

## 3.1. STRUCTURAL PHASE TRANSITIONS

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

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

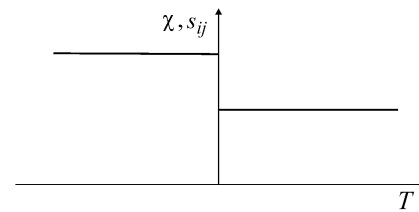


Fig. 3.1.2.10. Temperature dependence of the macroscopic susceptibility (or elastic compliance,  $s_{ij}$ ) in gadolinium molybdate. Compare with the ‘normal’ behaviour in Fig. 3.1.2.5(b).

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

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

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

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.