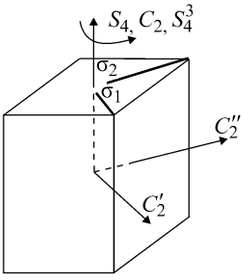

Fig. 3.1.2.9. Rotations/reflections belonging to the point group of gadolinium molybdate.

One can show, using the properties of the irreducible representations of the space groups, that the Fourier transform of the difference of densities given above is proportional to $\delta(\mathbf{K}-\mathbf{k})$, *i.e.* this Fourier transform is nonzero only for a $\mathbf{K}$ vector equal to the $\mathbf{k}$ vector indexing the order parameter. The implication of this property is that below T_c, the X-ray spectrum of the system will contain additional reflections whose locations in reciprocal space are defined by the vector of the order parameter. Experimentally, the vectors joining the Bragg spots existing in both phases to the *closest superlattice spots only appearing below* T_c are the vectors $\mathbf{k}$ defining partly the irreducible representation $\Gamma_{\mathbf{k},m}$ that specifies the symmetry properties of the order parameter.

In GMO, X-ray diffraction measurements show that superlattice spots appear below T_c at one of the four equivalent $\mathbf{k}$ vectors

$$\pm\frac{\mathbf{a}_1^* \pm \mathbf{a}_2^*}{2}. \qquad (3.1.2.28)$$

The operations of the point group $\bar{4}2m$ transform these vectors into each other. The star of $\mathbf{k}$ is therefore reduced to a single vector. On the other hand, consultation of available tables provides us with the possible representations $\tau_{\mathbf{k},m}$ necessary to construct the representation $\Gamma_{\mathbf{k},m}$ of the order parameter (the entries of the tables being the $\mathbf{k}$ vector determined and the space group G). There are three unequivalent $\tau_{\mathbf{k},m}$, which are reproduced in Table 3.1.2.2.

The ambiguity in the symmetry of the order parameter has now to be lifted. In this approach, the method is to work out for each τ_m the symmetries G of the phases that are possibly stable below T_c. One then compares the results with the observed space group below T_c, which, for GMO, is the orthorhombic space group *Pba*2.

The group F of interest is the invariance group of the density difference [equation (3.1.2.27)]. Note that this difference can be considered as a 'vector' with components η_i in the irreducible space of the order parameter. In each irreducible space, the action of the elements of G on a vector is represented by the set of matrices reproduced in Table 3.1.2.2. Let us first examine τ_1 in this table. Clearly, the matrices relative to $\{S_4|0\}$, $\{S_4^3|0\}$, $\{C_2'|\mathbf{t}\}$ and $\{C_2''|\mathbf{t}\}$ rotate by $\pi/2$ any vector of the two-dimensional space carrying the representation. These elements will not leave any direction unmoved and consequently they will not belong to F. The other elements either preserve any vector (and they then obviously belong to F) or they reverse any direction. However, in the latter case, the product of any two of these elements belongs to F.

Summarizing these remarks, we obtain a single possible group F consisting of the elements $\{E|0\}$, $\{C_2|\mathbf{a}_1\}$, $\{\sigma_1|\mathbf{t}\}$, $\{\sigma_2|\mathbf{t}+\mathbf{a}_1\}$ and by the infinite translation group generated by the vectors $(\mathbf{a}_1 \pm \mathbf{a}_2)$ and $\mathbf{a}_3$. The symbol for this space group is *Pmm*2.

A similar inspection yields for the representation τ_2 the group *Pba*2 and for τ_3 three possible groups (*P*4, *Pbm*2 and *P*2). Comparison with the experimental observation, recalled above, allows one to identify unambiguously the appropriate representation as τ_2. In conclusion, the irreducible representation associated with the order parameter of the transition in GMO can be denoted $\Gamma_{\mathbf{k},m}$. Its $\mathbf{k}$ vector is $\mathbf{k} = \pm(\mathbf{a}_1^* \pm \mathbf{a}_2^*)/2$, and its 'small representation' is $\tau_2(\mathbf{k})$. The number of components of the order parameter is two, equal to the dimension of $\Gamma_{\mathbf{k},m}$, which itself is equal to the product of the number of vectors in the star of $\mathbf{k}$ (one) and of the dimension of τ_2 (two).

3.1.2.5.2.2. *Construction of the free energy and stable states*

Denote by (η_1, η_2) the two components of the order parameter. The Landau free energy can be constructed by selecting the homogeneous polynomials of different degrees that are invariant by the *distinct* matrices of τ_2. There are four such matrices. It is easy to check that the most general form of fourth-degree polynomial invariant by the action of these four matrices is

$$F = F_0 + \frac{\alpha(T-T_c)}{2}\left(\eta_1^2+\eta_2^2\right) + \frac{\beta_1}{4}\left(\eta_1^4+\eta_2^4\right) + \frac{\beta_2}{2}\eta_1^2\eta_2^2 + \frac{\beta_3}{2}\eta_1\eta_2\left(\eta_1^2-\eta_2^2\right). \qquad (3.1.2.29)$$

A discussion of the minima of this free energy can be made according to the same method as in Section 3.1.2.3, by putting $\eta_1 = \rho\cos\theta$, $\eta_2 = \rho\sin\theta$. One then finds that, in accordance with the symmetry considerations developed in Section 3.1.2.5.2.1, there is a single possible symmetry below T_c. The equilibrium state of the system corresponds to an angle θ whose value depends on the values of the coefficients in the expansion. The modulus ρ has the standard temperature dependence $\rho \propto (T_c - T)^{1/2}$.

As in the model/example described in Section 3.1.2.2, below T_c there are several stable states having the same free energy. Indeed, one can easily check in expression (3.1.2.29) that if (η_1^0, η_2^0) is an absolute minimum of the free energy (3.1.2.29), the states $(-\eta_2^0, \eta_1^0)$, $(-\eta_1^0, \eta_2^0)$, $(-\eta_1^0, -\eta_2^0)$ are symmetry-related

Table 3.1.2.2. *Matrices defining the irreducible representations of Pba*2 *for* $\mathbf{k} = \mathbf{a}_1^* + \mathbf{a}_2^*$

	G										
	$\{E\|0\}$	$\{S_4\|0\}$	$\{C_2\|0\}$	$\{S_4^3\|0\}$	$\{\sigma_1\|\mathbf{t}\}$	$\{\sigma_2\|\mathbf{t}\}$	$\{C_2'\|\mathbf{t}\}$	$\{C_2''\|\mathbf{t}\}$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
τ_1	1 0 0 1	0 1 −1 0	−1 0 0 −1	0 −1 1 0	1 0 0 1	−1 0 0 −1	0 1 −1 0	0 −1 1 0	−1 0 0 −1	−1 0 0 −1	1 0 0 1
τ_2	1 0 0 1	0 1 −1 0	−1 0 0 −1	0 −1 1 0	−1 0 0 −1	1 0 0 1	0 −1 1 0	0 1 −1 0	−1 0 0 −1	−1 0 0 −1	1 0 0 1
τ_3	1 0 0 1	1 0 0 −1	1 0 0 1	1 0 0 −1	0 1 1 0	0 1 1 0	0 −1 1 0	0 −1 1 0	−1 0 0 −1	−1 0 0 −1	1 0 0 1