The Canadian Mineralogist
Vol. 34, pp. 1031-1038 (1996)

TWO-DIMENSIONAL PERIODIC ANTIPHASE BOUNDARIES IN A SYNTHETIC ALUMINATE SODALITE, $Ca_8[Al_{12}O_{24}](CrO_4)_2$

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Abstract

Transmission electron microscopy (TEM) has provided direct evidence for ordering of $[Ca_4{\cdot}CrO_4]^{6+}$ clusters in a synthetic aluminate sodalite, $Ca_8[Al_{12}O_{24}](CrO_4)_2$. The ordering of the above clusters causes antiphase domains that are separated by two-dimensional periodic antiphase boundaries (APBs). Such APBs are rare in minerals and inorganic solids, but they do occur in alloys. The APBs are at 90° to each other, parallel to {110} planes, and separated by about 54 Å. At high temperature, the $[Ca_4{\cdot}CrO_4]^{6+}$ clusters in the aluminate sodalite (space group $I\bar{4}3m$) are disordered, together with the framework oxygen atoms. As the temperature is lowered, the $[Ca_4{\cdot}CrO_4]^{6+}$ clusters are ordered and cause two-dimensional periodic APBs that are probably accompanied by positional modulations of the framework oxygen atoms.

Keywords: aluminate sodalite, transmission electron microscopy, modulated structure, periodic antiphase boundaries.

Sommaire

Une étude fondée sur la microscopie électronique à transmission a fourni de l'évidence directe à propos de la mise en ordre d'agencements $[Ca_4{\cdot}CrO_4]^{6+}$ dans un aluminate synthétique à structure de sodalite, $Ca_8[Al_{12}O_{24}](CrO_4)_2$. La mise en ordre de ces agencements mène à la formation de domaines antiphasés, qui sont délimités en deux dimensions par des fronts périodiques antiphasés. De tels fronts sont rares dans les minéraux et les solides inorganiques, mais sont plus courants dans les alliages. Ces fronts sont disposés à 90° l'un de l'autre, parallèles aux plans {110}, et à une distance d'environ 54 Å l'un de l'autre. A température élevée, les agencements $[Ca_4{\cdot}CrO_4]^{6+}$ dans cette structure (groupe spatial $I\bar{4}3m$) sont désordonnés, comme le sont les atomes d'oxygène de la trame. A mesure que la température diminue, les agencements $[Ca_4{\cdot}CrO_4]^{6+}$ deviennent ordonnés, et causent ces fronts antiphasés périodiques en deux dimensions, qui seraient aussi accompagnés de modulations dans la position des atomes d'oxygène de la trame.

(Traduit par la Rédaction)

Mots-clés: aluminate à structure de sodalite, microscopie électronique à transmission, structure modulée, fronts antiphasés périodiques.

Introduction

Synthetic aluminate sodalites $M_8[Al_{12}O_{24}](XO_4)_2$, with M representing Ca, Sr, ..., and X representing S, Cr, Mo, W, ..., have been the subject of recent studies (*e.g.*, Depmeier *et al.* 1987, Depmeier 1988a, b). According to Depmeier (1988a, b), the cubic high-temperature phases are characterized by disordered XO_4 groups over six orientational positions, and the transitions to the lower-temperature tetragonal and orthorhombic phases are triggered by ordering of the XO_4 groups over fewer than six orientations (see Fig. 2 of Depmeier 1988a).

The sulfatic aluminosilicate and aluminate sodalites that contain interstitial tetrahedral anion groups (*e.g.*, SO_4^{2-}, CrO_4^{2-}, WO_4^{2-}, *etc.*) display complex satellite reflections in diffraction patterns. However, the origins of the satellite reflections are not known in detail (*e.g.*, Hassan & Grundy 1984, 1989, 1991, Hassan *et al.* 1985, Hassan & Buseck 1989a, b, Xu & Veblen 1995).

This paper concerns two-dimensional periodic antiphase boundaries (APBs) in a synthetic aluminate sodalite, $Ca_8[Al_{12}O_{24}](CrO_4)_2$, with a pseudo-cubic cell parameter, a, of 9.222(2) Å (Depmeier 1988a). Other structural features are reported elsewhere (Hassan 1996a, b, c, d).

Electron Microscopy Results

Selected-area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy

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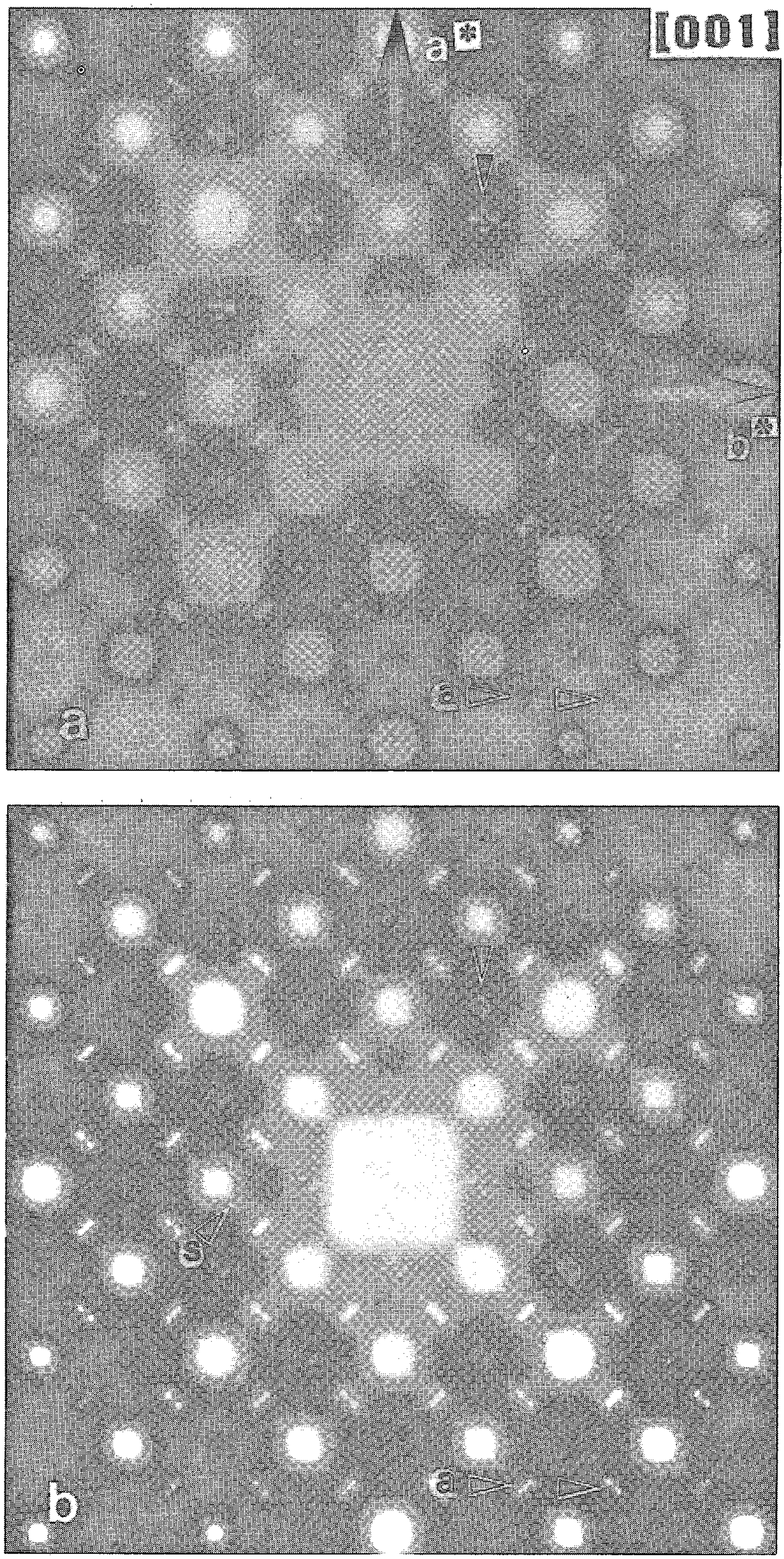

ı. [001] SAED pattern. ı) p'_s and r_s satellite :flections are shown. ifferent styles of p'_s and satellite reflections cur in (b); s satellite :lections (s_1 and s_2) and 'eaks occur along 10>* directions (arrow ›eled s).

(HRTEM) data were recorded from crushed crystals deposited on holey carbon support films and by using various microscopes (Hassan 1996a).

The main reflections in the cubic aluminate sodalite structure can be classified into two groups: one group of strong reflections satisfies the body-centered missing rule and is called type p (hkl: $h + k + l = 2n$), and the other group of weaker reflections that does not satisfy the body-centered rule is called type p' (hkl: $h + k + l = 2n + 1$; Fig. 1). The p' reflections are weak or missing at the intersection of the x reflections in the central region (*e.g.*, 100 in Fig. 1a).

The [001] SAED pattern shows strong subcell spots, diffuse streaking along <110>* directions, and various satellite reflections. One group of satellite reflections occurs at p' positions (*e.g.*, 100), but each spot is split into a group of four spots, which are denoted p'_s. The separation of the p'_s satellite reflections gives a periodicity of 42.4 Å. The splitting of the p'_s reflections occurs along **a*** and **b***. Another group of satellite reflections occurs midway between substructure spots along <110>* directions and is denoted r. However, each r reflection is split along <110>*, so they are denoted r_s. The r reflections are present in some places (Fig. 1b). Instead of a group of four p'_s spots (Fig. 1a), a group of six p'_s spots occurs (Fig. 1b). However, the extra pair of split spots occurs only along one of the <110>* direction and is similar to r_s spots. Still another group of s satellite reflections occurs along <110>* directions on either side of the main spots; the first- and second-order reflections are denoted s_1 and s_2, respectively. In some cases, second-order s_2 satellite reflections are present (arrow labeled s, Fig. 1b). Streaking also is present in the s satellite reflections and occurs along <110>* directions. Both the r_s and s satellite reflections give a periodicity of 53.5 Å. Different areas of the same single-crystal fragment show variable occurrence of satellite reflections (Figs. 1a, b); both patterns are from adjacent areas of the same single-crystal fragment.

The s and r_s satellite-reflection periodicity is expressed as nd_{110} (= 8.2 × 6.521 Å = 53.5 Å), whereas that for p'_s is na (= 4.6 × 9.222 = 42.4 Å). Because n is an irrational multiple of the basic substructure, the modulation is incommensurate for aluminate sodalite. The structure of the aluminate sodalite was imaged to determine which features cause the incommensurate modulations.

Two-Dimensional Periodic APBs and Modulations

Two-dimensional periodic APBs are parallel to {110} planes (Fig. 2). A typical SAED pattern corresponding to this image is shown (Fig. 1a). The set of APBs at the bottom is wave-like in appearance. A magnified image is shown in Figure 3. The two-dimensional periodic APBs occur at 90° to each other and are separated by about 54 Å. The optical diffractogram taken from the middle-right of the image contains the r_s satellite reflections that cause the APBs. Modulated fringes, s, occur at the left of the image, but the corresponding reflections are not obvious in the optical diffractogram. These s modulated fringes are wave-like in appearance along the horizontal direction (Fig. 3). The boundaries between the s modulated fringes are pointed out by arrows at the left. Across these boundaries, one set of periodic APBs occurs. The (110) planes are shifted by $\frac{1}{2}d_{110}$ spacing across the APBs. The alternating light and dark fringes are shifted back and forth, both horizontally and vertically, by one-half the (110) spacing across the APBs. The alternating light and dark fringes indicate ordering of $[Ca_4{\cdot}CrO_4]^{6+}$ clusters (see Hassan & Buseck 1988, 1989a, b). Differences in contrast are also seen along (100) and (200), and (010) and (020) planes, respectively, indicating cluster ordering (Fig. 3). The four double-headed arrows indicate additional modulated fringes (Fig. 3). Groups of four p'_s reflections occur in the optical diffractogram, so their corresponding modulations are present in the image and occur along the **a** and **b** directions. These modulations are seen as variation in the intensities of the white and dark spots on the image. The row of spots are white along a (100) plane, but they become dark at the APBs (see also below, Fig. 5). The repetition of the white and dark spots causes the p'_s satellite reflections.

The APBs occur at the boundaries between the s_1 modulation fringes (Fig. 4). This is clearly illustrated in this low-magnification image, in which the s_1 modulation fringes run vertically, and the boundaries coincide with the APBs. The features from the middle-left to upper-left of the image indicate the beginning of the second set of APBs. The APBs are best seen by viewing the image at a low angle horizontally and vertically, respectively.

Predominantly one-dimensional periodic APBs are shown (Fig. 5). Across an APB, one set of (110) planes is shifted by a value of $\frac{1}{2}d_{110}$. Two additional sets of fringes running off the vertical direction are also shifted by one-half the repeat unit, as indicated by the wave-like arrows at bottom left. The two symmetrically related double-headed arrows at the right of the image point out additional modulated fringes. Although this image shows that the APBs are predominantly one-dimensional, a second set of APBs is indicated on the optical diffractogram by pairs of r_s satellite reflections (arrowheads in insert). Adjacent regions of this crystal fragment contain only **a** × **b** substructure fringes (not shown), but part of this feature can be seen in the upper-left of the image. Although p'_s reflections do not occur in the optical diffractogram, their corresponding modulations are present in the image and occur along the **a** and **b**

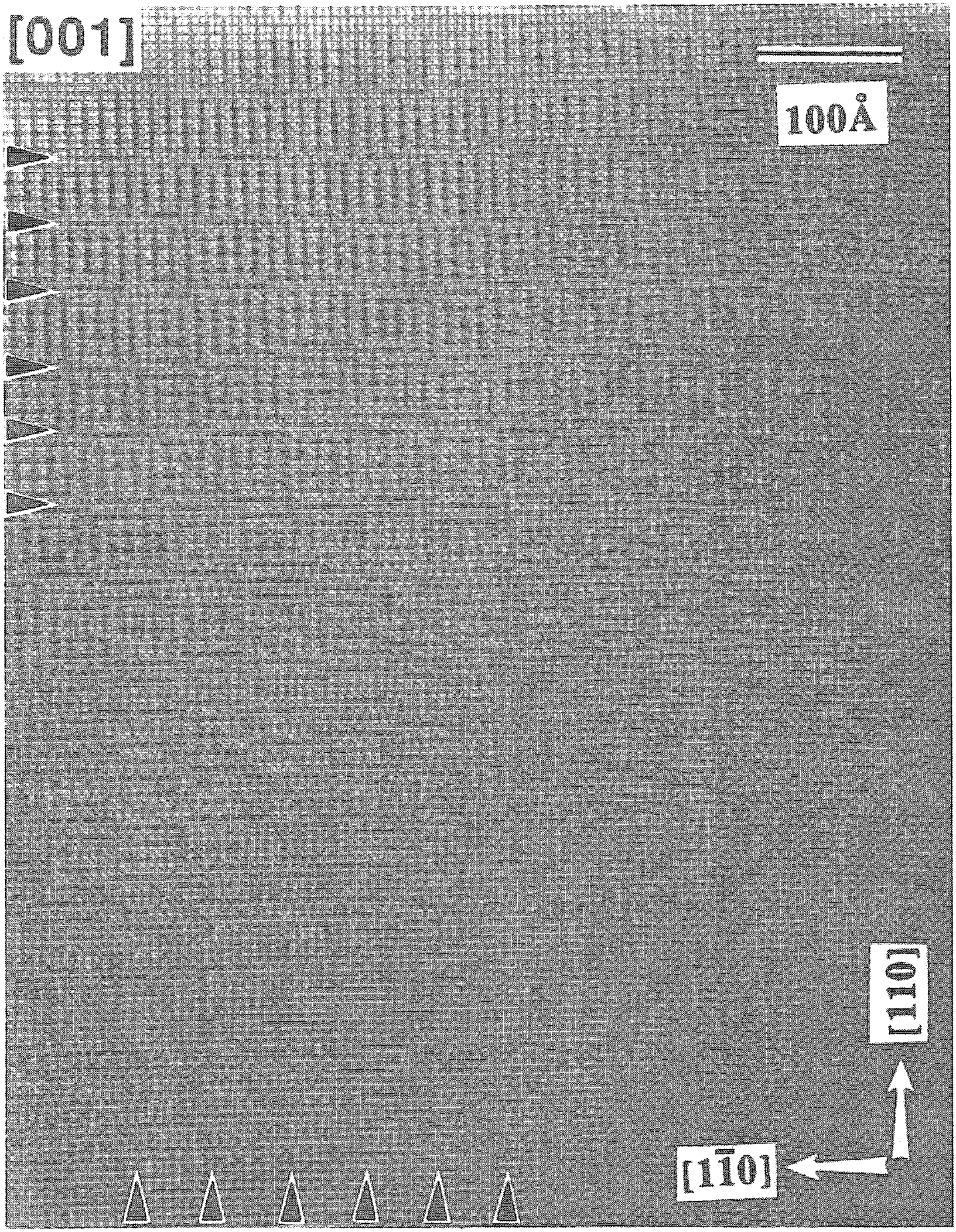

FIG. 2. APBs in [001] image of aluminate sodalite. Two-dimensional periodic APBs, parallel to {110} planes, are pointed out by sets of arrowheads at the upper-left and bottom.

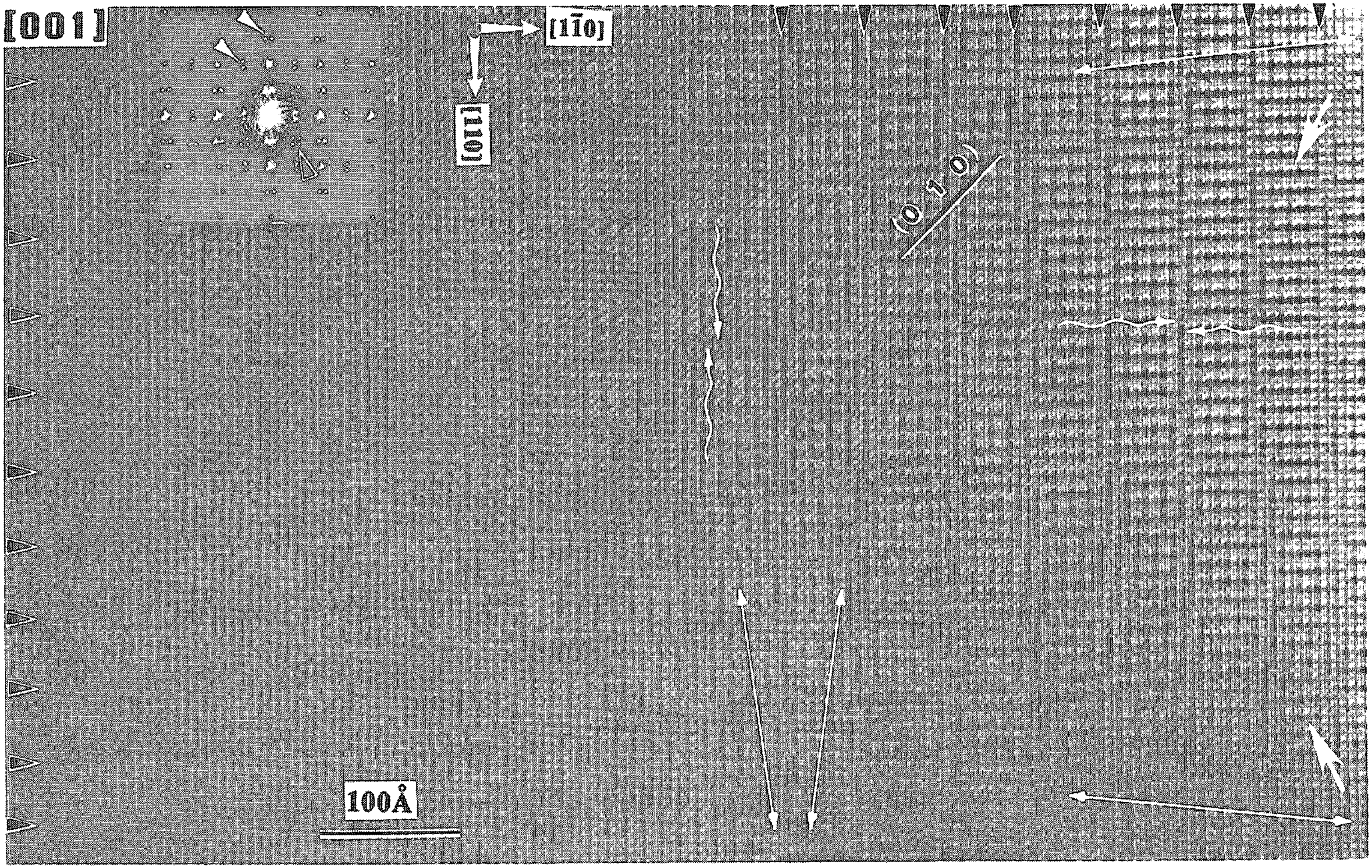

FIG. 3. APBs in [001] image of aluminate sodalite. Two-dimensional periodic APBs are shown (black arrowheads at the top and left). The {110} fringes are shifted by a value of $\frac{1}{2}d_{110}$ across the APBs (horizontal and vertical pairs of wave-like arrows). Symmetrical pairs of white arrows at the top right and bottom right point out fringes that are also shifted by one-half of the repeat unit, but these are difficult to see. Two different sets of symmetrical pairs of double-headed arrows point out additional modulated fringes. The optical diffractogram contains r_s reflections (white arrowheads in insert), and p'_s reflections (black arrowhead in insert).

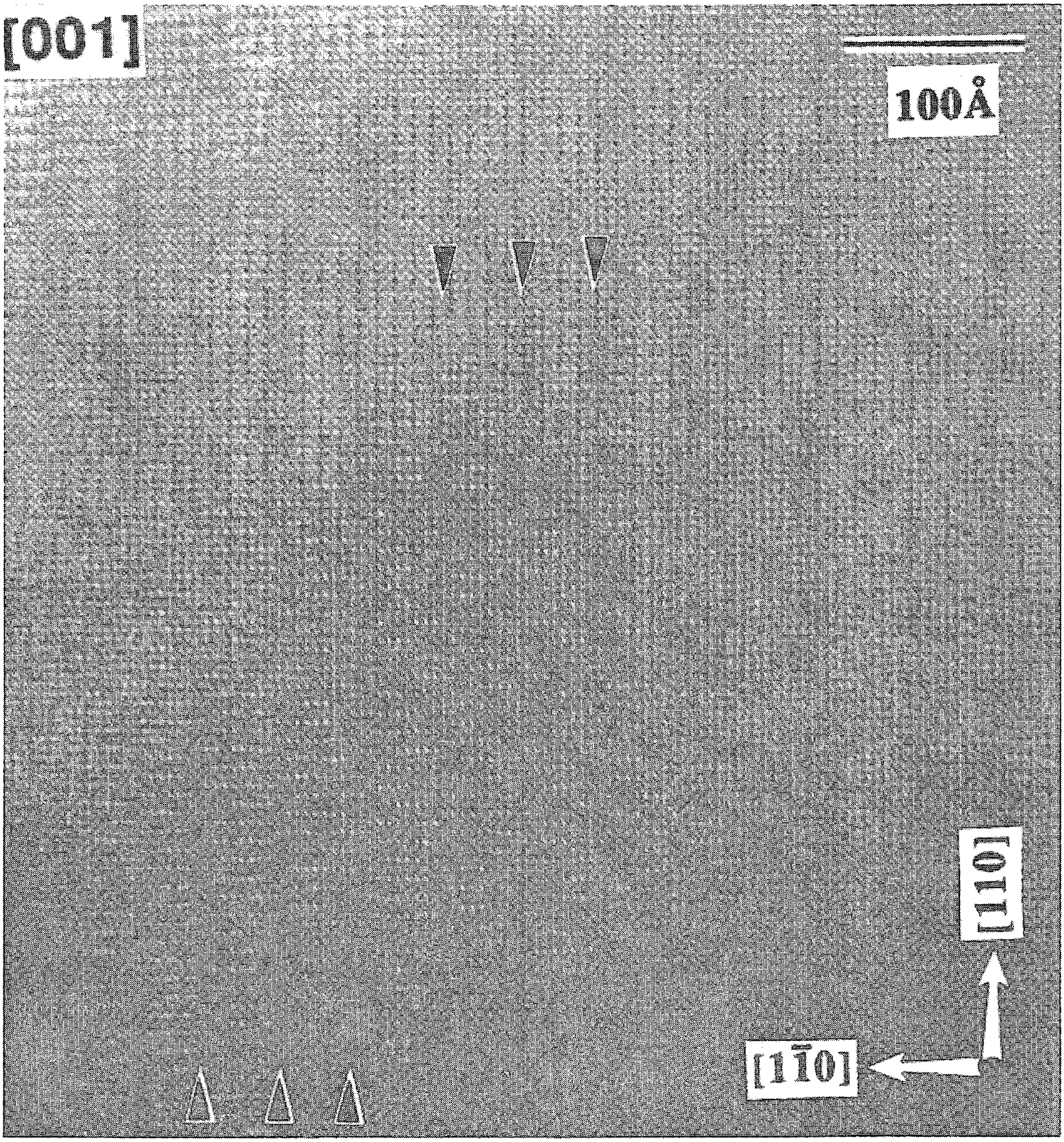

FIG. 4. APBs in [001] image of aluminate sodalite. One-dimensional periodic APBs parallel to (1$\bar{1}$0) planes are dominant (arrowheads), but the second set of APBs parallel to (110) planes occur in places. A magnified image is given in Figure 5.

directions. These modulations are seen as a variation in the intensities of the white and dark spots on the image. The row of spots are white along a (100) plane, but they become dark at the APBs (Fig. 5). This feature is best seen at the top and bottom of the image by viewing along the (100) plane at a low angle.

DISCUSSION

The SAED patterns indicate that the aluminate sodalite structure is modulated in several directions, notably <100>* and <110>*. The TEM images of the aluminate sodalite show that the structure is modulated in several directions in different parts of the crystal, and some parts are unmodulated. In the modulated parts, the framework oxygen atoms are probably positionally ordered on the O1 and O2 positions, whereas in the unmodulated parts they are disordered (see Hassan & Grundy 1989, 1991, Hassan *et al.* 1985, Hassan & Buseck 1989a, b). The disordered domains

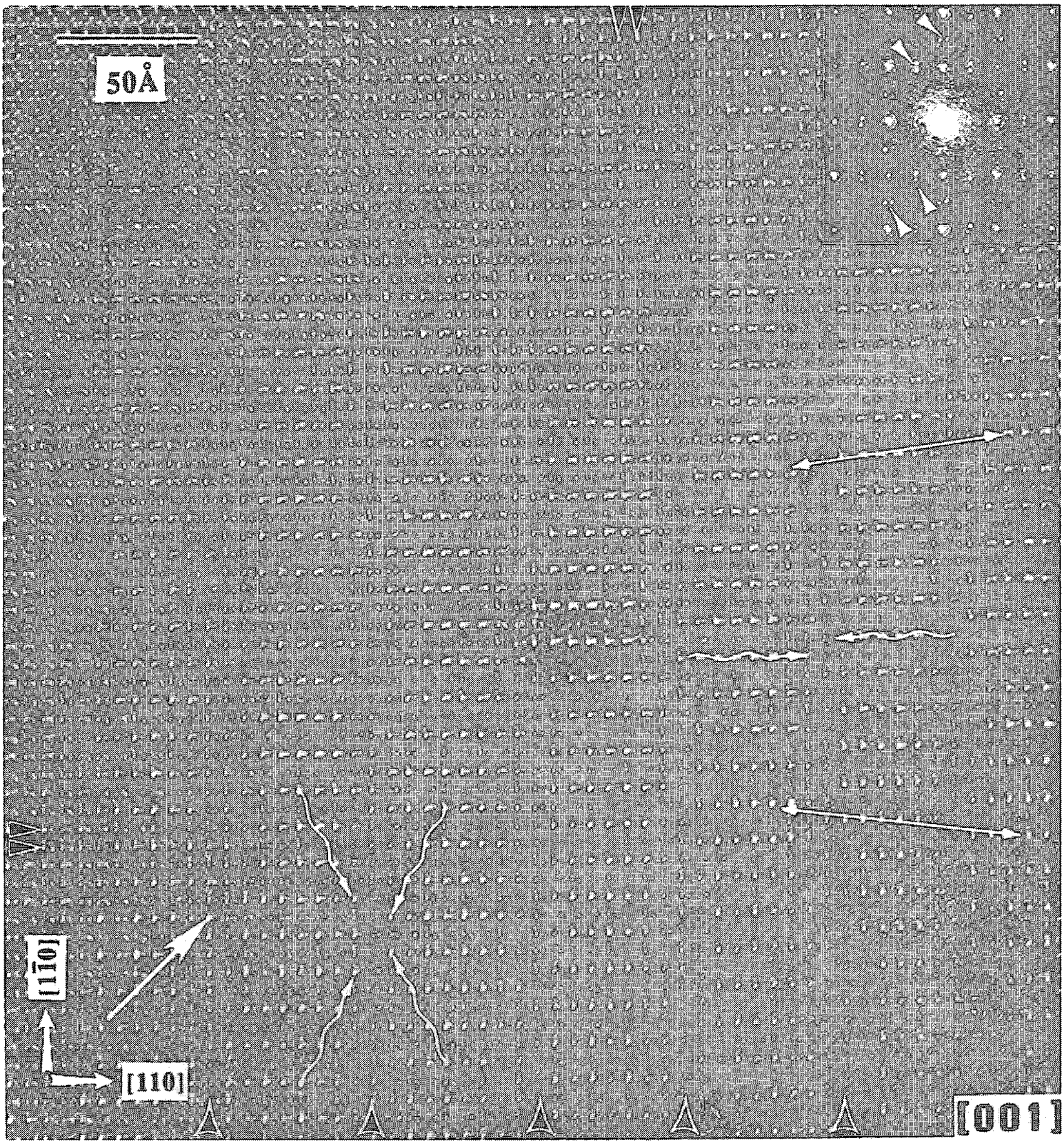

FIG. 5. APBs in [001] image of aluminate sodalite. One-dimensional periodic APBs are shown (bottom arrowheads). The (110) planes are shifted by a value of $\frac{1}{2}d_{110}$ across the APBs (pairs of wave-like arrows at middle right). APBs are absent in the thin part of the crystal (upper left), where the clusters are disordered. Symmetrical pairs of double-headed arrows point out additional modulated fringes. The (100) planes are indicated by a large white arrow at the lower left, and the $\frac{1}{2}d_{110}$ shift is pointed out by pairs of arrowheads at the lower-left and top. The optical diffractogram contains pairs of r_s reflections (arrows in insert).

may be compared to a high-temperature cubic phase, whereas the ordered domains can be considered analogous to a phase that is in a transitional state. The modulations of the framework oxygen atoms in aluminate sodalite cause the p'_s and s satellite reflections. However, a structure refinement is necessary to determine if indeed O1 and O2 positions occur in the aluminate sodalite.

The p' reflections imply that the contents of the cages centered at (0, 0, 0) and (½, ½, ½) are not equivalent. Nosean contains p' reflections and random APBs based on cluster ordering, so the average structure is best described in space group $P\bar{4}3n$, a subgroup of $I\bar{4}3m$. However, the p' reflections indicate that space group $P23$, a subgroup of $P\bar{4}3n$, is the most appropriate for the individual domains in nosean (Hassan & Grundy 1989, Hassan & Buseck 1989a). The simulated HRTEM images of nosean indicate that ordered $[Na_4{\cdot}SO_4]^{2+}$ and $[Na_4{\cdot}H_2O]^{4+}$ clusters can be recognized by HRTEM imaging. This ordering was observed as differences in contrast along (100) and (200), and (010) and (020) planes, respectively. This ordering of clusters leads to random APBs in nosean, analogous to those in scapolite-group minerals (Hassan & Buseck 1988, 1989a, b). If the cavity at (0, 0, 0) is occupied by $[Na_4{\cdot}SO_4]^{2+}$ clusters, then the cavity at (½, ½, ½) would be occupied by $[Na_4{\cdot}H_2O]^{4+}$ clusters; in the adjacent domain the occupancy of the cavities is reversed in nosean. In the aluminate sodalite, a similar type of cluster ordering occurs, but leads to two-dimensional periodic APBs. The alternating light and dark fringes are shifted back and forth, both horizontally and vertically, by one-half the (110) spacing across the APBs. The alternating light and dark fringes indicate ordering of $[Ca_4{\cdot}CrO_4]^{6+}$ clusters (see Hassan & Buseck 1988, 1989a, b). Differences in contrast also are seen along (100) and (200), and (010) and (020) planes, respectively (see Figs. 3, 5).

Two-dimensional periodic APBs are rare in minerals and inorganic solids, but they do occur in alloy systems (*e.g.*, AuCu). However, one-dimensional periodic APBs occur in minerals, for example, e-plagioclase (Nakajima *et al.* 1977).

Conclusions

At high temperature, the $[Ca_4{\cdot}CrO_4]^{6+}$ clusters in the aluminate sodalite (space group $I\bar{4}3m$) are disordered, together with the framework oxygen atoms. As the temperature is lowered, the $[Ca_4{\cdot}CrO_4]^{6+}$ clusters are ordered and cause two-dimensional periodic APBs along {110} planes. The APBs are separated by about 54 Å. These APBs cause the r_s satellite reflections. The formation of these APBs is probably accompanied by positional modulations of the framework oxygen atoms on the O1 and O2 positions. These modulations produce s and p'_s satellite reflections.

Acknowledgements

Dr. W. Depmeier and an anonymous referee are thanked for useful comments on this paper. Dr. John Barry is thanked for useful discussions and for his help in using the 4000EX microscope. The aluminate sodalite sample was provided by Dr. Yohan DeVellier. This work was financially supported by a University of Kuwait grant SG–038 to IH and by a NSF grant EAR–8708169 to Dr. P.R. Buseck; microscopy data were obtained at Arizona State University HREM Facility and at the University of Kuwait EM Centre.

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Received June 1, 1995, revised manuscript accepted June 8, 1996.