change from 10.8 to 9.48 Å, so making the interpillar gas comparable with the size of adsorbing molecules. Thus in (Hg-diamsar)–montmorillonite I the interpillar distances are big enough (15 Å) that the size of the adsorbate does not influence the specific surface appreciably. The surface area measured by hydrogen adsorption is then almost equal to that measured by nitrogen. Adsorption of hydrogen may also be influenced by the charge on the pillar's amino groups. If clays have pillars with diprotonated amino groups, the $S_{\text{hyd}}/S_{\text{nit}}$ ratio is much smaller. In general the $S_{\text{hyd}}/S_{\text{nit}}$ ratio increases from 1.02 to 4.56 with a decrease in interpillar distances (*d*) from 15 Å in (Hg-diamsar)–montmorillonite I to 9.48 Å in (Hg-diamsar)–fluorhectorite III.

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Role of High-Resolution Electron Microscopy in the Identification and Characterization of New Crystalline, Microporous Materials: "Reading Off" the Structure and Symmetry Elements of Pentasil Molecular Sieves

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The advantages of establishing the structure of new microporous, crystalline solids such as zeolites, porosils, and aluminum phosphates by using high-resolution electron microscopy are assessed and illustrated with reference to ZSM-5. In particular, it is shown that the structure and symmetry elements of this member of the pentasil family may, by comparison of computed and observed (at 200 and 1000 keV) images, be "read off" directly in real space. The technique is likely to be of especial value in characterizing many new structures, including those that, at the sub-unit-cell level, are composed of recurrent intergrowths of other structures.

The first synthesis of a zeolite with no natural counterpart was reported over 40 years ago.[1] In the intervening time more than 20 such zeolitic molecular sieves have been synthesized. In addition, apart from the naturally occurring and synthetic aluminosilicate molecular sieves, two other types of families of crystalline, microporous materials, called porosils and clathrasils,[2] have appeared on the scene. The porosils, through which molecules of small hydrocarbons may freely migrate, are the silica end-products of zeolites such as ZSM-5 and ZSM-11 (that is, silicalite I and silicalite II, respectively, the structures of which are shown in Figure 1). But they also encompass silica structures that may not have a zeolitic (aluminosilicate) counterpart. The clathrasils, on the other hand, typefied by naturally occurring melanophlogite and the recently synthesized nanosil and dodecasil 3C, possess intracrystalline cages the openings of which are too small to permit migration from cage to cage of the molecules that are trapped within these cavities as templates during synthesis.

Whereas the family of porosils continues to grow, its size is already dwarfed by yet another class of microcrystalline, microporous molecular sieves termed ALPOs, SAPOs, and MeALPOs—aluminum phosphates, silicon aluminum phosphates, and metal aluminum phosphates, respectively—first reported by workers at the Union Carbide Laboratories.[3,4] These consist of three-dimensional, four-connected (corner-sharing) tetrahedra of AlO_4 and PO_4 in the case of the ALPOs. The structures of some members of this large family are the same as their zeolitic (aluminosilicate and synthesized gallosilicate or aluminogermanate) counterparts, but others within the family are quite novel. Some 20 or so elements of the periodic table, including Li, Be, Ga, Si, As, Zn, Co, and Mg, can be accommodated in the framework of these porous aluminum phosphates, yielding a broad range of molecular sieves.

The majority of all these microporous solids can seldom be induced to grow as single crystals suitable for X-ray structural analysis, so that alternative, somewhat unconventional and certainly multipronged methods of structural analysis have to be utilized. These methods[5-7] entail the use of powder (X-ray and neutron) diffraction, solid-state NMR, and a range of other spectroscopies as well as high-resolution electron microscopy. Once a plausible

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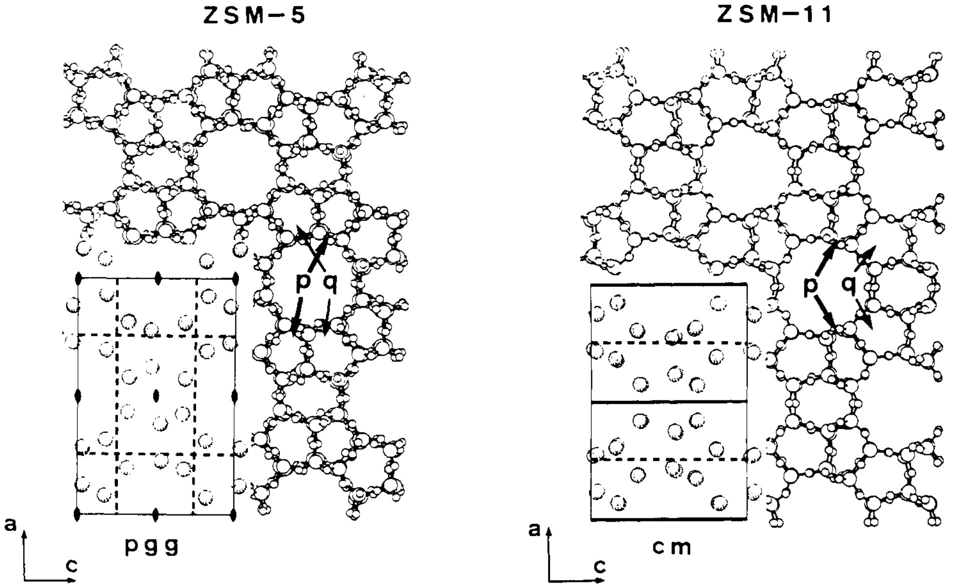

Figure 1. Framework structures of ZSM-5 (left) and ZSM-11 (right) projected along the [010] direction. Large circles denote tetrahedrally bonded atoms (Si and Al); small circles the bridging oxygens. In the lower left of each drawing are shown (tetrahedral atoms only) the symmetry elements. The symbols p and q refer to the smaller and larger five-membered rings, respectively (see also ref 28).

structural model can be postulated subsequent test procedures, including the so-called distance-least-squares (DLS) method,[8] are invoked.

Role of High-Resolution Electron Microscopy

One of the key contributions made by high-resolution electron microscopy to inorganic chemistry generally[9-11] is that new structures have been uncovered by its application. This is true not only of zeolites but also of many other types of solids such as complex oxide catalysts and warm superconductors.[19-21] High-resolution electron microscopy (HREM) has also brought to light the relatively widespread occurrence of intergrowths at the nanoscale level.[13,22,23] Such intergrowths are one of the causes that make conventional single-crystal X-ray structural procedures inapplicable for many zeolites. Intergrowths at the sub-unit-cell level are also now recognized[24] to be a fundamental feature of the architecture of large classes of inorganic solids. In particular HREM has recently shown[25] that the new zeolite ECR-1 is composed of recurrent sub-unit-cell sheets of the well-known zeolites mordenite and mazzite. Likewise HREM showns that zeolite β,[15] the structure of which had for long defied elucidation, is composed of intimate intergrowths of two polymorphic subunits called polymorphs A and B. Recurrent intergrowths, as shown by the early use of HREM, are a frequent occurrence in the structural chemistry of zeolites.[26,27]

All this demonstrates that HREM has an important role to play in identifying and characterizing the structures of new zeolites, porosils, and ALPOs. The technique, is essence, entails computing an image from a possible model of the structure—the electron microscopic image itself often providing vital clues for the construction of the model—and comparing that image with the experimentally observed one. In the nature of the comparison it is important to compute and observe the image under a variety of adjustable experimental conditions such as specimen thickness and extent of defocus of the objective lens. With the continued improvement in performance of electron microscopes—point-to-point resolutions of better than 1.7 Å are now achievable in certain commercial ones—HREM will undoubtably figure prominently in characterizing the new materials of the future since it provides a real-space projected image of the structure in question down a required crystallographic direction. For microporous solids, especially, it will soon become possible, with procedures such as those described below, to "read off" structural repeat units and to discern the symmetry elements that make up the structure. It transpires that, owing to the strong interaction between electrons and solids, it is often easier to establish symmetry relationships from images recorded from thick samples, where multiple scattering of electrons is pronounced, or by employing a range of focusing conditions.

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Experimental Section

Crystals of the ZSM-5 were gently crushed with an agate mortar under acetone and collected on a microgrid. They were examined by using two electron microscopes each fitted with a top-entry goniometer: a JEOL-200CX (coefficient of spherical aberration, C_s, of 0.8 mm, accelerating voltage 200 kV) and a JEOL-1000 (C_s of 11 mm, accelerating voltage 1000 kV). The theoretical point-to-point resolution limits of these two micrographs are, respectively, 2.4 and 2.0 Å.

As the ZSM-5 crystals, like those of most zeolites, are rather beam-sensitive,[22,26,27] high-resolution electron microscope images can be produced only if care is exercised to reduce the electron dose as low as possible. The procedure is, initially, to focus the specimen at much lower brightness than that required to record an image on a photographic emulsion. (Several factors are of relevance here, including the grain size and sensitivity of the film and the mechanical stability of the stage.) As neither of the two microscopes used here possess a special "minimum dose" attachment, a so-called dark-field mode of exposure was employed during the time-consuming processes of film advance and focus change, and then the electron beam was deflected immediately to the region of interest.

Fuji and Mitsubishi films were used, respectively, for the 200- and 1000-kV microscopes, and images were usually recorded at a magnification of normally less than 200 000.

Real-Space Study of the Structure, Symmetry, Elements, and Intergrowths of ZSM-5

We know from our earlier work[22,27] using HREM that specimens of ZSM-5, a well-known catalyst and the most widely studied member of the so-called pentasil family, tend to contain thin, intergrown sheets of another pentasil, ZSM-11. Each of these solids, as shown in Figure 1, possesses large 10-ring[28] pores of diameter ca. 5.5 Å. The space groups are *Pnma* for ZSM-[29] and $I\bar{4}m2$ for ZSM-11.[30] Structurally these pentasils have identical sheets parallel to (100), and the framework of ZSM-5 is produced by inversion of these sheets, whereas in ZSM-11 successive sheets are related to one another by mirror symmetry. ZSM-5 and ZSM-11 are the end members of an infinite series of intergrown structures.[31] The key question we pose in this investigation is whether, equipped with sufficiently powerful HREM, we can "see" directly the structures and symmetry elements of the archetype of the pentasil family, ZSM-5.

From their supposed structures, with their two distinct sizes of five-rings, designated p (smaller) and q (larger), the preferred direction for electron microscopic imaging of both ZSM-5 and ZSM-11 is along [010], parallel to the direction of the 10-ring channels.

For the space group *Pnma* the extinction conditions for $h0l$ reflections are $h00$ with h odd and $00l$ with l odd. Figure 2 shows a typical diffraction pattern of ZSM-5 with the electron beam along [010]. We note that reflections such as 100, 300, ..., and 001, 003, ..., are observed owing to multiple scattering. There are two types of structure factors for ZSM-5 for $h0l$ reflections, $F(h0l)$:

$$F(h0l) = F(\bar{h}0\bar{l}) = F(\bar{h}0l) = F(h0\bar{l}) \qquad \text{for } h + l = 2n$$

$$F(h0l) = F(\bar{h}0\bar{l}) = -F(\bar{h}0l) = -F(h0\bar{l}) \qquad \text{for } h + l = 2n + 1$$

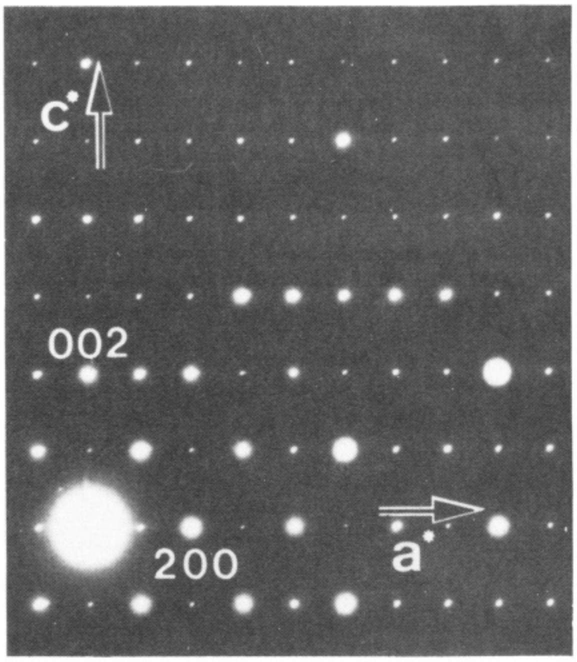

Figure 2. Typical electron diffraction pattern of ZSM-5 down the [010] zone axis.

Now the HREM image in the [010] projection is related to the projected potential density $V(x,z)$, which is proportional to the Fourier sum of the structure factors $F(h0l)$ for electrons. The first equation above gives the relation

$$V(x,z) = V(-x,-z) = V(-x,z) = V(x,-z)$$

that is, mirror symmetries for the planes $x = 0$ and $z = 0$. On the other hand, the second equation gives

$$V(x,z) = V(-x,-z) = -V(-x,z) = -V(x,-z)$$

which signifies 2-fold symmetry at the origin ($x = z = 0$). An acutal HREM image is the sum of both the terms above and, consequently, it should exhibit 2-fold symmetry. The second series is therefore important to enable us to have the true, 2-fold symmetry. But since the structure of ZSM-5 is such that the deviation from mirror symmetry is slight, it follows that only a few of the structure factors, within the range of easily attainable resolution limit, notably 102 (d = 6.35 Å), 203 (d = 4.08 Å), and 104 (d = 3.3 Å), are of significant magnitude. It is therefore essential that, in the imaging, these particular reflections must be picked up if we are to observe directly the symmetry elements of the structure in the real-space image.

Figure 3 consists of a set of simulated images,[32] the computations having been carried out at several values of specimen thickness and objective lens defocus. (The negative sign denotes overfocus). Note that in some of these images the 2-fold symmetry elements stand out very clearly.

The HREM image corresponding to the diffraction pattern of Figure 2 is shown in Figure 4. The sudden change of contrast apparent in this micrograph arises from a change in thickness. Figure 5 is an enlarged image of the thinner region of the specimen shown in Figure 4. This image, which clearly reveals the two different kinds of 5-ring apertures as well as the larger (10-ring) ones, is well matched (see inset) to the computed image for a thickness of 50 Å and a defocus setting, Δf, of 580 Å. It is immediately apparent from this optimal image that there are

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(28) A "10-ring" means an aperture with 10 tetrahedrally bonded atoms (either silicon or aluminium in this case) lining the opening. As there are bridging oxygens, in reality a 10-ring aperture consists of 20 atoms, 10 of which are oxygens.

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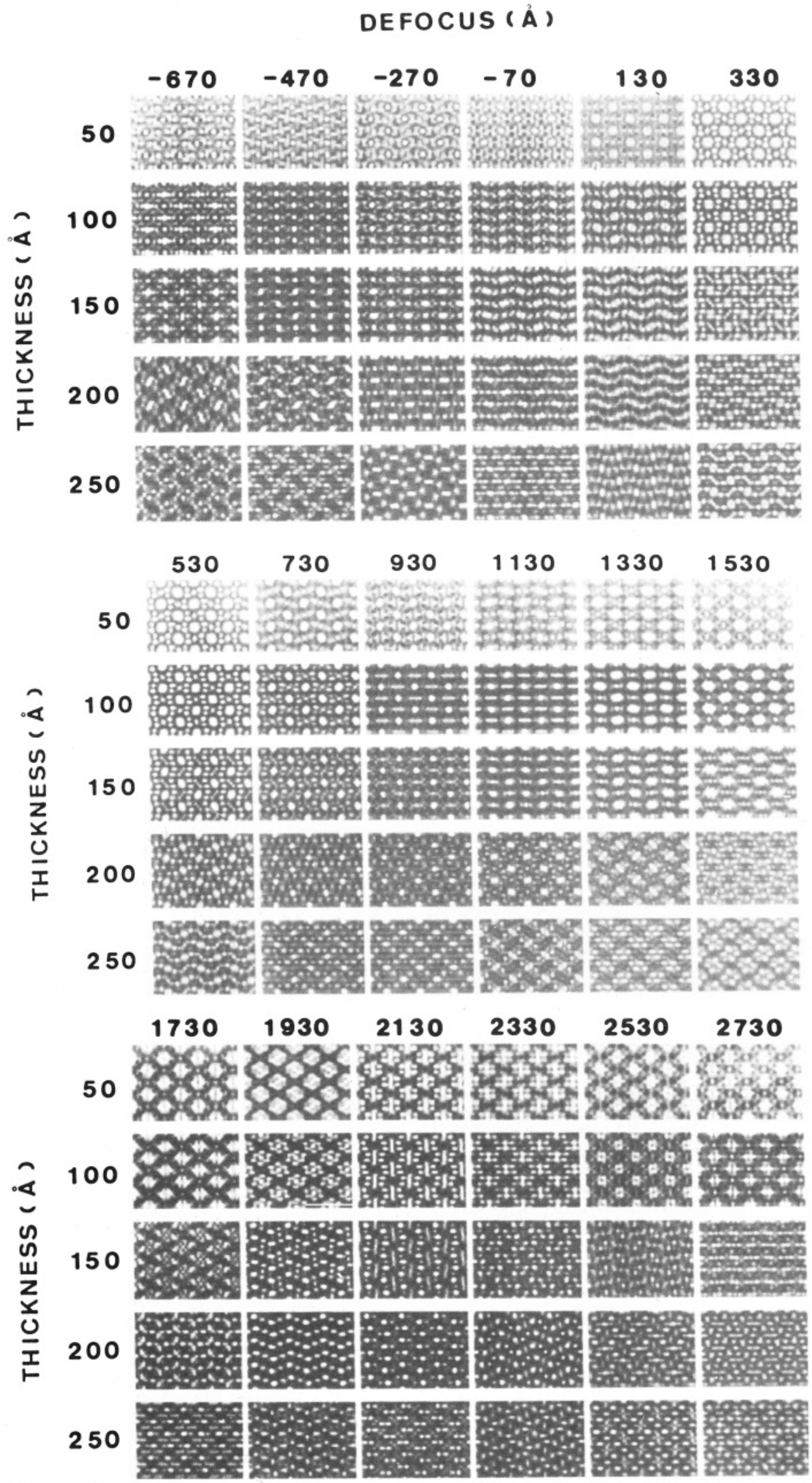

Figure 3. Computed images (derived from the multislice procedure) for ZSM for the JEOL 200CX electron microscope with C_s = 0.8 mm and objective aperture size (corresponding to the nominal resolution) of 2.8 Å.

2-fold axes at the positions marked by stars. There is no evidence that mirror planes (as would exist in ZSM-11) pass through the main channels. In the micrograph for the region straddling the thinner and thicker specimens (Figure 6), taken at an underfocus condition, it can be seen that it is somewhat easier to read off the symmetry of the structure from the thicker rather than the thinner regions (compare Figure 5). The images here, judging from the

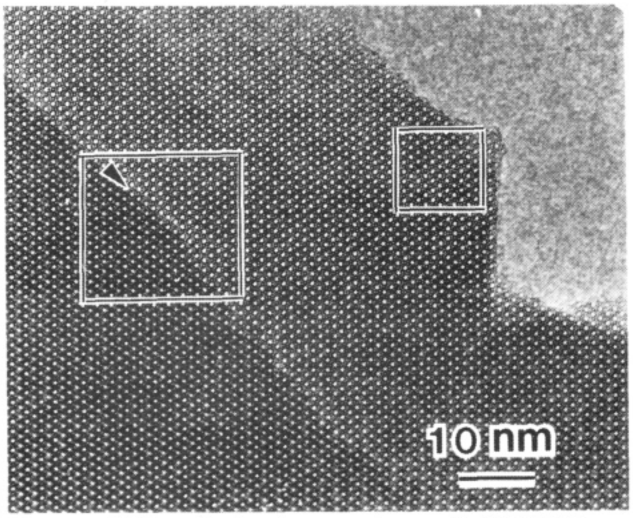

Figure 4. High-resolution electron microscopic (HREM) image (at 200 keV) of a ZSM-5 specimen, across which there is a step (arrow). The rectangular regions are shown enlarged in Figures 5 and 6.

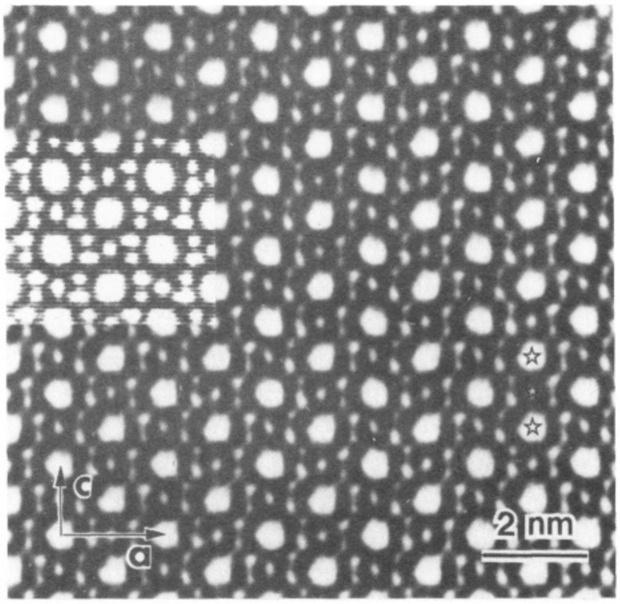

Figure 5. HREM image of the thinner region shown in Figure 4 along with (inset) the computed image for a thickness of 50 Å and a lens defocus seting of 580 Å. Note that the two distinct sizes of five-membered rings (p and q of Figure 1) are readily distinguished. The symmetry elements (center of inversion at the 10- and 6-membered rings) are also readily seen. Inversion symmetry is treated as 2-fold symmetry in the projection as indicated in the inset of Figure 1, left.

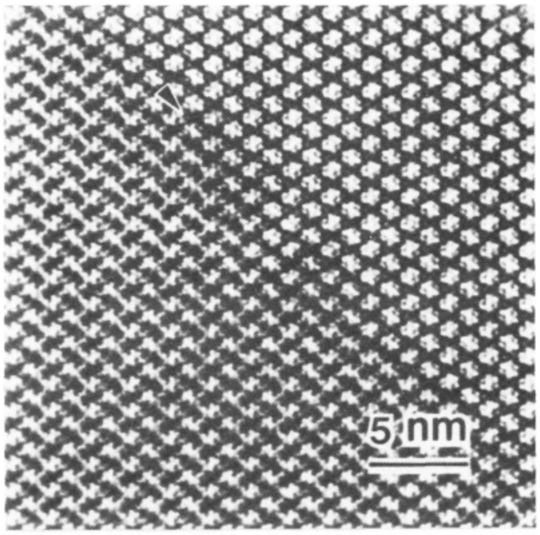

Figure 6. Enlarged HREM image of the thicker region shown in Figure 4, along with a portion of the thinner region. Note the step running from top left to bottom right.

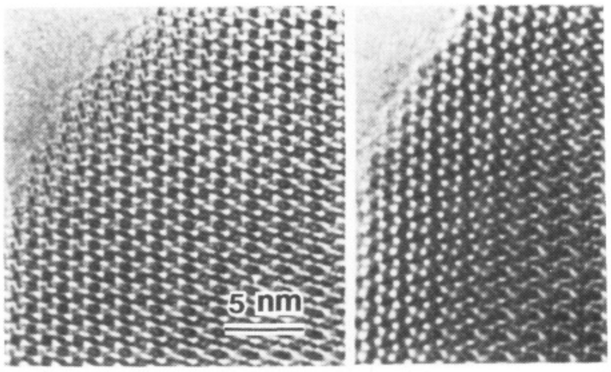

Figure 7. HREM images of ZSM-5 taken with a 1000-keV microscope. In these two images the 2-fold symmetry elements are clearly visible.

computer simulations (Figure 3), refer to a defocus $\Delta f = +1930$ Å and thicknesses of 50 and 150 Å (with a slight beam tilt). When images are recorded at 1000 keV (Figure 7), the 2-fold symmetry element stands out even more clearly than at 200 keV. On the basis of image-simulation computations, it is thought that the two images shown in Figure 7 would be obtained at $\Delta f = -400$ Å, $z = 250$ Å and $\Delta f = 4500$ Å, $z = 200$ Å.

Conclusions

HREM is a powerful method of reading off directly the symmetry elements of a projected structure from a real-space image. It is apparent that, with continuing improvements in resolution, structural motifs, especially five-, six-, eight-, and larger-membered rings in molecular sieves may be identified. This augers well for the direct determination of structures of solid sieves even more complicated than those hitherto reported.

When new solids are first prepared they are generally available only in a microcrystalline state. Whereas powder X-ray diffraction can often reveal the broad structural nature of such materials, it is high-resolution electron microscopic analysis, as illustrated here and in key references in the text,[12-16,21,25] that is likely to achieve the greatest insight into the nature of the new structures. Increasingly, it has been found that many "new" solids may be regarded as unit-cell composites or intergrowths—in the sense discussed in ref 24 and seen in the new zeolitic molecular sieve ECR-1[25] and comparable analogues[33] where there are recurrent slabs of two well-known zeolites (mazzite and mordenite)—and HREM offers a powerful method of observing such features directly in a real-space image.

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