Structural Correspondences and Mechanisms for the Polymorphic Transformations NaCl ⇌ CsCl Type and NaCl ⇌ Rhombohedral

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Experimental evidence is presented for a martensitic mechanism of transformation [NaCl] → [CsCl] type in supercooled NH₄Br crystals. Two published structural relationships are shown to be equivalent to the original Shoji–Buerger correspondence. The effect of conditions on the mechanism is discussed. Interface immobilization in transformations is attributed to relaxation of the interface structure.

1. Introduction

There are three main aspects of the mechanisms of polymorphic transformations in which there is a large change of structure: (1) the underlying structural correspondence, or its absence, (2) the structure of the interface, in particular the mode of accommodation of misregistry between the structures during transformation, and (3) initiation or nucleation.

The transformation NaCl type ⇌ CsCl type is a fundamental example of change between six and eight coordination in ionic crystals. Four apparently different structural correspondences or series of displacements have been proposed, and there have been different conclusions about the mechanisms. This paper, in discussing (1) and (2) above, establishes that three of the correspondences are closely related, elaborates on the other, and suggests that the total mechanism depends on conditions. It also includes experimental evidence for a particular martensitic mechanism.

It is often convenient to present the structural correspondence as extensions and contractions, that is, as a pure strain which converts the lattice, with nondiffusive consequential displacements of some of the atoms. (More generally, where small easily diffusing atoms are present, diffusive jumps of these could be incorporated.) Thus presented the correspondence makes clear that diffusive rearrangements are not inherent in the structure change. It permits the two factors of structure change and misregistry to be considered explicitly, it emphasizes that the principal strain axes are directions of maximum misfit, and it allows directions of unextended vectors in two or three dimensions to be calculated as an aid in finding lines or planes of optimum fit; in addition the strain can be resolved into extensions plus shears on any chosen plane of atoms. Without further adjustments, there will be no plane of fit between the structures unless one principal strain is zero, one positive, and one negative (1).

It will be convenient also to recall that where diffusive adjustments are not available, the requirement that the structures stay in register within the dimensions of atomic repeats can force the inclusion either of misfit

dislocations or of the required proportions of alternating twin options or twin-related displacements. This is the martensitic mechanism. It has the consequences that since there is no relaxation there is a predictable and observable shape change, and that since the tendency to align real rows of atoms is disturbed by the dislocations or proportion of twins, the precise orientation relation is irrational, and the orientations are multiplied by symmetry. This may be one of the reasons for difficulty in interpretation of diffraction patterns. On the other hand where activated adjustments are available one may expect that these requirements will be relaxed.

In the orientation relations which follow, subscripts C and N refer to CsCl and NaCl structure types, respectively, and square brackets denote structure type.

2. Structural Correspondence

2.1. First correspondence. The rhombohedral primitive cell of [NaCl] is converted to a cube, which is the [CsCl] cell, by a relative contraction along the common threefold axis [111] and a uniform expansion in the (111) plane (*2, 3*) (Fig. 1). The $\{100\}_N$ planes become three of the $\{110\}_C$ planes and a $\langle 010 \rangle_N$ becomes a $\langle 11\bar{1} \rangle_C$. The fcc cell becomes rhombohedral. The lattice dimensions of real compounds require a contraction of 40% and an extension of 19%; or conversely, for NH_4Br specifically, the principal distortions are 1.678 and 0.839. Intermediate amounts of deformation produce rhombohedral cells. In [NaCl] → [CsCl] because of the dimensional changes $\parallel$ and $\perp$ [111] failure to observe $[111]_C\parallel[111]_N$ experimentally tends to confirm rather than disprove this correspondence. In the cubic → cubic change hexagonal nets $\{11\bar{1}\}_N$ become square nets. Confirmation of this correspondence, especially in a mechanism with nondiffusive accommodation, would show that this
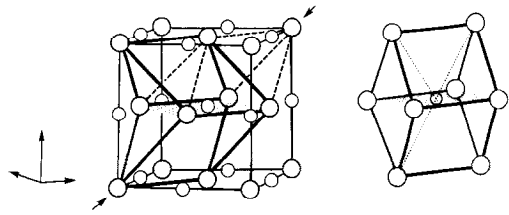
deformation of nets could occur in real crystals. This has consequences for other transformations.

An orientation observed, especially in supercooled crystals by Fraser and Kennedy (*4, 5*), and attributed to this correspondence was $[001]_N\parallel[11\bar{1}]_C$, $(100)_N\parallel(10\bar{1})_C$. This will be referred to as relation A. In the Shoji correspondence the $[001]_N$, $[11\bar{1}]_C$ row is little extended, as mentioned later.

In another view of this correspondence, the cube can be sheared along $\langle 001 \rangle_C$ on $\{110\}_C$, with dimensional adjustments (Fig. 1). These deformations combine to give the pure strain just described but now the plane $\{110\}_C$ to remain unrotated has been arbitrarily specified. Kennedy *et al.* (*6*) illustrated this view somewhat differently with $(110)_C$ unrotated and $[111]_C \rightarrow [111]_N$ consequently tilted through 19.48°. The resulting orientation relation (X) is then of the type $[011]_N\parallel[001]_C$, $(100)_N\parallel(110)_C$. This was observed, within 5°, by Chatterji *et al.*

(7) and Watanabe *et al.* *(8)*, in crystals at higher temperatures. In this aspect, the $\langle 1\bar{1}1 \rangle_C$, $\langle 100 \rangle_N$ row mentioned above lies in the $\{110\}_C$ plane, and the difference between relations A and X is a rotation of 9° in that plane. Relations A and X are thus connected. This is relevant to Sect. 2.3.

2.2. Second correspondence. This introduces the second correspondence, proposed by Hyde and O'Keefe *(9)* (Fig. 1). In this also $(100)_N \rightarrow (110)_C$, $[011]_N \rightarrow [001]_C$. The shear $[001](110)_C$ need not proceed in the same sense in successive layers. Since both the $(110)_C$ shear plane and the $\{110\}_N$ plane normal to the $[001]_C$ shear direction are mirror planes, equal shear in either sense will produce the same structure. This alternation of sense of shear is equivalent to alternation of two $\langle 111 \rangle$ symmetry options for the unique strain axis, the alternation occurring every half-cell. This produces the Hyde–O'Keefe correspondence. It is not evident why the strain options should alternate regularly on every $(110)_C$ plane. If they do not, then the deformation reduces to the Shoji correspondence combined with twinning displacements on $(110)_C$, which becomes $(001)_N$. This combination, where the twinning displacements provided the lattice invariant shear in a martensitic mechanism based on the Shoji correspondence, is the same which was considered to give the best agreement with experiment for highly supercooled NH$_4$Br crystals ((*5*), and Sect. 3).

Nevertheless if the shears on $(110)_C$ do alternate every half-cell, then these shears could be regarded as the consequential displacement of a new pure strain. These shear displacements are not slight: they amount to the $\{110\}_N$ spacing. Strain axes and principal distortions calculated for the present discussion are, for [NaCl] $\rightarrow$ [CsCl], in NH$_4$Br, $\eta_1 \| [001]_N = 0.845$, $\eta_2 \| [110]_N = 0.845$, $\eta_3 \| [\bar{1}10]_N = 1.194$. Here η_2 and η_3 lie in the $[110]_C \rightarrow (001)_N$ plane. This plane will be considered later. Though calculations show

that with slip-type accommodation this correspondence could satisfy martensite geometry, the combination amounts to the Shoji correspondence with two lattice-invariant shears, an unjustified combination. Thus this is another aspect of the Shoji correspondence for stoichiometry *MX*. Hyde and O'Keefe point out that for *MX*$_2$ the two correspondences produce different structures.

2.3. Third correspondence. Watanabe *et al.* *(8)* proposed a relatively complex sequence of displacements. Since these are coordinated displacements to convert a cell of [NaCl], they too should amount to a structural correspondence in the sense of the previous sections. We now enquire whether this correspondence differs from the others. Those authors note that $(110)_C$ and $(100)_N$ have the same sequences of ions and may therefore be interconverted by change of shape of the net. In further displacements, $[\bar{1}11]_C \rightarrow [010]_N$, $[110]_C \rightarrow [100]_N$. A zigzag layer consisting of $(101)_C$ and $(0\bar{1}1)_C$ "changes to the flat layer of $(001)_N$." To consider these displacements more quantitatively, we note that $(101)^\wedge(0\bar{1}1) = 120°$. This angle has to be increased to 180°. As this interplanar angle increases the row $[\bar{1}11]$ is displaced normal to itself along $[112]_C$. To produce the required structure there is a further displacement of alternate $[\bar{1}11]_C$ rows along $[\bar{1}11]_C$. However, further examination reveals that these two displacements add vectorially to constitute a displacement of the atoms in all the $[\bar{1}11]$ rows of alternate $(110)_C$ sheets along $[001]_C$, that is, these sheets are thus translated. The dimensions of the $(110)_C$ net, in which the net angle $\langle 1\bar{1}1 \rangle^\wedge \langle 11\bar{1} \rangle = 70.5°$, are adjusted to make it square. This translation of alternate $(110)_C$ planes along $(001)_C$, while $\langle 110 \rangle_C$ becomes $\| [100]_N$ and $[\bar{1}11]_C \rightarrow [010]_N$ is the Hyde–O'Keefe correspondence. The combination of the two planes $(1\bar{1}0)_C$ and $(101)_C$ *(8)* to one $(001)_N$ plane results from the alternation of symmetry options (every half-cell) which

relates the Hyde–O'Keefe to the Shoji correspondence. Thus the Watanabe–Tokonami–Morimoto displacements are equivalent to the Hyde–O'Keefe correspondence, which in turn is a special case of the Shoji correspondence.

2.4. Fourth correspondence. There remains a relationship independent of those above, introduced because of a secondary orientation, B, in NH_4Br N → C and $RbNO_3$ I(N) → II → III(C). We originally illustrated it as translation on alternate $(001)_N$ planes *(10)* but present it here as a pure strain (Fig. 2). Again $\langle 100\rangle_C$ becomes $\langle 110\rangle_N$. The cell of the primitive lattice of [CsCl] is deformed into a cell having $a = b = c = a_N/2^{1/2}$, $\alpha = \beta = 60°$, $\gamma = 90°$; that is, one face remains square: it becomes $(001)_N$. This converts the lattice and say the anion positions, but not the cation positions; but in the deformation of the anion array the cations are consequentially displaced from the cell center into the center of the cell face, or conversely. The principal distortions determined graphically in the present work are $\eta_1 = 0.64\|[130]_N$, $\eta_2 = 1.186\|[\bar{1}10]_C$ and $[010]_N$, $\eta_3 = 1.55\|[520]_N$. In the drawing in Fig. 2 there is an angle of 23° between initial and final directions of η_3.

2.5. Application to RbNO₃. An orientation relation of type B is more common in $RbNO_3$ than in NH_4Br. Like $BaCO_3$ I and II, $RbNO_3$ I is cubic [NaCl] related, II is primitive rhombohedral, calcite related. The observed orientation relation for $RbNO_3$ I → II was $[010]_I\,^\wedge\,[01\bar{1}]_{II} = 7°$. $(100)_I\,^\wedge\,(100)_{II} = 8°$ *(11)*. With different strains this fourth correspondence can also produce the rhombohedron. The cell previously selected from [NaCl] having $a = b = c$, $\alpha = \beta = 60°$, $\gamma = 90°$, has to change to the primitive rhombohedron of $RbNO_3$ II having $\alpha = 70.2°$. The principal distortions are $\eta_1 = 0.724\|[001]_I$ and $[11\bar{2}]_{II}$, $\eta_2 = 1.33\|[010]_I$ and $[1\bar{1}0]_{II}$, $\eta_3 = 1.15\|[530]_I$ and $[113]_{II}$.

The relevant type of orientation B probably arises when there is some diffusive adjustment in the interface. Similar geometry seems to describe the decomposition of cadmium carbonate to oxide *(21)*.

3. Experiments on NH₄Br

Figure 3 presents morphological evidence for a martensitic mechanism based on the Shoji correspondence in highly supercooled
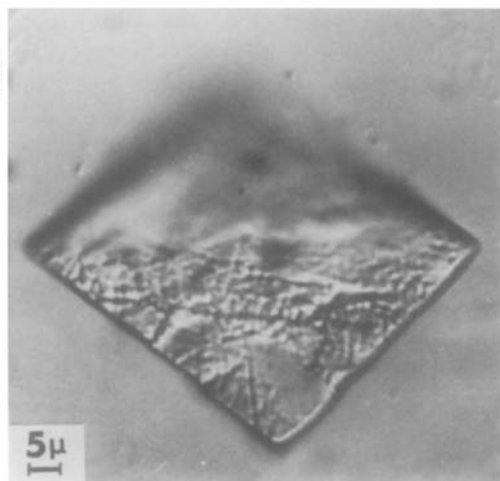
FIG. 3. A crystal of NH_4Br which has transformed suddenly to the [CsCl] form and contains two variants based on $\langle 111\rangle_N$ symmetry options. The diffuse region was originally in focus and tilted out of focus on transformation. Its original outline above the diffuse region, faintly discernible in the print, is marked by a row of specks of gold. Polarization interference contrast illumination.
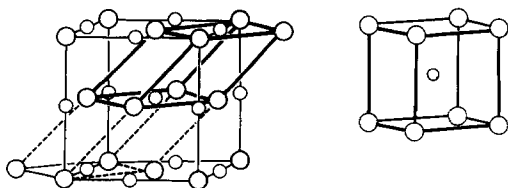

FIG. 2. An alternative structural correspondence. The subcell shown by the heavy lines is deformed to become a primitive cube, and the cation shown shaded is displaced into the center of it, giving [CsCl]. $(001)_N$ becomes $(001)_C$, $(101)_N$ becomes $(110)_C$, $\{11\bar{1}\}_N$ becomes $\{010\}_C$.

NH_4Br crystals which transformed from NaCl to CsCl type.

Such work needs crystals of well-defined morphology. These had typical NaCl morphology, the faces being {100}. They measured approximately 50 μm square × 10 μm thick, and were grown from solution in the high-termperature form above 147°C, as described by Fraser and Kennedy (4). They were lightly gold coated and observed by reflected light, interference contrast, by means of a small heater on a large microscope at a magnification of 600. They had supercooled to room temperature before transforming, then "clicked" into the new form.

The lattice deformation changes the interaxial angles of the NaCl cell from 90 to 109.46° and 70.54°. If different parts of the crystal were to choose say two symmetry options for the ⟨111⟩ contraction axis, one part of the transformed crystal would be tilted with respect to the other. Qualitatively this is seen in the photomicrograph, where the upper part, originally in focus, has risen up out of focus while the lower part has remained on the underlying coverslip. The original dimensions were visible from the trace of the gold coating. Quantitatively, if the mechanism is martensitic the lattice shape change will be modified. The resulting shape can be calculated by a shape change matrix, and values have been obtained from the computer output of the martensite calculations of Fraser and Kennedy (5). For the martensitic mechanism using $(110)[001]_C$ twinning, the predicted interedge angles are 79 and 101°. The measured angles for several crystals such as that shown are 80 and 100 ± 3°. As it has already been stated (5) that the orientation relations agree with experiment on supercooled NH_4Br this is in good agreement and supports this particular martensitic mechanism for supercooled crystals. Further details corresponding to various supercoolings will be published by Fraser and Kennedy (12, 13).

4. Types of Mechanism

Watanabe et al. (8) in studying the transformation of CsCl to the high-temperature form measured an expansion along ⟨110⟩$_C$ parallel to the microscope stage and concluded that this was not consistent with the martensite calculations (5). As the CsCl crystals were of irregular shape, and there was no assessment of the precision with which a component of shape change normal to the stage could be excluded, this shape measurement, though useful, should not be regarded as definitive. However, the conclusion that the mechanism of the C → N transformation was not martensitic under the operative conditions of higher temperature and slow propagation is in agreement with our discussion below. The expansion along ⟨110⟩$_C$ is nevertheless consistent with the Shoji correspondence, since in it each face of the unit cell expands along one of its ⟨110⟩ directions as the {100}$_C$ net changes from square to a 60° diamond net. The total change of shape would depend upon any alternation of symmetry options and on minor diffusive adjustments in the interface.

Kennedy et al. (6) illustrated a change of shape in an NH_4I platelet transforming C → N. As seen in projection this change is approximately an extension along ⟨110⟩$_N$. This again is consistent with the Shoji correspondence, even though other characteristics such as the curved interface do not suggest a martensitic mechanism. These observations suggest that the major atomic movements are similar when the interfacial accommodation is or is not martensitic: in each case the structural correspondence applies, though the modes of accommodation in the interface may differ.

A strictly martensitic mechanism is not necessarily to be expected in the transformation to the high-temperature form. The fine twins or dislocations are only required by the interface and they introduce interfacial or twin-boundary energy or both.

They are not likely to be favored if some diffusion is available. The availability of diffusion is a function of the rate of diffusion and the rate of propagation. The phenomena occurring are illustrated by $RbNO_3$. This transforms cubic → rhombohedral by the Shoji correspondence. Kennedy and Kriven (11) showed that when the transformation is performed almost instantaneously, it is martensitic. The martensite laths or plates and their internal twins are visible in the rhombohedral structure. After a short time all this substructure is eliminated by several different mechanisms, including amalgamation of the twins, followed by diffusive annealing (14). Were a similar transformation to take place over say 30 min the interface structure would be relaxed as quickly as formed and the mechanism would not appear to be martensitic. The optimum interface might then be describable by an extension of coincidence lattice site theory (15). Nevertheless since minimal diffusion will be favored, some structural deformation, usually the same one, will be followed. This is supported by the recent observation that there is the appropriate shape change in crystals of $RbNO_3$ transformed slowly by a single interface (16).

These various observations suggest that in general three stages of transformation can be distinguished: (1) martensitic, in relatively rapid transformation at temperatures low compared to the Tammann temperature and at sufficient driving force; (2) relaxed martensitic at intermediate temperatures; (3) nonmartensitic but with the structural relationship maintained. In the transformation to the high-temperature (NaCl) form in NH_4Br whiskers, Kennedy et al. (6) noted striations which in the absence of definitive evidence for type (1), may indicate type (2).

Representation of the structural relationship as a pure strain remains of value even when the mechanism is not strictly martensitic. It is common experience and was observed in NH_4Br that a closely packed direction is preserved. The particular closely packed row should be one in which the spacing is little altered, that is, it approximates to an unextended vector. The pure strain enables the cones which are the loci of unextended vectors to be calculated (1). The cones for the [NaCl] → [CsCl] transformation in NH_4Br are shown in Fig. 4. It is seen that a 17° tilt of the cone axis [111] is needed to preserve an unextended vector from parent to product, in addition to any secondary adjustments to produce an average plane of fit. In NH_4Br the $[100]_N \rightarrow [11\bar{1}]_C$ rows are close to the respective cones, and this row is preserved in the observation relation A.

5. Interface Immobilization

Relaxation suggests a reason for another problem of phase interface structure. When a moving interface is allowed to stop, either because of stresses or because the driving force is experimentally reduced, it is observed in some transformations that when the driving force (e.g., supercooling) is increased, the interface does not advance, but fresh nucleation occurs elsewhere. In metallurgy this is known as "stabilization." "Immobilization" might be a more descriptive term. It was observed in $TlNO_3$ (17), KNO_3 (but not discussed) (18), and NH_4Br (13). It has been attributed to segregation of
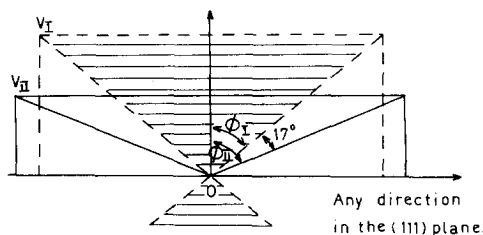

FIG. 4. Relative dimensions of the initial (inner) and final (outer) cones of unextended vectors for the Shoji–Buerger deformation. Any vector on the inner cone moves to the outer cone while retaining its length.

solutes (*19*). However, at least a martensitic interface needs a definite structure, to maintain its glissile quality (see (*19*) for a review). Relaxation, as discussed above, would modify this structure. There would then be no reason for the transformation to advance at the same site, rather than from another "active site." We suggest therefore that immobilization in these nonmetals is due also to relaxation of the interfacial structure.

6. Conclusion

One aim of the original investigations of the transformation [NaCl] – [CsCl] type was to ascertain whether this large structural deformation, with its change of 60° nets to 90° nets, and large volume change, can proceed cooperatively, and whether the orientation relations are consistent with the Shoji correspondence. Bearing in mind the analysis in Sect. 2.3, it seems that recent authors are basically in agreeement that it does proceed substantially cooperatively by this correspondence (*4, 8, 14*). It is strictly martensitic at high supercooling. This conclusion opens the way to consider large structural deformations relating other structure types (*20*),

Acknowledgments

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