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VITRIFICATION OF ZEOLITE Y IN THE TEM

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Vitrification of Zeolite Y in the TEM

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The metamict transformation of Y zeolite in the transmission electron microscope (TEM) has been studied in the range of accelerating voltages 80-200 kV. This study concentrates on the effects of accelerating voltage and Si/Al-ratio. The results show that the damage is due to radiolysis and that increasing the accelerating voltage and Si/Al-ratio prolongs the observation lifetime of the zeolite. A mechanism for the metamict transformation involving the cation is proposed. This mechanism is used to suggest ways of reducing the damage rate.

Keywords: Zeolite Y, TEM, damage, cations, Si/Al-ratio

INTRODUCTION

The damage of zeolites (and other silicates) upon examination in the transmission electron microscope (TEM) has been well documented.[1-6] Zeolites become amorphous during irradiation. This is known in the geological community as metamictization. Observations show that the damage rate of zeolites depends on the Si/Al-ratio, on the size of the cations,[2] and on the extent of hydration.[1] The goal of this work is to study the effects of varying the accelerating voltage and the Si/Al-ratio on the damage of Y zeolite in the TEM and to propose a model for the damage mechanism.

The types of damage possible in the transmission electron microscope (TEM) can be classified under two general headings: knock-on and radiolytic. "Knock-on" damage involves the interaction of the incident electron with the core of an atom in the specimen. An atom is "knocked" from its site, thereby changing the structure. Radiolytic damage involves the transfer of energy from the incident electron to the electrons in the specimen. The increase in energy of the specimen electrons results in bond breakage and consequently the possible alteration of the structure.

Knock-on damage

The cross-section for direct interaction of the probing electron and the nuclear core of an atom in the specimen is called the knock-on cross-section. For relativistic electrons this cross-section is given by[7,8]

$$\sigma_n = \left\{ \frac{4\pi a_o^2 U_R^2}{(mc^2)^2} \right\} \left\{ \frac{Z^2(1-\beta^2)}{\beta^4} \right\} \left\{ \left(\Omega_r\right) + 2\pi\alpha\beta \left(\Omega_r\right)^{1/2} - (\beta^2+\pi\alpha\beta) \ln\left(\Omega_r\right) - 1 - 2\pi\alpha\beta \right\} \quad (1)$$

where:

$$\Omega_r = \frac{T_{max}}{T_{th}} \qquad T_{max} = \frac{2\,U_p\,(U_p + 2mc^2)}{Mc^2}$$

$$\beta = \left\{ 1 - \frac{1}{\left(\frac{U_p}{mc^2} + 1\right)^2} \right\}^{1/2}$$

U_p is the incident beam kinetic energy (keV), and mc^2 is the rest energy of the electron (511 keV). Mc^2 is the rest energy of the nucleus, α is Z/137, Z is the atomic number, U_R is the Rydberg constant (0.0136 keV), and a_o is the Bohr radius (0.053 nm). The maximum energy that an incident electron can transfer to a nucleus is T_{max}. The minimum energy necessary to move an atom off its lattice site into some metastable position is T_{th},

which depends directly on the atomic number.

All materials undergo direct displacement of atoms above their specific threshold energy. For most metals the threshold energy, T_{th}, is 20-30 eV and σ_n=0 for accelerating voltages under 300 kV. However for lighter elements such as Al (or Mg), direct displacement is predicted and observed at accelerating voltages below 200 kV in the TEM.[9]

Above the threshold energy for the knock-on process, the cross-section for knock-on increases with increasing accelerating voltage. The potential damage due to electron-nuclear interaction becomes more severe as the incoming electron gets more and more energetic. At higher accelerating voltages the electron has enough energy to cause multiple damage events. The quantity, $N_d = \frac{T_{max}}{2\,T_{th}}$, takes into account the possible cascade of damage events. The knock-on damage cross-section includes the cross-section for displacement of an atom directly due to interaction with the electron wave and the probability of being displaced by another "knocked" atom, i.e., $\sigma_{kd}=\sigma_n \times N_d$. Its variation with accelerating voltage is shown in figure 1.

Radiolytic damage

The relativistic cross-section for the interaction between the incident electron and the specimen electron is given by[10]

$$\sigma_e = \left(\frac{8\,\pi\,a_o^2\,U_R^2}{mc^2}\right)\left(\frac{Z}{T'_{th}\,\beta^2}\right) \qquad (2)$$

where: T'_{th} is the minimum energy that must be transferred to the electrons of the solid to produce atomic nuclear movement, Z is the number of electrons (usually the atomic number) belonging to the target atom, and a_o, U_R, mc^2 and β have the meanings described previously. The minimum energy T'_{th} is specific to each unique atomic site

within the specimen and is related to the bond strength and the coordination number of the atom. The behavior of the cross-section for electronic interactions with accelerating voltage is determined by the parameter β^{-2}. This dependence is illustrated in figure 2 for the case of aluminum in zeolite Y. Note that the cross-section for ionization decreases significantly with increasing accelerating voltage up to 500 kV, then levels off to a constant value.

The experimental efficiency factor, ς, for radiolysis in silicates is 0.0001.[11] That is, for every ionization event that occurs, the probability of structural rearrangement is 1 in 10,000. The cross-section for radiolytic damage is thus given by

$$\sigma_r = \sigma_e \times \varsigma. \tag{3}$$

For zeolites the cross-sections for knock-on and radiolytic damage are of the same order of magnitude, and should both be considered when studying zeolites in the TEM, especially when accelerating voltages above 200 kV are used. Above the knock-on threshold for Al, the damage rate for a zeolite will increase with accelerating voltage rather than decrease, due to the increasing number of direct displacement events.

For alumino-silicates the cross-sections for knock-on and radiolytic damage predict that for an accelerating voltage below 200 kV, the damage should be due to a radiolytic process. The radiolytic cross-section can not, however, predict the actual structural relaxation (i.e., the mechanism) responsible for the damage.

EXPERIMENTAL

Samples of Y zeolite (with sodium cations) with Si/Al-ratios = 2.4, 18 and ∞ were investigated. Specimens for the TEM were prepared by embedding the zeolite powder in LR White acrylic resin and thin sectioning (50-80nm) with a diamond knife on a Dupont-Sorvall MT-6000 microtome.[12] The specimens were stored in a dessicator to

reduce the readsorption of water.

Experiments were carried out in a JEOL 200CX HREM operating between 80 and 200 kV. Typically HREM micrographs are recorded with a current density of $\approx 10^{23}\frac{e}{s}m^{-2}$, however, to slow the degradation for these experiments lower current densities were used. For specimens with Si/Al-ratios = 2.4 and 18, the current density to the specimen was $1.57\times10^{22}\frac{e}{s}m^{-2}$. For specimens with Si/Al-ratios = ∞, the current density was $6.28\times10^{22}\frac{e}{s}m^{-2}$; damage at lower current density was too slow to observe within reasonable times. Incident beam current was measured at the image plane with an electrometer and the current density at the specimen was determined using $\phi_{specimen}=(Mag)^2\phi_{image}$ (ϕ=current density). This dependence was verified by measuring the current density at the image plane while maintaining a constant current density at the specimen. Over the magnification range 19,000 to 100,000, the measured current density varied inversely with the square of the magnification.

The crystalline to amorphous transformation was monitored by recording on photographic film the loss of intensity in the Bragg reflections in the selected area diffraction (SAD) pattern with time. The SAD pattern was taken from a $5\mu m^2$ region in the center of a $20\mu m^2$ area of uniform current density. It is the long range periodicity of the crystalline solid that gives rise to strong intensity in the diffraction spots and as this long range periodicity is destroyed the intensity in the spots is reduced. Figure 3 shows some representative diffraction data. The upper three micrographs show the loss of crystallinity in the initial 9 minutes under the electron beam. The lower three micrographs show the final stages of the transformation that took 21 minutes to complete. For each specimen at every accelerating voltage, the transformation was monitored several times to

insure the reproducibility of the data. The dose to vitrification was calculated by multiplying the current density by the total time of exposure.

The measurement of current density was accurate to within 2% for all trials. For specimens with Si/Al-ratios = 2.4 and 18, the transformation time determinations were reproducible with an uncertainty of ≈9%. This results in an uncertainty in the dose to vitrification of ≈9%. For specimens with Si/Al-ratio = ∞, transformation time measurements were reproducible with an uncertainty of ≈12%, probably due to inhomogeneity in the crystals. The resulting uncertainty in the dose to vitrification was ≈12%, for specimens with Si/Al-ratio = ∞.

RESULTS

The metamict transformation took from 5 to 25 minutes to complete, depending on the Si/Al-ratio and the accelerating voltage. The dose to vitrification is plotted as a function of accelerating voltage for the three samples in figure 4. For all samples, increasing the accelerating voltage improved their radiation tolerance. This indicates that the damage is radiolytic and that knock-on damage is not significant up to 200 kV accelerating voltage. The difference between the dose to vitrification for the samples with Si/Al-ratios 2.4 and 18 is about 25%; for the sample with Si/Al =∞, the dose to vitrification is 3.5 and 5 times greater than that for the samples with Si/Al-ratios 18 and 2.4, respectively. Total replacement of all the aluminum by silicon produces a zeolite that is significantly more stable to electron irradiation as well as to elevated temperatures.

DISCUSSION

Radiolytic degradation of SiO_2 in the TEM has been explained as the weakening of Si-O bonds by the incorporation of H_2O in the structure.[10] Since zeolites are aluminosilicates where the aluminum occupies some of the tetrahedral positions of the silicon, the local structure is the same as SiO_2, i.e., the Si (or Al) are tetrahedrally coordinated to four O and the radiolytic degradation mechanism could be the same. If this mechanism is responsible for degradation of zeolites then the increase in dose to vitrification with Si/Al-ratio should be explained by the different cross-sections for radiolytic damage for Si and Al in the zeolite structure. Using equation 2, the ratio of the radiolytic cross-sections for an all Si containing zeolite versus an all Al containing zeolite is

$$\frac{\sigma_{Si}}{\sigma_{Al}}=0.80.$$

This predicts that a zeolite structure containing only aluminum atoms (all silicon atoms replaced with aluminum atoms) should degrade with a dose to vitrification 80% that for degradation of the same zeolite containing only silicon atoms (all aluminum atoms replaced with silicon atoms). This does not explain the data shown in figure 4, where the sample containing 29% Al (Si/Al=2.4) has a dose to vitrification 20% that of the Si/Al=∞ sample.

The data in figure 4 indicate that the mechanism and therefore the efficiency of radiolytic damage in zeolites is different from that in quartz. The important difference with aluminum in the structure is that each Al has a cation associated with it to balance the framework charge. This cation facilitates a different mechanism for the degradation of aluminum-containing zeolites.

Figure 5 shows a model of a silicon atom tetrahedrally coordinated to four oxygen atoms in the zeolite structure. It is difficult to describe the damage mechanism for a silicon site in a zeolite. If only one Si-O bond is broken the Si atom is rigidly held in place by the three other existing Si-O bonds and the requirement that Si be tetrahedrally coordinated causes the broken Si-O bond to reform without any structural changes. When two Si-O bonds are broken, the Si atom is free to rotate about the two existing Si-O bonds and form bonds in a configuration different from the original structure, however, this leaves some bonds unsatisfied unless several other nearby tetrahedra rotate and reform bonds simultaneously.

Figure 6a shows the case of Al tetrahedrally coordinated to four oxygen atoms in the zeolite framework. If one Al-O bond is broken (fig. 6b), the Al can remain coordinated to only three oxygens and the cation can bond to the fourth oxygen. The Al is stable with three bonds and the cation is still near it for local charge neutrality, but now the structure is permanently changed.

This mechanism can be used to explain why zeolite structures are less electron beam sensitive when dehydrated in vacuo,[1] when sodium ions are exchanged by larger cations,[2] or when the Si/Al-ratio is increased. At an aluminum site the larger the cation, the slower its movement into the proper position to bond to the dangling oxygen due to steric hindrance, and the greater the probability for reforming the original Al-O bond and preserving the structure. Therefore at a given Si/Al-ratio the zeolite with the larger cations will be more stable than the same zeolite framework with smaller cations. The same trend should be observed if the number of cations in the structure is reduced by using cations with greater ionic charge; i.e., Ca^{2+} instead of K^{+}. A cation such as La^{3+} should be strongly stabilizing due to its large size and charge. Adsorbed water in the

zeolite structure can fill the role of a cation in the damage mechanism. Adsorbed water can bond to the dangling oxygen atom resulting in a structural change at either a Si or an Al site. Thus, dehydrating the zeolite will always enhance its stability under the electron beam regardless of the Si/Al-ratio or type of cation present. As the Si/Al-ratio increases the number of possible degradation sites decreases and the zeolite is more stable to electron irradiation.

CONCLUSIONS

Experiments have confirmed that the damage of Y zeolites in the TEM is radiolytic and knock-on damage is not significant in the range 80-200 kV. Experimental evidence suggests a model for the degradation of zeolites in which structural relaxation is enhanced at Al sites due to the presence of a cation. When an Al-O bond is broken the cation moves into a position to bond to the dangling oxygen atom and the aluminum atom remains bound to only three oxygen atoms. Local charge neutrality is preserved, however, the structure is permanently changed.

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Running title: **Vitrification of Zeolite Y**

FIGURE CAPTIONS

1. Knock-on cross-section versus accelerating voltage for Al in Y zeolite

2. Radiolytic cross-section versus accelerating voltage for Al in Y zeolite

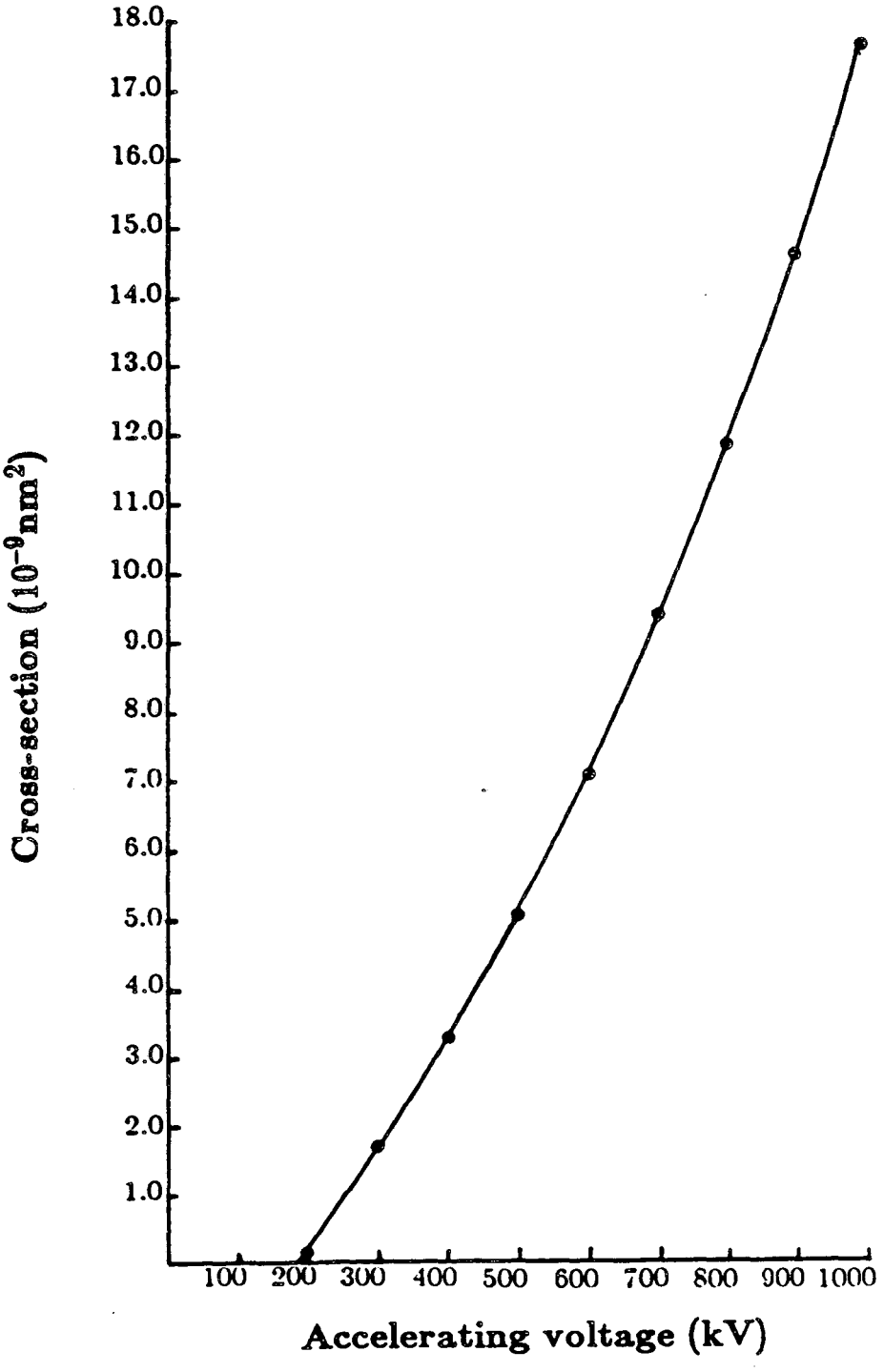
3. Fading of diffraction spots over 21 minutes at 200 kV, current density = $1.57 \times 10^{22} \frac{e}{s} m^{-2}$, Si/Al=18

4. Dose to vitrification versus accelerating voltage for Y zeolites with Si/Al = 2.4, 18, ∞

5. Silicon atom tetrahedrally coordinated to four oxygen atoms in the zeolite structure

6a. Aluminum atom tetrahedrally coordinated to four oxygen atoms in the zeolite structure

6b. Aluminum atom coordinated to three oxygen atoms in the damaged zeolite structure



XBL 8610-3776

Fig. 1

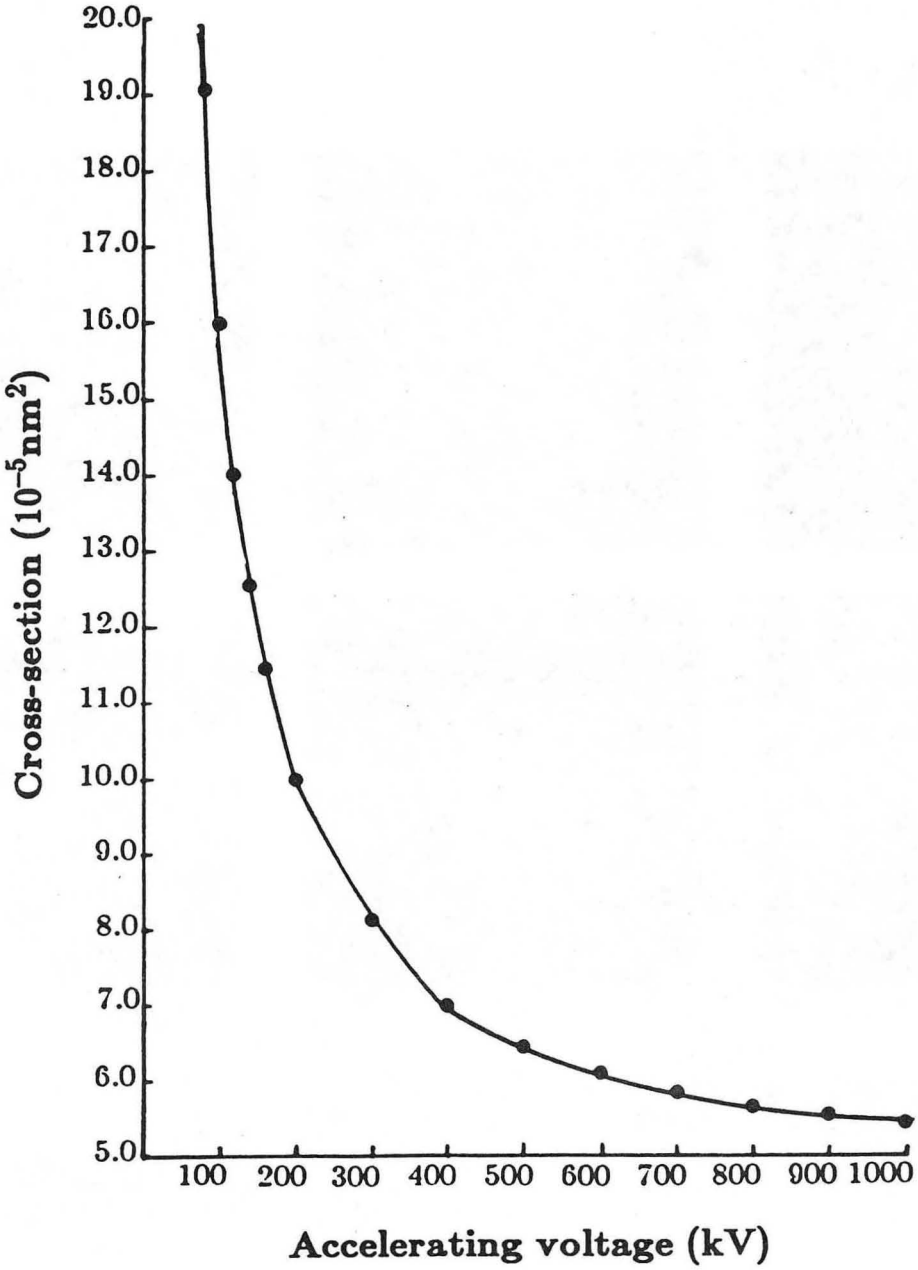


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Fig. 2

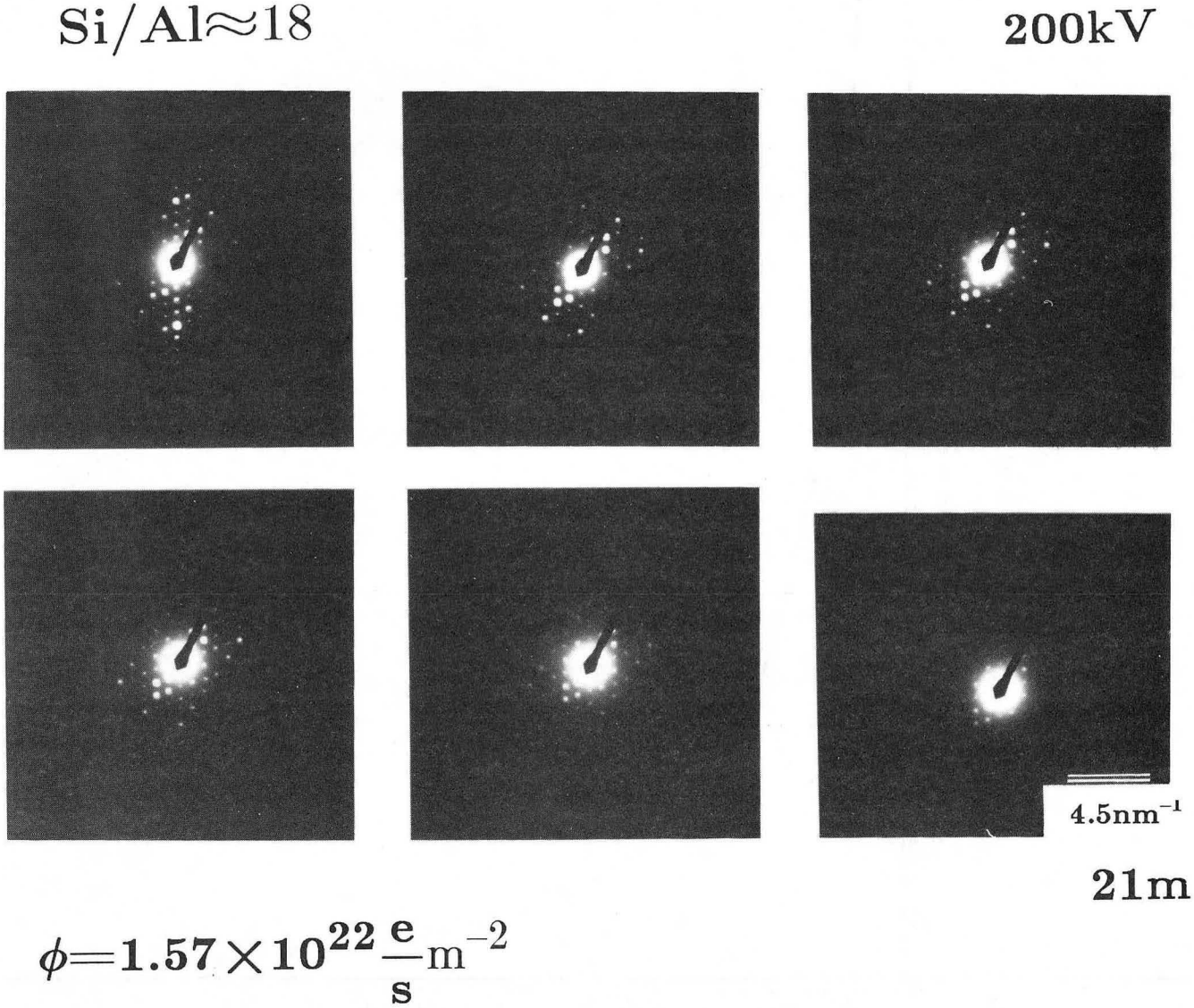

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Fig. 3

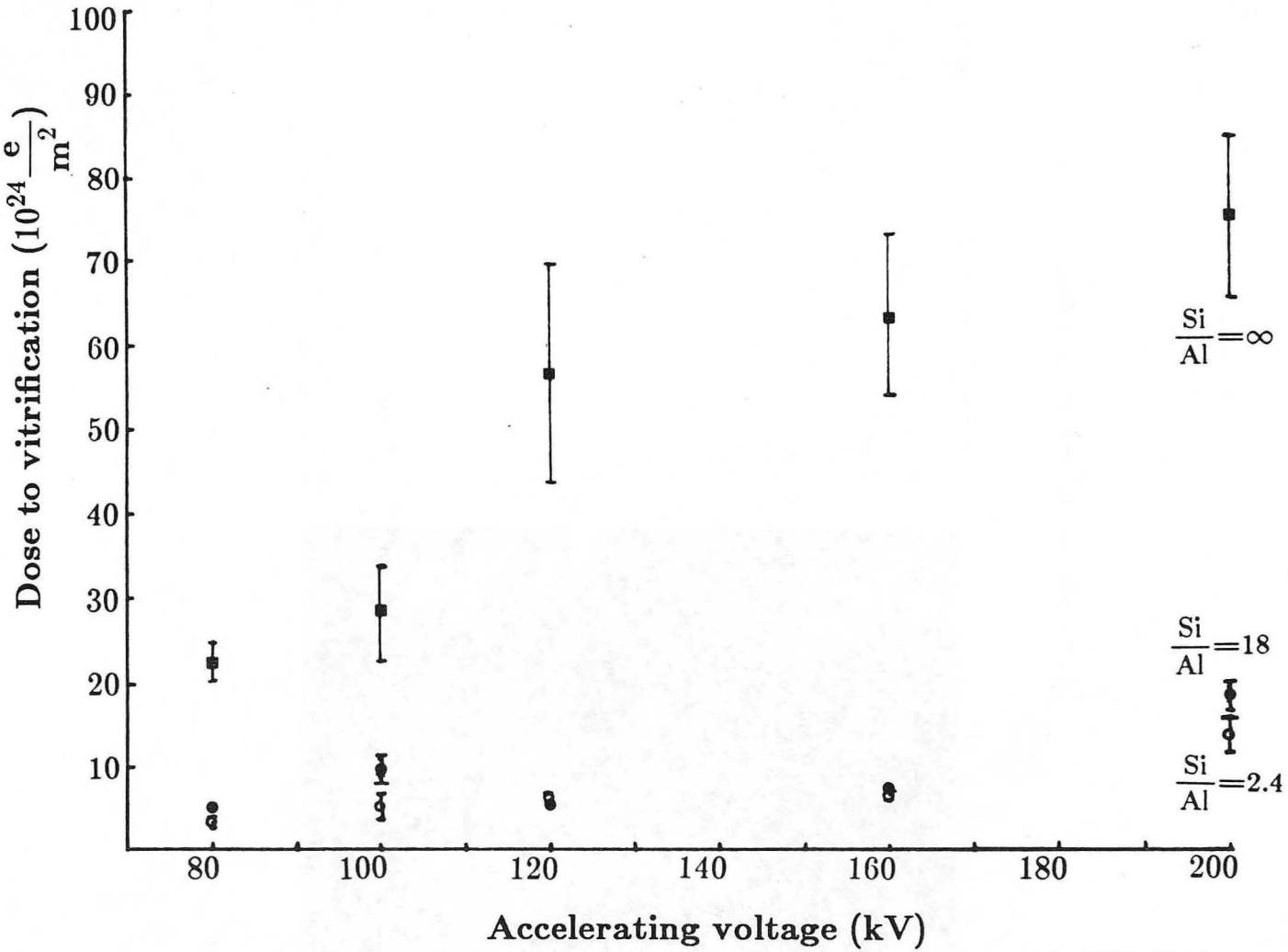

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Fig. 4

Tetrahedral Si in zeolite

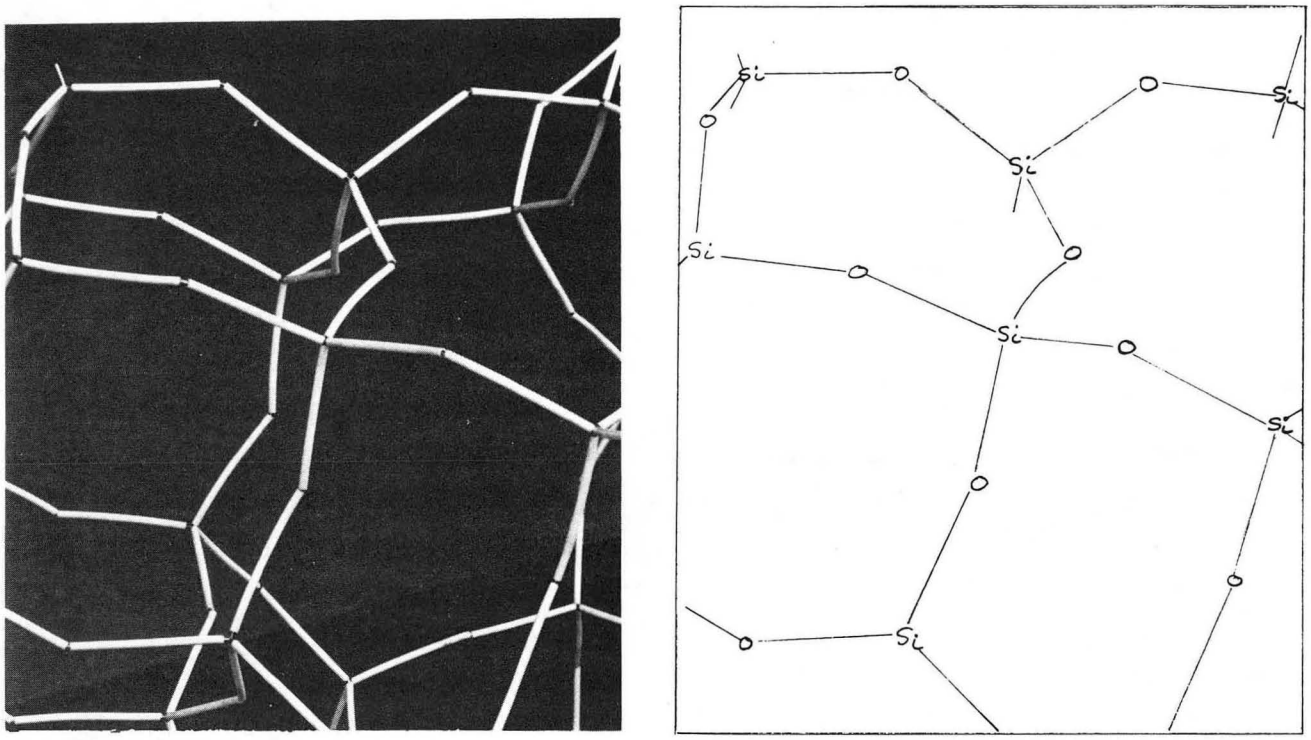

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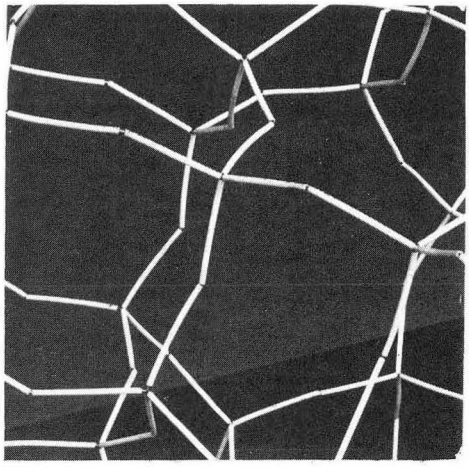
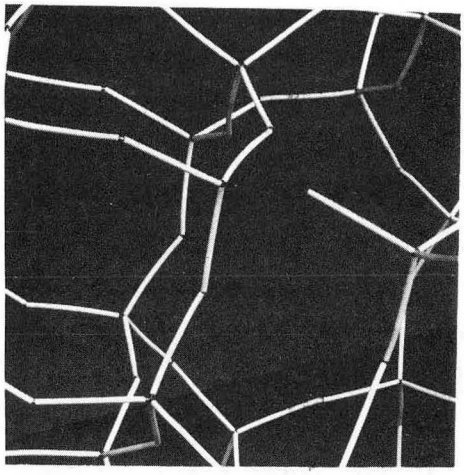
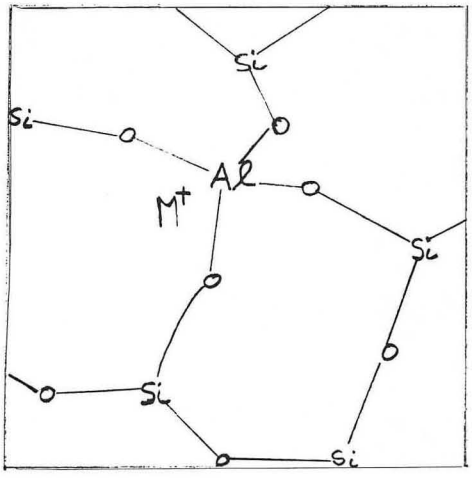
Fig. 5

Al in zeolite

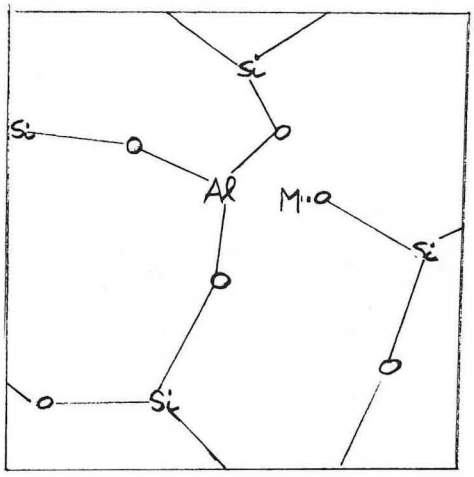






Al: 4 bonds

Cation: loosely bound



Al: 3 bonds

Cation: more tightly bound

XBB 867-5759

Fig. 6a

Fig. 6b

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