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THE 230 OR 1651 SPACE GROUPS?

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An analysis of ways by which the crystal structure transforms moments of force, has been made. The results indicate that crystals which can be librationally disturbed can exhibit, besides their crystallographic symmetry (230 space groups of colorless symmetry), another kind of symmetry called in this paper — the dynamic symmetry. Each crystallographic symmetry operator of a given real crystal structure has a corresponding dynamic polar, gray or black-white symmetry operator, which determines how the moments of force can be transformed by a considered structure during a librational disturbance. The dynamic symmetry should be described in terms of Shubnikov space groups and can be determined by diffraction methods.

1. Introduction

It is a well known fact that the different anisotropic properties of crystals give information about the crystal symmetry of different levels. It is customary to assume that a complete description of crystal symmetry can be made by means of colorless symmetry operations of the 230 space groups.

However, the purpose of this paper is to show that there are anisotropic quantities which characterize crystal structures, and which indicate that, in general, there are symmetry operations of crystal structures which should be classified beyond the colorless symmetry operations. These quantities are represented by axial vectors such as spin, moment of force etc. The symmetry relations which can appear between such quantities are described by the operations of the polar (one-color), gray, and black-white space groups. These kinds of symmetry operations were introduced by Shubnikov 26 years ago (Shubnikov 1951; Shubnikov et al. 1964), and until now have been used chiefly to describe magnetic spin alignments (Zamorzaev 1962). They are often called magnetic symmetry operations.

The following considerations illustrated by the examples given below, which are strongly connected with the dynamics of crystals, indicate that for crystal structures in

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which librational disturbances (represented by axial vectors) are possible, the application of Shubnikov symmetry operations is an imperative necessity not only for a systematic description of crystal symmetry, but also for an interpretation of physico-chemical properties of crystals and phase transitions.

2. *Dynamic symmetry of crystals*

Crystal structures which can be librationally deformed can exhibit another kind of symmetry, besides the crystallographic (colorless) one. Such structures can be treated as composed of the smallest congruent or enantiomorphous rigid elements, each of which has the same susceptibility to the action of moments of force or other quantities represented by axial vectors. These structural elements will be called the dynamic elements in this paper. The manner of bonding of dynamic elements, into a given real crystal structure, limits the number of its possible librational mode configurations and determines their possible symmetry.

Let us consider, for the sake of simplicity, the changes in crystallographic symmetry caused by phonons having librational modes of an infinite wavelength. Any particular symmetry operator of the crystallographic space group of a given crystal can at best become, in a certain configuration of a set of librational modes of an infinite wavelength, a crystallographic operator of either (a) the same order, or (b) order twice as large, or (c) order which is two times smaller, or (d) the same order for the spatial average librational mode configuration, as the one in the undisturbed structure. This depends on the kind of bonding between the dynamic elements of the considered crystal structure which determines the number and kinds of possible ways of transforming axial vectors of moments of force by the considered symmetry operator. If one of the above-listed possibilities occurs, then:

In case (a) the dynamic elements are bonded in such a way that axial vectors of moments of force can at best be transformed by the considered structure in the manner determined by the polar symmetry operator of the same order as the order of the corresponding crystallographic operator in the undisturbed structure.

In case (b) the structure made up of the centers of libration of dynamic elements of the considered structure has a symmetry operator of order twice as large as the corresponding symmetry operator in the considered structure. That means that every second equivalent dynamic element of the undisturbed structure is differently oriented in an antisymmetric manner and the moments of force can at best be transformed by the structure in a manner determined by the black-white symmetry operator of order twice as large as the corresponding crystallographic one in the undisturbed structure.

In case (c) the transformation of moments of force is at best determined by the black-white symmetry operator of the same order as the corresponding crystallographic one in the undisturbed structure.

In case (d) the transformation of the moments of force can at best be determined by the gray symmetry operator of the same order as the corresponding crystallographic one in the undisturbed structure.

It follows from the above that in the real crystal structure, in which dynamic elements are bonded, each crystallographic symmetry operator has a corresponding symmetry operator (polar, gray or black-white) which determines how the moments of force can be transformed. The characteristics of axial vectors of moments of force are congruent with Shubnikov space groups, and therefore, they can be used to describe the symmetry of their transformation by the crystal structure. Since this kind of symmetry is strongly connected with crystal dynamics, the present writer proposes to call it the dynamic symmetry.

It should be emphasized that crystals which belong to the same crystallographic space group can have a different dynamic symmetry, and crystals which belong to different crystallographic space groups can have the same dynamic symmetry.

The examples given below show how the polar and black-white operators of dynamic symmetry can be deduced by analysing the manners of transforming the axial vectors of moments of force by a considered structural configuration, or detected by making a comparison of symmetries of these configurations with symmetries of their librational modes. In these examples the considered configurations on the left of the drawings can be treated as librational modes of those on the right and vice versa.

The pair of one-period ribbon configurations *A* and *B* shown in Fig. 1 illustrates case (a). These configurations have the same crystallographic symmetries (*A′* and *B′*) described by the colorless translations of the same length in both configurations. The

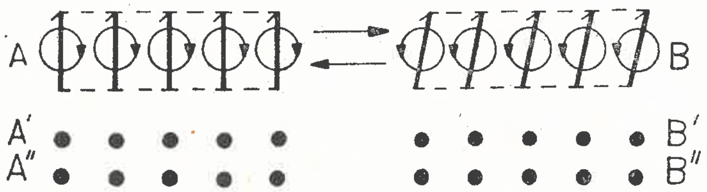

Fig. 1. One-period configurations *A* and *B* which can be mutually transformed by the actions of moments of force without a change of crystallographic symmetries. *A′* and *B′* — represent their Bravais crystallographic lattices. *A″* and *B″* — represent their dynamic Bravais polar lattices

dynamic structural elements are linked in both the configurations in such a way that the transformations of moments of force (represented in the drawing by circles) by the considered configurations indicate that their dynamic symmetries (*A″* and *B″*) are determined by the polar translations of the same length. As a result of the action of moments of force on the dynamic structural elements of these configurations, the librational transitions of both configurations, *A* into *B* and *B* into *A*, can occur. Such transitions do not change the crystallographic symmetries of the considered configurations and it means that their dynamic symmetry consists only of a polar translation.

Another pair of ribbon configurations *A* and *B* which illustrate cases (b) and (c) is shown in Fig. 2. These configurations are made up of the same structural elements as those in Fig. 1. However, the type of linkage in these configurations is different from that in Fig. 1. So the moments of force are transformed by these configurations in another way and the result of their action is a change in crystallographic symmetry. The crystallographic symmetry of the *B* configuration is described by the colorless translation twice as long as that of the configuration A (see A' and B'). The manner of transforming moments of force by the considered structures and differences in their crystallographic symmetries indicate that they have a common dynamic symmetry ($A'' \equiv B''$) described by the black-

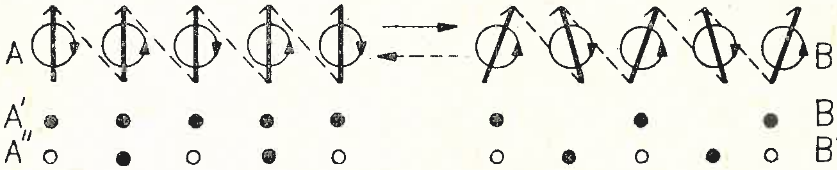

Fig. 2. One-period configurations A and B which can be mutually transformed by the actions of moments of force with a change of crystallographic symmetry. A' and B' — represent their Bravais crystallographic lattices. A'' and B'' — represent their dynamic Bravais black-white lattices

white translation. It should be noted that while the crystallographic symmetries of the configurations shown in the left-hand side of Fig. 1 and Fig. 2 are the same, their dynamic symmetries are different.

Further illustrations of cases (a), (b) and (c) are plane two-period configurations A and B in Fig. 3, which can be mutually transformed by the action of moments of force. Their

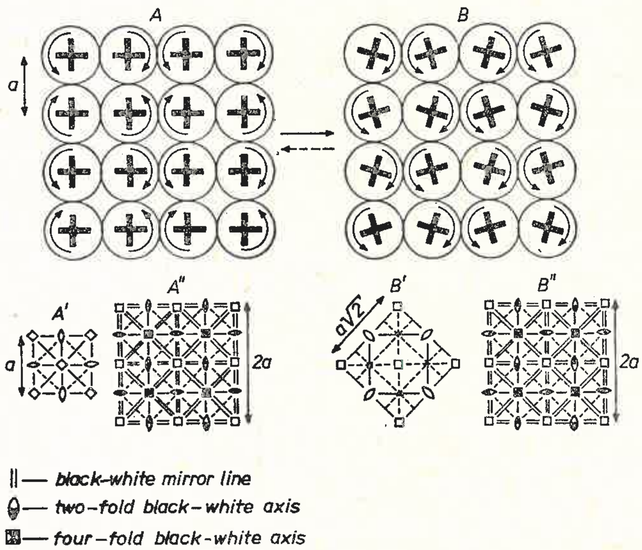

Fig. 3. Two-period plane configurations A and B which can be mutually transformed by the action of moments of force with a change of crystallographic symmetry. A' and B' represent their crystallographic symmetries, A'' and B'' represent their dynamic symmetries

crystallographic symmetries are different (A' and B'). On the other hand, the axial vectors of moments of force can only be transformed by these configurations in the same manner and according to their common dynamic symmetry (A'' and B''), which consists of polar and black-white operators. The polar operators of this dynamic symmetry correspond to those crystallographic operators whose orders remain unchanged; and the black-white ones, to those crystallographic ones whose orders are changed as a result of librational transition of both configurations, A into B and B into A.

The dynamic symmetry of a given tri-periodic crystal configuration can be likewise determined, that is, either by an analysis of the ways of transformation of moments of force by a considered configuration according to its particular possible dynamic symmetry operators, or by a comparison of crystallographic symmetry of this configuration with crystallographic symmetries of configurations of its possible librational modes. The latter method can be carried out experimentally for the real crystal structures, where the sources of librational disturbances are both thermal vibrations and stationary defects such as point defects, plane defects, or dislocations.

3. Determination of dynamic symmetry

In order to determine the dynamic symmetry operators it is necessary, at the final stage of the diffraction crystal structure analysis, to introduce into the expression for the structure factor a proper function which takes into account the existence of correlations between the phases of librational movements of different dynamic structural elements or the phases of librational disorientations of those elements caused by stationary structural defects.

If the dynamic symmetry consists of black-white symmetry operators, as in the cases (b) and (c), it is often possible to detect them without any computation, only by visual inspection of their diffraction pattern. Since librational disturbances of small amplitudes do not, in practice, change the positions of the centres of gravity of the dynamic elements in the lattice, the changes in crystallographic symmetry which are the result of librational disturbances affect characteristic extinctions of sharp reflections of a diffraction pattern of a considered crystal structure. It seems that the best method of observing these effects is through the X-ray topography of areas of the crystal disturbed librationally by stationary defects.

The effects of change of crystallographic symmetry as the result of dynamic symmetry were observed in the case of ethylidene-bis-N,N′-diacetamide crystals (Kołakowski 1977), whose structure was determined by the routine method (Kołakowski 1969).

4. Conclusions

A dynamic symmetry (represented by 1651 Shubnikov groups) which makes it possible to determine relations between moments of force or other quantities represented by axial vectors during their transformation by a given crystal structure depends to a large degree on the chemical bonding between structural elements. Thus determination of dynamic symmetry provides information about the nature of bonding, and can be used to interpret the phenomena which are symmetry sensitive — such as the spectra of elastic vibrations, creation transformation, and annihilation of quasiparticles in the crystal structure, phase transitions, crystal growth etc.

Finally it should be added that Opechowski and Dreyfus (1971) have shown that magnetic spin configuration can be equally described either by Shubnikov groups or by representations of 230 space groups. This can be probably applied to crystal dynamics as well. On the other hand Janner and Jansen (1976) do not deal with the color symmetry aspect in their description of the modulated symmetry using *n*-dimensional space groups ($n \geqslant 4$).

Nevertheless, the above presented concept of dynamic symmetry is more relevant, showing clearly that black-white symmetry operators really "exist" in crystals as do operators of classical crystallography. These two-color symmetry operators behave like colorless operators of the same order when crystal structure transforms quantities of colorless symmetry.

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