Direct Evidence to support the Proposal that ZSM-23 is a Recurrently Twinned Variant of Zeolite Theta-1

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High resolution electron microscopy reveals the presence of [110] twin boundaries in the zeolite Theta-1; this reinforces the view that ZSM-23 is a recurrently twinned variant of Theta-1.

Theta-1 is a highly siliceous zeolite (Si : Al ratio *ca.* 60 : 1) possessing a framework structure that has unidimensional ten-ring channel system [Figure 1(a)] oriented parallel to the [001] axis of the orthorhombic unit cell (space group $Cmc2_1$, a = 13.836, b = 17.415, c = 5.042 Å). (It is now recognized that ZSM-22 has the same framework topology as Theta-1.) If,

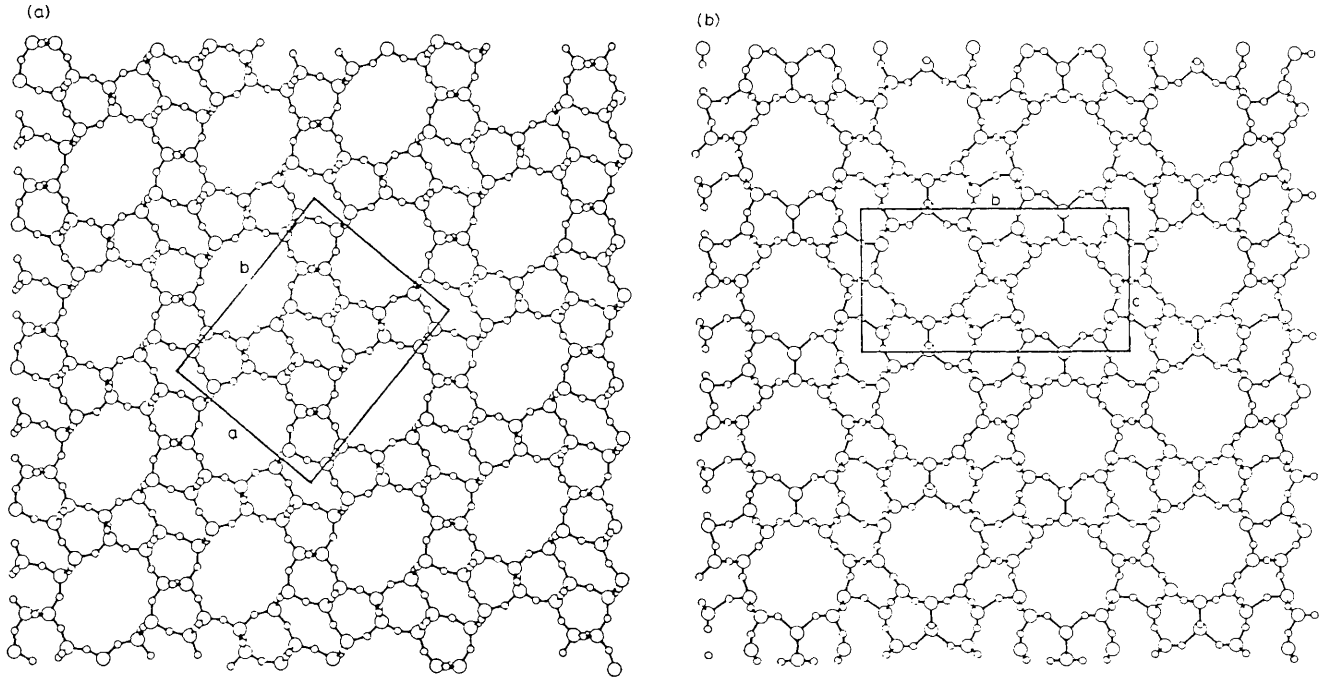

Figure 1. Schematic diagrams illustrating the similarity between the framework of Theta-1 (a) and ZSM-23 (b). Both structures are represented in equivalent projections ([001] for Theta-1 and [100] for ZSM-23) to show the large ten-membered channel systems. Recurrent twinning in Theta-1 on [110] planes [see Figures 2(b) and 3(b)] generates the ZSM-23 structure (mirror planes are signified by σ). The respective unit cell axes a, b and b, c are indicated.

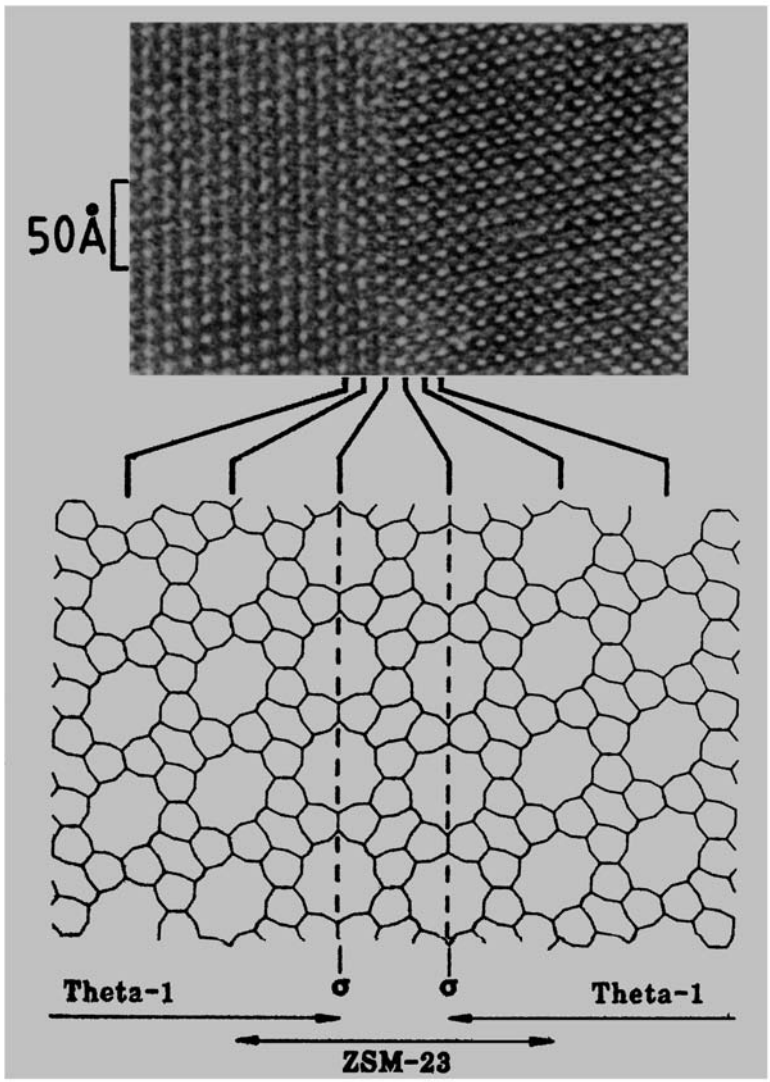

Figure 2. (a) Electron micrograph showing a single [110] twin boundary in a crystal of Theta-1 viewed along the [001] zone axis. (b) Schematic illustration of the framework structure at this boundary. σ indicates the position of the mirror plane.

however, the Theta-1 structure is twinned successively on all planes that lie parallel to the [110] planes and bisect the ten-membered rings, a new structure is generated [Figure 1(b)]; and there is good evidence,[1] both from *X*-ray and electron diffraction studies, that this recurrently twinned variant of Theta-1 constitutes the structure of ZSM-23 (orthorhombic, spacegroup *Pmmn* or *P2imn*, $a = 5.2$, $b = 21.7$, $c = 11.2$ Å). (The crystallographic axes of ZSM-23 have been chosen so that the channels are aligned in the [100] direction.)

High resolution electron microscopy (h.r.e.m.) enables two-dimensional projections of framework structures of zeolites to be directly recorded, and good structural images of Theta-1 and other zeolites have been reported earlier.[2] The practical difficulty of observing the typically c-elongated rod shaped crystals down a [001] zone-axis was overcome by embedding the sample in epoxy resin and preparing appropriate thin sections by ultra-microtomy. To improve the resistance of the zeolite to electron-beam damage, samples of Theta-1 were subjected to prior hydrothermal dealumination.[3]

Figure 2 shows an example of a single [110] twin, and Figure 3 an example of two successive twins in Theta-1. Schematic representations of these twin boundaries are also shown.

The observation that the Theta-1 structure does indeed possess some tendency to twinning lends further credence to the proposition that ZSM-23 is the fully recurrent twinned variant of Theta-1, prepared under different conditions.[4] Indeed, the two successive twins shown in Figure 3 can be considered as a short section ZSM-23 contained within a host matrix of Theta-1.

It has been shown elsewhere[5,6] that, in certain families of zeolites, there are common structural blocks and that individual members are related to others within a family by some appropriate symmetry operator. This is the case in the pentasils ZSM-5 and ZSM-11, the former consisting of

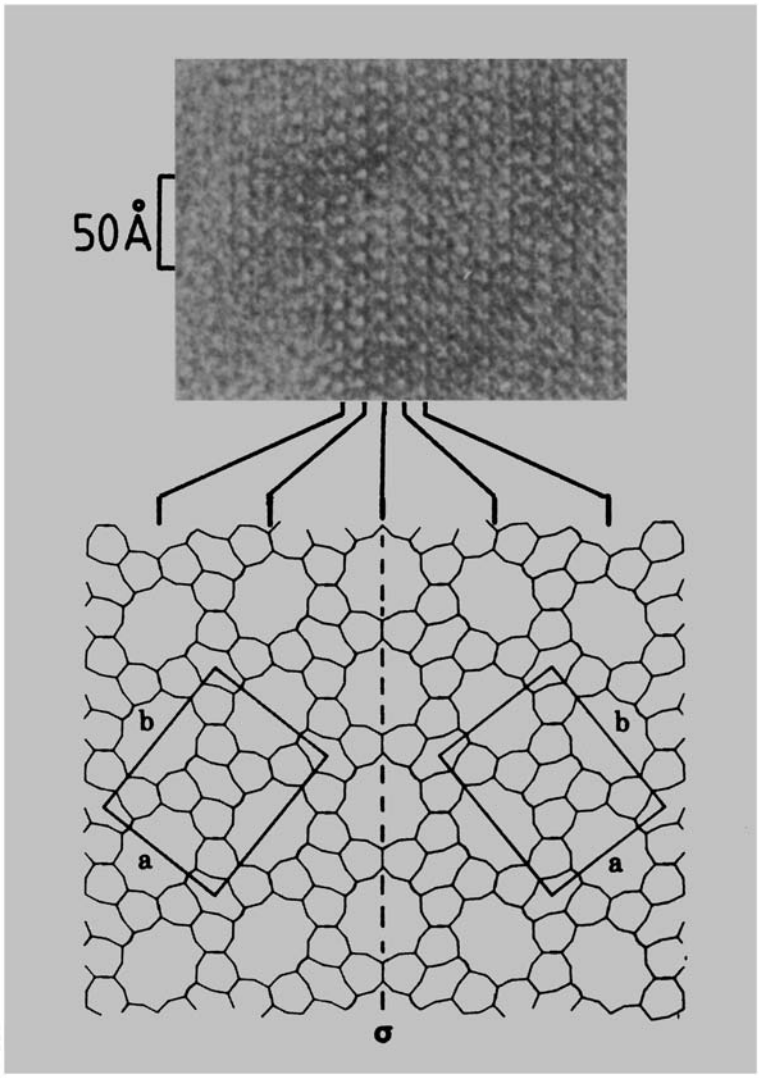

Figure 3. (a) Electron micrograph showing two successive [110] twin boundaries in a crystal of Theta-1. (b) Schematic illustration of the framework structure in this region. The arrangement can be considered as the insertion of a narrow strip of ZSM-23 within the host matrix of Theta-1.

recurrent inversion, the latter recurrent mirror operations.[6–8] In the ABC-6 family of zeolites, planar sheets of hexagonally arranged six-membered rings are stacked so that neighbouring sheets are connected in one of three possible ways (designated A, B or C). Depending on the sequence of connections, a large group of related structures can be formed (*e.g.* AABAAC is erionite, AAB is offretite, ABC is sodalite, AABB is gmelinite, *etc.*). This work confirms the structural kinship, proposed earlier,[1a] between Theta-1 and ZSM-23.

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