

## 3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

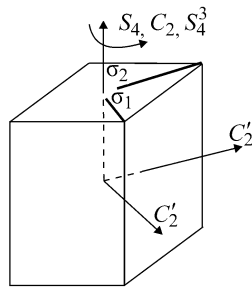


Fig. 3.1.2.9. Rotations/reflections belonging to the point group of gadolinium molybdate.

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

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

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  $\tau_m$  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  $Pba2$ .

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  $\eta_i$  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  $\tau_1$  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  $Pmm2$ .

A similar inspection yields for the representation  $\tau_2$  the group  $Pba2$  and for  $\tau_3$  three possible groups ( $P4$ ,  $Pbm2$  and  $P2$ ). Comparison with the experimental observation, recalled above, allows one to identify unambiguously the appropriate representation as  $\tau_2$ . 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  $\tau_2$  (two).

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

Denote by  $(\eta_1, \eta_2)$  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  $\tau_2$ . 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

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

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  $\theta$  whose value depends on the values of the coefficients in the expansion. The modulus  $\rho$  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  $(\eta_1^0, \eta_2^0)$  is an absolute minimum of the free energy (3.1.2.29), the states  $(-\eta_1^0, \eta_1^0)$ ,  $(-\eta_1^0, \eta_2^0)$ ,  $(-\eta_1^0, -\eta_2^0)$  are symmetry-related

 Table 3.1.2.2. Matrices defining the irreducible representations of  $Pba2$  for  $\mathbf{k} = \mathbf{a}_1^* + \mathbf{a}_2^*$ 

	$G$										
	$\{E 0\}$	$\{S_4 0\}$	$\{C_2 0\}$	$\{S_4^3 0\}$	$\{\sigma_1 \mathbf{t}\}$	$\{\sigma_2 \mathbf{t}\}$	$\{C_2' \mathbf{t}\}$	$\{C_2'' \mathbf{t}\}$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
$\tau_1$	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
$\tau_2$	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
$\tau_3$	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

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minima corresponding to the same value of the equilibrium free energy.

The intensities of the diffraction ‘superlattice’ spots, being proportional to the square of the atomic displacement  $\rho$ , vary linearly as a function of temperature. On the other hand, the diverging susceptibility associated with the order parameter is related to a rapid increase of the diffuse scattering of X-rays or neutrons at the location of the superlattice spots in reciprocal space. Hence, consistent with the macroscopic measurements, it is not related to a divergence of the dielectric susceptibility.

#### 3.1.2.5.2.3. Macroscopic behaviour of GMO

In GMO, macroscopic quantities are degrees of freedom that are distinct from the order parameter. Indeed, their symmetry properties are different, since any lattice translation will leave them invariant, while this is not the case for the order parameter (see Section 3.1.2.5.2.1). Nevertheless, certain of the macroscopic quantities behave singularly at the transition. These degrees of freedom can be decomposed, as shown in Section 3.1.2.4, as the sum of irreducible degrees of freedom. Having a symmetry different from that of the order parameter, they were neglected in the first step of the description of the phase transition. In a more detailed description, they have to be taken into account.

Let us, for instance, consider the  $P_z$  component of the dielectric polarization of GMO, as well as the  $\varepsilon$  component of the strain tensor which represents a shear in the  $xy$  plane of the crystal. The matrices in Table 3.1.2.3 recall the mode of transformation of the order-parameter components as well as those of these two quantities under the action of the  $G$  group.

We can complete the expression of the free energy of the system by adding to  $F$  in (3.1.2.29) the contributions of the preceding degrees of freedom up to the second degree (which, as will be seen, is comparable to the fourth degree used for the order parameter). The resulting expression is provided by (3.1.2.30) below, in which we have neglected a bilinear term in  $P_z$  and  $\varepsilon$  as this term does not change the qualitative result we want to establish.

$$F_1 = F + \frac{b}{2}P_z^2 + \frac{c}{2}\varepsilon^2 + \delta_1 P_z(\eta_1^2 - \eta_2^2) + \delta_2 \varepsilon(\eta_1^2 - \eta_2^2), \quad (3.1.2.30)$$

where  $F$  is provided by equation (3.1.2.29). At equilibrium, the derivatives of  $F_1$  with respect to  $P_z$  and  $\varepsilon$  vanish. These conditions yield

$$P_z = -\frac{\delta_1}{b}(\eta_1^2 - \eta_2^2); \quad \varepsilon = -\frac{\delta_2}{c}(\eta_1^2 - \eta_2^2). \quad (3.1.2.31)$$

As stressed in Section 3.1.2.5.2.2, the equilibrium direction in the order-parameter space corresponds to the trivial  $\theta = 0$  angle. Hence  $(\eta_1^2 - \eta_2^2) \neq 0$  below  $T_c$ , resulting in the fact that nonzero values of  $P_z$  and  $\varepsilon$  will onset below the transition temperature. Besides, the form (3.1.2.31) indicates that the two macroscopic quantities considered, which are proportional to the square of the order parameter, are expected to vary linearly as a function of temperature below  $T_c$ . Note that terms such as  $P_z^2$  are of the same order of magnitude as fourth-degree terms of the order parameter.

We can also determine the behaviour of the dielectric susceptibility  $\chi$ , by calculating the variations of the equilibrium

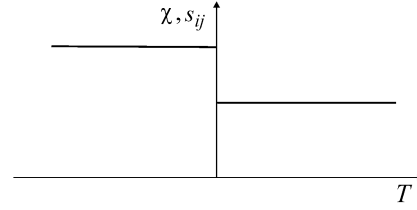


Fig. 3.1.2.10. Temperature dependence of the macroscopic susceptibility (or elastic compliance,  $s_{ij}$ ) in gadolinium molybdate. Compare with the ‘normal’ behaviour in Fig. 3.1.2.5(b).

value of  $P_z$  as a function of an applied electric field  $\mathbf{E}$  parallel to the polarization. We proceed as in Section 3.1.2.2, and minimize the potential  $G_1 = (F_1 - P_z E)$  with respect to the order parameter and to the polarization. In order to obtain the qualitative behaviour of  $\chi$ , we simplify the free energy by considering a single component of the order parameter. We also neglect the shear strain component  $\varepsilon$ . The set of simplified equations

$$\chi = \frac{\partial P_z}{\partial E} | E = 0; \quad bP_z + \delta\eta^2 = E \quad (3.1.2.32)$$

$$\frac{\partial F_1}{\partial E} = \eta \left\{ \alpha(T - T_c) + \left( \beta - \frac{2\delta_1^2}{b} \right) \eta^2 + \frac{2\delta_1}{b} E \right\}$$

yields the following expression of the susceptibility:

$$\chi = \frac{1}{b} \quad \text{for } T > T_c \quad \text{and} \quad \chi = \frac{1}{b} + \frac{2\delta_1^2}{b(\beta - 2\delta_1^2/b)} \quad \text{for } T < T_c. \quad (3.1.2.33)$$

We find an upward step of the dielectric susceptibility on cooling. Likewise, consideration of the ‘elastic’ susceptibility relative to the shear strain component  $\varepsilon$  would determine an upward step of the elastic compliance (Fig. 3.1.2.10). The more usually measured elastic constant, which is the inverse of the compliance, undergoes a downward step on cooling.

We have seen in the preceding paragraph that the low-symmetry phase of gadolinium molybdate possesses four equally stable states differing by the values of the order-parameter components. Equation (3.1.2.31) shows that two of the states are associated with the same sign of the polarization  $P_z$  or of the shear strain  $\varepsilon$ , while the two other states possess opposite values of  $P_z$  and  $\varepsilon$ . According to the definitions given in Section 3.1.1, gadolinium molybdate belongs to the category of ferroelectrics as well as to that of ferroelastics.

The example of GMO clearly shows that the ferroic classification is less informative than the one based on the order-parameter symmetry. The latter determines the full symmetry change (orientational and translational), while the former only specifies the orientational symmetry change. On the other hand, the ferroic classification is not informative about the physical behaviour as a function of temperature. Thus, the model ferroelectric in Section 3.1.2.2 has a diverging dielectric susceptibility at  $T_c$ , while a GMO-type ferroelectric keeps a finite susceptibility. The ferroic classification has nevertheless the advantage of specifying the nature of the macroscopic quantities that are expected to behave anomalously at the transition, and are therefore worth measuring.

Table 3.1.2.3. Action of the generators of  $Pba2$  on the order parameter and on the polarization and strain components

	$E$	$S_4$	$\sigma_1$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$
$\eta_1$	1 0	0 1	-1 0	-1 0	-1 0	1 0
$\eta_2$	0 1	-1 0	0 -1	0 -1	0 -1	0 1
$P_z$	1	-1	1	1	1	1
$\varepsilon$	1	-1	1	1	1	1