American Mineralogist
Vol. 57, pp. 439–444 (1972)

DIRECT OBSERVATION OF STACKING FAULTS IN THE ZEOLITE ERIONITE

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Abstract

Transmission electron microscopy of thin erionite rods show transverse fringes. These contrast lines are due to interference from the rotation of a layer in the erionite structure as well as to the junction of erionite and offretite regions within a crystal.

The confusion regarding the identity and structures of the zeolite offretite and erionite was resolved by Bennett and Gard (1967). Using electron diffraction they found crystals in a sample from Mt. Simiouse, Montbrison, Loire, France which were not identical with erionite from a number of other locations and from Durkee, Oregon. This is contrary to previous findings by Hey and Fejer (1962) using X-ray powder diffraction.

The aluminosilicate framework of erionite, space group $P6_3/mmc$, was first determined by Staples and Gard (1959) and is shown in Figures 1 and 2. This framework may be described as consisting of columns of cancrinite cages and hexagonal prisms linked together as shown in Figures 1 and 2. The cancrinite cages in every second layer are rotated through 60° giving an *AB* stacking sequence of cancrinite cages.

The framework, space group $P\bar{6}m2$, proposed by Bennett and Gard (1967) for offretite is related to that of erionite. If the stacking sequence of the cancrinite layers is *AA*, with no rotation, the offretite structure is described as shown in Figures 3 and 4. The twelve-membered ring channels parallel to the *c* parameter are not blocked as in the case of erionite.

Since offretite has a *c* parameter half that for erionite all the odd *l* reflections are missing. By changing the stacking sequence other structures are described similar to those in the gmelinite-chabazite series (Kokotailo and Lawton, 1964). In addition to the ordered stacking of layers in a well-defined manner as in erionite, errors in this regular sequence of layers known as stacking faults may occur. Random distribution of these stacking faults occur in the ordered sequence of the crystal as a whole (not a unit cell). This random distribution of stacking faults must be distinguished from the orderly arrangement of stacking that gives rise to polytypism. The presence

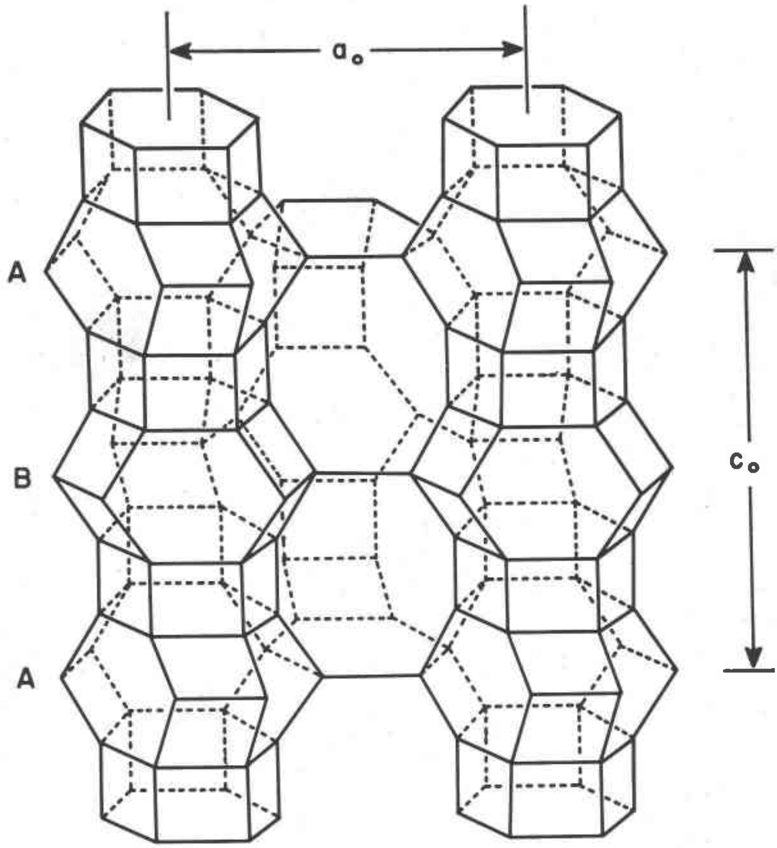

FIG. 1. View of erionite framework. Arrangement of cancrinite and erionite cages in columns parallel to c-axis. In Figures 1–4, the junction of the lines represent Si, Al; the oxygen atoms and cations are not shown.

of random disorder of layers or random stacking of layers has the effect of giving rise to X-ray reflections corresponding to $d_{001} = \infty$ or $c^* = 0$. This causes X-ray diffraction and electron diffraction photographs to show diffuse streaks along the reciprocal lattice rows parallel to c^*. Bennett and Gard (1967) observed this streaking in the case of offretite and Linde T. The ratio of the intensity of the diffuse scattering to that of the regular reflections is a measure of the amount of disorder in the crystal lattice (Jagodzinski, 1954). If some random stacking is superimposed on a structure with periodic stacking such as erionite the powder X-ray patterns are essentially the same, with the sharp odd l lines superimposed on broad lines with low intensity.

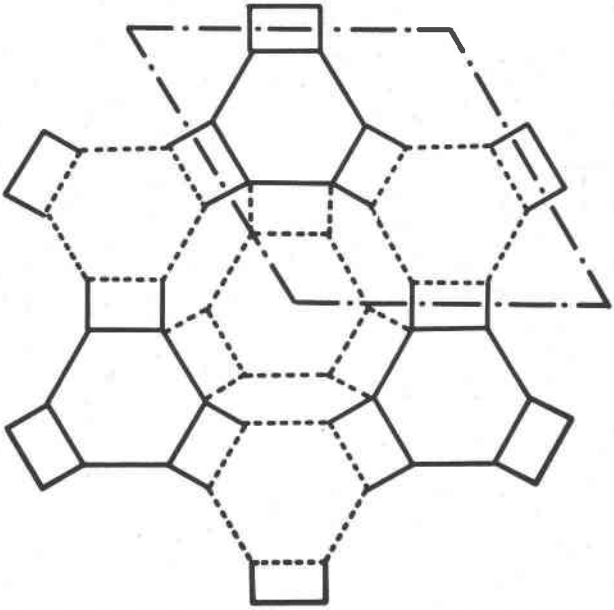

FIG. 2. 001 projection of erionite framework. $a = 13.2\text{Å}$ is indicated by the side of the parallelogram. The channel is a twelve-membered ring.

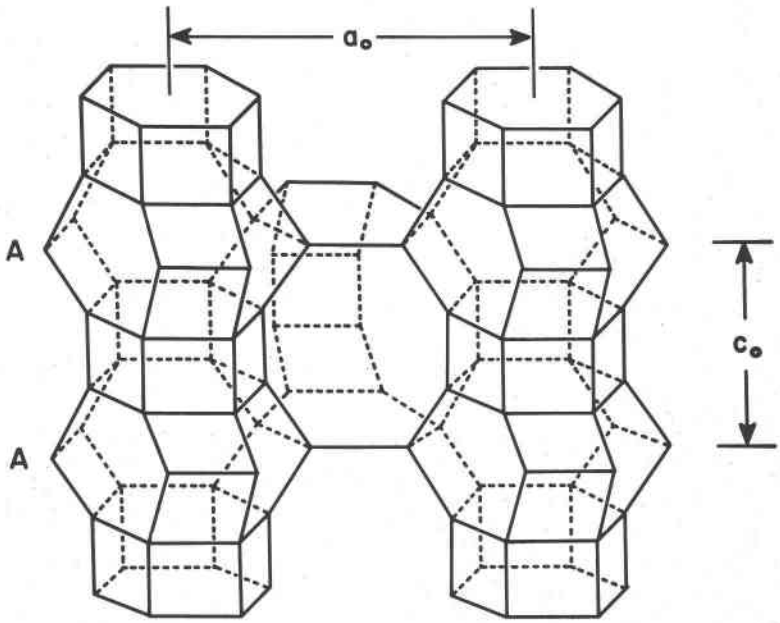

FIG. 3. View of offretite framework. Arrangement of cancrinite and gmelinite cages in columns parallel to c-axis.

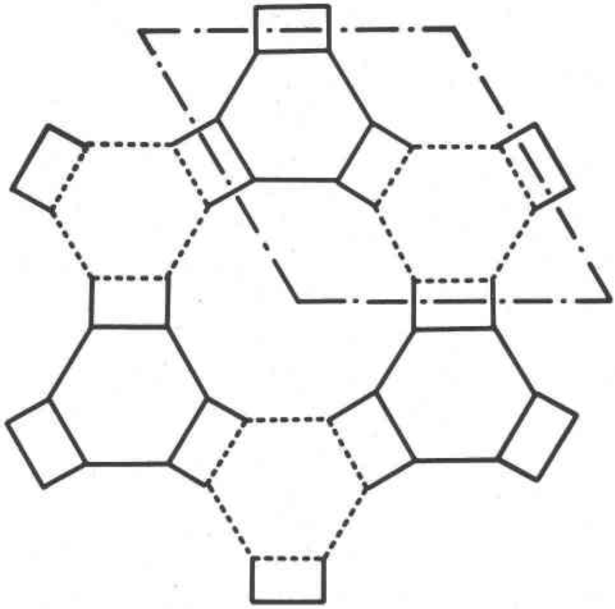

FIG. 4. 001 projection of the offretite framework. $a = 13.2\text{Å}$ is indicated by the side of the parallelogram. The channel is a twelve-membered ring.

This slight change in the wings at the base of the odd l lines is difficult to detect.

Phase contrast effects due to defects in thin metal crystals have been seen and studied by transmission electron microscopy (Bollman, 1956; Whelan *et al.*, 1956; Whelan, 1958; Swann and Nutting, 1960; Tomlinson, 1958; Heidenreich, 1949). It is possible to get resolutions of the order of 5 Å; thus details of very fine structure may be studied. Stacking faults in crystals are characterized in electron micrographs by contrast lines or fringes running parallel to the intersection of the fault with the surfaces. The stacking fault divides the crystal and the parts on each side of the stacking fault are displaced relative to each other by an amount equal to the partial displacement. In the case of erionite this displacement is obtained by rotation of the layer. This displacement causes a phase difference between the electrons scattered on either side of the fault and results in a corresponding change in the intensity of the diffracted beam. This phase difference may also be due to the junction of erionite and offretite regions.

Crystals of erionite from Pershing County, Nevada, were examined by transmission electron microscopy. These crystals showed contrast fringes as shown in Figure 5. The rod-like crystals, with the c axis

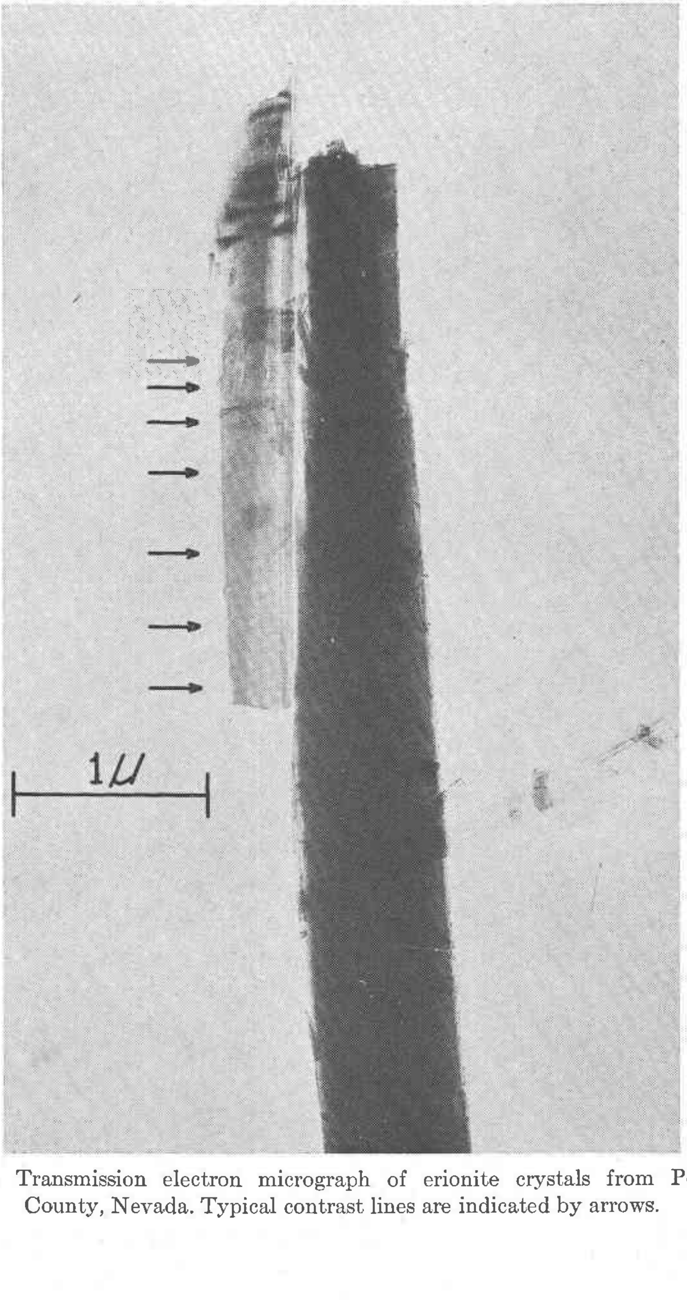

FIG. 5. Transmission electron micrograph of erionite crystals from Pershing County, Nevada. Typical contrast lines are indicated by arrows.

parallel to the axis of the fiber exhibiting contrast lines perpendicular to the axis of the fiber, had a diameter of less than 5000 Å. The distance between contrast lines, which is also the distance between stacking faults, is as small as 150 Å, about ten unit cells. The sharp contrast lines indicate that the planes of the stacking faults are perpendicular to the *c*-axis.

Thus we have found that some crystals of the zeolite erionite are not completely ordered but have some superimposed random stacking as was previously shown for zeolites offretite and Linde T (Bennett and Gard, 1967). This random stacking in erionite is difficult to detect with powder X-ray diffraction but can be shown for individual small crystals with transmission electron microscopy.

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Manuscript received, August 30, 1971; accepted for publication, October 13, 1971.