3.1.3. Equitranslational phase transitions. Property tensors at ferroic phase transitions

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In the Landau theory, presented in the preceding Section 3.1.2, symmetry considerations and thermodynamics are closely interwoven. These two aspects can be, at least to some extent, disentangled and some basic symmetry conditions formulated and utilized without explicitly invoking thermodynamics. Statements which follow directly from symmetry are exact but usually do not yield numerical results. These can be obtained by a subsequent thermodynamic or statistical treatment.

The central point of this section is Table 3.1.3.1, which contains results of symmetry analysis for a large class of equitranslational phase transitions and presents data on changes of property tensors at most ferroic phase transitions. Notions and statements relevant to these two applications are explained in Sections 3.1.3.1 and 3.1.3.2, respectively. Table 3.1.3.1 with a detailed explanation is displayed in Section 3.1.3.3. Examples illustrating possible uses of the table are given in Section 3.1.3.4.

3.1.3.1. *Equitranslational phase transitions and their order parameters*

A basic role is played in symmetry considerations by the relation between the space group $\mathcal{G}$ of the high symmetry *parent* or *prototype* phase, the space group $\mathcal{F}$ of the low-symmetry *ferroic* phase and the order parameter η: The low-symmetry group $\mathcal{F}$ consists of all operations of the high-symmetry group $\mathcal{G}$ that leave the order parameter η invariant. By the term *order parameter* we mean the primary order parameter, *i.e.* that set of degrees of freedom whose coefficient of the quadratic invariant changes sign at the phase-transition temperature (see Sections 3.1.2.2.4 and 3.1.2.4.2).

What matters in these considerations is not the physical nature of η but the transformation properties of η, which are expressed by the representation Γ_η of $\mathcal{G}$. The order parameter η with d_η components can be treated as a vector in a d_η-dimensional carrier space V_η of the representation Γ_η, and the low-symmetry group $\mathcal{F}$ comprises all operations of $\mathcal{G}$ that do not change this vector. If Γ_η is a real one-dimensional representation, then the low-symmetry group $\mathcal{F}$ consists of those operations $g \in \mathcal{G}$ for which the matrices $D^{(\eta)}(g)$ [or characters $\chi_\eta(g)$] of the representation Γ_η equal one, $D^{(\eta)}(g) = \chi_\eta(g) = 1$. This condition is satisfied by one half of all operations of $\mathcal{G}$ (index of $\mathcal{F}$ in $\mathcal{G}$ is two) and thus the real one-dimensional representation Γ_η determines the ferroic group $\mathcal{F}$ unambiguously.

A real multidimensional representation Γ_η can induce several low-symmetry groups. A *general vector* of the carrier space V_η of Γ_η is invariant under all operations of a group Ker Γ_η, called the *kernel of representation* Γ_η, which is a normal subgroup of $\mathcal{G}$ comprising all operations $g \in \mathcal{G}$ for which the matrix $D^{(\eta)}(g)$ is the unit matrix. Besides that, *special vectors* of V_η – specified by relations restricting values of order-parameter components (*e.g.* some components of η equal zero, some components are equal *etc.*) – may be invariant under larger groups than the kernel Ker Γ_η. These groups are called *epikernels* of Γ_η (Ascher & Kobayashi, 1977). The kernel and epikernels of Γ_η represent potential symmetries of the ferroic phases associated with the representation Γ_η. Thermodynamic considerations can decide which of these phases is stable at a given temperature and external fields.

Another fundamental result of the Landau theory is that components of the order parameter of all continuous (second-order) and some discontinuous (first-order) phase transitions transform according to an irreducible representation of the space group $\mathcal{G}$ of the high-symmetry phase (see Sections 3.1.2.4.2 and 3.1.2.3). Since the components of the order parameter are real numbers, this condition requires irreducibility over the field of real numbers (so-called *physical irreducibility* or *R-irreducibility*). This means that the matrices $D^{(\eta)}(g)$ of *R*-irreducible representations (abbreviated *R-ireps*) can contain only real numbers. (Physically irreducible matrix representations are denoted by $D^{(\alpha)}$ instead of the symbol Γ_α used in general considerations.)

As explained in Section 1.2.3 and illustrated by the example of gadolinium molybdate in Section 3.1.2.5, an irreducible representation $\Gamma_{\mathbf{k},m}$ of a space group is specified by a vector $\mathbf{k}$ of the first Brillouin zone, and by an irreducible representation $\tau_m(\mathbf{k})$ of the little group of $\mathbf{k}$, denoted $G(\mathbf{k})$. It turns out that the vector $\mathbf{k}$ determines the change of the translational symmetry at the phase transition (see *e.g* Tolédano & Tolédano, 1987; Izyumov & Syromiatnikov, 1990; Tolédano & Dmitriev, 1996). Thus, unless one restricts the choice of the vector $\mathbf{k}$, one would have an infinite number of phase transitions with different changes of the translational symmetry.

In this section, we restrict ourselves to representations with zero $\mathbf{k}$ vector (this situation is conveniently denoted as the Γ point). Then there is no change of translational symmetry at the transition. In this case, the group $\mathcal{F}$ is called an *equitranslational* or *translationengleiche* (*t*) *subgroup of* $\mathcal{G}$, and this change of symmetry will be called an *equitranslational symmetry descent* $\mathcal{G} \Downarrow^t \mathcal{F}$. An *equitranslational phase transition* is a transition with an equitranslational symmetry descent $\mathcal{G} \Downarrow^t \mathcal{F}$.

Any ferroic space-group-symmetry descent $\mathcal{G} \Downarrow \mathcal{F}$ uniquely defines the corresponding symmetry descent $G \Downarrow F$, where G and F are the point groups of the space groups $\mathcal{G}$ and $\mathcal{F}$, respectively. Conversely, the equitranslational subgroup $\mathcal{F}$ of a given space group $\mathcal{G}$ is uniquely determined by the point-group symmetry descent $G \Downarrow F$, where G and F are point groups of space groups $\mathcal{G}$ and $\mathcal{F}$, respectively. In other words, a point-group symmetry descent $G \Downarrow F$ defines the set of all equitranslational space-group symmetry descents $\mathcal{G} \Downarrow^t \mathcal{F}$, where $\mathcal{G}$ runs through all space groups with the point group G. All equitranslational space-group symmetry descents $\mathcal{G} \Downarrow^t \mathcal{F}$ are available in the software *GI★KoBo*-1, where more details about the equitranslational subgroups can also be found.

Irreducible and reducible representations of the parent point group G are related in a similar way to irreducible representations with vector $\mathbf{k} = \mathbf{0}$ for all space groups $\mathcal{G}$ with the point group G by a simple process called *engendering* (Jansen & Boon, 1967). The translation subgroup $\mathbf{T}_G$ of $\mathcal{G}$ is a normal subgroup and the point group G is isomorphic to a factor group $\mathcal{G}/\mathbf{T}_G$. This means that to every element $g \in G$ there correspond all elements $\{g|\mathbf{t} + \mathbf{u}_G(g)\}$ of the space group $\mathcal{G}$ with the same linear constituent g, the same non-primitive translation $\mathbf{u}_G(g)$ and any vector $\mathbf{t}$ of the translation group $\mathbf{T}_G$ (see Section 1.2.3.1). If a representation of the point group G is given by matrices $D(g)$, then the corresponding engendered representation of a space group $\mathcal{G}$ with vector $\mathbf{k} = \mathbf{0}$ assigns the same matrix $D(g)$ to all elements $\{g|\mathbf{t} + \mathbf{u}_G(g)\}$ of $\mathcal{G}$.

From this it further follows that a representation Γ_η of a point group G describes transformation properties of the primary order parameter for all equitranslational phase transitions with point-symmetry descent $G \Downarrow F$. This result is utilized in the presentation of Table 3.1.3.1.

3.1.3.2. *Property tensors at ferroic phase transitions. Tensor parameters*

The primary order parameter expresses the 'difference' between the low-symmetry and high-symmetry structures and can be, in a microscopic description, identified with spontaneous displacements of atoms (frozen in soft mode) or with an increase of order of molecular arrangement. To find a microscopic interpretation of order parameters, it is necessary to perform mode analysis (see *e.g.* Rousseau *et al.*, 1981; Aroyo & Perez-Mato, 1998), which takes into account the microscopic structure of the parent phase.

