of NaSn up to the melting point. Furthermore, the similar behavior of the quasielastic scattering between the disordered solid and liquid phases [4] suggests structural similarities between the two phases. Thus, the existence of isolated polyanions in the liquid above the melting point must still be considered an open question. It would be extremely interesting to measure the ionic conductivity σ_i along the different crystal axes. Unfortunately this is not easy because of the high electronic conductivity. An upper limit for its averaged value just above the $\beta \rightarrow \alpha$ transition is given by the total conductivity at that temperature, $\sigma = 5\ \Omega^{-1}\,\mathrm{cm}^{-1}$ [2], but probably it is considerably lower than that. Insulating fast ion conductors generally have ionic conductivities on the order of 1–5 $\Omega^{-1}\,\mathrm{cm}^{-1}$ just above T_c. Ramasesha and others [16] have pointed out that an attractive interaction between fast ions and mobile electrons or holes can exist in such systems, leading to a mutual enhancement of the fast-ion conduction and the population of mobile fermions. If this is the case in α-NaSn, the dramatic rise in α with temperature over the temperature range of the α phase implies a similar large increase in the population of mobile ions.

In conclusion, the neutron diffraction measurements presented here show that the $\beta \rightarrow \alpha$ transition in NaSn is associated with a lowering of crystal symmetry that appears to be unique among disordering transitions. In the α phase, the ${Sn_4}^{4-}$ polyanions undergo translational as well as orientational disorder, while the Na^+ cations lie on two types of sites, fixed sites that maintain the rigidity of the lattice and mobile sites that provide convoluted pathways for the fast migration. The fixed sites may also be starting to disorder as the temperature is raised in the α phase, accompanied by a dramatic increase in the number of mobile electronic charge carriers. The crystal finally melts when this disorder becomes so large that the lattice rigidity can no longer be maintained.

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[1] M.-L. Saboungi, G. K. Johnson, and D. L. Price, in *Statics and Dynamics of Alloy Phase Transformations*, edited by P. E. A. Turchi and A. Gonis (Plenum, New York, 1994), p. 195.
[2] J. Fortner, M.-L. Saboungi, and J. E. Enderby, Phys. Rev. Lett. **74**, 1415 (1995).
[3] M.-L. Saboungi, J. Fortner, W. S. Howells, and D. L. Price, Nature (London) **365**, 237 (1993).
[4] D. L. Price, M.-L. Saboungi, and W. S. Howells, Phys. Rev. B **51**, 14 923 (1995).
[5] R. D. Stoddard, M. S. Conradi, A. F. McDowell, M.-L. Saboungi, and D. L. Price, Phys. Rev. B **52**, 13 998 (1995).
[6] W. Müller and K. Volk, Z. Naturforsch **32B**, 709 (1977).
[7] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).
[8] J. Schneck and J. Primot, Solid State Commun. **21**, 57 (1977), and references therein.
[9] H.-J. Bleif and H. Dachs, Acta Crystallogr. Sect. B **38**, 470 (1982).
[10] M. Krauzman, R. M. Pick, N. Le Calvé, and B. Pasquier, J. Phys. (Paris) **44**, 849 (1983).

[11] D. McK. Paul *et al.*, Phys. Rev. Lett. **58**, 1976 (1987); J. D. Axe *et al.*, Phys. Rev. Lett. **62**, 2751 (1989); S. J. L. Billinge *et al.*, Phys. Rev. Lett. **72**, 2282 (1994).
[12] R. Mukhopadhyay, S. L. Chaplot, and K. R. Rao, Phys. Status Solidi (a) **92**, 467 (1985).
[13] G. Seifert, G. Pastore, and R. Car, J. Phys. Condens. Matter **4**, L179 (1992); M. Schöne, R. Kaschner, and G. Seifert, J. Phys. Condens. Matter **7**, L19 (1995).
[14] B. P. Alblas, W. van der Lugt, J. Dijkstra, W. Geertsma, and C. van Dijk, J. Phys. F **13**, 2465 (1983).
[15] W. Geertsma and M.-L. Saboungi, J. Phys. Condens. Matter **7**, 4803 (1995).
[16] S. Ramasesha, J. Solid State Chem. **41**, 333 (1982); Y. Y. Gurevich and Y. I. Kharkats, Sov. Phys. Solid State **27**, 1188 (1985).