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Homometric Polytypes in Cadmium Iodide

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Abstract

Two sufficient criteria on homometric polytypes are derived. They are applied to CdI_2. In addition to the known pairs of homometric structures, infinite sets of other pairs may be constructed. Examples of possible pairs of homometric CdI_2 polytypes for all space groups in CdI_2 are given.

Introduction

Homometrics are two or more structures that are neither congruent nor enantiomorphous, but would give identical diffraction patterns. Examples of homometric structures are to be expected particularly among polytypes. Sufficient conditions have been formulated for MX and MX_2 structures (Dornberger-Schiff & Farkas-Jahnke, 1970; Jain & Trigunayat, 1977; Ohsumi & Nowacki, 1981).

Jain & Trigunayat (1977) have formulated two criteria for MX_2-type structures, a proof of which has been given by Chadha (1981). Firstly, a Zhdanov symbol consisting of only even digits and its literally reversed sequence would be either congruent or else homometric. For CdI_2 and PbI_2 no actual example of this kind may exist because of the restrictions in the arrangement of molecular sheets in these compounds (Wahab & Trigunayat, 1980). Secondly, if a Zhdanov symbol of a structure consists of only 2's and pairs of 1's, then this structure and its literally reversed sequence are either congruent or else homometric. Ohsumi & Nowacki (1981) have given a criterion that permits homometric CdI_2 polytypes to be derived from homometric cyclotomic sets (Patterson, 1944; Buerger, 1976). In the present paper, both the criteria valid for CdI_2 are generalized.

Possible CdI_2 structures, homometric according to one of the known criteria, have space group $P3m1$ or $P6_3mc$. It will be shown that there may also exist pairs of homometric structures with space group $P\bar{3}m1$, $R3m$ and $R\bar{3}m$, respectively. A pair of homometric CdI_2 polytypes with different space groups is constructed.

Two theorems on homometrics among polytypes

Theorem 1. Let P_I be a polytype satisfying the following conditions:

(i) P_I is composed of two kinds of parallel layers S and T;

(ii) the origins of S and T may be chosen such that there is a straight line through the origins of all the layers of P_I.

Let P_{II} be the polytype whose structure is described by the reverse stacking sequence of layers S and T in P_I. Then the structures of P_I and P_{II} are either congruent or enantiomorphic or homometric.

The proof of this theorem is based on formula (1) derived by Marumo & Saito (1972) for layered structures satisfying conditions (i) and (ii).

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$$|F(hkl)|^2 = N_S|F_S|^2 + N_T|F_T|^2 + \sum_m \sum_n N_{S(S^mT^n)S}|F_S|^2 \cos 2\pi l r_{S(S^mT^n)S} + \sum_m \sum_n N_{T(S^mT^n)T}|F_T|^2 \cos 2\pi l r_{T(S^mT^n)T} + \sum_m \sum_n N_{S(S^mT^n)T}(F_S F_T^* + F_S^* F_T) \times \cos 2\pi l r_{S(S^mT^n)T}, \quad (1)$$

where F_S and F_T are the layer structure factors of S and T layers, respectively. N_S and N_T are the numbers of S and T layers, respectively (per period along the c axis). $N_{S(S^mT^n)S}$ is the number of pairs S–S separated by m S layers and n T layers. $r_{S(S^mT^n)S}$ is the distance between the origins of two S layers separated by mS layers and nT layers. $N_{T(S^mT^n)T}$, $N_{S(S^mT^n)T}$, $r_{S(S^mT^n)T}$ and $r_{T(S^mT^n)T}$ are defined correspondingly. The equality $N_{S(S^mT^n)T} = N_{T(S^mT^n)S}$ holds for any combination of m and n in any periodic structure (Marumo & Saito, 1972). As the stacking sequences of P_I and P_{II} are the reverse of each other,

$$N_S^{(I)} = N_S^{(II)}, \qquad N_T^{(I)} = N_T^{(II)},$$
$$N_{S(S^mT^n)S}^{(I)} = N_{S(S^mT^n)S}^{(II)}$$
$$N_{T(S^mT^n)T}^{(I)} = N_{T(S^mT^n)T}^{(II)}, \quad (2)$$
$$N_{S(S^mT^n)T}^{(I)} = N_{T(S^mT^n)S}^{(II)} = N_{S(S^mT^n)T}^{(II)}.$$

From (1) and (2) it follows that $|F^{(I)}(hkl)|^2 = |F^{(II)}(hkl)|^2$, *i.e.* P_I and P_{II} are congruent, enantiomorphic or homometric.

According to the approach of Ohsumi & Nowacki (1981), a pair of homometric polytypes is derived from homometric cyclotomic sets. In Fig. 1 an example of cyclotomic sets is given. If any white point is replaced by a sandwich layer ($A\gamma B$) and instead of black points sandwich layers ($C\alpha B$) are taken, a pair of homometric polytypes results. More generally, for homometric cyclotomic sets the layers S and T may be taken instead of white and black points, respectively. Thus, a sufficient criterion results:

Theorem 2. Let P_I and P_{II} be polytypes for which the conditions (i) and (ii) of theorem 1 are valid and additionally the following conditions hold:

(iii) S is as thick as T;

(iv) the distributions of the S layers in P_I and P_{II} correspond to the distribution of black points in two enantiomorphic or homometric cyclotomic sets, respectively.

Then, P_I and P_{II} are congruent, enantiomorphic or homometric polytypes.

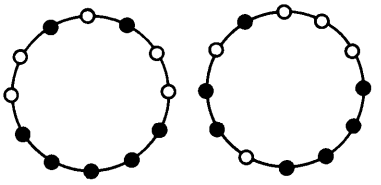

Fig. 1. The two cyclotomic sets are homometric with each other. The first set has a symmetrical arrangement of points, the second does not.

The proof of theorem 2 follows again from (1). As the layer S is as thick as the layer T, (1) may be simplified to

$$|F(hkl)|^2 = N_S|F_S|^2 + N_T|F_T|^2 + \sum_n (N_{S(X^n)S}|F_S|^2 + N_{T(X^n)T}|F_T|^2) \cos 2\pi l(n+1) r_{ST} + \sum_n N_{S(X^n)T}(F_S F_T^* + F_S^* F_T) \times \cos 2\pi l(n+1) r_{ST}. \quad (3)$$

In (3), X^n stands for n layers of any kind. Theorem 2 is proved if we show that for P_I and P_{II} the corresponding numbers N in (3) are equal. As the S layers in P_I and P_{II}, respectively, are distributed according to homometric cyclotomic sets, it follows that

$$N_S^{(I)} = N_S^{(II)}, \qquad N_{S(X^n)S}^{(I)} = N_{S(X^n)S}^{(II)}.$$

The complementary cyclotomic sets describe the distribution of the T layers in P_I and P_{II}, respectively. According to Patterson (1944) and Buerger (1976), the complementary cyclotomic sets are also homometric. Hence,

$$N_T^{(I)} = N_T^{(II)}, \qquad N_{T(X^n)T}^{(I)} = N_{T(X^n)T}^{(II)}.$$

In any polytype, $N_{S(X^n)S} + N_{S(X^n)T} = N_S$. Thus,

$$N_{S(X^n)T}^{(I)} = N_{S(X^n)T}^{(II)}$$

Application of the theorems to CdI_2

In the simplest case, both layers S and T consist of only one molecular layer (sandwich) each: $S = (A\gamma B)$, $T = (C\alpha B)$. Then the second criterion of Jain & Trigunayat (1977) follows from theorem 1, and the criterion of Ohsumi & Nowacki (1981) follows from theorem 2. Besides, the criterion of Jain & Trigunayat may also be deduced from theorem 2 as the distribution of S and T layers corresponds to enantiomorphic cyclotomic sets. Thus, the previous section contains proofs of the criteria mentioned and shows their close relationship.

All the 20 known pairs of homometric CdI_2 structures have space group $P3m1$, but the criterion of Jain & Trigunayat allows pairs of homometrics with space group $P6_3mc$ to be constructed.

Example 1: Polytypes with Zhdanov symbol $(221121111)_2$ and $(221111211)_2$ are homometric and have space group $P6_3mc$.

In the following, more complex layers will be considered, each consisting of several sandwiches. Further, we suppose that neighbouring layers *SS*, *TT*, *ST*

or TS have one common sandwich. The condition that the origins of all layers are on a straight line means that there is a straight line through cadmium ions of all boundary sandwiches between two successive S or T layers. For the construction of suitable examples, the *thr* notation (Fichtner, 1984, 1983) is used. This notation describes any CdI_2 polytype as a sequence of pairs of neighbouring sandwiches (Fig. 2). The sequences may only contain letters h, $\bar{h}$ and t because of the restriction for CdI_2 (Wahab & Trigunayat, 1980). As the layers S have to be parallel, the total number of letters h and $\bar{h}$ in any layer S or T has to be even.

Example 2: $S = h_2$, $T = t_2$, cyclotomic sets of Fig. 3. The homometric polytypes are $h_6t_4h_2t_4$ and $h_4t_2h_4t_6$ with Zhdanov sequences $(22)_3(11)_422(11)_4$ and $(22)_2(11)_2(22)_2(11)_6$.

Example 3: $S = h_2$, $T = \bar{h}_2$, S_2TST_2 and S_2T_2ST. Both $24H$ polytypes, 222123212223 and 222122232123, have space group $P\bar{3}m1$.

Example 4: $S = \bar{h}h$, $T = t_3$, S_3T_2ST and S_3TST_2. This is a pair of $102R$ polytypes with space group $R3m$. The aperiodic parts in the Zhdanov sequences are

$$(13)_3(11)_613(11)_3$$

$$(13)_3(11)_313(11)_6.$$

In this example, the straight line through the origins of the layers S and T is not perpendicular to the layers.

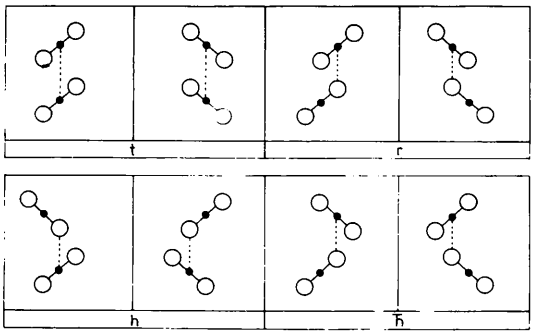

Fig. 2. The *thr* notation for the description of stacking sequences in CdI_2-type structures.

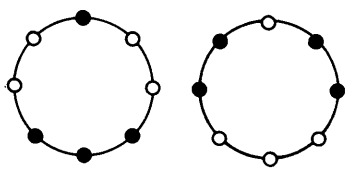

Fig. 3. Simplest example of a pair of homometric cyclotomic sets. Black and white points are interchanged.

Example 5: $S = h\bar{h}t$, $T = th\bar{h}$, S_3TST_3 and S_3T_3ST. S and T are centrosymmetric to each other and have the same inclination per sandwich. One period contains eight symmetrically arranged layers. Hence, the space group is $R\bar{3}m$. The two $144R$ polytypes have the Zhdanov sequences

$$(1311)_311131311(1113)_3$$

$$(1311)_3(1113)_313111113.$$

Example 6: $S = (\bar{h}h)_2$, $T = (ht_2\bar{h})$, cyclotomic sets of Fig. 1, *viz* $S_5T_2STST_2$ and $S_4TS_2TST_3$. As the total number of points in the cyclotomic sets is a multiple of three, the polytypes are hexagonal. In each of the two layers S and T, the arrangement of sandwiches is centrosymmetric. The first cyclotomic set has a symmetric arrangement of points, the second not. Thus, the first polytype has space group $P\bar{3}m1$ and the second $P3m1$. The Zhdanov sequences of the two $96H$ polytypes are

$$(13)_92(11)_213(11)_2123132(11)_2123132(11)_213(11)_2123$$

$$(13)_72(11)_2123(13)_32(11)_212313(2(11)_213)_2(11)_2123.$$

This example demonstrates that homometric polytypes may have different space groups.

Concluding remarks

In addition to the known pairs of homometric polytypes of CdI_2, infinitely many other examples may be constructed, governed neither by the criterion of Jain & Trigunayat nor by that of Ohsumi & Nowacki. Compared with observed CdI_2 polytypes, the stackings in examples 1-3 are of moderate complexity. Thus, it may be expected that actual examples will be found that are not governed by the criterion of Jain & Trigunayat or do not have space group $P3m1$. The polytypes of example 3 consist of only h_2 and $\bar{h}_2$ in their stacking sequence. Such polytypes have been observed, *e.g.* $20H_{14}$: $(22)_32123 = h_8\bar{h}_2$ (Pałosz & Gierlotka, 1984) or $40H_2$: $(22)_621(22)_223 = h_{14}\bar{h}_6$ (Pałosz, 1983).

The theorems of this paper may also be applied to polytypic substances other than CdI_2. For instance, in $CdBr_2$ pairs r of sandwiches and triples $\bar{h}h$ exist in the observed polytypes. Thus, a pair of homometric $18H$ polytypes may exist: $S = r$, $T = \bar{h}h$, S_2TST_2 and S_2T_2ST, with the Zhdanov sequences 531333 and 533313, respectively.

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Compound Identification and Characterization using Lattice-Formula Matching Techniques

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Abstract

A lattice-formula matching technique has been developed to be used in conjunction with the *NBS Crystal Data File* [(1982), National Bureau of Standards, Gaithersburg, MD] for the identification and characterization of crystalline materials. This technique is reliable, efficient and highly selective. In the first step of the identification/characterization procedure, a unit cell defining the lattice is determined. The cell is reduced and derivative supercells and subcells are calculated. These cells are then checked against the *NBS Crystal Data File* in which all lattices have been represented by standard reduced cells. By routinely calculating derivative supercells and subcells and matching against the file of known compounds, it is possible to find related materials and/or to make an identification in spite of certain types of errors made by the experimentalists (*e.g.* missing rows of spots on diffraction photographs or the diffractometer *etc.*). Finally, the identification obtained by lattice matching is verified using known chemical data. Practical experience and an analysis of the data in the *NBS Crystal Data File* have proved that the lattice-formula combination is highly characteristic of a crystalline material. Since the method is subject to precise mathematical techniques, the entire procedure can be highly automated. Both the unit-cell determination and the identification/characterization procedure can be carried out in the same instrument. A Fortran program and the *NBS Crystal Data File* are available.

Introduction

We have designed a lattice-formula matching technique to be used in conjunction with the *NBS Crystal Data File* (1982) for the characterization and identification of crystalline materials. The NBS Crystal Data Center maintains a data base that contains evaluated crystallographic and chemical data on approximately 60 000 materials. The data fall into the following categories: organics, organometallics, metals, intermetallics, inorganics and minerals. There are two fundamental ways that large crystallographic data bases can be used. As a source of critically evaluated data, the data base can be used as a basis for scientific research, or as an aid to scientific research (*e.g.* to identify unknown compounds, to locate certain molecules, to obtain bibliographic data *etc.*). The type of data that can be obtained through search and retrieval programs includes chemical name and formula, cell parameters and cell volume, crystal system, space-group symbol and number, density, bibliographic data, plus additional data. Since the data base is formatted, many of these data items may be searched readily using systems software available at a particular institution. However, general systems software will not be adequate for certain types of information search and retrieval operations. One such example is the identification of unknown compounds by matching unit-cell parameters and, if available, some chemical data. Although simple in principle, lattice-formula matching is a complex operation that requires a specialized scientific background in order to design a practical computer search algorithm.

Three relatively recent developments have given the lattice-formula method for compound identification great potential as a routine analytical tool. Firstly, automated methods to determine a unit cell

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