Canadian Mineralogist
Vol. 27, pp. 173-180 (1989)

CLUSTER ORDERING AND ANTIPHASE DOMAIN BOUNDARIES IN HAUYNE

ISHMAEL HASSAN* AND PETER R. BUSECK
Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

High-resolution transmission electron microscopy indicates ordering of $[Na_3Ca{\cdot}SO_4]^{3+}$ and $[K_2Ca{\cdot}OH]^{3+}$ clusters in hauyne, ideally $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$. Reflections of type *hhl*, $l = 2n + 1$, indicate that space group $P\bar{4}3n$ is an average for hauyne, and that space group $P23$, a subgroup of $P\bar{4}3n$, applies for each domain, as was found in nosean and lazurite. Antiphase domain boundaries, arising from ordering of the clusters, occur in hauyne. In general, diffraction patterns of sulfatic sodalite samples show complex satellite reflections in several directions that arise from well-defined modulations of the framework oxygen-atom positions; in the sample of hauyne that was studied here, however, diffuse streaked reflections instead of satellite spots occur in directions such as <001>, <110>, and <112>. The diffuse, streaked reflections mark the beginning of superstructure formation. Some parts of the crystal show superstructure fringes, and others do not, thus indicating another type of domain structure. The ordering of the cage clusters does not significantly affect the positions of the framework oxygen atoms, suggesting that $[Na_3Ca{\cdot}SO_4]^{3+}$ and $[K_2Ca{\cdot}OH]^{3+}$ clusters give rise to similar geometrical effects. Contrary to previous work, this study indicates an incomplete nosean–hauyne solid-solution series.

Keywords: sodalite group, hauyne, HRTEM, cluster ordering, antiphase domain boundaries, nosean–hauyne solid solution, nosean, lazurite.

SOMMAIRE

Une étude par microscopie électronique par transmission à haute résolution indique une mise en ordre de groupements $[Na_3Ca{\cdot}SO_4]^{3+}$ et $[K_2Ca{\cdot}OH]^{3+}$ dans la hauÿne, de formule idéale $Na_6Ca_2[Al_6Si_6O_{24}](SO_4)_2$. La présence de réflexions de type *hhl*, $l = 2n + 1$, indique que le groupe spatial $P\bar{4}3n$ constitue une moyenne pour la hauÿne, et que le groupe spatial $P23$, sous-groupe de $P\bar{4}3n$, régit chaque domaine, tout comme pour noséane et lazurite. La hauÿne contient donc des parois entre domaines déphasés, qui sont l'expression d'une mise en ordre des groupements. En général, les clichés de diffraction d'échantillons de sodalite sulfatée révèlent des réflexions satellites complexes dans plusieurs directions, qui résultent de modulations bien définies dans la position des atomes d'oxygène de la trame; dans les échantillons de hauÿne étudiés, toutefois, nous observons des réflexions étirées diffuses plutôt que des taches satellites le long de <001>, <110> et <112>. Ces réflexions étirées diffuses témoignent d'un début de formation de surstructure. Les franges de la surstructure sont présentes dans certaines portions d'un cristal, et absentes dans les autres, ce qui impliquerait la présence d'une autre sorte de structure en domaines. La mise en ordre des agencements des cages n'a qu'une faible influence sur la position des atomes d'oxygène de la trame, ce qui fait penser que les agencements $[Na_3Ca{\cdot}SO_4]^{3+}$ et $[K_2Ca{\cdot}OH]^{3+}$ produisent des effets géométriques semblables. Cette étude nous conduit à proposer une solution solide incomplète entre noséane et hauÿne, contrairement à l'opinion courante.

(Traduit par la Rédaction)

Mots-clés: groupe de la sodalite, hauÿne, microscopie électronique par transmission à haute résolution, mise en ordre des agencements, parois des domaines déphasés, solution solide noséane-hauÿne, noséane, lazurite.

INTRODUCTION

This work is part of a broad study of complex framework aluminosilicate minerals, the purpose of which is to characterize the role of volatile elements that are of petrological importance. Hauyne and nosean commonly are considered to form a solid-solution series mainly because they contain SO_4^{2-} as a principal interframework anion and because substitution has been demonstrated in experimental work (Van Peteghem & Burley 1963). Taylor (1967) proposed the general formula $(Na_{5-7}Ca_{0-2}K_{0-3})[Al_6Si_6O_{24}])(SO_4)_{1-2}$ for hauyne, and $(Na_{5-8}Ca_{0-2}K_{0-1}\square_{0-1})[Al_6Si_6O_{24}](SO_4)_{1-2}{\cdot}nH_2O$ for the nosean–

---

*Present address: Department of Geology, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A.

hauyne series. Nosean and lazurite exhibit ordering reflections of the form *hhl*, $l = 2n + 1$, but in hauyne such reflections were undetected using X-ray-diffraction techniques (Taylor 1967, Hassan 1983, Hassan *et al.* 1985, Hassan & Grundy 1989). These studies indicate a change in space group between nosean and hauyne (see Taylor 1967), and they raise the question addressed here as to whether nosean and hauyne do form a solid-solution series.

Hauyne is a framework aluminosilicate mineral in which the TO_4 (T = Al, Si) tetrahedra are fully ordered. The structure is characterized by six- and four-fold rings of TO_4 tetrahedra parallel to {111} and {100} planes, respectively. The linkage of the TO_4 tetrahedra results in cubo-octahedral cages (see Fig. 1 of Hassan & Grundy 1984). The cages contain $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters (Hassan 1983). Nosean cages contain $[Na_4{\bullet}SO_4]^{2+}$ and $[Na_4{\bullet}H_2O]^{4+}$ clusters, and they are ordered because of net differences in charge and size between the clusters (Hassan & Grundy 1989, Hassan & Buseck 1987, 1989). For hauyne, such cluster ordering cannot be predicted *a priori*; the establishment of the possible existence of such ordering is, therefore, another goal of this study.

Sulfatic sodalites such as nosean, lazurite, and hauyne generally show complex, incommensurate satellite spots (Saalfeld 1961, Taylor 1967, Schulz 1970, Hassan *et al.* 1985, Hassan & Buseck 1989). In general, the satellite reflections occur as sharp spots along several directions, but in the hauyne studied here they occur as diffuse, streaked reflections that mark the beginning of superstructure formation. Structures of this hauyne and a similar one have been determined (Lohn & Schulz 1968, Hassan 1983). This material, therefore, provides an opportunity to study a sulfatic sodalite that is not complicated by strong satellite spots.

Here we present results on ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters in hauyne as well as on antiphase domain boundaries (*APBs*) arising from ordering of these clusters. The space group for each domain is *P*23. Moreover, ordering of the framework oxygen-atom positions occurs randomly in parts of the hauyne crystal, as evident by diffuse, streaked reflections along many directions. In [110] high-resolution transmission electron microscopy (HRTEM) images, large parts of the crystal do not show superstructure fringes, but other parts of the crystal do contain superstructure fringes, thus indicating another type of domain structure. This study also suggests the existence of an interrupted nosean–hauyne series.

PREVIOUS WORK

Transmission electron microscopy (TEM) has been used to study sulfatic sodalites showing well-developed satellite reflections (Morimoto 1978, Tsuchiya & Takéuchi 1985, Hassan & Buseck 1989). Incommensurate modulations of the framework oxygen-atom positions give rise to complex satellite reflections along directions such as <001>, <110>, <112>, and $<41\bar{2}>$.

Ordering of clusters such as $[Na_4{\bullet}SO_4]^{2+}$ and $[Na_4{\bullet}H_2O]^{4+}$ occurs in nosean. The differences in size and net charge between these clusters give rise to two well-defined framework oxygen-atom positions in nosean and lazurite, but only one oxygen-atom position exists in hauyne (Hassan 1983, Hassan *et al.* 1985, Hassan & Grundy 1989).

Two different types of domains occur in nosean. One type of domain is based on positional ordering of the framework oxygen-atom positions because parts of the crystal are modulated and contain superstructure fringes; other parts of the crystal are not modulated. The other type of domain is based on cluster ordering, and these domains are separated by antiphase boundaries. Based on reflections of the type *hhl*, $l = 2n + 1$, space group *P*23, a subgroup of $P\bar{4}3n$, is the space group for the domains that arise from cluster ordering in nosean and lazurite (Hassan & Grundy 1989, Hassan & Buseck 1989).

ELECTRON MICROSCOPY

The sample used in this study (Royal Ontario Museum sample M35731, from Sacrafano, Italy) also was used to extract a crystal for structure refinement (Hassan 1983). Its composition is close to $Na_{4.5}Ca_2K[Al_6Si_6O_{24}](SO_4)_{1.5}(OH)_{0.5}$, and the cell parameter is 9.116(5) A. Based on the structure analysis and composition, 75% of the cages contain $[Na_3Ca{\bullet}SO_4]^{3+}$ clusters, and the remaining 25% of the cages contain $[K_2Ca{\bullet}OH]^{3+}$ clusters. The latter clusters contain a vacant cation site, so that cation-vacancy ordering is possible. If the clusters are ordered, the excess $[Na_3Ca{\bullet}SO_4]^{3+}$ clusters can be distributed randomly through the structure or they can be segregated into domains. Such domains contain one type of cluster, and they are not expected to give rise to ordering reflections unless the SO_4^{2-} group has different orientations and, thus, different coordinations.

Fragments of hauyne suitable for study were obtained by crushing in acetone using an agate mortar and pestle. Crystals in suspension were deposited on holey carbon support films, and TEM data were recorded from thin regions. Electron microscopy was performed using JEOL 200CX and 4000EX microscopes operated at 200 keV and 400 keV, respectively. TEM images were recorded at a magnification of less than 250,000. Hauyne did not damage as rapidly in the 4000EX microscope as in

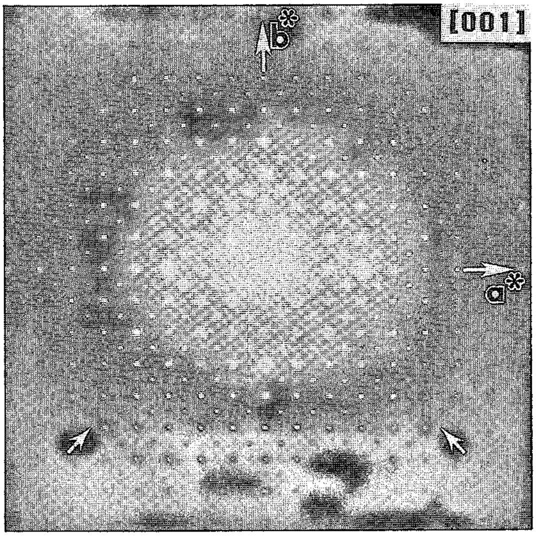

FIG. 1. [001]-zone SAED pattern of hauyne. Alternating rows of weak type-p' reflections (arrows) occur parallel to $<110>^*$ directions.

the 200CX microscope because the former was operated in the "minimum exposure" mode to minimize the electron-beam irradiation.

DIFFRACTION PATTERNS

The [001]-zone selected-area electron diffraction (SAED) patterns contain reflections of the form hhl, $l = 2n + 1$) *e.g.*, {100} reflections, denoted type p'; Fig. 1). Type-p' reflections (general: hkl, $h + k + l = 2n + 1$) are absent in space group $P\bar{4}3n$, which allows reflections of class hhl, $l = 2n$ (type p; general: hkl, $h + k + l = 2n$). The type-p' reflections are related to ordering of the cage clusters and indicate that the space group for hauyne is $P23$. Diffuse reflections occur around the edges of Figure 1, but in other sulfatic sodalites these reflections occur as sharp spots (Hassan & Buseck 1989). Type-r reflections, which occur midway between the main spots along $<110>$ directions (Figs. 2,3), are absent in [001] zones (Fig. 1). The occurrence and intensities of reflections of type r and p' are variable; they occur in some hauyne fragments and are absent in others (Figs. 2, 3). Such spots cannot arise from double diffraction.

Diffuse, streaked, type-q reflections are parallel to $<112>$ directions, and they have the appearance of an X (Figs. 2b, c). The lengths of the streaks increase (*i.e.*, the X becomes bigger; arrows in Fig. 2c) as the orders of the reflections increase, which is characteristic of positional modulations (Smith 1974, Buseck & Cowley 1983). Of particular importance is the absence of satellite spots or streaking in $<111>$ directions. The interframework atoms are located along these directions, so that absence of satellite reflections indicates that the interframework atoms are disordered along $<111>$ directions, as is also the case for nosean and lazurite (Hassan & Buseck 1989).

Some [111]-zone SAED patterns contain type-r reflections (Fig. 3). Around each main spot are groups of six type-r reflections, and they tend to have equal intensities (Fig. 3b). However, this equality of intensity is not observed in all crystal fragments (Fig. 3c). The variability of intensities and occurrences of types p' and r reflections in hauyne suggests a domain structure and indicates subtle local changes in ordering and chemistry.

TEM IMAGES

An optical diffractogram of a [001] image (insert in Fig. 4) indicates that the hauyne crystal was well oriented and, in particular, the diffractogram contains the 100 and 010 reflections (arrows), as in the SAED pattern (Fig. 1). The image shows differences in contrast along adjacent (100) and (200), and (010) and (020) planes (Fig. 4; arrows). This contrast difference arises from ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters. The interpretation of this image is based on simulated images (inserts), which are based on the following 200CX microscope parameters: 200 keV, objective aperture 0.76 A^{-1}, spherical aberration coefficient 1.2 mm, defocus −120 A, depth of focus 50 A, divergence angle 0.1 millirad, and thickness 91 A. For the model in which the clusters are ordered, the unit cells contain central spots that are considerably darker than the white spots at the corners of the cells. In contrast, in the image where the clusters are disordered, all the spots have equal intensities (Fig. 4; inserts of simulated images). However, radiation damage can cause varied degrees of disordering among the clusters. This effect occurs in places of the image and is also reflected in the SAED patterns by the loss of p' reflections. The simulated images confirm that radiation damage gives rise to disordering of clusters, so that care is necessary in recording images showing cluster ordering. It is difficult to obtain good matches between experimental and calculated images for materials that suffer damage because of the associated noise. Nevertheless, to confirm cluster ordering in hauyne, it is sufficient to show that ad-

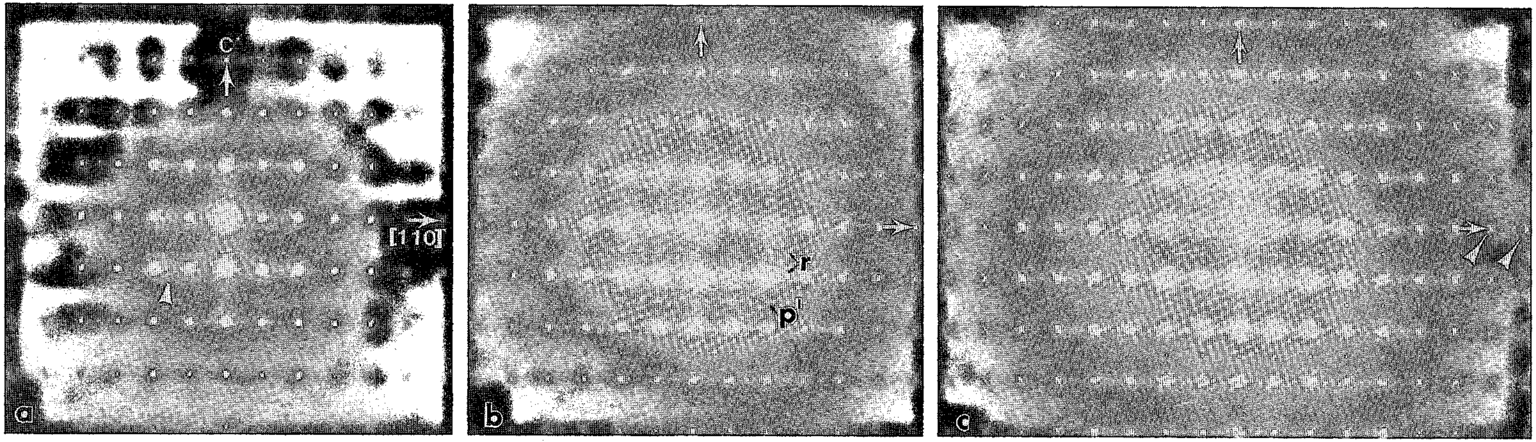

FIG. 2. [110]-zone SAED patterns from different crystal fragments. Some fragments contain weak type-*r* reflections (a; arrow), others contain strong types *p'* and *r* reflections (b), and yet others contain type-*p'* but weak type-*r* reflections on alternating horizontal rows (c). The streaked X-like type-*q* spots occur toward the edges (b, c; arrows).

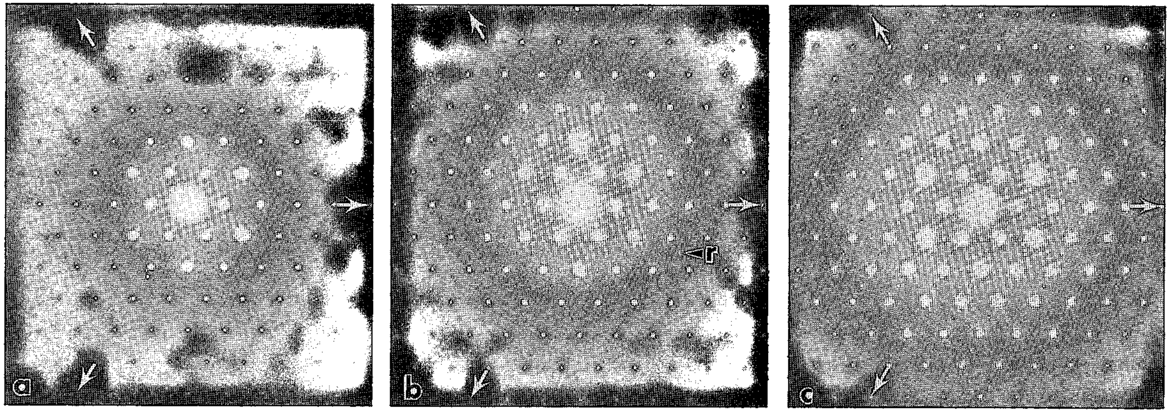

FIG. 3. [111]-zone SAED patterns from different crystal fragments. Arrows point along three <110>* directions. Type-*r* reflections are absent in (a), but occur in (b) (arrow), and their intensities are variable (c).

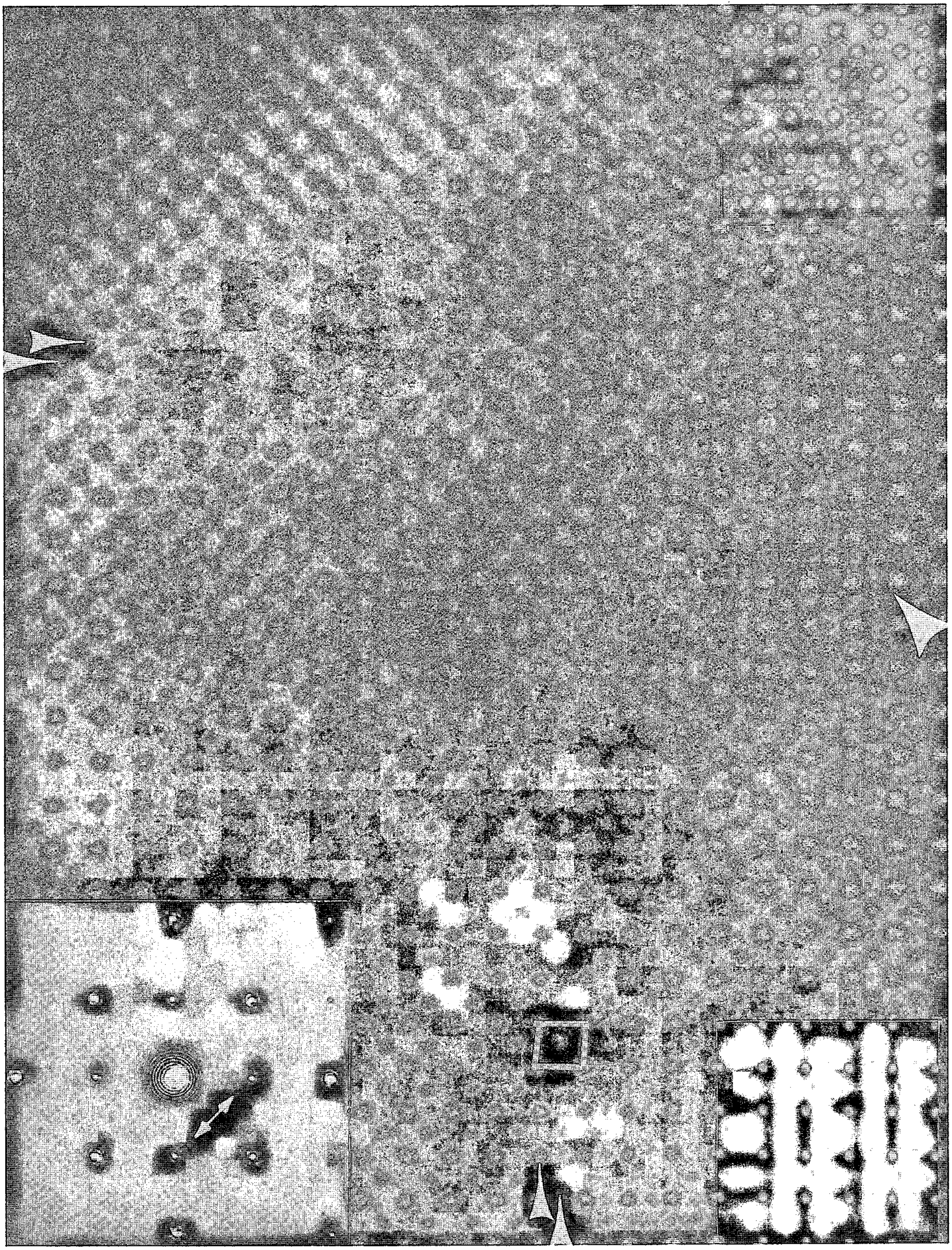

FIG. 4. [001] image, optical diffractogram, and simulated images. A unit cell is outlined. The $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters occur at the corners and centers of the cubic cells, and their ordering is manifested as differences in contrast along adjacent arrows, as confirmed by the simulated image based on cluster ordering (lower right). The white patches (*e.g.*, right-center region pointed out by arrow) indicate the result of radiation damage, which causes disordering of the clusters; this interpretation is supported by the simulated image based on cluster disordering (upper right).

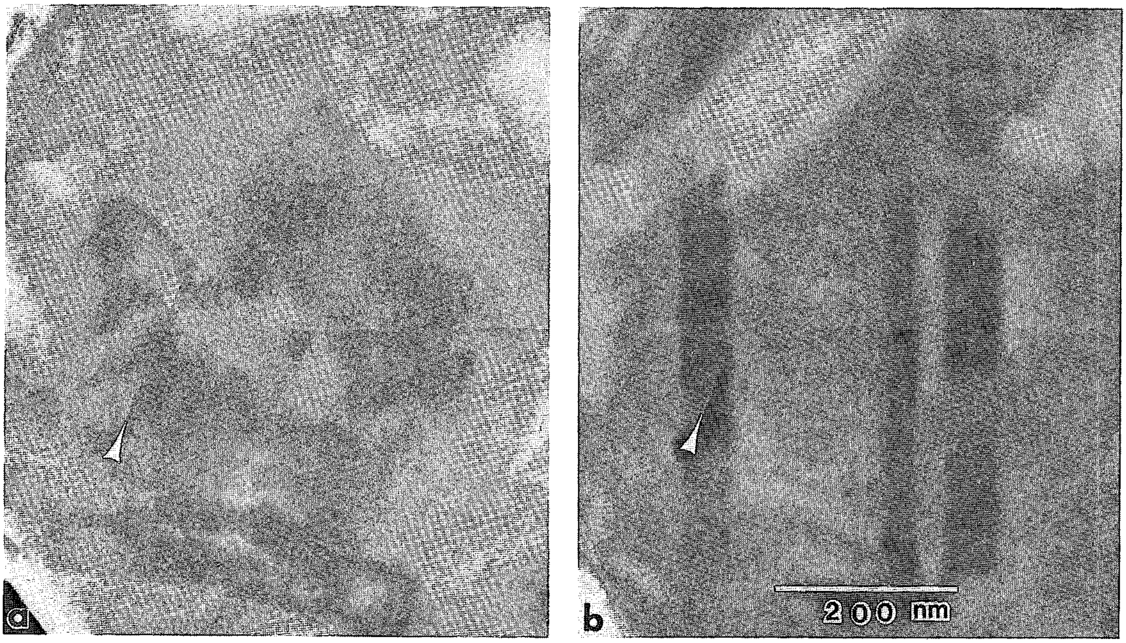

FIG. 5. [111] images showing *APB*s: (a) dark field, (b) bright field. The arrows point out one such boundary.

jacent rows contain significant contrast differences, whereas for cluster disordering they do not. Cluster ordering also was observed in other sulfatic sodalites and scapolite-group minerals (Hassan & Buseck 1988, 1989).

The ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters can give rise to *APB*s in hauyne, similar to *APB*s in nosean and scapolite-group minerals. If the cage at (0,0,0) is occupied by $[Na_3Ca{\bullet}SO_4]^{3+}$ clusters, then the (½. ½, ½) cage is occupied by $[K_2Ca{\bullet}OH]^{3+}$ clusters; in the adjacent domain the occupancy of the cages is reversed. *APB*s can only be imaged by chance in the HRTEM mode; however, conventional microscopy was used to show *APB*s in hauyne by imaging with types *p'* and *r* reflections.

Figures 5a,b show [111] images for the same area of a hauyne crystal. For the dark-field image, an objective aperture of 10-μm radius was centered around a type-*r* reflection, but it also included main reflections (see Fig. 3b). For the bright-field image, the aperture was centered around the incident beam, and it included type-*r* reflections. Both images show many sharp boundaries and resemble an aggregate of euhedral grains. However, the SAED pattern is that of a single crystal, indicating that these are domain boundaries. Because the boundaries are based on type-*r* reflections, they indicate *APB*s, which is a special case of out-of-phase boundaries.

DISCUSSION

The SAED patterns (Figs. 1, 2, 3) show type-*p'* reflections, indicating that space group $P\bar{4}3n$ is not appropriate for hauyne. The SAED patterns also contain streaked reflections along directions such as <100>, <110>, and <112>. HRTEM [110] images locally contain superstructure fringes that indicate a domain structure. The HRTEM image (Fig. 4) indicates ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters, implying that the cages centered at (0,0,0) and (½, ½, ½) are not chemically equivalent. These results suggest that space group *P*23, a subgroup of $P\bar{4}3n$, is appropriate for each domain in hauyne. However, the occurrence of *APB*s indicates that the average structure of hauyne is represented by space group $P\bar{4}3n$.

The interframework cations and the oxygen atoms of the SO_4^{2-} and OH^- groups are positioned along the body diagonals in hauyne. However, the SAED patterns do not show satellite reflections or streaking along <111> directions, indicating that the interframework atoms are disordered along such directions.

Evidence indicating that the diffuse reflections in hauyne are related to positional ordering of the framework oxygen-atom positions is provided by X-ray structure refinements (Hassan 1983, Hassan *et al.* 1985, Hassan & Grundy 1989). All sulfatic sodalites show similar types of disorder of interframework ions. In hauyne, the framework oxygen atoms are on one set of positions, but in nosean and lazurite they are on two sets of well-defined positions. These dual oxygen-atom positions permit positional ordering. Sharp satellite reflections occur in nosean and lazurite, but only diffuse streaks occur in SAED patterns of hauyne. The diffuse streaks in hauyne suggest inclusions of "nosean-like" components where the oxygen atoms occupy dual positions that allow for positional modulations.

In nosean, the ordering of the $[Na_4{\bullet}SO_4]^{2+}$ and $[Na_4{\bullet}H_2O]^{4+}$ clusters, which is enhanced by net differences in their charge and size, affects the oxygen atoms in a different manner and accounts for the two well-resolved framework oxygen-atom positions. In hauyne, the $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters behave similarly to each other and give rise to framework oxygen atoms on one position instead of two.

It is of interest to speculate on the nosean–hauyne series in view of the present results. Ordering of $[Na_4{\bullet}SO_4]^{2+}$ and $[Na_4{\bullet}H_2O]^{4+}$ clusters occurs in nosean, and ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters occurs in hauyne. To form a complete nosean–hauyne series, all four clusters must be miscible. The net differences in charge between the clusters indicate that complete miscibility is not possible and suggest that nosean clusters would be separated from hauyne clusters in a single crystal, even though the framework is continuous. Such a separation is suggested by the results given in this paper, and a similar interrupted series was observed in the scapolite-group minerals (Hassan & Buseck 1988b).

CONCLUSIONS

The SAED patterns of hauyne suggest that the framework oxygen-atom positions are randomly ordered, as indicated by diffuse, streaked reflections in many directions. Absence of satellite reflections along <111> directions indicates that the interframework atoms are disordered along such directions. Ordering of $[Na_3Ca{\bullet}SO_4]^{3+}$ and $[K_2Ca{\bullet}OH]^{3+}$ clusters is indicated in [001] images, but this ordering does not significantly affect the framework oxygen-atom positions. The ordering of clusters gives rise to *APB*s, and the space group for each domain is *P*23. The local occurrence of superstructure fringes indicates domains based on framework oxygen-atom positional ordering. The variability of intensities and occurrences of types *p′* and *r* reflections in hauyne indicate subtle changes in ordering and chemistry in different crystal fragments. Finally, our results suggest an interrrupted nosean–hauyne solid-solution series.

ACKNOWLEDGEMENTS

We thank Dr. John Barry for his help in using the 4000EX microscope. Hauyne samples were provided by courtesy of Dr. Fred J. Wicks of the Royal Ontario Museum. This work was supported by NSF grants EAR-8408169 and EAR8708169; microscopy was done at the Arizona State University High-Resolution Electron Microscopy Center, which is supported by NSF and ASU.

REFERENCES

BUSECK, P.R. & COWLEY, J.M. (1983): Modulated and intergrowth structures in minerals and electron microscope methods for their study. *Am. Mineral.* **68**, 18-40.

HASSAN, I. (1983): *The Crystal Chemistry and Crystal Structure of the Sodalite and Cancrinite Groups of Minerals.* Ph.D. thesis, McMaster Univ., Hamilton, Ontario.

______ & BUSECK, P.R. (1987): The incommensurate-modulated structures of sodalite-group minerals. *Geol. Soc. Am., Abstr. Programs* **19**, 695.

________ & ________ (1988): HRTEM characterization of scapolite solid solutions. *Am. Mineral.* **73**, 119-134.

________ & ________ (1989): The incommensurate-modulated structure of nosean, a sodalite-group mineral. *Am. Mineral.* **74**, 394-410.

________ & GRUNDY, H.D. (1984): The crystal structures of sodalite-group minerals. *Acta Crystallogr.* **B40**, 6-13.

________ & ________ (1989): The structure of nosean, ideally $Na_8[Al_6Si_6O_{24}]SO_4{\bullet}H_2O$. *Can. Mineral.* **27**, 165-172.

________, PETERSON, R.C. & GRUNDY, H.D. (1985): The structure of lazurite, idealy $Na_6Ca_2(Al_6Si_6O_{24})S_2$, a member of the sodalite group. *Acta Crystallogr.* **C41**, 827-832.

LÖHN, J. & SCHULZ, H. (1968): Strukturverfeinerung am gestörten Hauyn, $(Na_5K_1Ca_2)Al_6Si_6O_{24}(SO_4)_{1.5}$. *Neues Jahrb. Mineral., Abh.* **109**, 201-210.

MORIMOTO, N. (1978): Incommensurate superstructures in transformation of minerals. *Recent Prog. Nat. Sci. Japan* **3**, 183-206.

SAALFELD, H. (1961): Strukturbesonderheiten des Hauyngitters. *Z. Kristallogr.* **115**, 132-140.

SCHULZ, H. (1970): Struktur- und Uberstrukturuntersuchungen an Nosean-Einkristallen. *Z. Kristallogr.* **131**, 114-138.

SMITH, J.V. (1974): *Feldspar Minerals. 1. Crystal Structure and Physical Properties.* Springer-Verlag, New York.

TAYLOR, D. (1967): The sodalite group of minerals. *Contrib. Mineral. Petrol.* **16**, 172-188.

TSUCHIYA, N. & TAKÉUCHI, Y. (1985): Fine texture of hauyne having a modulated structure. *Z. Kristallogr.* **173**, 273-281.

VAN PETEGHEM, J.K. & BURLEY, B.J. (1963): Studies on solid solution between sodalite, nosean and hauyne. *Can. Mineral.* **7**, 808-813.

Received February 15, 1988, revised manuscript accepted July 27, 1988.