1.5. MAGNETIC PROPERTIES

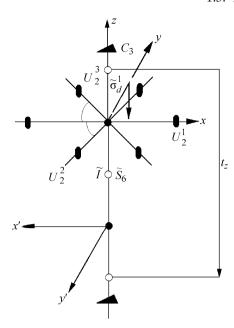


Fig. 1.5.3.1. Arrangement of the symmetry elements of the group $\widetilde{\boldsymbol{D}}_{3d}^6$.

group \mathcal{T} in the ordered state does not contain primed elements. Therefore, there is no need to consider the whole crystal space group \mathcal{G} . It will suffice to consider the cosets of \mathcal{T} in \mathcal{G} . Such a coset consists of all elements of \mathcal{G} that differ only by a translation. From each coset, a representative with minimum translative component is chosen. We denote a set of such representatives by \mathcal{G} ; it can be made into a group by defining AB $(A, B \in \mathcal{G})$ as the representative of the coset that contains AB. Obviously, \mathcal{G} is then isomorphic to the factor group \mathcal{G}/\mathcal{T} and therefore to the point group \mathcal{P} of \mathcal{G} .

Once more, we should like to stress that to construct the magnetic structures and the magnetic groups of a given crystal it is not enough to consider only the point group of the crystal, but it is necessary to perform the analysis with the help of its space group in the paramagnetic state or the corresponding group of coset representatives. An example of such an analysis will be given in the following section.

1.5.3.1. Magnetic structures in rhombohedral crystals

Following Dzyaloshinskii (1957*a*), we consider crystals belonging to the crystallographic space group $D_{3d}^6 = R\bar{3}c$. To this group belong α -Fe₂O₃ and the carbonates of Mn²⁺, Co²⁺ and Ni²⁺. Weak ferromagnetism was first observed in these materials.

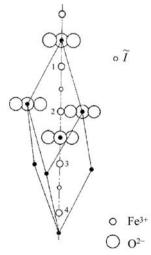


Fig. 1.5.3.2. Crystallographic structure of transition-metal oxides of the type $\alpha\text{-Fe}_2O_3$.

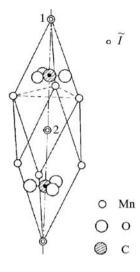


Fig. 1.5.3.3. Crystallographic structure of transition-metal carbonates of the type ${\rm MnCO}_3$.

 ${\rm Cr_2O_3}$, in which the magnetoelectric effect was discovered, also belongs to this group. The magnetic ordering in these materials occurs without change of the unit cell.

The representatives of the cosets $\boldsymbol{D}_{3d}^{6}/T$ form the group $\boldsymbol{\widetilde{D}}_{3d}^{6}$. Its symmetry operations are shown in Fig. 1.5.3.1. Directed along the z axis is the threefold axis C_3 and the sixfold roto-inversion axis \tilde{S}_6 . Three twofold axes U_2 run through the points \bullet at right angles to the z axis. One of these axes is directed along the x axis. Arranged normal to each of the U_2 axes are three glide planes $\tilde{\sigma}_d$. The y axis is directed along one of these planes. The centre of inversion \tilde{I} is located at the point \circ , lying on the z axis halfway between two points \bullet . The sign means that the corresponding operation is accompanied by a translation along the z axis through half the period of the crystal (\tilde{I} means that the inversion centre is shifted from the point \bullet to the point \circ). In Fig. 1.5.3.1, the elementary period of translation along the z axis is marked by t_z . Thus the crystallographic group \tilde{D}_{3d}^{6} has the following elements:

$$E, 2C_3, 3U_2, \tilde{I}, 3\tilde{\sigma}_d, 2\tilde{S}_6 \quad \{1, \pm 3_z, 3(2_{\perp}), \tilde{\tilde{\mathbf{1}}}, 3(c = \tilde{\boldsymbol{m}}), \pm \tilde{\tilde{\mathbf{3}}}_z\}.$$

$$(1.5.3.1)$$

In two types of crystals, considered below, the magnetic ions are arranged on the z axis. If we place the magnetic ion at point 1 located between points \circ and \bullet (see Fig. 1.5.3.2), then using symmetry operations (1.5.3.1) we obtain three additional positions for other magnetic ions (points 2, 3, 4). Thus, the elementary cell will contain four magnetic ions. This is the structure of oxides of trivalent ions of iron and chromium (Fe₂O₃, Cr₂O₃). The structure of these oxides is shown in Fig. 1.5.3.2. If the positions of the magnetic ions coincide with the positions of the inversion centre \circ , we obtain the structure of the carbonates of the transition metals (MnCO₃, CoCO₃, NiCO₃, FeCO₃), which is shown in Fig. 1.5.3.3.

Evidently, the formation of a magnetic structure in the crystal does not result in the appearance of new elements of symmetry. The magnetic groups of magnetically ordered crystals may lack some elements contained in the crystallographic group and some of the remaining elements may happen to be multiplied by R (primed). Let us find the groups of symmetry that correspond to all possible collinear magnetic structures in rhombohedral crystals with four magnetic ions in the elementary cell. We shall assume that the magnetic moments are located at the points of the ion positions 1–4; they will be marked μ_{α} . The symmetry transformations cannot change the length of the vectors of the magnetic moments but they can change the direction of these vectors and interchange the positions of the sites $1 \leftrightarrow 2$, $3 \leftrightarrow 4$