3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

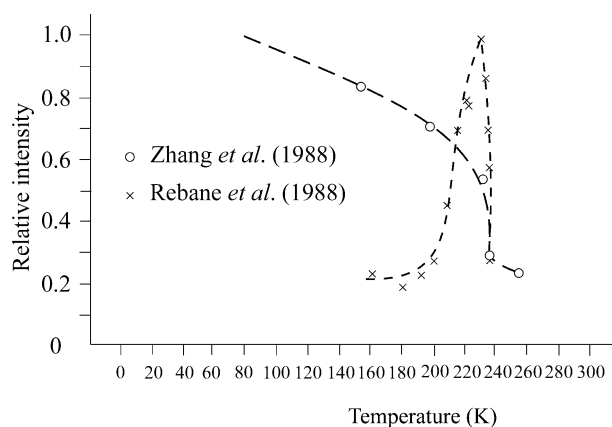Fig. 3.1.5.25. Raman spectra of $YBa_2Cu_3O_{7-x}$ below an apparent phase transition at *ca.* 235 K (Zhang *et al.*, 1988).

Table 3.1.5.1. *Low-temperature ferroelectrics*

Formula	Curie temperature T_c (K)	Curie constant C (K)	Entropy change ΔS (cal mol^{-1} K^{-1})
$NH_4Al(SO_4)_2 \cdot 12H_2O$	71	?	?
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	88	400	0.15
$(NH_4)_2Cd(SO_4)_3$	95	?	?
$CdTiO_3$	55	4.5×10^4	?
$Pb_2Nb_2O_7$	15.3	?	?
$LiTlC_4H_4O_6 \cdot H_2O$	10.5	?	?
$K_3Li_2Nb_5O_{15}$	7	?	?

LO (longitudinal optical) phonon in the semiconducting $YBa_2Cu_3O_{6+x}$ material, suggesting that the supposed phase transition at 235 K may be not a structural transition but instead a chemical transition in which oxygen is lost or gained at the surface with temperature cycling.

3.1.5.3. *Low-temperature ferroelectric transitions*

It has historically been difficult to establish the nature of ferroelectric phase transitions at cryogenic temperatures. This is simply because the coercive fields for most crystals rise as the temperature is lowered, often becoming greater than the breakdown fields below *ca.* 100 K. As a result, it is difficult to demonstrate *via* traditional macroscopic engineering techniques (switching) that a material is really ferroelectric. Some authors have proposed (*e.g.* Tokunaga, 1987) on theoretical grounds the remarkable (and erroneous) conjecture that no crystals have Curie temperatures much below 100 K. A rebuttal of this speculation is given in Table 3.1.5.1 in the form of a list of counter-examples. References may be found in the 1990 Landolt–Börnstein Encyclopedia of Physics (Vol. 28a). The original work on pure cadmium titanate and on lead pyrochlore (Hulm, 1950, 1953) did not demonstrate switching, but on the basis of more recent studies on mixed crystals $Ca_{2-2x}Pb_{2x}Nb_2O_7$ and $Ca_xCd_{1-x}TiO_3$, it is clear that the pure crystals are ferroelectric at and below the stated temperatures.

Hence, in Table 3.1.5.1 we see examples where X-ray structural studies may establish the symmetries requisite for ferroelectricity without the macroscopic switching being demonstrated. This is the converse case to that primarily emphasized in this section (*i.e.* the use of techniques complementary to X-ray scattering to determine exact crystal symmetries); it is useful to see these reverse cases to demonstrate the full complementarity of X-ray crystallography and dynamic spectroscopic techniques.

3.1.6. Group informatics and tensor calculus

By V. Kopský and P. Boček

We shall briefly describe here the intentions and contents of the accompanying software package *GI⋆KoBo*-1 (*Group Informatics*, first two letters of authors names, release 1). A more detailed description is contained in the manual; the user may consult this file on the screen, but we recommend that it is printed out and that the printout is followed in order to become familiar with the theoretical background as well as with more detailed instructions for the use of the software.

The main purpose of this software is to describe the changes of tensor properties of crystalline materials during ferroic phase transitions, including basic information about domain states. The

software provides powerful information in a standardized manner and it is based on a few advanced methodical points that are not yet available in textbooks. These points are:

(i) The introduction of *typical variables*, which was inspired by the *symbolic method* of the old invariant theory (Weitzenböck, 1923).

(ii) The method of Clebsch–Gordan products (Kopský, 1976*a*,*b*). The name stems from Clebsch–Gordan coefficients, known in quantum mechanics as coefficients of momentum addition. In this case, the coefficients are connected with the orthogonal group $\mathcal{O}(3)$; analogous coefficients were later introduced and calculated for crystal point groups (Koster *et al.*, 1963). They appear in Clebsch–Gordan products, which represent a better adaptation of results for our purposes.

(iii) Tables of *tensorial covariants* (Kopský, 1979*a*,*b*). The name covariant may sound rather unusual now, but it was originally used by Weyl (1946); it is equivalent to *symmetry-adapted bases* (*form-invariant bases* and other terms are also used). The term covariant is classical and its semantical use is easier.

(iv) Tables of *fine structures of domain states* (Kopský, 1982). These are contained in a booklet which is practically unknown though, together with tables of tensorial covariants, it contains all answers concerning changes of tensor properties at ferroic phase transitions.

Remark. The original term *fine domain structure* corresponds to the term *degenerate domain structure* in Chapter 3.4.

(v) *Extended integrity bases* (Patera *et al.*, 1978; Kopský, 1979*c*). These represent finite sets of polynomial invariants and covariants suitable for the calculation of all types of interactions in symmetric systems.

(vi) *Lattices of subgroups* (Ascher, 1968; Kopský, 1982). Subgroups of a group constitute a partially ordered set of special properties called a *lattice*. The unfortunate coincidence of the term (in English) with crystallographic lattices should be disregarded; it is always possible to see from the context what we mean by this term.

These methods provide good ammunition for all types of group-theoretical considerations where work with characters is insufficient and knowledge of the explicit bases of irreducible representations is necessary. This is exactly the case for the theory of structural phase transitions, and the consideration of domain states, pairs of domain states and domain walls or twin boundaries. The main results of the software are contained in tables of symmetry descents $G \Downarrow H$ and/or $G \Downarrow F_i$, where G is the parent point group, H its normal subgroup and F_i is the set of conjugate subgroups. These tables provide information about changes of tensors at ferroic phase transitions as well as basic information about interactions, and they are also supplemented by tables of equitranslational subgroups of space groups.

To make this exposition quite clear, we begin in the manual from the beginning with a brief review of elementary group-theoretical concepts used in the software. Relevant elementary tables (listed below in Section A) are followed by more advanced information proceeding towards the central goal of providing information for all symmetry descents (Section B). To achieve this goal, it was also necessary to introduce our own standard

notation for specifically oriented groups, for their elements and for irreducible representations (ireps). The reasons for the introduction of these standards are twofold: (i) There is no unique and commonly accepted notation in the literature. The recent book by Altmann & Herzig (1994) contains slight inconsistencies (different symbols for elements in a group and in its subgroup) and is also not compatible with another prominent source (Bradley & Cracknell, 1972). (ii) We need a strict specification of groups and their subgroups with reference to a Cartesian coordinate system and a strict specification of matrix ireps; neither is available in the literature. This does not mean that we introduce brand-new symbols; we simply adapt those that are already in use and we take extreme care that every symbol has a unique meaning.

It is recommended that users follow the manual when first using the software. The tabular content is as follows:

A. *General information*

On opening the program, a panel *Crystallographic* appears on the screen. In the left-hand part are listed crystallographic geometric classes in a tree form wrapped to crystallographic systems (families). A click on a system brings to the screen a list of its crystallographic geometric classes as either Hermann–Mauguin, Schoenflies or Shubnikov symbols (the latter are used only on this level).

The default choice for the notation is set in a table *Options* under the pull-down menu *File*. Hermann–Mauguin or Schoenflies symbols are offered for groups, standard or spectroscopic notation for group elements, classes of ireps and classes of conjugate elements. The temporary notation, under the pull-down menu *Notation*, also includes the choice of Shubnikov symbols.

When the user clicks on a geometric class, all specifically oriented groups of this class used in the software appear in the right-hand part of the panel. At the top appear the groups in standard orientation that are further used as the standard parent groups, all remaining groups appearing below. For some groups two or three standard orientations are available, for reasons explained in the manual. The option of using Hermann–Mauguin or Schoenflies symbols for groups is available throughout; up to a certain point there are options for using either standard symbols of group elements and of ireps (as defined here) or spectroscopic symbols. A specific group is picked using the left mouse button, then a click with the right mouse button opens a pull-down menu. The following information is available under the titles:

(1) *Basic info*: This contains information relevant to each group of the geometric class, such as the number of elements, generators, isomorphism type, normalizer, number of conjugacy classes and the standard orientations.

(2) *Group elements*: Activates the group calculator, the keys of which list elements of the group. Performs calculation of products (strings) of up to ten elements by left or right multiplication.

(3) *Correlation stnd./spectro*: Symbols of groups, elements and classes of ireps for standard and spectroscopic notation are correlated.

(4) *Class structure*: Symbols of classes of conjugate elements are defined and elements of classes are listed.

(5) *Class multiplication table*: Displays class multiplication formulae.

(6) *Character table*: Standard and spectroscopic symbols of classes of ireps are specified and kernels of ireps are presented.

(7) *Kronecker products*: Tables of Kronecker products of classes of ireps are displayed. Up to this point, both standard and spectroscopic notation are used.

(8) *Ireps and standard variables*: Irreducible matrix representations (ireps) are explicitly defined. These also define the standard symbols of typical variables.

Brief: Brief tables specify matrices of ireps for generators of the group.

Full: Full tables provide these matrices for each group element. Kernels of ireps are presented. From this point onwards only the standard notation is used.

(9) Clebsch–Gordan products: Up to orthorhombic groups, one Clebsch–Gordan product table is given. For groups of higher systems, there are two options: *complex* Clebsch–Gordan tables, where variables $(\xi_\alpha, \eta_\alpha)$ are used, and *real* Clebsch–Gordan tables, with variables (x_α, y_α) for two-dimensional real ireps.

(10) *Tensorial covariants*: Decomposition of tensors up to fourth rank into their covariant components is displayed.

B. *Ferroic phase transitions*

(11) *Subgroups*: Choice of this item displays a panel with the lattice of subgroups of the originally chosen point group G either in Schoenflies or in Hermann–Mauguin symbols. The pull-down menu *Graph* in the upper bar enables handling of the lattice: each item can be picked and moved to another place, the rearranged lattice can be fixed as default or reset, and the lattice can be sent to a printer. Notice that sets of conjugate subgroups are stacked like a pile of sheets of paper and can be unstacked. Consecutive clicks activate individual subgroups of the set. In the upper part of the panel, ireps of the parent group G in spectroscopic symbols are listed; these are followed by boxes in which it is possible to scroll for special vectors of the respective carrier space in terms of typical variables. Clicking on a vector marks its stabilizer (epikernel of the irep) in the lattice and activates it at the same time. With each irep is associated a table of the extended integrity basis; the table is called either by the option *Integrity bases* under the pull-down menu *View* or directly by using the right mouse button in the box of this irep. If the Ctrl key is pressed after the choice of one vector, another vector may be chosen; as a result, an intersection of the respective epikernels is marked in the lattice.

Each subgroup of the lattice may also be activated independently. Lattices of subgroups serve themselves as menus for consideration of specific symmetry descents. Clicking on a subgroup H or on one of the stack of conjugate subgroups F_i activates the following information about symmetry descent $G \Downarrow H$ or $G \Downarrow F_i$:

(1) *Domain*: This option brings to the screen the main table that describes changes of tensor properties in chosen ferroic descent. The option is available under the pull-down menu *View* or directly at the subgroup in the case of normal subgroups. The change of tensor properties is given with reference to the first domain state and hence to the group F_1 from the set of conjugate subgroups. It is given for all tensors listed in Section 3.1.2.3 in a slightly different manner than in Table 3.1.3.1. Namely, principal and secondary tensor parameters of the transition are distinguished. In other words, the onsetting tensor components are distinguished according to the ireps to which they belong. From this information, one can deduce the *fine structure of domain states* with all possible crossovers when some tensor properties are identical in several domains. In tables for those symmetry descents where the subgroup is not an epikernel of a certain irep, expressions of the subgroup as possible intersection of epikernels are presented.

To each table is attached information about G-invariant forms of interactions. This consists of:

Integrity basis: of invariants in the primary order parameter.

Faint interactions: These are those interactions of the primary order parameter with secondary (faint) parameters that are responsible for the occurrence of faint parameters.

Electric switching interactions: The interactions of all order parameters with an external electric field.

Elastic switching interactions: The interactions of all order parameters with an external stress field.

(2) *Integrity bases*: Needs activation of the box of ireps as explained above. Displays the *extended integrity basis* of polynomials in variables of the chosen irep. This consists of the

integrity basis of polynomial invariants and of the linear bases of polynomial covariants.

(3) *Twinning group*: This option works for the first group of the set of conjugate subgroups only. It displays a table that contains consecutive normalizers of the set of conjugate subgroups, left, right and double coset resolutions of the parent group G with respect to the subgroup F_1, and the twinning groups assigned to double cosets. This is the basic information concerning pairs of domain states.

Lattices of equitranslational subgroups of the space groups. The importance of these lattices was realized by Ascher (1968), who prepared the first tables. However, his tables do not contain full information about subgroups; neither the parent group nor the subgroups are completely specified. The current version gives the full information about subgroups including their settings and origins. The pull-down menu *Groups* contains two options: *Point* and *Space*. The choice of the second option brings to the screen another panel, in the right-hand part of which are listed space groups of the geometric class G through Hermann–Mauguin symbols corresponding to all settings and cell choices where applicable. The number of the space-group type, the Schoenflies symbol, the setting and the cell choice are shown in the left-hand part of the panel when you click on one of these Hermann–Mauguin symbols. At the same time, the symbols of the point groups in the lattice change to Schoenflies symbols of oriented space-group types. As you click on any of these subgroups, the Hermann–Mauguin symbol that specifies the subgroup completely appears in the lower bar of the panel, reserved for this information. Though the embellished lattice symbols used in this presentation are self-explanatory, consultation of the manual is recommended.

The option *Point* returns the lattice to its original form of the lattice of point groups.

The following is a list of tabular appendices contained in the manual:

Appendix A: correlation of various notations and Jones' faithful representation symbols;

Appendix B: Schoenflies and Hermann–Mauguin symbols of groups in standard orientations and of their subgroups;

Appendix C: isomorphisms used for defining irreducible representations;

Appendix D: standard polynomials;

Appendix E: labelling of covariants and conversion equations;

Appendix F: list of symmetry descents;

Appendix G: nonstandard lattice letters.

Our symbols for point-symmetry operations are compared with other sources in Appendix A. Symbols of all groups used in the software are given in Appendix B and isomorphisms in Appendix C. Standard polynomials in Appendix D are abbreviated symbols for more complicated polynomials that appear in the main tables. Appendix E is of primary importance for consideration of the relationship between tensor parameters and their contribution to Cartesian tensor components as already indicated in the text explaining Table 3.1.3.1. In Appendix F are listed and classified all symmetry descents considered in the main table. Consultation of Appendix G is strongly recommended to all users who want to use the lattices of equitranslational subgroups of the space groups.

3.1.7. Glossary

(*a*) Groups

G	point-group symmetry of the parent (prototype, high-symmetry) phase
$\mathcal{G}$	space-group symmetry of the parent (prototype, high-symmetry) phase
F	point-group symmetry of the ferroic (low-symmetry) phase (domain state not specified)
$\mathcal{F}$	space-group symmetry of the ferroic (low-symmetry) phase (domain state not specified)
F_1	point-group symmetry of the first ferroic single domain state
$\mathcal{F}_1$	space-group symmetry of the first ferroic single domain state
$G \Downarrow F$	point-group symmetry descent from G to F
$\mathcal{G} \Downarrow \mathcal{F}$	space-group symmetry descent from $\mathcal{G}$ to $\mathcal{F}$
$\mathcal{G} \Downarrow^t \mathcal{F}$	equitranslational symmetry descent from $\mathcal{G}$ to $\mathcal{F}$
Γ_η	representation of $\mathcal{G}$ (or of G) according to which η transforms
$D^{(\eta)}$	irreducible matrix representation of the order parameter η
χ_η	character of the matrix representation $D^{(\eta)}$
R-irep	physically irreducible representation
n_F	number of subgroups conjugate under G to subgroup F_1
n_f	number of ferroic single domain states
n_a	number of ferroelastic single domain states
n_e	number of ferroelectric single domain states

(*b*) Physical quantities

c	specific heat
$d_{i\mu}$	piezoelectric tensor
F, G	free energy
g_μ	optical activity
P_i	dielectric polarization
S	entropy
s_{ij}	elastic compliance
T_c	Curie temperature
u_{ij}, u_μ	strain tensor
V	cell volume
χ	dielectric susceptibility
ε	enantiomorphism, chirality
ε_{ij}	dielectric permittivity
η	order parameter (primary)
λ	order parameter (secondary)
ω_{LO}	longitudinal optic mode frequency
ω_{TO}	transverse optic mode frequency
$\pi_{\mu v}$	piezo-optic tensor

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