

Study of the Fine Structure of Zeolites and Materials Confined in Zeolites

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The fine structures of zeolites, compositional fluctuations and planar faults have been studied by high-resolution electron microscopy. Lead iodide, a material incorporated into the spaces of zeolite LTA, has also been studied.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Zeolites, represented by the general formula $M_{x/m}Si_{1-x}Al_xO_2 \cdot nH_2O$, where M is an exchangeable cation of valence m , and n is the number of water molecules, have been synthesized for use as ion exchangers, catalysts and molecular sieves.¹ However, on a molecular scale, the crystallization process is not well understood at this stage, and research on the fine structure of zeolites is important, not only in order to understand the growth process, but also to seek the best conditions for tailoring their chemistry. For the absorption forces in zeolites, on the other hand, Andersson and his group in Lund have given a fascinating explanation, using the differential geometry term 'curvature' of the minimal surface.² Zeolites have also been used as containers for materials which can be confined in the zeolite spaces.³⁻⁵ In addition, several systems have been reported in which quantum size effects are observed.^{6,7}

Since all these systems are in the crystalline state, diffraction is the main method used to solve their structures. There are two types of diffraction methods. One is X-ray or neutron diffraction, which gives atomic coordinates, occupation probabilities etc., i.e. information from within the unit cell.⁸ The other is electron microscopy, which is an extremely powerful technique used to observe fine structure on the unit-cell scale. In the case of zeolites, it is used for the observation of planar faults such as twins and intergrowths and the detection of very weak superlattice reflections, and for the direct observation of confined materials which usually are distributed randomly in the zeolite spaces.

In this paper some examples will be shown of HREM images of the fine structure of zeolites and the materials confined in the spaces, and the importance of the contributions of Andersson and his coworkers to our studies will be pointed out.

Experimental

Specimen preparation and other experimental techniques have been described in previous papers.^{4,5,7} 1 MV, 400 kV

and 200 kV electron microscopes were used for observations. Under appropriate conditions of Scherzer defocussing and crystal thickness, the contrast in the HREM images resembles the projected potentials, and so the channels or cavities (spaces) are imaged as white dots, unless there are materials confined in the spaces.

Results and discussion

Composition modulation of Si/Al in mordenite (MOR). Both compositional and phase modulations give effects observed in diffraction. For composition modulation in zeolites, two types must be considered. One is the ordered arrangement of Al and Si atoms in the zeolite framework structure of the unit cell; this can be detected by ion exchange of heavy cations into the zeolite, although the difference in scattering amplitudes between the two is very small for both X-rays and electrons. In Cs ion-exchanged Na-MOR, superlattice spots were observed which were not present in the original material. This forms the main part of the structure determination, together with an analysis of cations and water molecules. The other is composition modulation, the wavelength of which is larger than the unit cell, and this type will be shown here. In principle, from an analysis of the EDS X-ray emission spectra in the scanning electron microscope (SEM) we can obtain information on compositional variations, such as the Si/Al ratio across large particles, although the effective resolution is of the order of 10 nm.

We tried to introduce Se atoms into the channels of mordenite (Se-MOR), with the intention of making isolated Se-chains and observing them directly by HREM. During this study, we observed an unusual black and white contrast in the HREM image (Fig. 1) that was due to modulation of the Se content along [010], and found it difficult to explain the origin of this modulation.⁴ Immediately after being shown these HREM images Blume and Andersson suggested that the origin of this might correspond to the compositional fluctuation of Si/Al in the

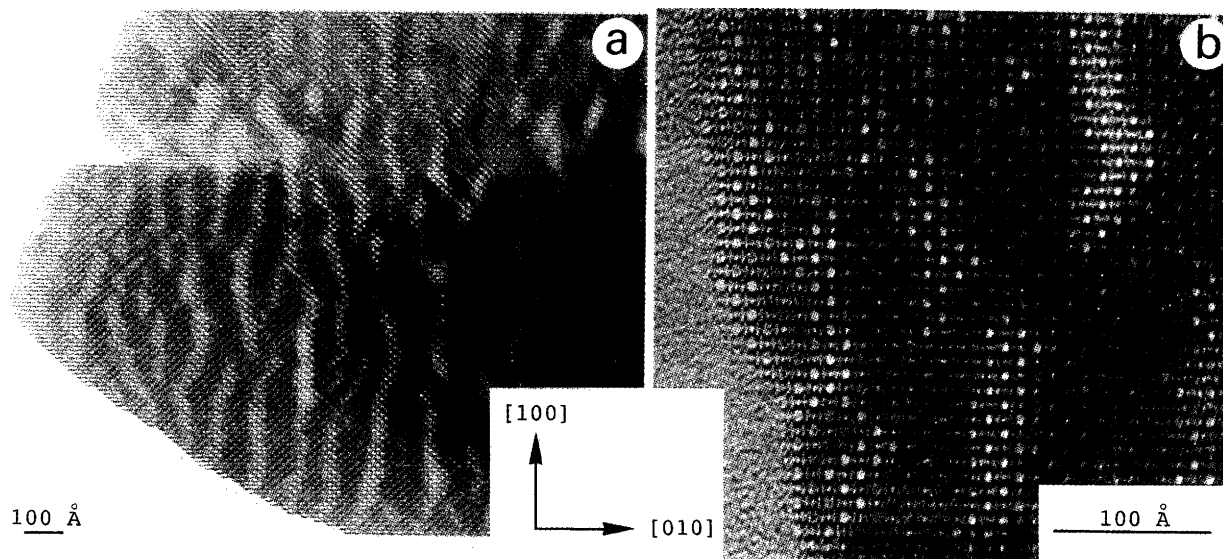


Fig. 1. HREM images of Se-MOR taken on 1 MV EM. (b) is a high-magnification image corresponding to (a).

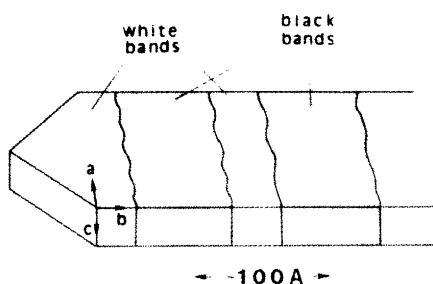


Fig. 2. Schematic drawing of the shape of MOR and the manner of its compositional variation along [010]. Dark bands correspond to Al-rich regions.

framework and that the Se concentration should be high in Al-rich regions, where the growth rate might be larger. I am now convinced that their explanation was right, particularly after our recent experiment on the optical absorption spectra of Se confined in the spaces. This showed that a finite number, 10–20, atoms of Se are physically adsorbed at each dipole induced by AlO_4^- and the cation.⁹ I want to stress, therefore, that Se atoms can be used as probes to detect compositional variations of Al in the unit cell size by producing contrast in the HREM images. The crystalline state of MOR, shown schematically in Fig. 2, was determined by this technique. The crystal has a plate-like character, long along the *b*-axis and thin along the *c*-axis, which is quite different from natural MOR, which is needle-shaped along the *c*-axis. Compositional modulation may be responsible for this shape, through a dependence of the crystal growth rate on the Si/Al ratio.

Planar faults

Twins in faujasite-type zeolite (FAU). The structure of FAU is composed of sodalite cages which are arranged in a

diamond-type lattice, through double-hexagonal rings. The stacking of sodalite cages along $[111]_{cub}$ forms the cubic stacking AA'BB'CC', where the midpoints between A and A', B and B', and C and C' correspond to the centres of the double-hexagonal rings, which are the inversion centres. In other words, double-hexagonal rings parallel to $[111]_{cub}$ form a face-centred cubic (FCC) lattice, and this arrangement produces the big cavities which also form the diamond lattice. The latter is shown schematically in the right and left parts of Fig. 3, while in the central part, the hexagonal stacking of sodalite cages, AA'CC', is inserted. In this case, the planes passing through the centres of A and A', and C and C', perpendicular to $[001]_{hex}$, are mirrors. There have been several reports on twins in FAU,¹⁰ and we have observed the same twins in FAU many times.

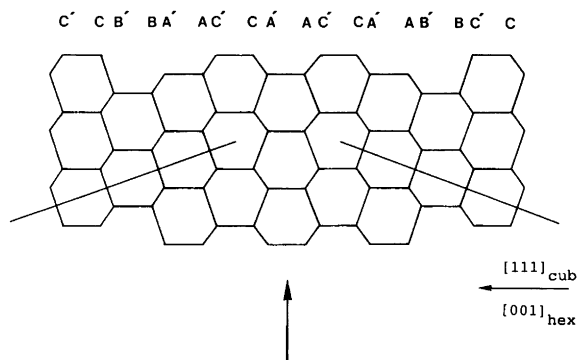


Fig. 3. Schematic drawing of stacking of sodalite cages. Intersecting points correspond to the positions of sodalite cages, and their stacking sequence along $[111]_{cub}$ and $[001]_{hex}$ are shown by A, A', B, B', C and C'. Hexagonal stackings are inserted between cubic ones. The lines and the arrow correspond to those in Fig. 5.

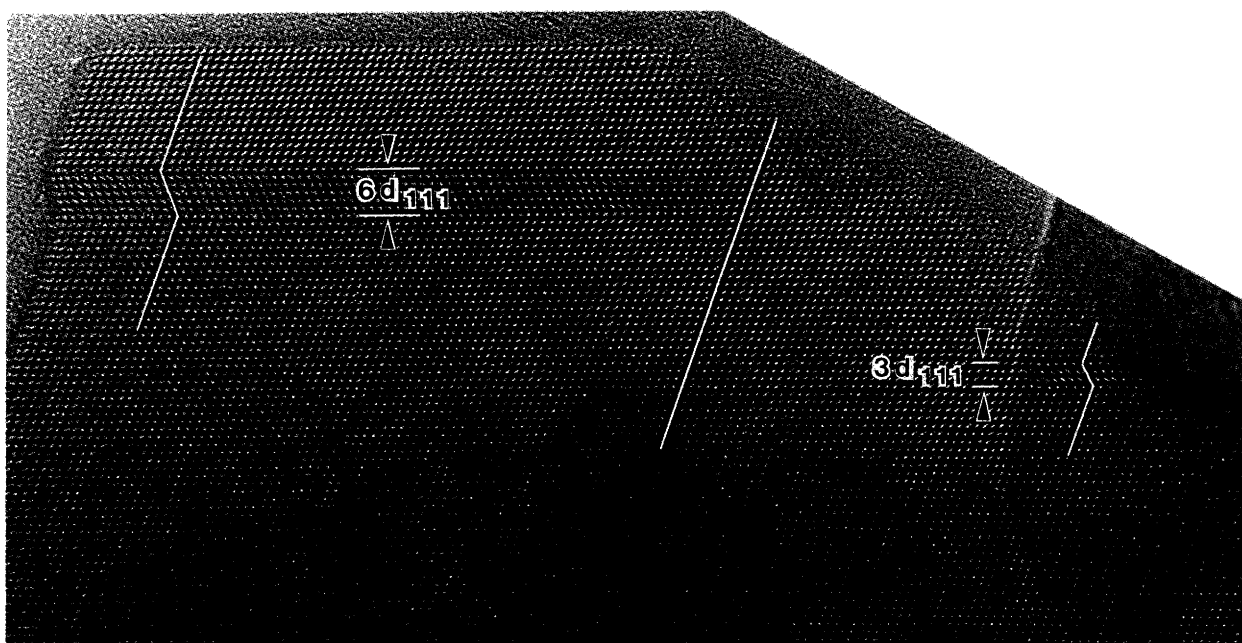


Fig. 4. An HREM image of a twin in FAU(USY) taken on a 1 MV electron microscope.

Fig. 4 shows an HREM image of twins. If there are twins in the crystal, the lines of white dot arrays, corresponding to the main channels, exhibit a zig-zag arrangement, in contrast to the straight line which is seen when there are no

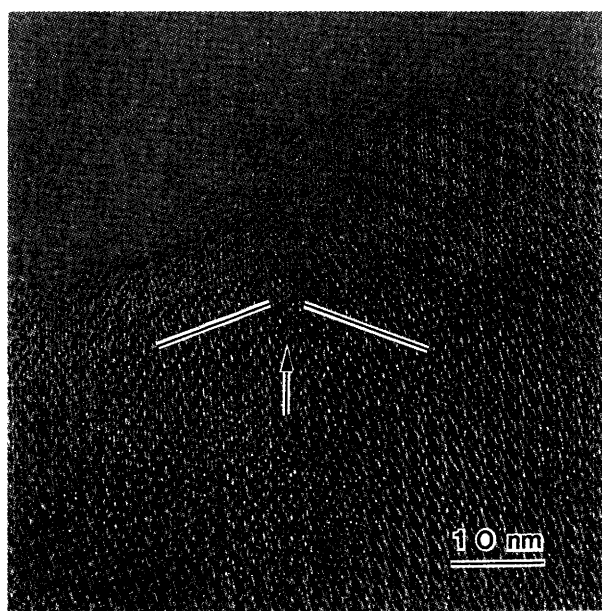


Fig. 5. An HREM image of a twin in FAU(USY) taken on a 400 kV electron microscope. Hexagonal stacking of sodalite cages is clearly visible in comparison with Fig. 3. The diffraction condition changes slightly across the fault, so the white dots corresponding to the main channels are less clear in the right-hand part of the figure.

twins. In Fig. 4 the twin plane does not penetrate the whole crystal, but is terminated within the crystal. This suggests that the framework structure is so flexible that the lattice strain around the terminated edge can be accommodated. Another interesting HREM image is shown in Fig. 5. It is easy to recognize that the arrangement of channels at the twin boundary is different from that in Fig. 4, but corresponds exactly to that in Fig. 3. This type of stacking has been suggested^{11,12} already, but as far as I know, this is the only observation of this type in USY, which is dealuminated FAU, synthesized without organic templates. If the sheet of sodalite cages is a building unit in the crystal growth process, then we should expect this type of stacking more often. All these HREM observations were made possible by using hydrophobic ultra-stable Y-zeolite (called USY), because zeolites are so sensitive to electron beams that the crystals become amorphous very easily if they contain many Al atoms in the framework (and therefore many water molecules).¹³ This material, with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 680$, was produced by the Tosoh Corporation, based on Andersson's suggestion. Synthetic cubic and hexagonal FAU can be obtained by using crown-ethers as templates.^{14,15} We have succeeded in changing the densities of this type of intergrowth, as shown in Fig. 5, and observing them directly in the HREM images. These studies are continuing, and details will be published elsewhere.

Intergrowth in the ERI/OFF system. The infinite set of the ABC-6 family of zeolites is obtained by linking parallel six-membered by tilted four-membered rings. The planes consist of hexagons, and their centres can take three different positions, A, B or C, in the projection perpendicular to the plane shown in Fig. 3. Erionite (ERI), offretite (OFF)

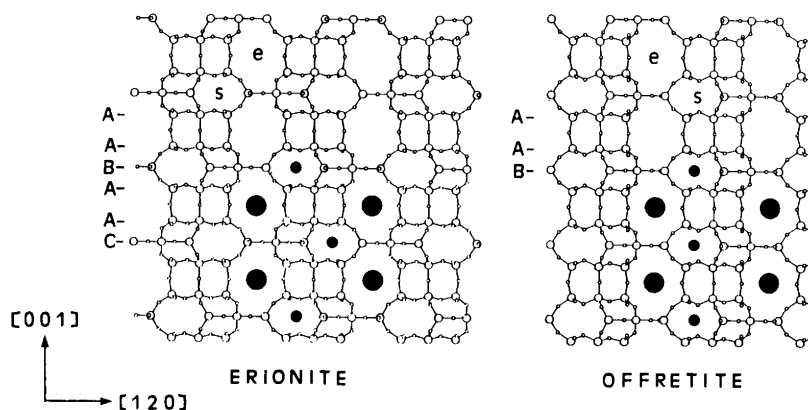


Fig. 6. Projections of ERI and OFF along $[100]$ to show the stacking sequence and the role of the double six-membered rings, AA. The letters s and e represent six- and eight-membered rings, respectively, and these are also shown by small and large solid circles.

and sodalite (SOD) are known to be members of this family, and their structures are described by the stacking sequence perpendicular to the plane, e.g., they are AA-BAAC, AAB and ABC for ERI, OFF and SOD, respectively. The nomenclature, ABC-6, is correct for an intuitive description of the framework structure, but there are some differences from the stacking problem in hard-sphere models. Special attention should be paid to the calculation of diffuse intensity distributions, because we must take into account the effect produced from tilted four-membered rings. $[100]$ incidence is a good orientation to detect the stacking sequence. The maximum number of successive stacks of the same type is two, as in AA, BB or CC, forming double six-membered rings, in contrast to the hard-sphere model, where more than one is not allowed. These double six-membered rings form eight-membered rings next to them in the same stack, and this helps us to solve the stacking sequence, as shown schematically in

Fig. 6 by differentiating between eight- and six-membered rings through a difference in contrast. Fig. 7 (a)–(c) show several different electron diffraction patterns of ERI/OFF taken with $[100]$ incidence. The manner of diffuse streaking along $[001]$ suggests fairly periodic intergrowths for (a) and (b), and random intergrowths for (c). We have reported both OFF and SOD intergrowths in ERI, the occurrence of which was very rare.¹⁶ An example of an HREM image showing OFF intergrowths in ERI with high density, is given in Fig. 8. Triangles show the positions where OFF intergrowths are present, and we can expect the appearance of diffuse maxima in the electron diffraction pattern from the density and spatial correlation of the intergrowths.

PbI₂ in LTA. PbI_2 is a layered semiconductor with hexagonal CdI_2 -type structure. An absorption band for crystalline bulk PbI_2 is observed at 2.5 eV in the orange region of the

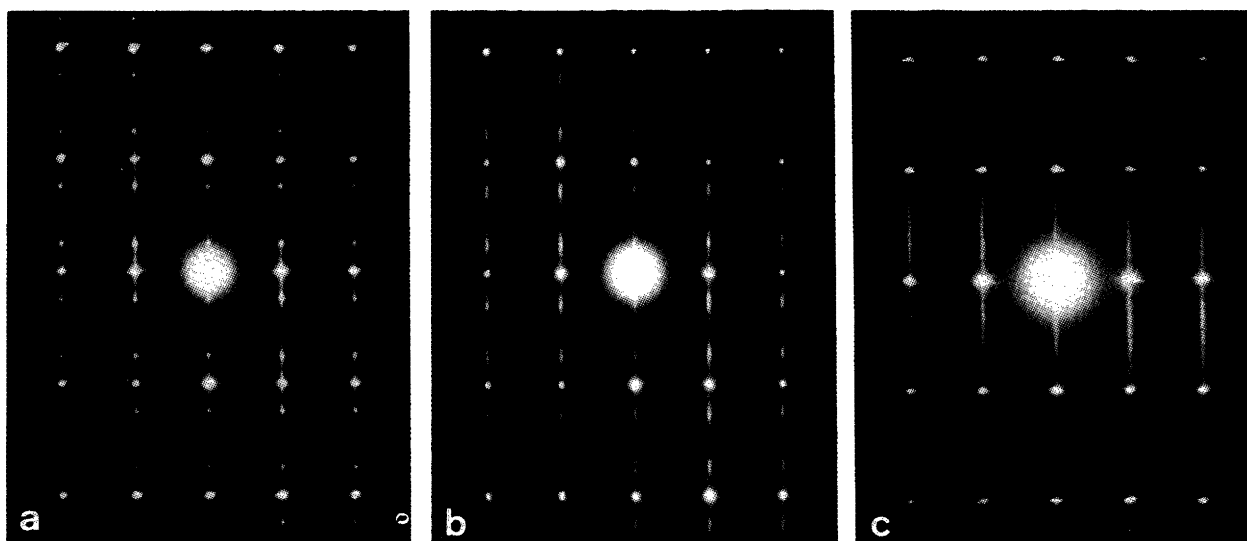


Fig. 7. Electron diffraction patterns of ERI/OFF showing various types of intergrowths.

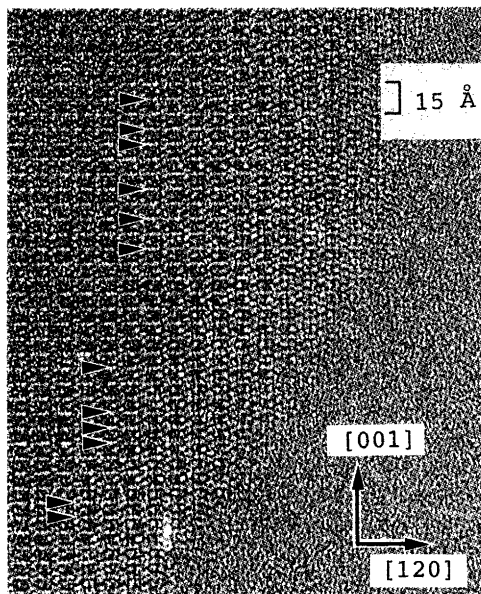


Fig. 8. An HREM image of ERI/OFF taken on a 400 kV electron microscope.

visible spectrum and is due to bulk exciton energy. Remarkable blue shifts to 3.0–3.6 eV and quantum size effects were observed in the optical absorption band of PbI_2 confined in the spaces of LTA zeolites.⁷ The structure of LTA is described in terms of sodalite cages, which are connected through double four-membered rings, and larger α -cages are produced. The α -cages are arranged in a simple cubic lattice of dimension 12.3 Å (space group $Pm\bar{3}m$), and if the ordering of Si and Al atoms in the framework structure is taken into account, the space group changes to $Fm\bar{3}c$, with $a = 24.6$ Å.¹⁷ Direct observation of PbI_2 in an HREM image was sought in order to confirm the results of the optical absorption measurements. Fig. 9 shows the HREM image taken on 200 kV EM, in which we can see dark contrast at the centres of the channels; some of them are

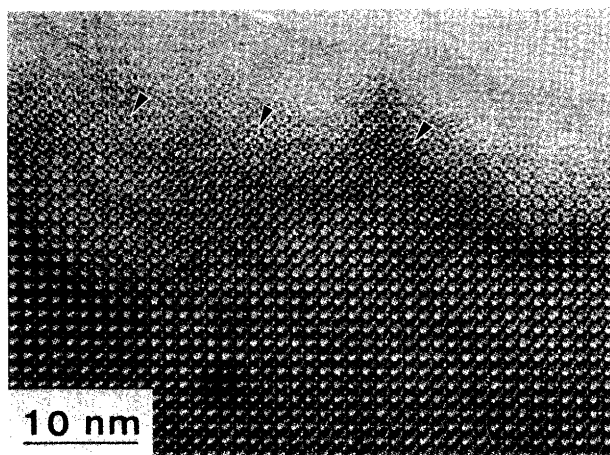


Fig. 9. An HREM image of PbI_2 confined in the cavities of LTA, at [001] incidence and taken on a 200 kV electron microscope.

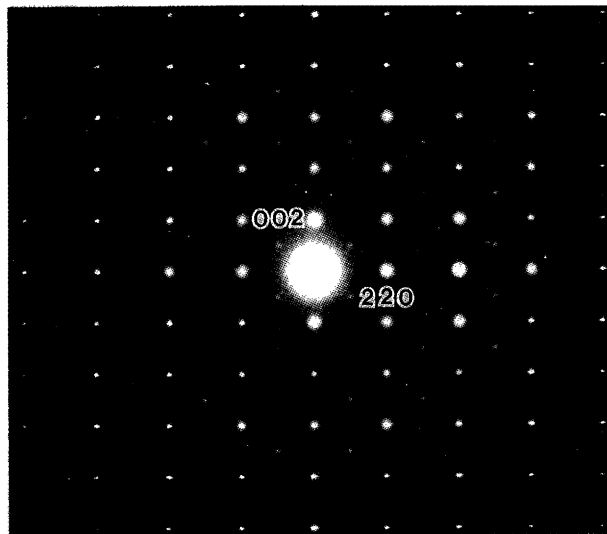


Fig. 10. An electron diffraction pattern of PbI_2 confined in the cavities of LTA at $[1\bar{1}0]$ incidence.

shown by triangles, although the incorporation of PbI_2 is not uniform. An electron diffraction pattern with $[1\bar{1}0]$ incidence from part of a crystal shows superlattice reflections (hhl) with $h, l = \text{odd}$, which are forbidden for the $Fm\bar{3}c$ space group (Fig. 10). The most simple model which produces these superlattice reflections may be of two different confined materials, arranged alternately, and since the intensity of the superlattice reflections is very weak, the difference in scattering power of the neighbouring confined materials is very small, such as might result from a different number or different orientation of PbI_2 molecules. The incorporated PbI_2 produces a new symmetry, which suggests an artificial superlattice of PbI_2 confined in the spaces of LTA. This structural problem remains unsolved.

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