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LETTER TO THE EDITOR

The ferroelastic phase transition of betaine borate and maleinate

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Abstract. The ferroelastic orthorhombic–monoclinic transition of betaine hydrogen maleinate $(\text{CH}_3)_3\text{NCH}_2\text{COO}(\text{CH})_2(\text{COOH})_2$ and betaine borate $(\text{CH}_3)_3\text{NCH}_2\text{COO B}(\text{OH})_3$ has been studied by x-ray diffraction. The temperature dependence of the spontaneous strain and the orientational correspondence of the domains to the parent lattice has been established.

The great success of triglycine sulphate as a ferroelectric material stimulated interest in the physical properties of other adducts of amino acids. In our laboratories the crystal growth and the physical properties of betaine compounds are studied systematically. It has been shown that some members of this family, like betaine phosphate and betaine calcium chloride dihydrate, have outstanding dielectric properties [1]. In the present article we report x-ray diffraction results on the ferroelastic phase transition of betaine borate $(\text{CH}_3)_3\text{NCH}_2\text{COO B}(\text{OH})_3$ ('BB') and betaine hydrogen maleinate $(\text{CH}_3)_3\text{NCH}_2\text{COO}(\text{CH})_2(\text{COOH})_2$ ('BHM').

Large single crystals of the two compounds have been grown from aqueous solution. At room temperature both crystals are orthorhombic with space group $Pm\bar{c}n$ and have (100) cleavage planes [2, 3]. An x-ray structure determination on BB shows that the borate and the carboxyl group as well as the betaine backbone of one molecule are (100) coplanar [4]. Chains of alternating borate and carboxyl groups linked by hydrogen bonds propagate along [001]. The ferroelastic low-temperature phase of BB is monoclinic, $P2_1/c$, which in fact is a maximal isomorphic subgroup of $Pm\bar{c}n$. The changes of internal coordinates induced by the phase transition are small. For both crystals, the elastic shear constant c_{55} of the orthorhombic phase shows an almost complete softening with decreasing temperature T [2, 3]. This was the first indication that these crystals are ferroelastically unstable. (Note that the present article and [4] interchange the crystal axes with respect to [2, 3].)

The x-ray diffraction experiments of the present study have been carried out on a two-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation, from room temperature down to about 20 K. The temperature stability of the cryogenic set-up is 0.1 K. The crystals, of typical size $0.5 \times 0.5 \times 0.5 \text{ mm}^3$, have been mounted in two different settings, with [010] and [100] perpendicular to the scattering plane. For both compounds the systematic extinctions observed are consistent with the space group given above. The room temperature lattice parameters ($a = 7.776 \text{ \AA}$, $b = 9.875 \text{ \AA}$, $c = 11.976 \text{ \AA}$ for BB; $a = 6.695 \text{ \AA}$, $b = 26.528 \text{ \AA}$, $c = 12.745 \text{ \AA}$ for BHM) agree with the values cited previously [2, 3, 4]. Selected peaks have been scanned in longitudinal and transverse directions as a function of temperature. The spontaneous strain and the formation of domains in the low- T

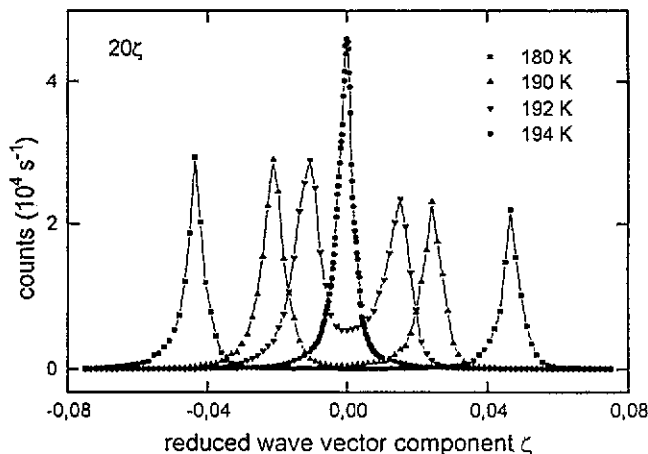


Figure 1. The splitting of the (200) reflection of BHM upon the ferroelastic phase transition, as observed in transverse scans along (20ζ) .

phase leads to a splitting of reflections—see, e.g., figure 1. Leaving aside a complication that occurred in some of the BB crystals, the crystals obey the following transformation rule.

The directions of the a - and the b -axis are conserved. The c -axis is rotated about the b -axis by an angle of $\pm\Delta\beta$, $\Delta\beta = \beta - 90^\circ$. $\Delta\beta$ is directly accessible from the splitting of $(h00)$ peaks in the transverse direction—that is, in scans along $(h0\zeta)$; see figure 1. The ζ -position of the split components is found to be proportional to the node index h , a fact that proves that the deformation of the lattice is a pure homogeneous shear. The integrated intensity of the split components amounts to about half of the intensity of the $(h00)$ parent peak. Thus the two domain states have about the same statistical weight. These observations strongly suggest that the domains form a regular zigzag twin pattern with (001) domain walls. This conclusion is in agreement with a recent optical inspection of the domain pattern [5]. The temperature dependence of the spontaneous shear order parameter $\sin(\Delta\beta) \simeq \Delta\beta$ of the two compounds is shown in figure 2. The order parameter follows the mean-field power law $\sim (T_c - T)^{1/2}$ within experimental accuracy down to about 50 K with a tendency towards saturation at lower T . The transition temperature T_c is 136.3 ± 0.5 K for BB and 193.0 ± 0.1 K for BHM. Figure 3 shows the T -dependence of the cell volume. One notes a kink rather than a jump at T_c . This point, the apparently continuous onset of the order parameter (and the deep softening of c_{55}) suggest that the transition is close to second order. Of course the finite mosaic width and the finite experimental resolution in combination with small values of the order parameter and with diffuse scattering from the low-lying acoustic phonon branch in the vicinity of T_c render fits of the scan profiles somewhat arbitrary. In particular it is difficult to decide whether the profile at temperatures around T_c is better described by a profile of two split components or by a three-peak profile with an additional peak remaining at $(h00)$ which would represent a coexisting orthorhombic fraction. Nevertheless we can exclude the possibility of an orthorhombic–monoclinic coexistence region being broader than 1 K.

The fact that the ferroelastic order parameter of many compounds follows the mean-field power law over a wide T -range has been recognized and attributed to the long range of elastic interactions by Salje and co-workers [6]. The eventual saturation of the order parameter at low T has been described by a quantum mechanical version of the mean-field model [7].

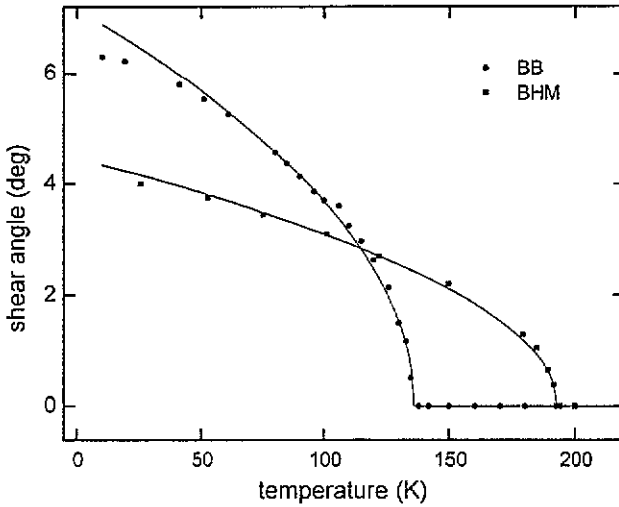


Figure 2. The spontaneous shear angle $\Delta\beta$ of the ferroelastic phase of BB and BM.

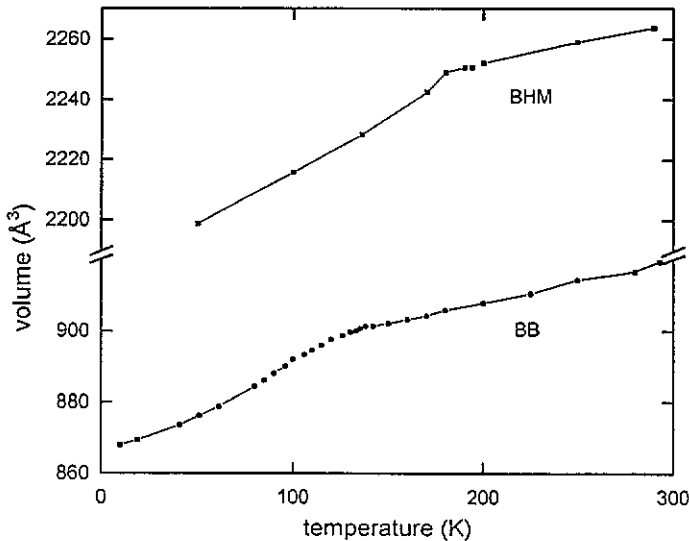


Figure 3. The temperature dependence of the cell volume.

In some of the BB crystals more complex peak profiles have been observed in the ferroelastic state: scans along $(\epsilon 0k)$ and $(h0\zeta)$ show both three-peak profiles, namely a peak unshifted at the central positions, $(00k)$ and $(h00)$, and a pair of side peaks at $(\pm\delta 0k)$ and $(h0\pm\Delta)$. Thus there are peaks at $(h00)$ and $(\pm\delta 0k)$ in addition to those that have been already observed for the transformation scheme discussed above. The additional peaks can be attributed to a second twin pair, with a (100) twin plane. As for the primary pair, the statistical weights of the twins are about equal. Both types of domain twin have the same spontaneous strain $\Delta\beta(T)$. In those cases where the secondary pair appears, it does so about 2 K below T_c and eventually represents about 20% of the crystal volume.

The present compounds show particularly simple, perhaps even prototypic examples of a ferroelastic transition. They belong to the ferroelastic species $mmmF2/m$, which has just two orientation states [8]. The transition is due to a condensation of the long-wavelength acoustic phonons, the velocity of which is proportional to $c_{55}^{1/2}$. Such purely transverse modes occur in mutually perpendicular pairs whose displacement and propagation directions, here [100] and [001], may be interchanged. For a second-order ferroelastic transition in the absence of symmetry-breaking external fields the domain wall normals correspond to these acoustic axes. This rule follows directly from the soft-mode concept [9], but can also be derived from the criterion of strain compatibility at the domain boundary [10]. For $mmmF2/m$ the predicted domain walls are (100) and (001) in agreement with the experimental observation. The question of what type of twin pair actually appears or whether both types coexist is a matter of higher-order terms of the strain energy and of possible crystal defects which lead to inhomogeneous stresses. In this context the appearance of the secondary domain pair (with (100) walls) in BB some K below T_c is presumably induced by residual stresses set up by the formation of the primary domain pattern.

The appearance of a shear instability in a layered crystal is of course not unexpected. Nevertheless the microscopic origin of the ferroelastic instability is not yet known. Recent Raman measurements show that Γ -point optical modes are coupled to the soft acoustic mode [5] and thus may help to establish a microscopic model. It has been shown for BHM that well above T_c the elastic shear constant c_{44} is even lower than the critical mode c_{55} [2]. It is only a few K above T_c that c_{55} falls below c_{44} . Nevertheless this unusual behaviour does not affect the phase transition.

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