A New Type of Stacking Fault in Zeolites: Presence of a Coincidence Boundary ($\sqrt{13}.\sqrt{13}\,R32.2°$ Superstructure) Perpendicular to the Tunnel Direction in Zeolite L

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Real-space imaging has revealed a tendency for zeolite-L to form well-defined coincidence boundaries by rotation of 32.2° of one part of a crystal with respect to another; the generated interface has a superlattice repeat of $\sqrt{13}$ times that of the original, and the number of continuous tunnels intersecting unit area of interface is *ca.* 8% of that in the unfaulted crystal.

Zeolites possess pores or cages in the size range 3—10 Å, the precise value being governed by the particular framework structure and, to a lesser degree, by the size and co-ordination of the exchangeable cation. The wide use[1,2] of zeolites as ion-exchangers, molecular sieve adsorbents, and shape-selective or other types of catalysts takes advantage of the existence of these accessible cavities, which permit both ready ingress of reactants and egress of products. But many industrially important zeolitic preparations display features which suggest that transport of molecular or ionic species through the highly porous solids is, to a greater or lesser degree, hindered. In addition the product distribution in reactions catalysed by certain zeolites implies that there are structural irregularities in these solids. The occurrence of stacking faults perpendicular to the tunnels in mordenite or offretite, or the presence of so-called detrital impurities in these tunnels, has been postulated to account for the diminished diffusivity of reactant and product species.[1] In shape-selective zeolites such as ZSM-5, intergrowths of closely similar structures (*e.g.* ZSM-11) have been proposed[3] and recently identified[4,5] by high-resolution electron microscopy (H.R.E.M.) and optical diffractometry.

In zeolite-L (idealised formula $Na_3K_6Al_9Si_{27}O_{72}.21H_2O$; space group *P6/mmm*, $a_O = 18.4$, $c_O = 7.5$ Å) the plan view of the framework structure is as shown[6] in Figure 1. In projection along [00.1] the real space image is, typically, as seen in Figure

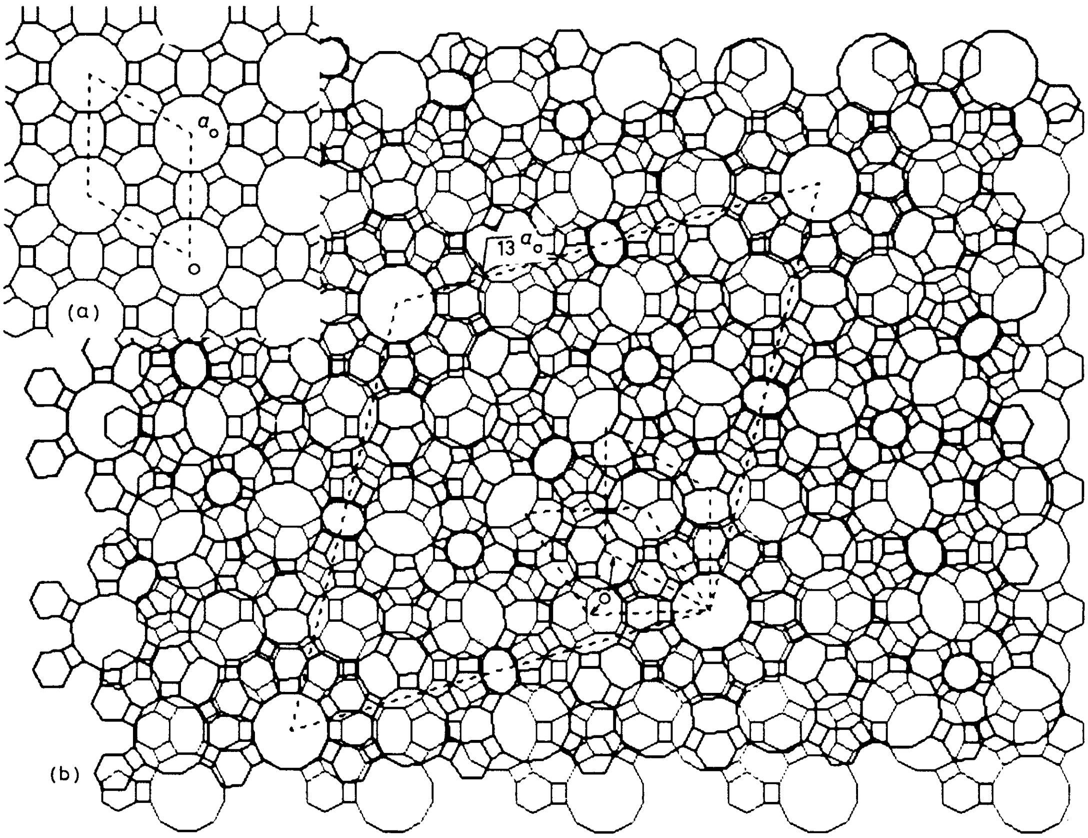

Figure 1. (a) Plan view (down [00.1]) of a single sheet of the zeolite-L structure. Each vertex denotes a tetrahedral (T ≡ Si or Al) site joined to other such sites *via* oxygens (not shown). (b) Plan view of the coincidence boundary ($\sqrt{13}.\sqrt{13}\,R32.2°$) generated by rotating one part of the crystal of zeolite-L, about [00.1], by 32.2° with respect to another. The hexagonal repeat mesh now exceeds the dimension of the original hexagonal mesh (a_O = 18.4 Å) by $\sqrt{13}$. The evidence for this superlattice is shown in Figure 2.

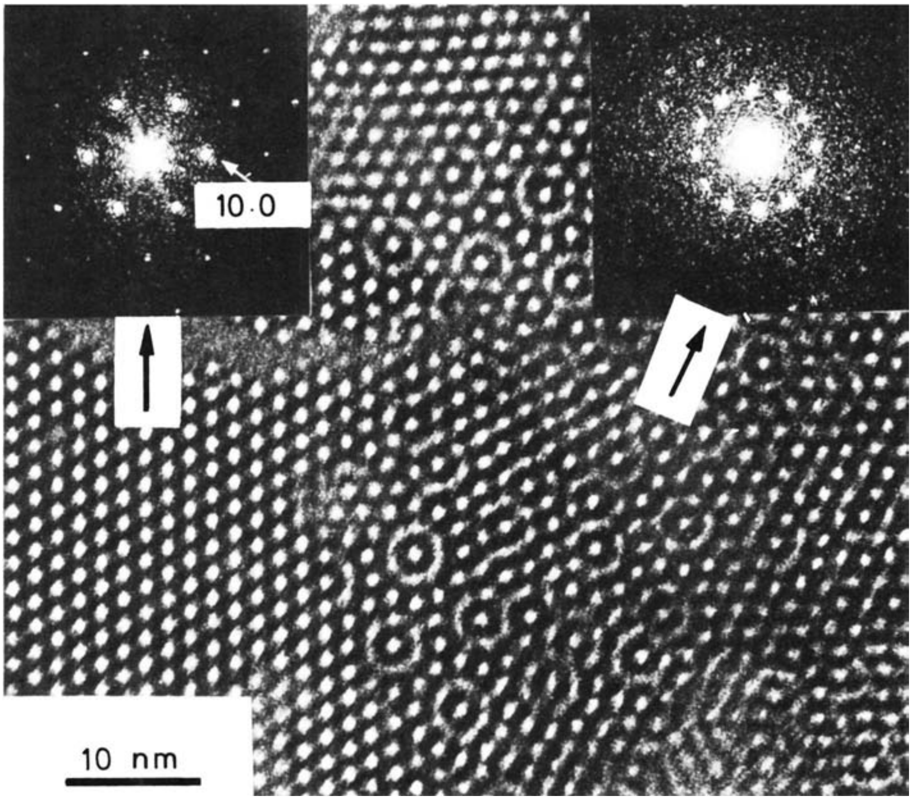

Figure 2. High-resolution electron microscopic image of partially dealuminated zeolite-L crystal. Left portion of the image shows the arrangement of main tunnels in zeolite-L; the optical diffractogram obtained from this region (top left) shows the six {10.0} type reflections. The image on the right shows the $\sqrt{13}.\sqrt{13}$ $R32.2°$ superlattice repeats which tend to occur in domains. The corresponding optical diffractogram (top right) shows the twelve {10.0} type reflections from the coincidence of tunnels. See Figure 1(b) for interpretive drawing.

2. Our detailed studies,[7] by H.R.E.M.,[8] of partially dealuminated zeolite-L have brought to light a new type of planar fault which has not hitherto been discussed in the structural chemistry of zeolites (Figures 1 and 2). The schematic drawing (Figure 1) represents the plan view, down [00.1], of the interface created within a crystal of zeolite-L when one part is rotated about [00.1] by 32.2°. Such a rotation sets up at the interface a coincidence boundary in which the repeat distances are $\sqrt{13}$ times the unit cell repeat, a_O, of the normal structure. A rotation (R) of 32.2° is read off from the micrograph, and a rotation of close to 30° is also discernible in the diffraction pattern. From the high resolution micrograph it can be seen that there is some tendency for such boundaries to occur in domains.

It is not yet known how frequently these coincidence boundaries occur in zeolite-L (or in other zeolites), and whether the concentration of these non-equilibrium faults can be boosted or suppressed by appropriate change in preparative procedure or of exchangeable cation. What is apparent, however, is that the diffusivity of guest species is likely to be considerably diminished by the presence of this type of coincidence boundary. Note that, if there is only one such boundary per crystallite of zeolite at the interface, the number of primary tunnels (nominal diameter 7.1 Å per unit area), is reduced to *ca.* 8% of the number in the unfaulted crystal.

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