Digital Computer Laboratory
Massachusetts Institute of Technology
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLVII

To: Group 63 Engineers

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In order to obtain an understanding of the spinel structure of ferrites a short discussion of some of the basic crystal structures will be given at this meeting.

One of the most important features of crystals is their symmetry and one method of defining this feature is in terms of the axis of symmetry. On rotating a crystal about a line or axis, the crystal structure may present identical patterns at regular intervals of rotation. When this happens the axis of rotation is an axis of symmetry and the number of times that the same pattern appears per 360° rotation is called the numerical value of symmetry of that axis. This may be better understood in terms of a particular example. If a cubic crystal is rotated about an axis a, as shown in figure 95, it is evident that after being rotated through a quarter turn (90°) it would appear unchanged. On rotating through 360° there would therefore be four positions at which the crystal would appear identical, and the cube is said to exhibit a four-fold axis of symmetry about a. Similarly, the cube exhibits a three-fold axis of symmetry about b.

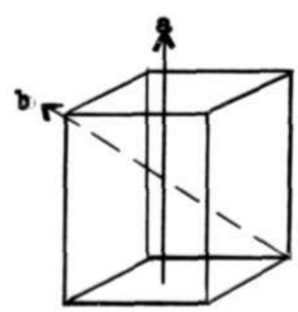


FIGURE 95

CUBIC CRYSTAL WITH AXES OF SYMMETRY SHOWN

Since the spinel structure forms octahedrons and tetrahedrons, let us look at these forms. The cube and octahedron bear a very simple relationship with each other; if a cube is planed away at the corners it passes through a series of forms into a regular octahedron. This is indicated in figure 96*.

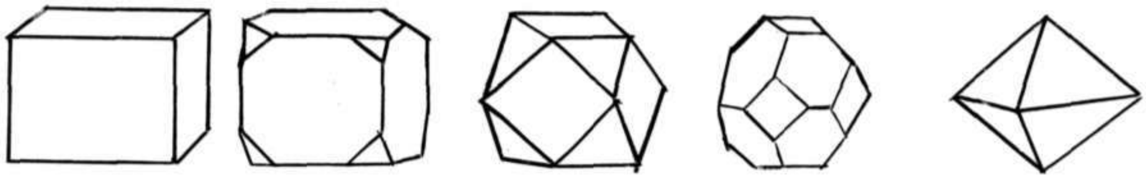
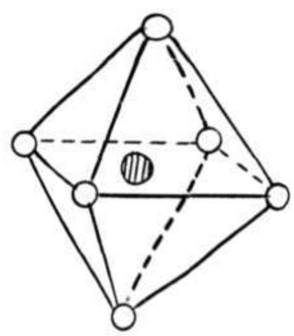


FIGURE 96

GRADUAL DERIVATION OF OCTAHEDRON FROM CUBE

Figure 96 demonstrates that the cube and the octahedron have the same axes of symmetry; they are said to belong to the same crystallographic classification. All crystal forms shown in figure 96 may occur in nature, and are classified as cubic crystals.



In spinel lattice

FIGURE 97

Octahedron Configuration

The octahedron, shown as the last diagram of figure 96 is reproduced in enlarged form in figure 97.

The tetrahedron can similarly be derived from the cubic structure by planing away a cube at four of the eight corners, as shown in figure 98. Its symmetry is lower than that of the cube, but rotation through 90° about an axis bisecting a pair of opposite, mutually perpendicular edges followed by a 180° rotation of the axis itself still reproduces the original pattern.

* T. V. Barker, "The Study of Crystals", Thomas Murby and Co., London, 24 (1930).

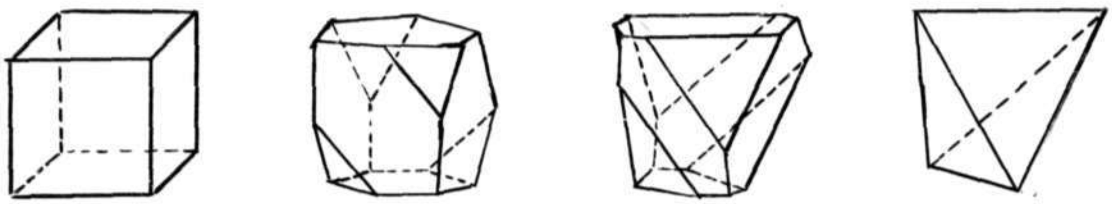


FIGURE 98

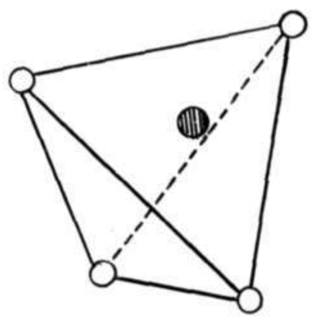


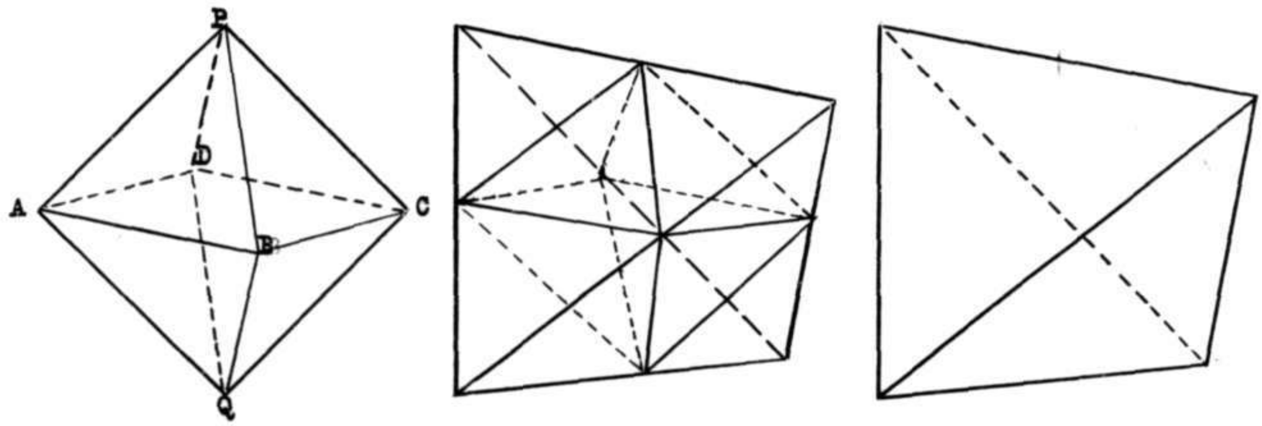
FIGURE 99

Ferrites have the general formula $M^{++}O^{=}Fe_2^{+++}O_3^{=}$ where the M^{++} represents a divalent metal such as Fe^{++}, Ni^{++}, Mg^{++} etc. They have a spinel structure. The oxygen ions form a face centered cubic structure while the metal ions arrange themselves at the center of octahedrons and tetrahedrons, surrounded by four and six oxygen ions respectively. Twice as many octahedral sites as tetrahedral sites are occupied in a unit cell. This is shown more clearly in figures 97 and 99.

The metallic ions in the tetrahedron are said to occupy the A sites, while those in the octahedron are said to be in the B sites. In general, the larger ions tend to go into the A sites, but other factors may alter this arrangement. The divalent ion is usually larger than the trivalent ion, so there is a strong tendency for the divalent ion to occupy the A (tetrahedron) sites. There are twice as many trivalent ions as divalent ions, and these go to the B (octahedron) sites. This ionic arrangement is known as the normal spinel structure.

In the inverse spinel structure the divalent ions occupy the B sites. Since there are twice as many B sites as divalent ions, the divalent ions can occupy only half the B sites. The remaining half of the B sites and all the A sites are then occupied by the trivalent ions. All ferrites which display high magnetization properties are of this inverse spinel type.

Figure 100 shows the relation between tetrahedral and octahedral sites. Figure 100 a) denotes an octahedron; its eight faces are described by the terms "upper" and "lower", "front" and "back", "left hand" and "right hand". Thus face ABP is the upper front, face QBC the lower right hand face. When four tetrahedra are attached to the upper left and right hand and the lower front and back faces, as shown in figure 100 b), a tetrahedron is formed, as shown in figure 100 c). The spinel structure does have a tetrahedral symmetry; figure 100 b) shows the relative positions of tetrahedral and octahedral sites.



a) b) c)

FIGURE 100

Signed ____________________
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Approved ____________________
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