Short Communications

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Acta Cryst. (1973). A**29**, 305

A note on the derivation of Heesch groups.

By KRISHNA K. DAYANIDHI*, *Department of Applied Mathematics, Andhra University, Waltair, A.P., India*

(*Received* 19 *April* 1972; *accepted* 1 *August* 1972)

Starting with an aspect group which is the observed nuclear magnetic resonance symmetry, an extended aspect-group technique is employed to construct the set of all Heesch groups corresponding to the given aspect group.

Originally Heesch (1930) introduced a non-spatial double-valued quantity, thus generalizing the concept of symmetry which is found to be important in the study of magnetic crystals (Donnay, Corliss, Donnay, Elliott & Hastings, 1958). Addition of the two-valued attribute which is identified as the time-reversal operation (Shubnikov, 1951) produced a generalization of 32 ordinary crystallographic point groups to 122 magnetic point groups (Donnay & Donnay, 1959; Donnay, 1967) or Heesch groups (Riedel & Spence, 1960), and 230 crystallographic space groups to 1651 magnetic space groups (Opechowski & Guccione, 1965) or Shubnikov groups (Shubnikov & Belov, 1964).

In a recent paper Spence & van Dalen (1968) have shown that the question as to whether the magnetic space group of a magnetically ordered crystal contains an anti-translation or anti-inversion can be answered by nuclear magnetic resonance. According to these authors, the criterion for answering the question depends on whether number of elements in two groups which they call the Heesch group and the aspect group is the same or differs by a factor of two. The Heesch group describes the symmetry of the array generated by translating the set of equivalent axial vectors scattered through the magnetic unit cell to a single point. In this sense a Heesch group is 'point-like', but it is important to note that such groups contain an anti-identity if the magnetic space group from which they were derived contains an anti-translation. The aspect group describes the symmetry of the same array of vectors as the Heesch group but treats the vectors as if they were polar rather than axial vectors. In other words, the aspect group is the symmetry that would be attributed to the same figure if the axial vectors were replaced with polar vectors.

The results of Spence & van Dalen are formulated in terms of the elements of Heesch groups which lead to the construction of an aspect group corresponding to a set of Heesch groups. The purpose of the present note is to point out that one can write down the set of Heesch groups corresponding to a given aspect group using the idea of extended aspect group. The set of extended aspect groups G_a^e with respect to a given group G_a is defined as the set which when one replaces centre of inversion $\bar{1}$ by the identity E will be identical with G_a.

The way one can develop the technique is to classify the 32 aspect groups into three categories (Sumberg, Dayanidhi, Parker & Spence, 1972); the set of groups containing (i) only pure rotations (ii) a centre of inversion as an element by itself (iii) rotation and rotatory inversion axes. Then G_a^e of G_a consists of G_a, $G_a+\bar{1}.G_a$ and $G_x+\bar{1}.(G_a-G_x)$ where G_x is any subgroup of G_a of index two (Lomont, 1959). It is important to note that in case (ii), by definition, G_a^e consists of only one group G_a, the given aspect group.

Finally, the set of Heesch groups G_a^h corresponding to a given aspect group G_a is constructed for the three cases using G_a^e as the intermediate set of groups.

In case (i) G_a^h reduces to G_a^e as there are no coloured or anti-elements in the Heesch groups and the 32 ordinary point groups or uncoloured Heesch groups thus belong to pure rotational aspect groups.

In case (ii) in which there is centre of inversion, G_a^h contains either $1'$, the time reversal or $\bar{1}'$ or both and all grey groups correspond to this type of aspect group. To obtain the set G_a^h, consider G_a^e whose only element is G_a for this case and all its subgroups 'G_y' of index two with the criterion that by replacing $\bar{1}$ by E, G_y reduce to G_R, the pure rotational invariant subgroup of index two of the given G_a (Sumberg *et al.*, 1972). One obtains grey groups by adjoining time reversal to all of these groups and coloured Heesch groups by adding the coloured elements $1'.(G_a-G_y)$ to each G_y. These grey and coloured groups together constitute the required set G_a^h. For example, consider the aspect group $4/mmm$. The subgroups 'G_y' are 422, $4mm$ and $\bar{4}2m$. Then G_a^h is the set consisting of grey groups $422{\cdot}1'$, $4mm{\cdot}1'$, $\bar{4}2m{\cdot}1'$ and $4/mmm{\cdot}1'$ and coloured groups $4'/m'm'm(\bar{4}2m)$, $4/m'mm(4mm)$ and $4/m'm'm'(422)$. For coloured groups, the corresponding G_y is given in paranthesis.

In the third type of aspect group neither $1'$ nor $\bar{1}$ is present. Only coloured Heesch groups correspond to this kind of aspect group. Since set G_a^e consists more than one group we choose G_y in accordance with the definition given earlier from each G^e of G_a^e. The coloured groups from G_y will be obtained in the usual manner, *i.e.* by adding the coloured elements $1'.(G^e-G_y)$ to the corresponding G_y and they constitute the set of Heesch groups G_a^h of the given G_a. As an example, we take the aspect group $6mm$. The elements or groups of the set G_a^e are $6mm$, 622 and $6/mmm$. The subgroups G_y' are given by 6, $\bar{6}$ and $6/m$. Thus the set G_a^h corresponding to $6mm$ consists of the colour groups: $6m'm'(6)$, $62'2'(6)$, $\bar{6}2'm'(\bar{6})$ and $6/mm'm'(6/m)$ which coincides with the list given by Spence & van Dalen (1968).

* Present address: Department of Physics, Andhra Post-Graduate Centre, Gutur-5, Andhra pradesh, India.

One can thus arrive at the set of Heesch groups noting to what the given aspect groups belongs.

I wish to thank Professor R. D. Spence for his valuable assistance and suggestions.

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Acta Cryst. (1973). A**29**, 306

On the use of unit-weight matrices in the least-squares determination of rigid-body vibration tensors.

By H. KÜPPERS, *Institut für Kristallographie der Universität Köln, Germany (BRD)* and C. SCHERINGER, *Institut für Kristallographie der Universität Karlsruhe, Germany (BRD)*

(*Received* 20 *November* 1972; *accepted* 22 *November* 1972)

The transformation laws for the weighting and covariance matrices of the components of the atomic vibration tensors are derived. It is shown that the use of unit-weight matrices in the least-squares determination of the rigid-body vibration tensors **TLS** from the atomic vibration components leads to incompatible results when the **TLS** parameters are refined in different Cartesian coordinate systems. Numerical results for some molecules showed that the differences in the obtained components of **TLS** usually lie within the range of two standard deviations. If the covariances of the atomic vibration components are taken into account in some simple form the incompatibilities vanish.

The components of the rigid-body vibration tensors **TLS** are usually determined from the components of the atomic vibration tensors U_r by means of the least-squares method. In the majority of cases a Cartesian coordinate system and unit weights for the components U_r^{ik} are used. With the structure of lithium succinate (Klapper & Küppers, 1973) we first noticed that the principal components of the libration tensor **L** were not uniquely determined when it was refined in two different Cartesian coordinate systems and unit weights were employed. The differences found between the respective principal components could not be ascribed to rounding-off errors. In this paper we shall give further examples where this happens.

Discrepancies of this type arise because the unit matrix as weighting matrix does not transform into the unit matrix under rotation of axes. In an earlier paper (Scheringer, 1966*a*) – hereafter referred to as SCHE – we stated the transformation law without proof for the 6×6 weighting matrices of the components U_r^{ik} when the base vectors were transformed. Hirshfeld & Shmueli (1972) have recently derived the transformation law for the respective 6×6 covariance matrices by reducing it to the transformation law of a 4th rank tensor. In this paper we want to show first how the transformation law can be obtained simply from the basic equations of the least-squares method.

In SCHE we showed that the weighting matrix for the refinement of the parameters **TLS** should be the normal matrix M of a structure-factor least-squares refinement of the components U_r^{ik}. The covariance matrix C is then proportional to M^{-1}. We now assume that in the last cycle of the structure-factor refinement we have only refined the $6n$ independent components U_r^{ik} of the n atoms of the (nearly) rigid molecule, *i.e.* we neglect all covariances to other types of parameters. Then M and C consist of n^2 6×6 blocks. We define the change of the coordinate system by the transformation

$$\mathsf{X}' = \mathsf{A}\mathsf{X} \tag{1}$$

of the (contravariant) components of a vector X in direct space. Then the (contravariant) components U_r^{ik} of the rth atom transform according to

$$\mathsf{U}_r' = \mathsf{A}\mathsf{U}_r\mathsf{A}^T, \tag{2a}$$

(Scheringer, 1966*b*). If we now arrange the 6 independent components U_r^{ik} in a 6×1 column matrix V_r in the sequence 11, 22, 33, 12, 13, 23 then, by rearranging the terms in equation (2*a*), it can be shown that the transformation law

$$\mathsf{V}_r = \mathsf{L}\mathsf{V}_r \tag{2b}$$

corresponds to the law (2*a*). The elements of the 6×6 matrix L are given in SCHE. (Formally, L is obtained by reducing the 9×9 outer product $\mathsf{A}\times\mathsf{A}$ to a 6×6 matrix). The transformation laws (2*a*) and (2*b*) also hold for the shifts ε_r^{ik} of the components U_r^{ik}. Let the normal equations for refining the components U_r^{ik} from diffraction data in the two coordinate systems be

$$\mathsf{M}\varepsilon = \mathsf{N}, \quad \mathsf{M}'\varepsilon' = \mathsf{N}', \tag{3}$$