in which U is the lattice energy (i.e. the magnitude of the solid state electrostatic cohesion in an alkali halide); A, B and m are constants; N is Avogadro's number; Z_1 and Z_2 are the charges ($Z_1 = Z_2 = 1$ for alkali halides) on the ions; e is the electrostatic charge and R is the internuclear distance. A higher lattice constant for an alkali halide implies a higher R and, correspondingly, a lower U value. The latter, of course, signifies weaker solid state cohesion and hence a relatively easier dielectric breakdown on application of a given field, as deduced above (Fig. 1). It should be added that the same conclusion would be reached even when U is calculated from other relationships such as the Born-Mayer equation, Kapustinski's equation or the Born-Haber cycle etc [7].

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Relationships for crystal structure transformations: MX, MX_2, MXO_3

The detailed crystallographic treatment of transformations of crystal structure depends upon the existence of a deformational relationship between the structures. This relationship implies that during the lattice deformation the displacements of atoms do not require any activated interchange of neighbours. The structures of many chemical compounds, however, contain so many atoms per unit cell that detailed examination of the displacements becomes necessary to decide whether particular structures are deformationally related ([1] and references therein). Most proposals for relationships and mechanisms for large changes of structure [2, 3] have concentrated on the sequence of displacements with little explicit attention to the lattice deformation and consequent misregistry and transformation twinning. The anion array has commonly been taken as the framework of the structure, or the relative arrangements of co-ordination polyhedra, usually octahedra, have been compared. This note points out some new deformational relationships referred either to a sub-cell which indicates the relationship or to a true cell from which the principal strains can be derived. Simple relationships between the well-known basic MX types are expected to be fundamental to the geometry for more complex stoichiometries.

In Fig. 1 either set of circles could represent anions, or the points of a sub-lattice. When small circles represent cations, Fig. 1 shows that the NiAs and CsCl structures are related by a pure strain, the site occupied by the central ion being displaced by the deformation. Quite similar geometry can be shown to relate the WC, MnP and NiAs structures.

When alternate pairs of cation sites are vacant, Fig. 1a represents rutile, TiO_2, regarded as having approximately hcp anions. The base of the prism corresponds to $(010)_r$. When the prism has been deformed to become two cubes the anion is at the centre of a tetrahedron, the anion array is simple cubic, and the result is the fluorite structure.

If the small black circles of Fig. 1 represent centres of triangular (CO_3^{2-}, NO_3^-) or flat pyramidal (BrO_3^-) anions then Fig. 1a represents the aragonite ($CaCO_3$) or KNO_3II structure (planes of anions parallel to the base of the prism) and Fig. 1b represents the cubic and distorted pseudo-cubic $CaNO_3$, $TlNO_3$ and low $RbNO_3$ structures which probably include that of KNO_3IV to which KNO_3II transforms under pressure. Except for aragonite it is convenient to

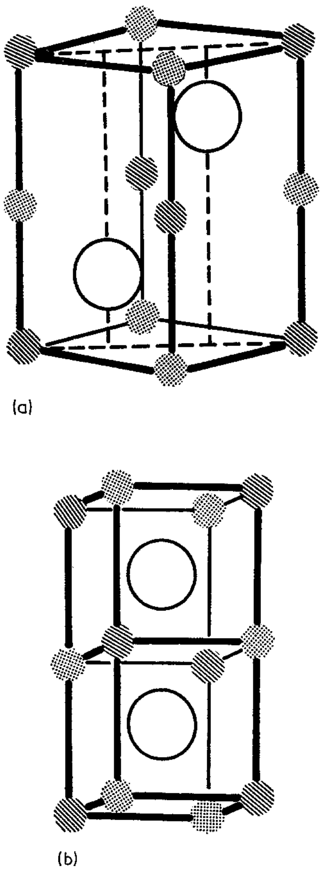

Figure 1 When the prism (a) is converted by pure strain to the two cubes (b) the unit denoted by the open circles is automatically displaced to the centre of the cube. In (a) atoms shown by large open circles are arranged as in hcp. The deformation represents NiAs → CsCl when all the small circles represent cation sites; rutile → fluorite when the dot-shaded circles mark empty sites; and aragonite → $CsNO_3$ when all small circles denote anion sites.

let the small circles represent cations. The anion tilts within the cation cage. The unusual structure of $AgNO_3$II, which did not appear to fit into this series, is then found to correspond to a deformation intermediate between KNO_3II and $TlNO_3$, the basal net containing an angle of 70°, with some distortion of the cation array. These relationships are novel. Previously it has been shown that relative extension along the cube body diagonal of Fig. 1b gives the calcite-like structures as in $RbNO_3$III → II for which an orientation relationship has been observed in this laboratory. The implied tilts of the anion without disruption of the deformational relationship has been confirmed for $RbNO_3$ [4] and are expected

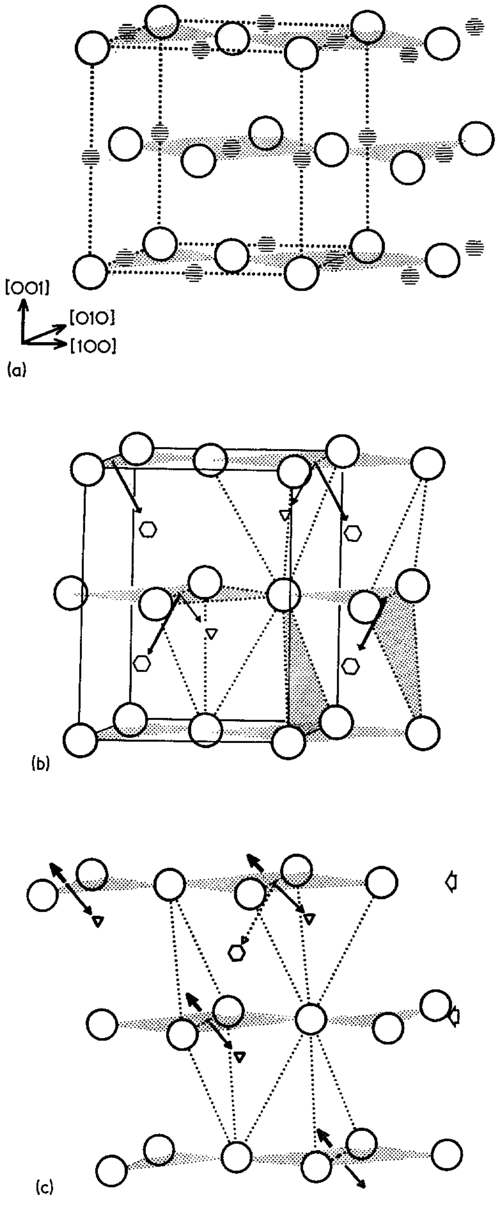

Figure 2 Relative contraction along the [010] direction of the NaCl structure (a) besides requiring minor adjustments of the [001] stacking (b, c) necessarily displaces the ions shown by shaded circles. In (b) they can fall into new octahedral sites (hexagons) giving the NiAs structure or new tetrahedral sites (triangles) giving the wurtzite structure. In (c) if they fall into half the tetrahedral sites (thin arrows) the result is the zinc blende structure. The deformation (a) → (c) can in an abbreviated way represent a rutile-fluorite relationship if the [001] axis is shortened and the shaded circles mark the middle of a line joining two anions. These become displaced into all the tetrahedral sites (indicated by full thin and thick arrows).

to occur generally. This geometry relates polymorphs of MXO_3 carbonates, nitrates, halates, some borates and some nitrites MXO_2. Details will be discussed in connection with structure-determinations [5] and martensite geometry.

Fig. 2 shows that the six-co-ordinated NaCl structure is deformationally related to the hexagonal NiAs type and to both the cubic zinc blende and hexagonal wurtzite structures both of which have tetrahedral co-ordination of cations, but that these two are not so related to one another. Accordingly the interconversion wurtzite-zinc blende is in practice slow. By the same argument, a deformational relationship is lacking for the hexagonal olivine to cubic spinel transformation because tetrahedral sites are occupied in both. This is important for the response of the earth's mantle to pressure increase or shock.

In these relationships the square (001) net of NaCl-type becomes hexagonal. Proof that square-hexagonal deformations can actually occur comes from experiments on the NaCl–CsCl transformation, in which $\{11\bar{1}\}_{\mathrm{NaCl}}$ becomes $\{100\}_{\mathrm{CsCl}}$ [6]. A deformational relationship such as that in Fig. 2 is required to explain the rapidity [7] of the wurtzite-NaCl transformation in NH_4F under pressure; and the observation that in CdS the shock-induced transformation from the wurtzite to the zinc-blende structure actually proceeds through the NaCl structure [8] is evidence that these particular relationships are the basis of mechanisms.

As an example of quantitative application, in the NaCl to wurtzite change in MnS the principal distortions, parallel to the NaCl cube axes, are $\eta_1 = 0.88$, $\eta_2 = 0.76$, $\eta_3 = 1.23$. These are reasonable for compounds. Similarly, for NiAs to NaCl-type in MnTe, $\eta_1 = 1.32$, $\eta_2 = 0.76$, $\eta_3 = 1.23$. Such deformations imply that there is no plane of fit between the lattices. The misregistry could be accommodated by a martensitic mechanism.

The rutile and fluorite types, which have been the subject of much experimental work, can be related in two new ways. From the rutile structure (Fig. 3), a fc tetragonal array of cations, having axes $a\sqrt{2}$ $a\sqrt{2}$, and c, can be selected. With adjustment of dimensions, this can be represented by the fcc array of open circles in Fig. 2a. The filled circles then correspond to the point midway between two anions, which lie in the shaded planes (001). In the deformation (Fig. 2c) these pairs lie either in the edges or the faces of nascent tetrahedra, and are displaced to fill both apex-up and apex-down tetrahedra. This may be verified with ball-and-spoke models. The resulting fcc array of cations with anions in all the tetrahedral sites is the conventional crystallographic description of fluorite. Here $(001)_r \rightarrow (111)_f$.

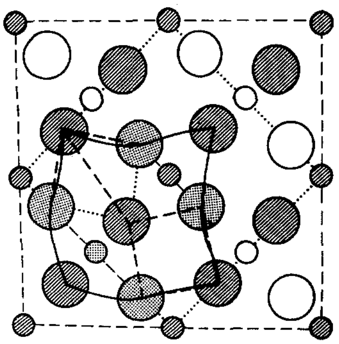

Figure 3 Four cells of the rutile structure projected down the *c*-axis. A pseudo fc tetragonal array of anions is outlined by curved lines and a corresponding primitive cell by broken lines. Large circles denote anions, small circles cations, and line shading denotes atoms at height 0 and 1.

Alternatively, a pseudo-fc tetragonal array of anions can be selected (Fig. 3). Minor displacements are needed to make the curved lines straight. The primitive cell of this array can be converted to a primitive cubic sub-cell of fluorite by a deformation of which one component is a contraction along [111], just as the primitive rhombohedron of NaCl becomes the CsCl cell [6]. In MX_2 the cations require consequential displacements (shuffles). Half are found to lie in the faces and half in the edges of the primitive sub-cells. Those in the faces are displaced into the interior, all in the same direction, filling a "first set" of sub-cells, and those in the edges are displaced from the edge to the interior of the particular sub-cell which shares an edge with the first set. The result is the fluorite structure, in which filled CsCl-type sub-cells share edges.

It may be concluded that (1) many structures (not only all lattices) are deformationally related (2) some structures are not, (3) several structural correspondences may be feasible. Experimentally the operative correspondences might be identified not only by the orientation relations but also by the transformation twinning derived from the lattice deformation. For theory criteria such as minimum principal strains are required to decide between alternative correspondences. The problem of finding whether and how atoms in the more complex structures can shift without interchange to their sites in the product structure, although rather complex, is fundamentally mathematical.

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On the extension of the crystal lattice along the chain direction in polyethylene single crystals from X-ray line widths

The breadth of the 002 X-ray reflection of polyethylene should provide a measure of the extension of the crystal lattice along the chain direction. Once in possession of this information, the total layer thickness of a chain-folded single crystal lamella provided by low-angle scattering data should be subdivisible into a crystalline core and fold surface region, information much required in polymer crystal studies. Earlier work in this field relating to drawn fibres [1] and single crystals [2] established a correlation between the low-angle X-ray spacing and the crystal size deduced from the 002 reflection where the latter was somewhat smaller than the full periodicity. Some years ago we embarked on a programme of work along these lines in aid of wide ranging studies on the nature of the fold surface. One byproduct, the detection of a small negative thermal expansion coefficient along the chain direction has already been reported [3]. The main body of the work, while unpublished, has formed the basis of further investigations commenced in these laboratories by Windle [4]. As because of this the reporting of the original work is no longer opportune at this date, there is nevertheless, one remaining aspect which may have noteworthy implications and is not included elsewhere. The purpose of the present note is to place this on record.

The X-ray work was performed on mats of single crystals obtained at 70° C from xylene with a long spacing of 109 Å. The mats were exceptionally well oriented, on the standards normally achievable on such samples, with the chains perpendicular to the mat surface (Fig. 1). This degree of orientation was achieved through forming very thin layers at a time by sedimentation from suspension and by building up the required mat thickness by plying new layers onto those already prepared. These mats proved to be prerequisites not only for the present work but also for all further studies on the 002 line width

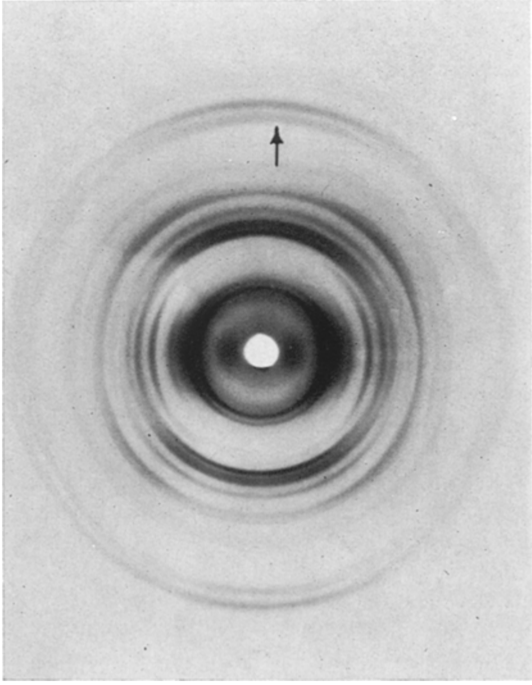

Figure 1 X-ray diffraction pattern of a typical sedimented mat of polyethylene single crystals such as used for the present study. The beam is parallel to the mat surface which itself is horizontal. The 002 reflection is marked by an arrow. (Photograph by A. H. Windle.)