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SMALL DEVIATIONS FROM THE APPARENT SYMMETRY OF CRYSTALS

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Years ago a crystal-structure determination required a great deal of heavy work of collecting intensities and performing calculations. It also required skillful application of the space-group theory supported by intuition and personal experience.

With the advance of automatic diffractometers and powerful computing facilities in the majority of cases the determination of a crystal structure becomes now a routine task which conforms nicely to the wellestablished concepts of classical group theory. There are, however, crystal structures (sometimes called "not well behaved") which offer considerable difficulties. Among them are structures with unusual atomic arrangement or very large molecules requiring more ingenious methods of crystal structure analysis. There are also other kinds of structures which are "not well behaved" due to pseudosymmetry or small deviations from the apparent symmetry.

Some of these structures are disordered and can not be regarded as fully periodic. They are often observed in the vicinity of phase transformations and, therefore, seem to be important for the theory of solidstate phase transitions.

In this survey the following problems connected with small deviations from the apparent symmetry will be presented:

1. True symmetry of the paraelectric, and more generally high-temperature phases.
2. Asymmetry induced by external or internal fields.
3. Isosymmetric phase transitions.
4. Conclusion.

1. Symmetry of paraelectric phases.

We consider only those phase transitions in crystals which do not destroy completely the crystal structure, but starting from a single crystal do result in a single or polydomain crystal. That means that at least a small volume of the monocrystal transforms into a monodomain region with closely related lattice. It is usually possible to find a basic structure called prototype or sometimes aristotype with the highest symmetry. This prototype structure may actually exist at sufficiently high temperatures or in some other cases the crystal may melt or deteriorate before reaching the supposed high--temperature phase transition.

We will concentrate on phase transitions from a ferro- to a paraelectric phase (which is not necessarily the prototype). It was generally believed that a polar (that is ferroelectric) phase is more interesting due to its remarkable physical properties. The non-polar, paraelectric phase was supposed to be an "ordinary" crystal structure which at the Curie point underwent for some unknown reason a spontaneous polarization, thus becoming ferroelectric. The X-ray crystal structure analysis proves that this is not true. In fact, a precise crystal-structure determination of the paraelectric phase is more complicated and requires a special approach. As an example let us consider the crystal structure of the well-known ferroelectric triglycine sulfate (TGS) and the isomorphous triglycine fluoberylate (TGFB). The crystal structure of the polar ferroelectric phase is shown in Fig.1a. The space group is P2. There are two important features in this structure: a non-polar glycine I with a nitrogen atom pointing in the b--axis direction, and an asymmetric hydrogen bond connecting glycines II and III. In the early crystal-structure determination of the paraelectric phase the glycine I was assumed to be planar in keeping with the space group P2/m. This was, however, proved not to be true. In fact the paraelectric phase is disordered (Fig.1b) with the nonplanar molecule of glycine I oriented at random.

The crystal-structure determination of the paraelectric phase is always connected with difficulties arising from symmetry and ordering. In general, one of the following assumptions may be chosen:

i) The crystal structure is ordered and the symmetry of the lattice cell conforms to the macroscopic symmetry.

ii) Some atoms or molecules are disordered and the remaining

part of the lattice cell is considered to be ordered and conforming to the macroscopic symmetry.

iii) The whole lattice cell is disordered and the statistical structure consists of two overlapping lattice cells of opposite polarity.

iv) The crystal structure is being refined in the noncentrosymmetry space group. After possible introduction of the symmetry centre the final result of the refinement becomes equivalent to (ii) and serious difficulties in the refinement procedure can be easily overcome.

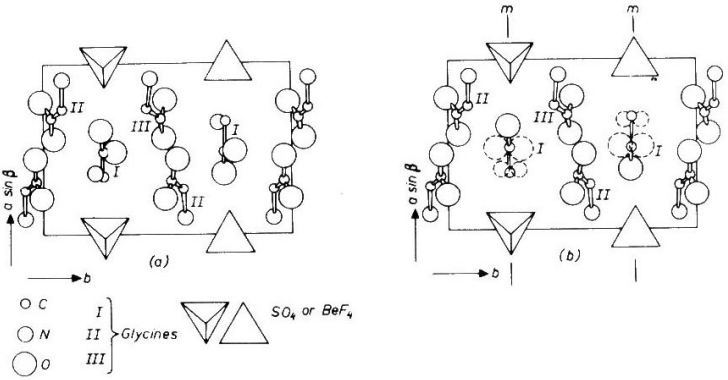


Fig. 1. The crystal structure of TGS (or TGFB)
a) Ferroelectric phase b) Paraelectric phase

Many paraelectric phases have been solved and reasonably well refined under assumption (i). In the case of the TGS family this approach is not feasible due to considerable disorder of glycine I. The crystal structure of paraelectric TGS has been solved, assuming (ii), in space group $P2_1/m$ with disordered glycine I contrasting with the ordered and centrosymmetric pair of glycines II and III. This, however, imposes the assumption that the asymmetry in one part

of the lattice cell does not influence the symmetry of the remaining part of the cell, thus neglecting any interactions between glycine I and the remaining two glycines.

The approach (iii) has been applied by Sato [3] in refining the paraelectric phase of diglycine nitrate. The attempts to refine the paraelectric TGFB under assumption (iii) failed due to very high correlations between positional and thermal parameters of almost overlapping atoms. These atoms appeared to be indistinguishable to the full-matrix least-squares program which caused a formal exchange of some pairs of oxygens between two glycine molecules.

It has, therefore, been decided to refine the crystal structure of paraelectric TGFB in space group $P2_1$ in order to reveal the correlation between the orientation of glycine I and the conformation of glycines II and III. The validity of such an approach can be justified by assuming a short - or perhaps medium - range ordering in the paraelectric phase even at 27K above the T_c. After completing the refinement without serious difficulties the R-index, expressing the average discrepancy between the calculated and measured structure amplitudes, dropped to 0.0583. Let us now introduce an additional parameter G to the structure-factor formula:

$$F = A + iBG$$

where A and B are the real and imaginary components of F.

By decreasing G from 1 to 0, we introduce a centre of symmetry resulting in a structure model consisting of two overlapping lattice cells with opposite polarity. It has been shown that the best agreement between the experimental and calculated structure amplitudes corresponds to G equal to 0.75 with the origin of the lattice cell defined by the position of the beryllium atom with $y_B = 0.2525$.

The crystal structure of paraelectric TGFB should, therefore, be regarded as consisting of noncentrosymmetric lattice cells with short-range order resulting in a structure model with the apparent symmetry intermediate between $P2_1$ and $P2_1/m$.

Small deviations from the apparent symmetry have also been observed in another ferroelectric crystal, $RbHSeO_4$. In the ferroelectric phase it is triclinic, I1, and in the paraelectric phase it is supposed to be monoclinic, I2. The temperature dependence of the lattice para-

meters a, b and c is shown in Fig. 2a. There are only small anomalies at the Curie point. The angles α, β and γ, shown in Fig. 2b, undergo much more pronounced changes. Note that in the region of about twelve degrees above T_c small (but definitely outside the experimental error) deviations of the α and β angles from 90° are observed, contradicting the monoclinic symmetry. These deviations which are observable only with the very high precision of the experiment have not been fully explained so far. They may result from some ferroelectric interactions still existing above the Curie point or from the residual strains in the crystal.

Discussing the structure and symmetry of the paraelectric phases one should also mention an ingenious idea of Comes, Guinier and Lambert [5]

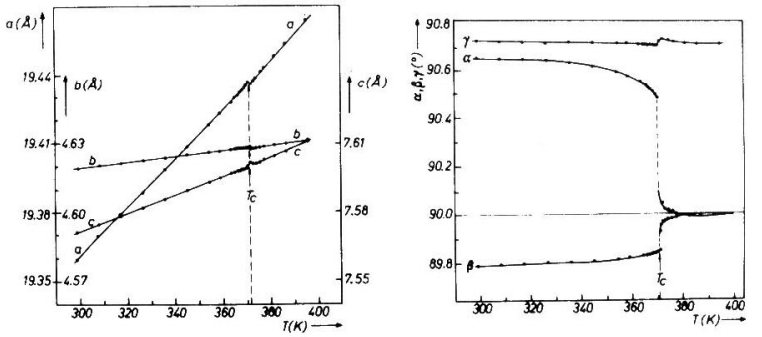


Fig. 2. Lattice parameters of $RbHSeO_4$ as a function of temperature [1]

a) a, b and c b) α, β and γ

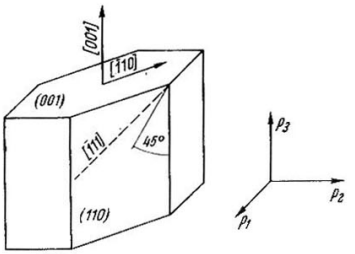
who explain the crystal structure of the prototypic high-temperature phase of barium titanate and other perovskites by assuming that the titanium atom can occupy at random one of the 8 equivalent sites displaced from the average position along the <111> directions inside the titanium-oxygen octahedron. The displacements are, however, correlated in successive unit cells along <100> chains of 10 to 20 octahedra. The diffraction pattern of this structure consists of diffuse rings accompanying the usual sharp reflections.

All these phenomena seem to be closely related to the phenomenon of the central peak due to fluctuation and formation of clusters both static and dynamic |6|. Bruce, Müller and Berlinger |7| express this as follows: "With the onset of criticality, the growth in correlations drives a crossover from a weakly anharmonic ("displacive") regime to a strongly anharmonic ("order-disorder") regime, whose short-range order is manifested in clusters, in which the average value of the ordering variable ("cluster coordinate") is nonzero for a time long in comparison with typical inverse phonon frequencies. The central peak may thus be regarded as the short-range-order-induced dynamic precursor of the Bragg peak to appear below T_c,....". There is certainly some need for development of the theory of symmetry which might account for and describes properly what really happens in crystals in the vicinity of the phase transition.

2. Asymmetry induced by an external or internal field

We shall consider a few examples of symmetry reduction induced by a field. The point group of the crystal upon which a field is acting must be a subgroup of both the point group of the crystal without field and of the point group of the field. Within these general frames interesting processes may be observed in the crystal.

A symmetry reduction induced by light has been observed by Damm and Łukaszewicz |8|. A potassium chloride (KCl) crystal had been coloured by X-irradiation and then exposed to visible light, both polarized and unpolarized, penetrating along different crystallographic directions. The crystal with carefully cut and polished planes is shown in Fig. 3 and the results are summarized in Table 1.



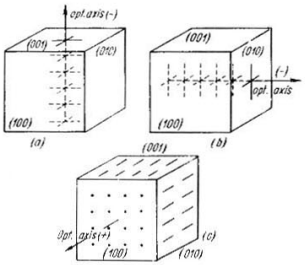


Fig. 3. View of the specimen cut from a KCl crystal, with crystallographic directions |8|

Fig. 4. Distribution of linear defects in the optically uniaxial negative (a and b) and positive (c) KCl crystals |8|

It appears that by the action of light almost every kind of optical anisotropy can be induced in the previously cubic KCl crystal. The physical nature of this effect is suprisingly simple. Irradiation by γ-rays generates in a KCl crystal different kinds of defects. Among them are linear defects comprising two adjacent anion positions and distributed at random along the three equivalent [100] crystallographic directions. The incident visible light destroys only those defects which are parallel to the electric vector of the light beam. The remaining defects induce an optical anisotropy (Fig.4).

The next example is taken from the outstanding paper by Kobayashi, Uesu and Enmoto |9| on the influence of an electric field on the ferroelectric phase transition of KH_2PO_4 (KDP). KDP in the paraelectric phase above 122 K is tetragonal, space group I42d. The field was applied parallel to the tegragonal c-axis, resulting in the orthorhombic deformation of the lattice cell. This can be explained by comparing the point group 42m of KDP with the point group ∞ m of the field. The highest common subgroup is the orthorhombic point group 2mm. In Fig. 5 the lattice parameters a and b of the KDP crystal are shown as a function of the temperature for different electric fields. It follows that even a rather small field results in the orthorhombic destortion of the lattice cell.

Table 1

Optical properties of coloured KCl crystals (i) in dependence on illumination direction and localization of electric vector of light

Direction of electric vector	Direction of optical axis	Optical sign	Remarks
direction of incident light [100]			
ordinary light	[100]	(+)	
[010]	[010]	(-)	
[011]	[100]	(+)	
[012]	biaxial crystal, main directions of indicatrix [100] [010] [001]		
direction of incident light [110]			
ordinary light	[001]	(-)	weak effect
[001]	[001]	(-)	
[110]	[001]	(+)	
[111]	.....	.....	optically isotropic
direction of incident light [111]			
ordinary light	.....	.....	optically isotropic
[110]	[001]	(+)	
[121]	[010]	(-)	weak effect

With increasing field the transition temperature increases but the jump of the lattice parameters at the transition point decreases and at some critical value of the field the transition becomes continuous.

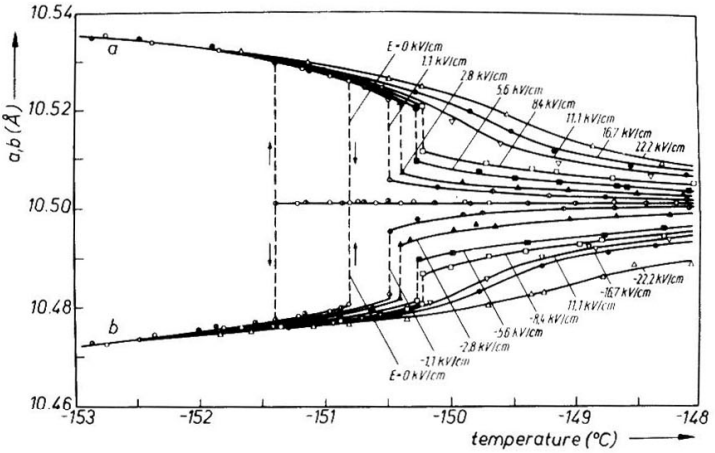


Fig. 5. Temperature dependence of lattice parameters a and b of KDP under various biasing fields (after Kobayashi, Uesu and Enmoto [9])

Another example of artifical reduction of symmetry may be taken from the paper by Keve, Bye, Whippers and Annis [10] on doping of TGS crystals by alanine. The polarity of the ferroelectric TGS crystal is closely related to the conformation and orientation of the molecule of glycine I. The free glycine molecule has a symmetry plane. In the TGS crystal the glycine molecule is flexible enough to assume both asymmetric conformations and to switch from one conformation to another, resulting in polarity reversal of TGS (Fig. 1). The alanine molecule, however, is similar in shape but due to substitution of one hydrogen by the methyl group becomes asymmetric (Fig. 6).

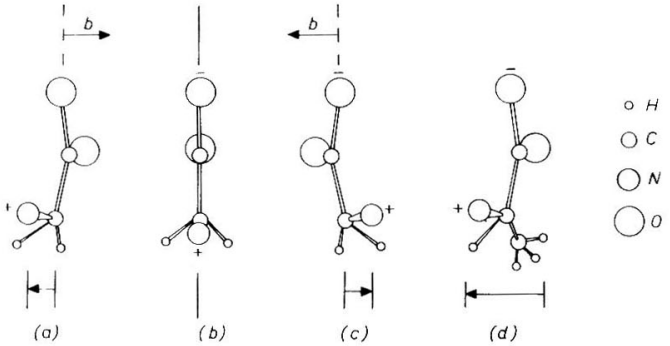


Fig. 6. Comparison of the glycine I molecule in: a) one polar state, b) possible prototypic or non polar state, c) state of opposite polarity, and d) L-alanine molecule of fixed polarity (after Keve, Bye, Whipps and Annis |10|)

Even a very small amount of alanine doped into the TGS crystal induces chirality of the whole system due to the loss of the symmetry center. Alanine molecules substitute glycine in the lattice of TGS and due to their inherent asymmetry predetermine the direction of polarity of the ferroelectric phase. In fact, the situation is similar to the application of the electric field. A doping with asymmetric molecules can be regarded as influence of an internal field with symmetry $\infty\infty$. The point group of the paraelectric TGS is 2/m and the common subgroup is 2, the same as that of ferroelectric TGS. The paraelectric phase of doped TGS is at least potentially polar and the phase transition in such a crystal should be regarded as isosymmetric, i.e., proceeding without change of symmetry.

3. Isosymmetric phase transitions

The isosymmetric phase transitions are often considered as something unusual. Pawley and Dietrich |11| published in 1975 a paper on the phase transformation in octafluoronaphtalene with both phases belonging to space group P2/c. The authors explain this by assuming two equilibrium positions of the close packing of the molecules (Fig. 7). In their opinion this transformation, although not unique,

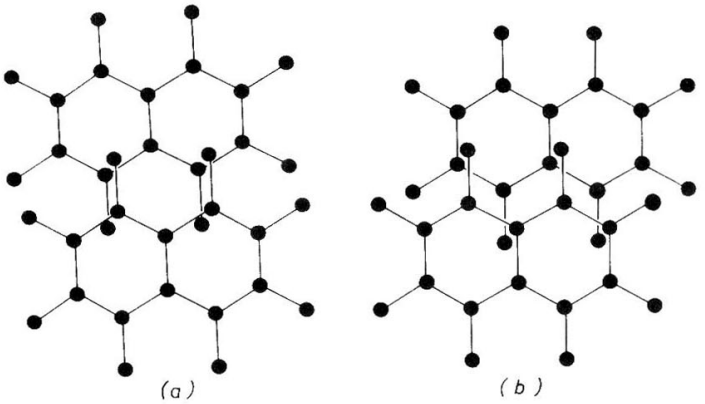


Fig. 7. Superposition of molecules of octafluoronaphtalene in a) upper phase and b) lower phase (after Pawley and Dietrich [11])

is probably the first of its kind to be discovered in molecular systems. They conclude that this establishes the existence of a rather remarkable solidstate phase transition in which there is no change in space-group symmetry.

Another example of a phase transition apparently without any change of symmetry can be taken from the investigation by Malinowski [12] on the crystal structures and phase transitions of the ferroelectric lead germanates $Pb_5Ge_3O_{11}$ and $Pb_5Ge_2SiO_{11}$. The crystal structures of $Pb_5Ge_3O_{11}$ in both ferro- and paraelectric phases were already known, the space groups being P3 and $P\bar{6}$, respectively (Fig. 8).
Since $P\bar{6}$ is the same as P3/m the paraelectric structure can readily be obtained by introducing a mirror plane perpendicular to the c-axis. The paraelectric phase is obviously not prototypic as one can easily foresee a further symmetry enhancement to $P\bar{6}2m$ by introducing additional mirror planes parallel to the c-axis. In the paper by Salnikow et al. [13] it has been reported that the second-harmonic generation study of lead germanate indicates a second phase transition at about 593K. We were able to confirm this transition by very precise lattice-parameter determinations as well as by dielectric permittivity measurements. A careful crystal-structure determination of this

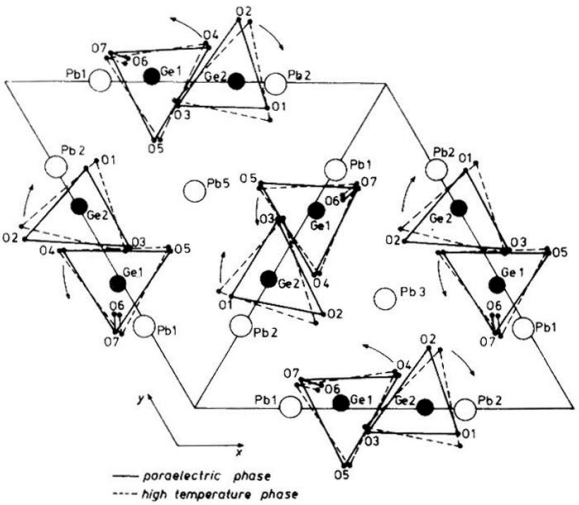


Fig. 8. The crystal structure of $Pb_5Ge_3O_{11}$ a) paraelectric phase (full lines) b) high-temperature phase (dashed lines |8|)

high-temperature phase has proved, however, that there is no symmetry enhancement and the space group above the second phase transition remains the same, $P\bar{6}$.

4. Conclusion

A space group G describing the symmetry of a crystal structure usually refers to the ideal crystal which is virtually infinite, perfectly periodic and completely ordered. In the case of a real crystal with lattice defects of any kind a special approach would be desirable. Lattice defects play also an important rôle in phase transitions and the further development of the theory of phase transformations in solids should certainly take them into account. In my opinion the symmetry of real imperfect crystals in the nearest future will become one of the main frontier topics in the application of group theory in crystallography.

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