

HREM Study of the Fine Structures of Zeolites and Materials Confined in Their Spaces: Are Zeolites Good Enough as Containers for Confined Materials?

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Fine structures have been studied for zeolites with one-dimensional (LTL and MOR) and three-dimensional (FAU and EMT) channels by high resolution electron microscopy. The importance of choosing better quality zeolite crystals was stressed, especially for making new low-dimensional materials in the spaces of zeolites. HREM images of confined materials were also shown. © 1993 Academic Press, Inc.

1. Introduction

Zeolites belong to the class of aluminosilicates and their framework structures are produced by a three-dimensional network of corner sharing of TO_4 tetrahedran ($T = \text{Si or Al}$); consequently they contain spaces of molecular size, called cages, cavities, and channels, inside the crystal. This characteristic structure might be responsible for their shape selectivity in chemical reactions and at the same time the spaces are very attractive for making new low dimensional materials which will show physical properties different from bulk crystals due to quantum confinement effects (1, 2). But the above structure descriptions are too idealized to be applied to zeolites used as containers in real systems. For example, even a planar defect crossing the channels changes the effective size of the apertures enormously (3). Zeolite crystals normally contain many different types of fault and, further, synthetic zeolites are about $1 \mu\text{m}$ in size. High resolution electron microscopy (HREM) coupled

with electron diffraction (ED) is therefore the most powerful technique for characterizing the defects of zeolites, although zeolites are very electron beam sensitive (3-6). This characterization is a key to understanding their chemical properties and for developing synthesis conditions to improve their crystallinities.

Zeolites are attractive especially for making wires in their one-dimensional channels and isolated clusters or "cluster crystals" in well-defined three-dimensional network of large cavities (2). The basis of "cluster crystals" is of course the cluster itself and its three-dimensional arrangement, which is different from that of the bulk, is given by zeolite frameworks; for example, a simple cubic or diamond structure arrangement if we use LTA or FAU. Furthermore, we can control the degree of overlap of electron wave functions belonging to neighboring clusters; therefore the "cluster crystal" is a very interesting system to use to reinvestigate solid state physics. The characteristic features of zeolites as containers for con-

finer materials may be summarized as follows (7, 8);

1. The crystal has basically the same composition as quartz and is therefore optically transparent for a wide range of energy and chemically stable.

2. The space has a unique size (about 6–15 Å), arranged regularly with a period of ca. 10 Å, and hence has a high density of ca. 10^{20} cm⁻³.

3. Different geometrical shapes and connectivities of spaces can be chosen from many different kinds of zeolite. Moreover, we can fine tune the size of the aperture to the spaces by exchanging cations with different sizes or even by removing them.

The quantum size effect is well known. The basic idea is that the average separation of electron energy levels is inversely proportional to the number of atoms in a cluster (J). The level is not continuous but discrete, if the separation is larger than thermal energy, kT , or Zeeman energy, $g\mu H$, then we observe the quantum confinement effect. The average spacing of Na with a 100 Å cube (2.5×10^4 atoms) is about 1.5×10^{-4} eV or $k \times 1.3$ K.

Interesting results for alkaline metal clusters in zeolite Y (FAU), that is, ionic clusters M_4^{3+} ($M = \text{Na, K}$) inside a sodalite cage have been studied by the Cambridge group (9). This is regarded as an electron confinement in a potential well produced by an $(M^+)_4$ cluster. Dr. Nozue and his colleagues in our department have measured optical absorption spectra of sodium clusters incorporated into LTA (10). They observed absorption bands originating from electronic excitation of the ionic clusters at lower loadings, and then those from surface plasmon-like and electron-hole excitations of clusters in α -cages as well at higher loadings of sodium clusters. Recently they observed ferromagnetism of K-clusters in K-LTA (11).

The aim of this report is twofold; to report here the advantages of HREM for the study of the fine structures of zeolites and to show an example of our attempts to

make new materials in their spaces, stressing the importance of choosing high quality zeolites.

2. Experimental

For HREM study, crystals were dispersed on grids without crushing, in order to avoid sample preparation artifacts. HREM images were taken by JEM-4000 at 400 kV unless otherwise stated.

3. HREM Study of Fine Structure of Zeolites

(a) One-Dimensional, Zeolite L (LTL) and Mordenite (MOR)

LTL contains a one-dimensional channel with a constricting aperture of 12-membered rings and has space group $P6/mmm$ and unit cell dimensions $a = 18.4$ Å, $c = 7.5$ Å. The channels are well separated by the framework atoms and therefore very attractive to make a one-dimensional system. We have reported coincidence boundaries which block most of the one-dimensional channels when a crystal grows on the other with rotation by a nonmultiple of 60° along the c -axis (3). An example is shown in Fig. 1. More than 90% of channels are blocked in region B, but in region A channels may be perfect. A few different boundaries or faults are shown by white arrows in Figs. 2a and 2b. These do not change the one-dimensional character but only decrease a small number of channels near the faults. By changing synthesis conditions, we can obtain a crystal with few coincidence boundaries, which is desirable for a container, and also we can control the crystal growth morphology due to the anisotropy in growth rate showing facets.

As stated later, the number of physically adsorbed Se atoms is approximately proportional to the number of Al atoms in the framework structure. The compositional fluctuation of the Si/Al ratio in the framework can be observed through the concentration modulation of Se. In HREM images

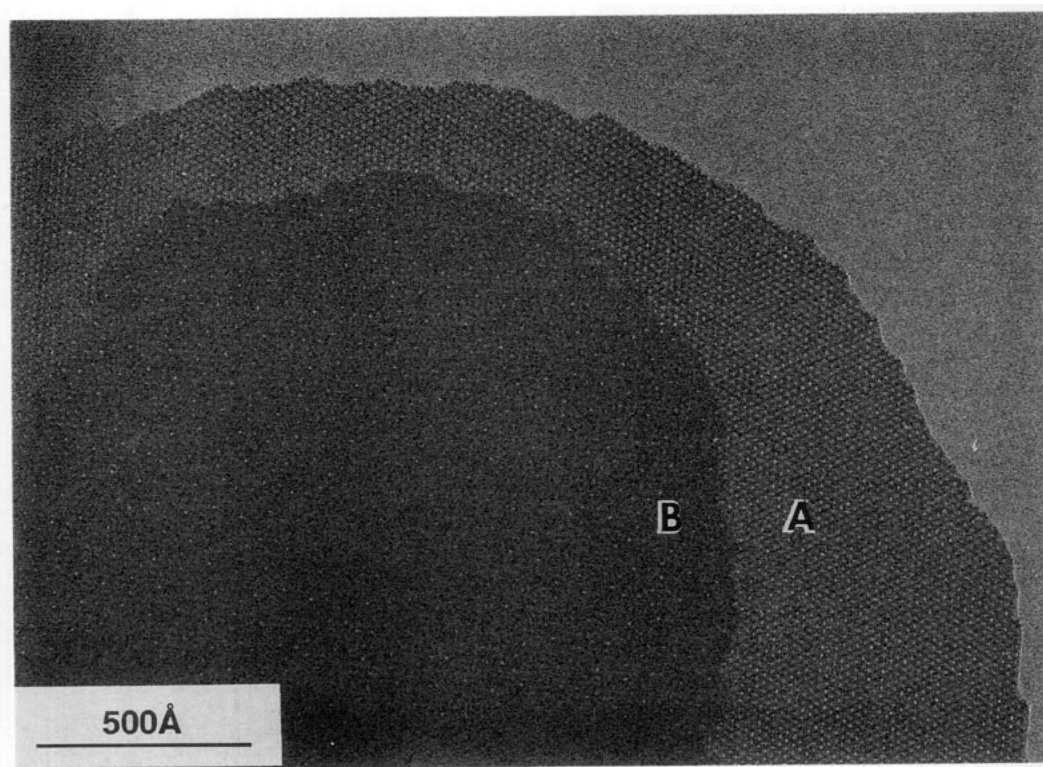


FIG. 1. An HREM image of LTL taken with $[001]$ incidence. Overlapping crystals are easily observed as moiré effect. The crystals block each other's channels.

of MOR taken with $[001]$ incidence, black and white bands, which are perpendicular to the b -axis and correspond to Al-rich and Si-rich regions respectively, were clearly observed (4, 12). An example is shown in Fig. 3.

(b) *Three-Dimensional, Faujasites, FAU (cubic) and EMT (hexagonal)*

FAU has one of the most open cubic framework structures with space group $Fd\bar{3}m$. Figure 4 shows an HREM image of FAU taken on a 1 MeV EM with incidence $[110]$. Twins are observed on $\{111\}$ as shown in the zigzag lines at both the left and right hand sides in the image. The structure at the boundaries corresponds locally to the hexagonal. In Fig. 4 the structure of the central part looks perfect, as shown in the straight line, so the twin planes do not pene-

trate the whole crystal. This suggests that the zeolite framework is so flexible that the lattice strain around the terminated edges can be easily accommodated and turned into a "perfect" structure (4). In an electron diffraction pattern, we can observe twin reflections, streaks perpendicular to the twin planes, due to the effect of thin twin plates and very weak diffuse intensity from the strain. But in powder X-ray diffraction, only twin reflections are observable as shoulders.

Recently a hexagonal type of FAU has been synthesized using 18-crown-6 as a template and has been coded as EMT (13). But there are sometimes many twins in a FAU crystal and ZSM-20 is believed to be FAU with numerous twins or an EMT/FAU intergrowth. Thus an argument may be raised that there is no essential difference between ZSM-20 and zeolite synthesized using 18-crown-6 if we cannot find a pure hexagonal

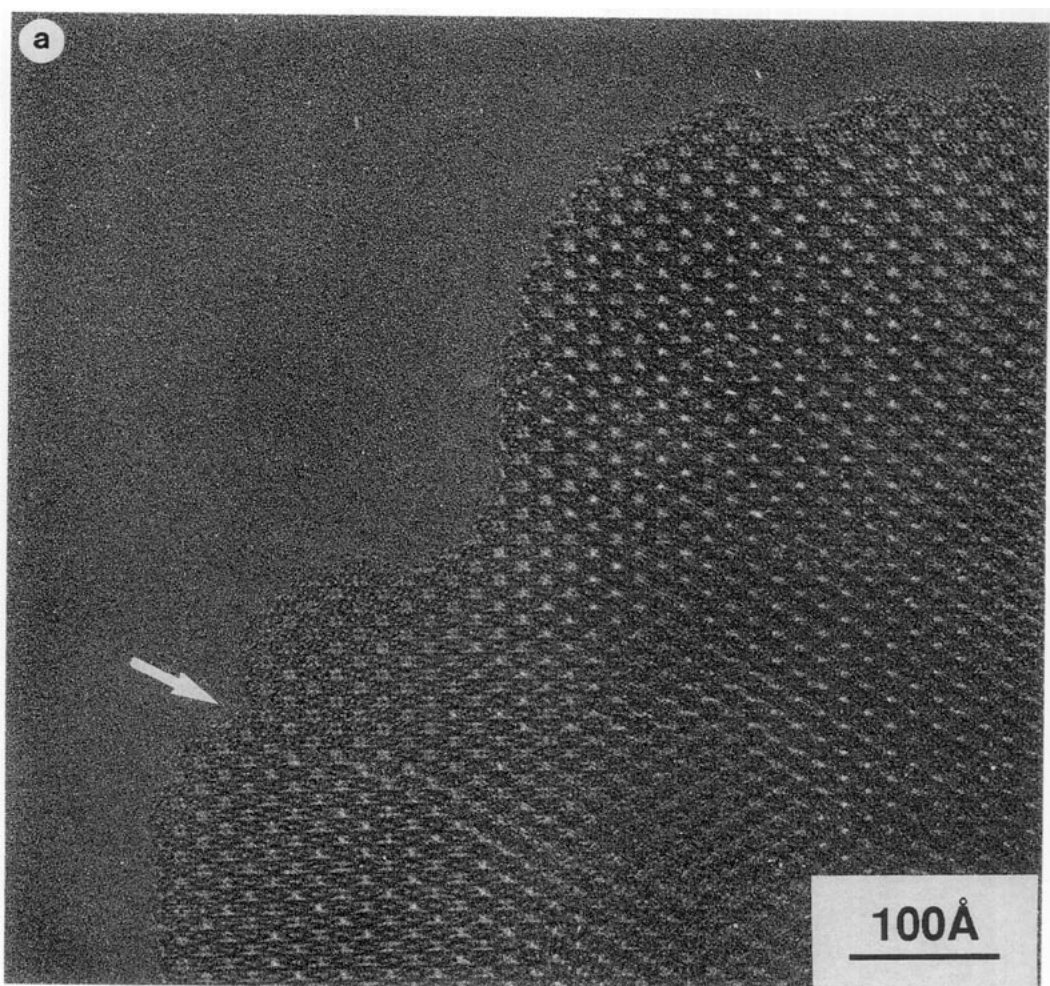


FIG. 2. (a) and (b) HREM images of LTL. Faults or boundaries are indicated by white arrows. Flat {100} surface is shown by triangles.

phase, because it is very difficult to detect a small amount of an intergrowth (second phase) from X-ray powder diffraction patterns or scanning electron micrographs. Figure 5a shows a SEM image of EMT synthesized by the use of 18-crown-6, taken with the [100] incidence, and Fig. 5b shows an HREM image. This is the first direct evidence showing that we can make a pure hexagonal phase, EMT (Tosoh Coop.), although most crystals contain EMT/FAU intergrowth. We have then a new channel system having one-dimensional main channels along the c -axis and slightly smaller ones

which are in the c -plane and intersect each other by 120° . By changing the relative concentrations in a mixture of 18-crown-6 and 15-crown-5, we can control the density and the manner of intergrowth of FAU/EMT (14, 15). From our experiences we know that we can extend the lifetime of zeolites under an electron beam by removing zeolitic water or by dealumination procedures. But from hydrated ordinary FAU with Si/Al = 2.8 we have found that we can take very nice HREM images, and we believe this is due to the good quality of the crystal, i.e., its crystallinity. We have also found by HREM

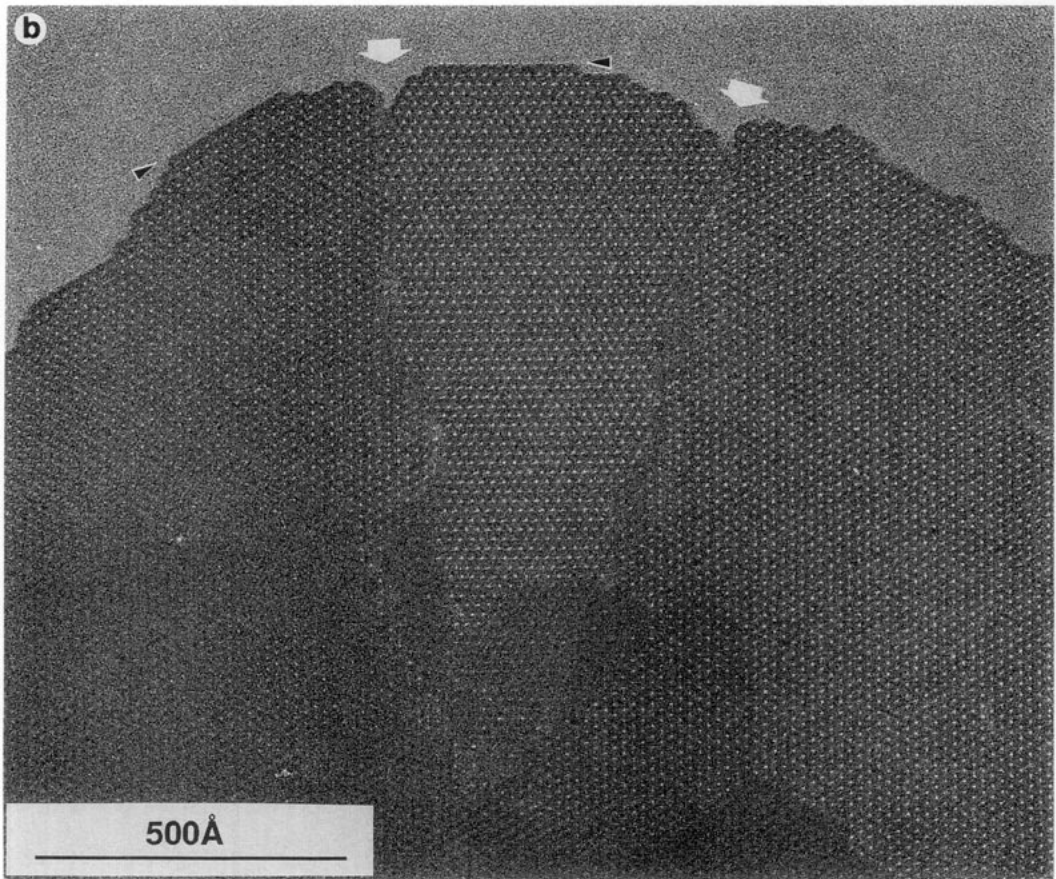


FIG. 2—Continued

the importance of choosing good crystals in that this FAU crystal, quite differently from others, is not damaged after the incorporation of Mo-oxide clusters by oxidation of adsorbed $\text{Mo}(\text{CO})_6$ as shown in Fig. 6 (collaboration with Dr. Y. Okamoto, Osaka University).

We have succeeded in taking HREM images which clearly show surface steps from both FAU and EMT. The images enable us to discuss the crystal growth process. They will be published elsewhere.

(c) *Confined Materials in the Spaces of Zeolites*

The electronic configuration of Se is $[\text{Ar}]3d^{10}4s^24p^4$. The six electrons per atom

therefore occupy s states, the bonding p -like states (called σ -bonds), and the non-bonding or lone-pair states. The Fermi level falls between the nonbonding and the antibonding p -like states. Se atoms are two-fold coordinated and the structure is made up of helical chains or puckered rings. Se chains or rings were successfully incorporated into different types of zeolite (FAU, MOR, LTA and LTL). The number of adsorbed Se atoms per Al was estimated to be 10–20 by optical absorption intensity change of Se in FAU as a function of $\text{Al}/(\text{Al} + \text{Si})$. The absorption bands appear at 2.5–3.0 eV and 3.5 eV and they are assigned to the transition from the lone-pair and bonding states to the antibonding state, depending on their geo-

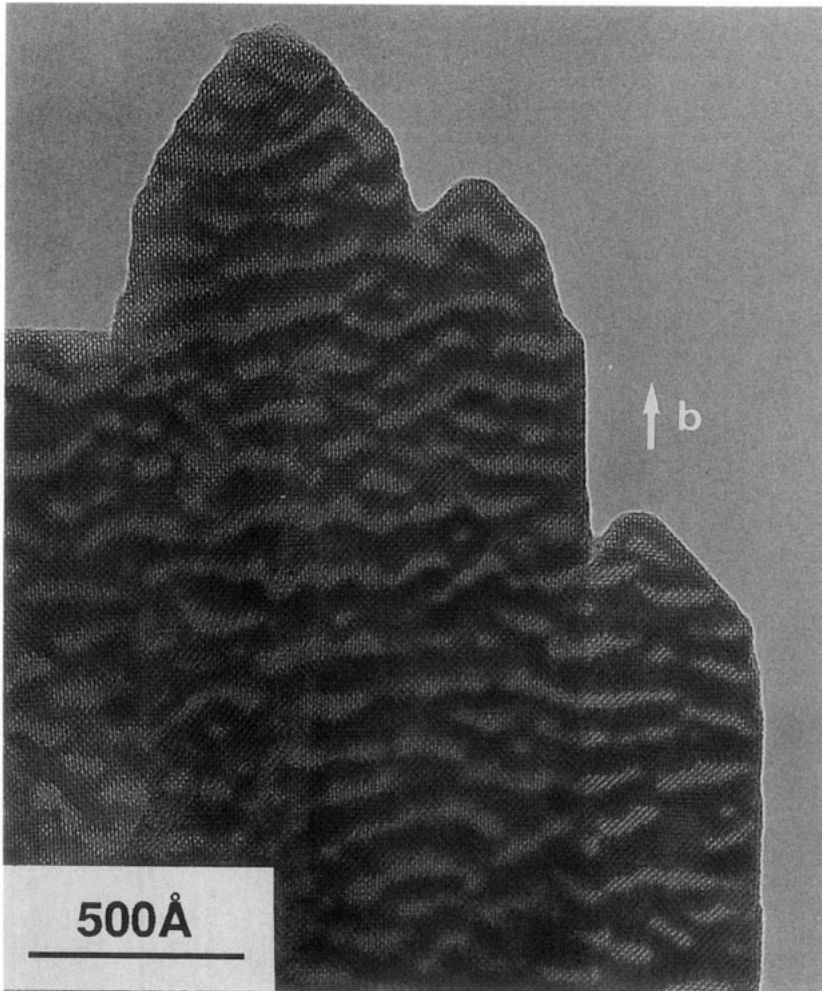


FIG. 3. An HREM image of MOR taken with [001]. Black and white bands can be observed.

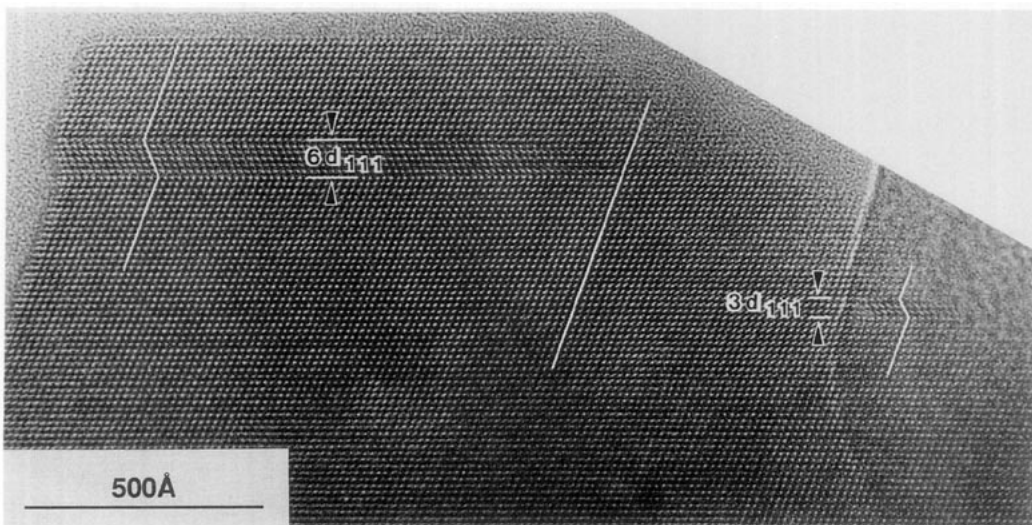


FIG. 4. An HREM image of FAU taken on 1 MeV EM with [110] incidence.

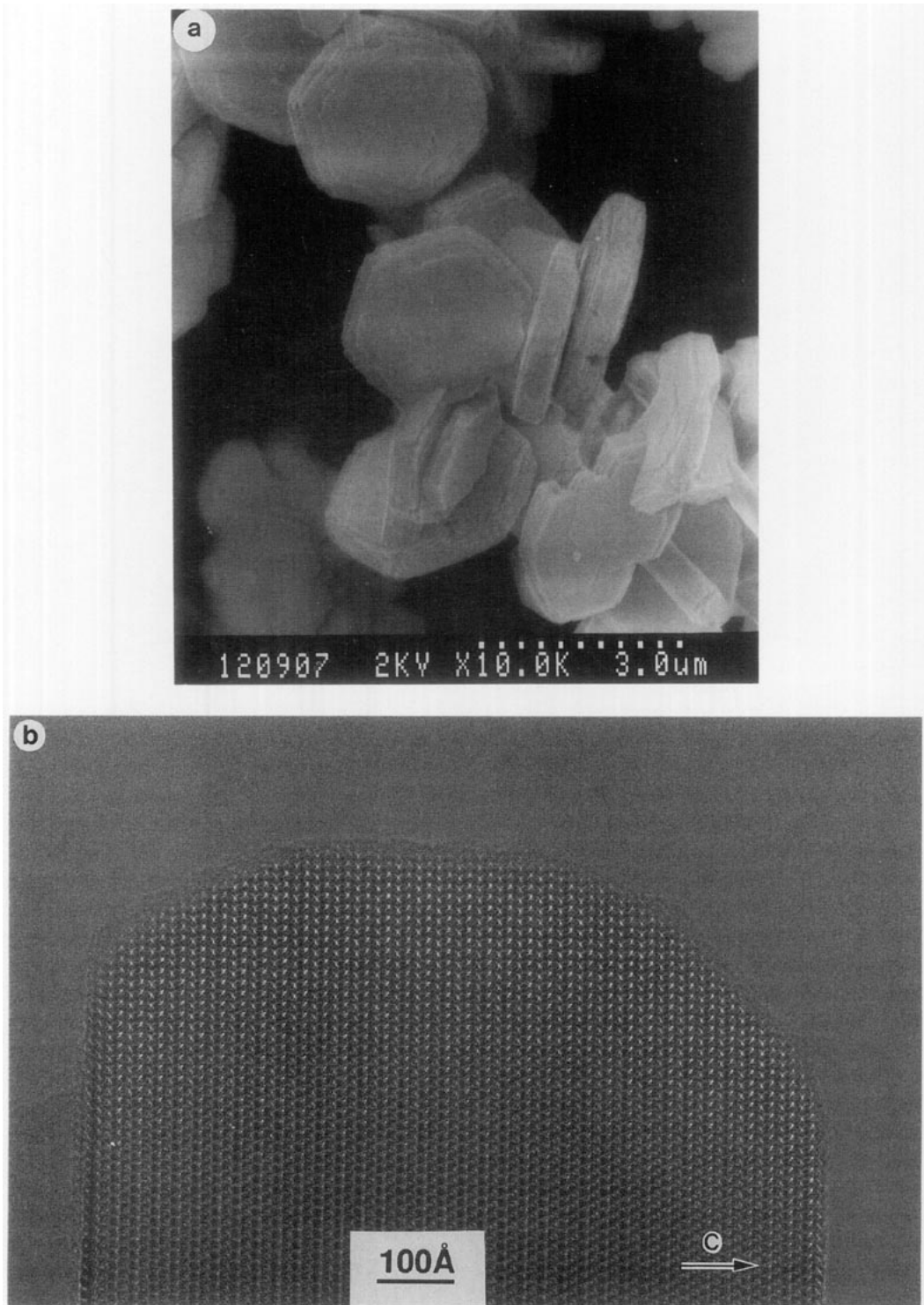


FIG. 5. (a) A SEM image of EMT. (b) An HREM image of EMT taken with [100] incidence.

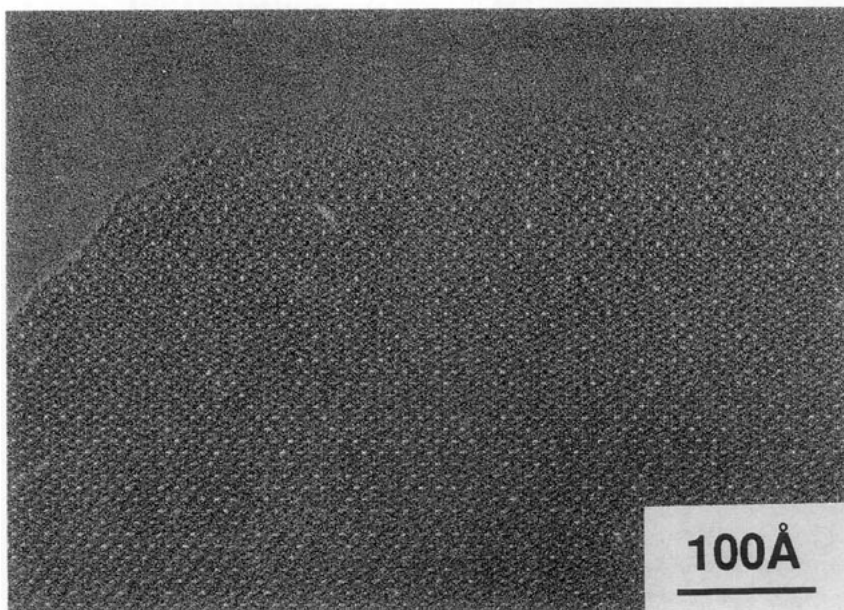


FIG. 6. An HREM image of $(\text{MoO}_3)_n$ incorporated Na-FAU taken with $[110]$ incidence.

metrical constraints and on the Si/Al ratio. From the difference in absorption spectra, the structures of Se in MOR, LTA, and LTL are expected to be isolated chains, double parallel rings (which may be Se_8), and double parallel chains, respectively. In FAU they are isolated clusters, isolated chains, and chains with neighboring chains for high, medium, and low silica content (16).

If the size of the semiconductor cluster is much smaller than the effective Bohr radius exciton, then the lowest excitation energy of the electron-hole pair is shifted toward higher energy, i.e., blue shift due to quantum confinement. It is easy to observe this effect through the absorption spectra. The effective Bohr radius of exciton for PbI_2 is about 19 Å. When PbI_2 clusters are incorporated into the spaces of LTA through the vapor phase, the zeolite powder changes color from white to light yellow. Absorption spectra of PbI_2 clusters in Na-LTA were measured as a function of the density of the clusters, and we could observe several blue shifted absorption peaks which are assigned to different sizes of molecular clusters (17,

18). By HREM imaging we could confirm that the LTA crystal keeps its periodicity (crystallinity) after the incorporation and that the clusters are formed in α -cages (4). Maximum loading density is estimated to be four molecules per α -cage. In an electron diffraction pattern taken from a maximum loaded specimen with $[1\bar{1}0]$ incidence, hhl ($h, l = \text{odd}$) reflections, which are forbidden for $Fm\bar{3}c$ of LTA, are observed. Our model is that two different clusters arranged alternately in an α -cage may lower the space group symmetry, probably to $P4_232$. Figure 7 shows an HREM image of maximum loaded LTA with $[100]$ incidence. Although this image shows quite fine details, including the effect from clusters, we could not extract proper information on clusters as yet.

The most exciting report on clusters in zeolite spaces is for potassium, K, clusters in K-LTA. These show ferromagnetism. Figure 8 shows the temperature dependence of magnetic susceptibility from the specimen of K in K-LTA observed by Nozue *et al.* (11). This curve is observed from the specimen of ca. 4 electrons per α -cage,

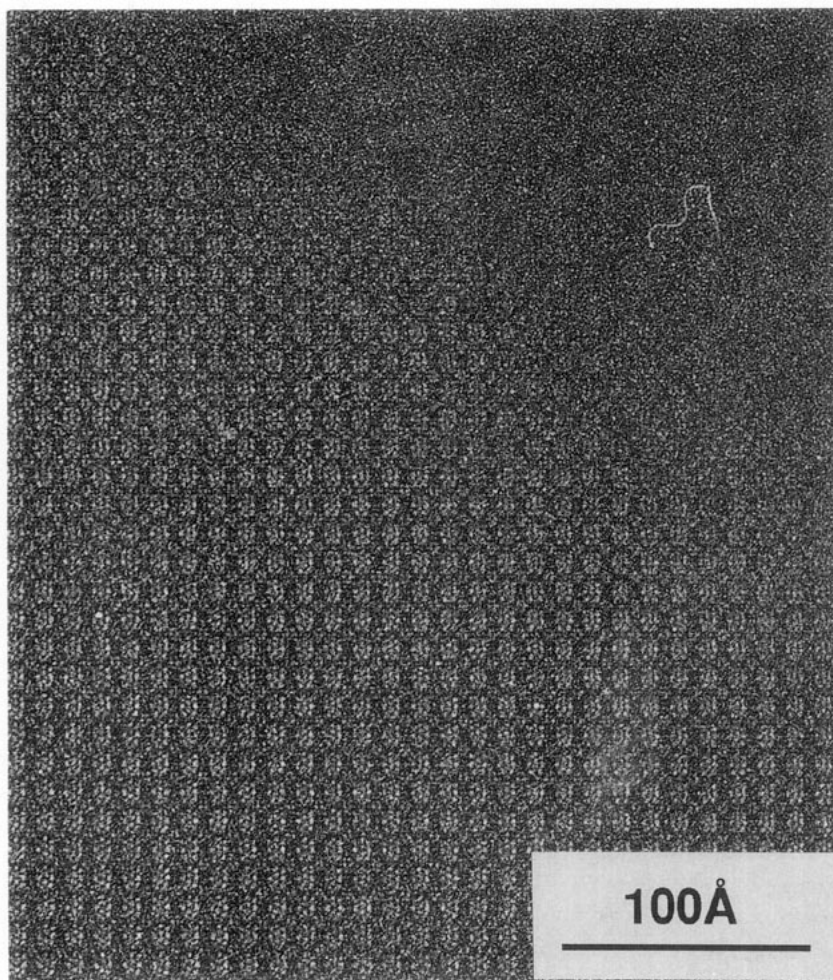


FIG. 7. An HREM image of PbI_2 -maximum loaded Na-LTA taken with [100] incidence.

which is estimated by the analysis of the diffuse reflection spectrum, and shows ferromagnetism below about 4 K. Nozue *et al.* assumed for simplicity a spherical quantum-dot potential with an infinite barrier. Therefore $4s$ -electrons confined in the $1p$ molecular orbital are responsible for the ferromagnetism shown in Fig. 8 and this is only plausible when electron wave functions belonging to neighboring K clusters overlap each other. The effective magnetic moment per supercage was estimated to be about $0.13 \mu_B$ at 1.7 K. It is to be noted that K clusters in Na-LTA do not show this kind of phenomena.

4. New Zeolites¹

The maximum size of the aperture in a zeolite is a 20-membered ring for CLO, but VPI-5 as a container has the biggest aperture with 18-membered ring. It is very important to obtain zeolites with larger apertures. We should know for this trial what directions we must direct our efforts in; I believe the following is one such direction.

Some zeolite structures have been well described by Sten Andersson and his col-

¹ This part was based on discussion with Sten Andersson and Z. Blum, and was presented at the 29th Kaya Conference, Aug. 25–28, 1991, Bandai, Japan.

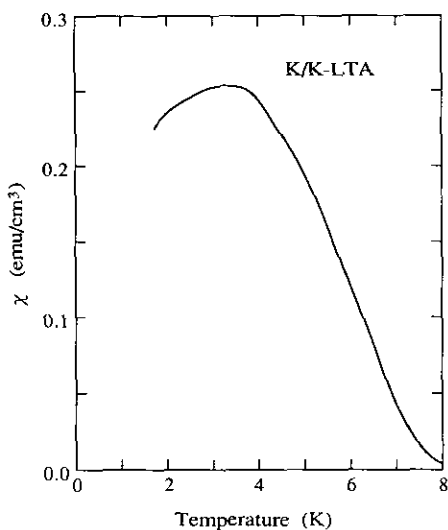


FIG. 8. Temperature dependence of the ac magnetic susceptibility of K-loaded K-LTA observed by Nozue *et al.* (11).

leagues (19, 20) as frameworks lying on infinite periodical minimal surfaces (IPMS). Negative charges carried by a zeolite framework and organic cations may be separated by IPMS, as the constant electrostatic potential surfaces are very close to the surfaces for many interpenetrating lattices of oppositely charged points. If the framework does not carry net charges (for example, pure silica or AlPO_4), neutral molecules of hydrophobic character may act as structural directing agents. Amphiphilic molecules assemble into bilayers and form periodic arrangements of P, F, G surfaces of IPMS for cubic arrangements or hexagonal arrangements of rod shape (21). If we can use these as templates then we will be able to synthesize new zeolites with quite large apertures, the size of which may be tunable.

5. Conclusion

The above-mentioned strongly suggests that zeolite synthesis is still in its early stages and that we must pay much attention to improving or choosing better qualities of zeolites. It is needless to say that the quality

of zeolite has an effect on physical properties of guests, and I believe this is also true for shape selectivity in catalytic reactions. I agree with the statement in the reports on "Research Opportunities on Clusters and Cluster-Assembled Materials" that in order to remove the problem of the presence of defects in both the zeolite hosts and clusters, a better quality of zeolite crystals and improved synthetic procedure are needed (22). I add that we can find good zeolite crystals, and I am sure the time will come soon when crystals will be checked out not by HREM but by X-ray topography after a large good single crystal has been made.

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References

1. R. KUBO, *J. Phys. Soc. Jpn.* **17**, 975 (1962).
2. V. N. BOGOMOLOV, *Sov. Phys. Usp.* **21**, 77 (1978).
3. O. TERASAKI, J. M. THOMAS, AND G. R. MILLWARD, *Proc. R. Soc. London Ser. A* **395**, 153 (1984).
4. O. TERASAKI, *Acta Chem. Scand.* **45**, 785 (1991).
5. G. R. MILLWARD, J. M. THOMAS, O. TERASAKI, AND D. WATANABE, *Zeolites* **6**, 91 (1986).
6. O. TERASAKI, J. M. THOMAS, G. R. MILLWARD, AND D. WATANABE, *Chem. Mater.* **1**, 158 (1989).
7. O. TERASAKI, *Nippon Kinzoku Gakkai Kaiho* **30**, 17 (1991). [In Japanese]
8. O. TERASAKI, *Solid State Phys.* **27**, 601 (1992). [In Japanese]
9. M. R. HARRISON, P. P. EDWARDS, J. M. KLINOWSKI, J. M. THOMAS, D. C. JOHNSON, AND C. J. PAGE, *J. Solid State Chem.* **54**, 330 (1984).
10. T. KODAIRA, Y. NOZUE, AND T. GOTO, *Mol. Cryst. Liq. Cryst.* **218**, 55 (1992).
11. Y. NOZUE, T. KODAIRA, AND T. GOTO, *Phys. Rev. Lett.* **68**, 3789 (1992).
12. O. TERASAKI, K. YAMAZAKI, J. M. THOMAS, T. OHSUNA, D. WATANABE, J. V. SANDERS, AND J. C. BARRY, *Nature (London)* **330**, 5 (1987), and *J. Solid State Chem.* **77**, 72 (1988).
13. F. DELPRATO, L. DELMOTTE, J. L. GUTH, AND L. HUVE, *Zeolites* **10**, 546 (1990).

14. M. W. ANDERSON, K. S. PACHIS, F. PREBIN, S. W. CARR, O. TERASAKI, T. OHSUNA, AND V. ALFREDSSON, *J. Chem. Soc. Chem. Commun.*, 1660 (1991).
15. O. TERASAKI, T. OHSUNA, V. ALFREDSSON, J-O BOVIN, D. WATANABE, S. W. CARR, AND M. ANDERSON, *Chem. Mater.* **5**, 452 (1993).
16. Y. NOZUE, T. KODAIRA, O. TERASAKI, K. YAMAZAKI, T. GOTO, D. WATANABE, AND J. M. THOMAS, *J. Phys. Condens. Matter* **2**, 5209 (1990).
17. Z. K. TANG, Y. NOZUE, AND T. GOTO, *J. Phys. Soc. Jpn.* **60**, 2090 (1991).
18. O. TERASAKI, Z. K. TANG, Y. NOZUE, AND T. GOTO, "Materials Research Society Symposia Proceedings," Vol. 233, pp. 139-143, Materials Research Society, New York (1991).
19. S. ANDERSSON, S. T. HYDE, K. LARSSON, AND S. LIDIN, *Chem. Rev.* **88**, 221 (1988).
20. Z. BLUM AND S. T. HYDE, *Chem. Mater.* **2**, 312 (1990).
21. Y. BOULIGAND, "Geometry in Condensed Matter Physics" (J. F. Sadoc, Ed.), pp. 193-231, World Scientific, Singapore (1990).
22. R. A. ANDRES, R. S. AVERBACK, W. L. BROWN, L. E. BRUS, W. A. GODDARD, III, A. KALDOR, S. G. LOUIE, M. MOSCOVITS, P. S. PEERCY, S. J. RILEY, R. W. SIEGEL, F. SPAEPEN, AND Y. WANG, *J. Mater. Res.* **4**, 704 (1989).