Section 2.13 Magnetic Symmetry Groups

Not all empirically observed point symmetry groups of physical crystals coincide with one of the 32 crystallographic point groups. In particular it has been found that the crystallographic point groups do not adequately explain the magnetic properties of crystals. To understand this, we consider a model of a magnetic crystal as a periodic distribution of atoms. The magnetic property of the crystal is introduced by the assumption that some of the atoms are spinning. The spin axes are parallel to one another although some of the atoms spin in a clockwise direction about their spin axes (spin up) and others spin in a counterclockwise direction (spin down). A geometrical symmetry operation of such a crystal may not be a physical symmetry since the geometrical symmetry may map a spinning atom onto an atom with the opposite spin orientation. To describe the symmetries of such crystals we enlarge the group $O(3)$ of possible point symmetry operations by adding to it the operator $\underline{R}$ which acts geometrically as the identity except that it reverses the spin orientation of each atom. The operator $\underline{R}$ is sometimes called the time reversal operator since when the direction of time is reversed the spin orientation of an atom is also reversed.

Since $\underline{R}^2 = \underline{E}$, the operator $\underline{R}$ generates a cyclic group of order 2, $R = \{\underline{E}, \underline{R}\}$. Furthermore the extended symmetry group $O'(3)$ generated by $\underline{R}$ and $O(3)$ is the direct product

$$O'(3) = O(3) \times R = \{O(3), \underline{R}\,O(3)\}$$

The elements $\underline{g}$ of $O'(3)$ are either of the form $\underline{g} = \underline{O}$ or $\underline{g} = \underline{R}\underline{O} = \underline{O}\underline{R}$ $\underline{O} \in O(3)$, depending on which of the two $O(3)$-cosets of $O'(3)$ they belong to. It is clear that $\underline{g}$ can be a point symmetry of some magnetic crystal only if the orthogonal part $\underline{O}$ of $\underline{g}$ satisfies the crystallographic restriction. A <u>magnetic symmetry group</u> G is a finite subgroup of $O'(3)$ such that the orthogonal part of each $\underline{g} \in G$ satisfies the crystallographic restriction. In so far as our model of a magnetic crystal has validity it follows that the point symmetry group of a magnetic crystal must be one of the magnetic symmetry groups. In particular, the point symmetry group of a magnetic crystal must be finite. Furthermore, it can be shown that for every magnetic symmetry group G there exists a model of a magnetic crystal with G as its point symmetry group.

The mathematical procedure for deriving magnetic symmetry groups from the 32 crystallographic point groups is almost identical to the procedure for obtaining point groups of the second kind from point groups of the first kind. In essence the answer is given by theorem 2.6 and we merely need to translate this theorem so as to apply to the new groups and operators introduced here.

Let G be a magnetic symmetry group and consider the homomorphism $\mu: G \to R$ defined by $\mu(\underline{g}) = \underline{R}$ if $\underline{g} = \underline{R}\underline{O}$ and $\mu(\underline{g}) = \underline{E}$ if $\underline{g} = \underline{O}$ for some $\underline{O} \in O(3)$. Let K be the kernel of μ. Clearly $K = G \cap O(3)$ There are two possibilities: Either 1) $G = K$ or 2) K is a subgroup of G with index 2.

If the first possibility occurs then $G = K$ is a crystallographic point group. We know that there are 32 conjugacy classes of such groups. These groups correspond to magnetic crystals in which every atom is spinning with the same spin orientation.

If the second possibility occurs then

$$G = \{K, \underline{g}_0 K\}$$

where $g_0 \in G$ is any element of the form $\underline{R}\underline{Q}$, $\underline{Q} \in O(3)$. Thus, half of the elements of G belong to the crystallographic point group K and the other half belong to $O'(3)$ but not to $O(3)$. Again there are two possibilities: Either 1) $\underline{R} \in G$ or 2) $\underline{R} \notin G$.

In the first case $G = \{K, \underline{R}K = K'\}$ so G is just the direct product of K and R. Clearly, there are 32 conjugacy classes of such groups G, since there are 32 classes of crystallographic point groups K. Since $\underline{R} \in G$, such a symmetry group corresponds to a nonmagnetic crystal, i.e., a crystal in which no atom is spinning.

In the second and most complicated case, $R \notin G$, we proceed by copying the corresponding part of the proof of theorem 2.6. Thus, the group

(13.1) $$K^+ = \{\underline{R}\underline{g} : \underline{g} \in G, \underline{g} \notin K\}$$

can be shown to have the following properties:

1) $K^+ \subsetneq O(3)$
2) $K^+ \cap K = \phi$
3) $n(K^+) = n(K)$.

Furthermore, the crystallographic point group $G^+ = K \cup K^+$ is isomorphic to G. This isomorphism acts like the identity on K and maps $\underline{g} \in K'$ into $\underline{R}\underline{g} \in K^+$. Conversely, given any pair of crystallographic point groups G^+, K with K a subgroup of index 2 in G^+, there exists a magnetic symmetry group of the third kind $G = K \cup K'$, isomorphic to G^+ and related to K^+ by (13.1).

It follows that to find all conjugacy classes of magnetic symmetry groups of the third kind it is enough to determine all pairs of crystallographic point groups $\{G^+, K\}$ with K a subgroup of index 2 in G^+. (Two pairs $\{G^+, K_1\}, \{G^+, K_2\}$ are identified if K_1 and K_2 are conjugate subgroups of G^+.) A straightforward though tedious examination of the subgroup relations among the crystallographic point groups shows that there are 58 such pairs. (See [ ], page .)

We conclude that in addition to the 32 nonmagnetic point groups there are $32 + 58 = 90$ magnetic point groups.

The magnetic symmetry groups are also called color groups. In this interpretation we think of a periodic distribution of (spinless) atoms in which each atom is colored either black or white. The operator $\underline{R}$ changes white atoms to black and black to white. The color groups correspond to the possible symmetry groups of these colored patterns.

We could extend this type of analysis by allowing more than two colors or by allowing the atoms to have both color and spin. Of course, the enumeration of possible symmetry groups becomes increasingly difficult as more symmetry operations are added to $O(3)$.

The magnetic point groups describe the observed macroscopic symmetries of magnetic crystals. To describe the microscopic symmetries of these crystals it is necessary to compute the possible magnetic space groups. Mathematically this amounts to the determination of all subgroups G of $E'(3) = E(3) \times R$, such that $G \cap E(3)$ is a space group. Clearly, there are 230 such groups (the nonmagnetic space groups) of the form $H \times R$ where H is an ordinary space group and 230 magnetic space groups of the form $G = H$ where H is an ordinary space group. Finally, there are 1191 magnetic space groups G such that $G \neq G \cap E(3)$ and $\underline{R} \notin G$. The derivation of these groups is left as an excercise for the reader.