8

Ferroelectric Crystals

A *ferroelectric* crystal is defined as a crystal which exhibits a spontaneous electric dipole moment; in other words, a crystal for which even in the absence of an applied electric field the center of positive charge does not coincide with the center of negative charge. It can be shown that it is a necessary, but not sufficient, condition for ferroelectricity that the crystal lack a center of symmetry. All ferroelectric will be piezoelectric, but not all piezoelectric will be ferroelectric (e.g. quartz). The occurrence of ferroelectricity is generally interpreted to be the result of a polarization catastrophe as treated in the preceding chapter; we discuss this at greater length below.

After a ferroelectric crystal is polarized in a given direction, the action of the polarization outside the crystal is gradually neutralized by the collection on the crystal surface of free charges from the atmosphere and by conduction within the crystal. In a number of substances the polarization appears to have a very high coercive force— the direction of the spontaneous polarization may not be changed by an electric field of the maximum intensity which it is possible to apply without causing electrical breakdown of the crystal. We are often able to observe the spontaneous moment in these substances only when they are heated, as raising the temperature changes the value of the polarization. These crystals, such as tourmaline, which develop an observable spontaneous electric moment only on heating are called *pyroelectric*, while crystals with a lower coercive force, such that the direction of the spontaneous moment can be altered by an electric field, are called *ferroelectric* and often have very high dielectric constants.

ELECTRETS

There is another class of substances known as *electrets*, discovered by Eguchi in 1925, which may display "permanent" electric moments. Electrets are produced by the solidification of mixtures of certain organic waxes in a strong electric field. Some of the wax molecules

carry permanent dipole moments; they are oriented by the electric field, and frozen in their orientation by the solidification. The moments produced in this way may persist for several years, yet it is generally believed that the polarized state of an electret is only metastable, and that the stable state would be unpolarized. We shall not consider electrets here; for a review of their properties the reader is referred to a paper by Gutmann.[1]

CLASSIFICATION OF FERROELECTRIC CRYSTALS

We list in Table 8.1 some of the crystals which are commonly considered ferroelectric, along with the transition (Curie) temperature T_c at which the crystal changes from the low temperature polarized state to the high temperature unpolarized state. Rochelle salt has both an upper and a lower Curie point, between which the crystal is ferroelectric. The maximum value of the spontaneous polarization P_s is listed where known. It is useful in converting units to recall that $P(\text{esu})$ is obtained by multiplying $P(\mu\text{coul}/\text{cm}^2)$ by 3×10^3 and by multiplying $P(\text{coul}/\text{m}^2)$ by 3×10^5.

The crystals considered in the table may be classified into several quite natural groups. First there is Rochelle salt[2] and the associated isomorphous salts. Rochelle salt is a quite complicated crystal, and little progress has been made toward understanding its behavior on a microscopic basis, although Mueller[3] and others have formulated a phenomenological theory which correlates a number of experimental facts. It seems possible that the ferroelectric behavior of Rochelle salt is connected intimately with the action of the molecules of water of hydration in the crystal. This is suggested by the observation that the substitution of D_2O for H_2O changes the range in which the crystal is ferroelectric from 41.7°C for the ordinary Rochelle salt to 57°C for the deuterated salt,[4] which is quite a large effect. It may be noted, however, that the observed spontaneous polarization 800 esu is considerably less than the polarization which would result from the parallel orientation of all the water molecules; there are 1.52×10^{22} of these per cubic centimeter, and the moment per molecule is 1.83×10^{-18} esu (in the vapor), corresponding to a polarization of 28,000 esu, while the observed spontaneous polarization is only 800 esu.

[1] F. Gutmann, Revs. Modern Phys. 20, 457 (1948).

[2] Discovered by J. Valasek, Phys. Rev. 17, 475 (1921); for summary of properties see H. Mueller, Ann. N.Y. Acad. Sci. 40, 321 (1940).

[3] H. Mueller, Phys. Rev. 57, 829 (1940); 58, 565 (1940).

[4] Holden, Kobzarev, Mason, and Morgan, Phys. Rev. 56, 378 (1939); J. Hablützel, Helv. Phys. Acta. 12, 489 (1939).

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Vasily Yanchilin

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