SYMMODES: a software package for group-theoretical analysis of structural phase transitions

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1. The crystallographic problem

Group-theoretical methods are widely used in the investigation of phase transitions in crystals. On the one hand, important structural aspects concerning the relation between the low- and the high-symmetry structures follows from the the group–subgroup relations of the space groups $\mathcal{G} > \mathcal{H}$ describing the symmetry of the two phases. For example, the number of low-symmetry domain states equals the index of $\mathcal{H}$ in the parent group $\mathcal{G}$, while their symmetry groups are conjugate subgroups $\mathcal{H}_j$ (isomorphic to $\mathcal{H}$) of $\mathcal{G}$. The splitting schemes of the occupied atomic orbits for the symmetry break $\mathcal{G} > \mathcal{H}$ (known also as splitting of Wyckoff positions) determine the structural relation between the two phases.

Further, an essential feature of a continuous or quasicontinuous displacive phase transition is the appearance of a symmetry-breaking distortion in the low-symmetry phase (with respect to the high-symmetry one) which is mainly caused by the freezing of some mode, the so-called primary mode. In addition, secondary modes are also triggered by the phase transition and can also have non-zero spontaneous amplitudes in the distorted structure. The so-called symmetry-mode analysis allows the 'separation' of the frozen primary mode from the contributions of modes of different symmetry present as a secondary effect, but for its application it is necessary first to calculate the symmetry modes of the parent phase, compatible with the low-symmetry phase, and then using their orthonormality properties to decompose the global distortion as a sum of the contributions of each of them.

Such a symmetry analysis of phase-transition phenomena is rather complex as it requires full use of group-theoretical methods, including detailed knowledge of the group–subgroup relations of space groups and their irreducible representations ('irreps'). The goal of the developed software package *SYMMODES* is to provide the necessary tools for a group-theoretical analysis of a structural phase transition, including (i) a detailed group–subgroup description of the chain $\mathcal{G} > \mathcal{H}$ and (ii) a calculation of the primary and secondary modes for the symmetry break $\mathcal{G} \rightarrow \mathcal{H}$.

2. Method of solution

The software package *SYMMODES* combines modules of the programs *SUBGROUPGRAPH* (Ivantchev *et al.*, 2000), *WYCKSPLIT* (Kroumova *et al.*, 1998) and the program *SOPD* (subgroup graph order-parameter displacements), which is a specific segment of the package *ISOTROPY* (Stokes & Hatch, 1998).

Consider a structural phase transition with a symmetry change $\mathcal{G} \rightarrow \mathcal{H}$, where the low-symmetry space group $\mathcal{H}$ is a subgroup of the high-symmetry group $\mathcal{G}$. The main steps of the symmetry analysis carried out by *SYMMODES* can be summarized as follows.

(i) Given the space-group types of $\mathcal{G}$ and $\mathcal{H}$, and their index, the *SUBGROUPGRAPH* module constructs the lattice of maximal subgroups relating $\mathcal{G}$ and $\mathcal{H}$. All possible subgroups $\mathcal{H}_j$ of the type $\mathcal{H}$ are listed, and their distribution into classes of conjugate subgroups is indicated. In addition, the program also supplies the corresponding transformation matrices relating the (conventional) bases of $\mathcal{G}$ to each of the subgroups $\mathcal{H}_j$. By specifying the relevant subgroup $\mathcal{H}_j$ of $\mathcal{G}$, the module returns the particular graph of maximal subgroups for $\mathcal{G} > \mathcal{H}_j$. The results on the group–subgroup relations for the chain $\mathcal{G} > \mathcal{H}$ obtained by the program *SUBGROUPGRAPH* are based on the data of maximal subgroups of space groups available in the *International Tables for Crystallography*, Vol. A1 (2003).

(ii) For a given symmetry break $\mathcal{G} \rightarrow \mathcal{H}_j$ and a crystal structure specified by the Wyckoff positions of the occupied atomic orbits, the program calculates (*a*) the number and the patterns of the primary and secondary modes. The symmetry of each mode is characterized by an irreducible representation of the high-symmetry group, the direction of the order parameter in the representation space, and the corresponding isotropy subgroup from the $\mathcal{G} > \mathcal{H}_j$ graph. (*b*) The splitting schemes of the Wyckoff positions during the symmetry break $\mathcal{G} > \mathcal{H}_j$ are calculated by the *WYCKSPLIT* module. The decomposition of an orbit O^G of $\mathcal{G}$ into O_i^H suborbits of $\mathcal{H}$ is achieved *via* the splitting of the general position of $\mathcal{G}$.

3. Software and hardware environment

The package *SYMMODES* runs under any Unix or Unix-like operating system (Digital Unix, HP-UX, Sun, BSD, Linux *etc.*). It is written in C. Only standard library functions are used. Modules, used for extracting data from CIF files, are written in Perl. No overlay structure has been applied. The program is designed to be used, without local installation, *via* any computer with a WWW browser (Unix, VMS, Macintosh, DOS, Windows *etc.*)

4. Program specifications

4.1. Input

The space-group types $\mathcal{G}$ and $\mathcal{H}$ specified by their sequential numbers as listed in the *International Tables for Crystallography*, Vol. A (1995), and their index or the transformation matrix that relates the bases of $\mathcal{G}$ and $\mathcal{H}$, are required as input. The crystal structure is specified by selecting the Wyckoff positions of the occupied orbits of the atoms.

4.2. Output

As a first step, the program lists all different subgroups of the type $\mathcal{H}$, distributed into classes of conjugate subgroups with respect to $\mathcal{G}$. After selecting the relevant subgroup $\mathcal{H}_j$, *SYMMODES* returns the maximal subgroups graph $\mathcal{G} > \mathcal{H}_j$ and the splitting schemes of the occupied Wyckoff positions. The output also includes the polarization vectors of all pertinent displacive modes, the symmetry of which is specified by the corresponding irreducible representations of $\mathcal{G}$, the directions of the order parameter in the representation carrier space, and the isotropy subgroups. The labels of the irreducible repre-

sentations follow the notation scheme of Miller & Love (1967), and the irreducible-representation matrices coincide with those used by the program *ISOTROPY*.

5. Documentation and availability

The program *SYMMODES* forms part of the Bilbao Crystallographic Server, http://www.cryst.ehu.es (Kroumova *et al.*, 1998, 2003), and uses the databases and the results from other programs available on that server. The program can be accessed *via* the Internet by any computer with a WWW browser. The URL is http://www.cryst.ehu.es/cryst/symmodes.html, where an on-line manual is also available with a description of the program input and output.

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