Transmission electron microscopy study of optically anisotropic and isotropic haüyne

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ABSTRACT

Optically anisotropic and isotropic haüyne has been observed in phonolite from Niang-niang Hill, Jiangsu Province, southeastern China. Selected-area electron diffraction (SAED) and transmission electron microscopy (TEM) studies show the anisotropic haüyne has a one-dimensional superstructure with a period of $6d_{110sub}$ along one of the $\langle 110 \rangle$ directions of the ideal cubic haüyne subcell. The superstructure may be considered as a periodic arrangement of (110) layer domains with $P23$ symmetry along [110]. Neighboring domains are related by a twin relationship. The unit-cell parameters for this haüyne superstructure are thus metrically orthorhombic, with $a_{sup} = 2d_{\bar{1}10sub}$, $b_{sup} = 6d_{110sub}$, $c_{sup} = c_{sub}$, but the most likely space group is monoclinic, Pn. SAED patterns and TEM images of two optically isotropic haüyne samples show they have either a three-dimensional superstructure or no superstructure. The average structure of the isotropic haüyne with the superstructure is cubic, even though it is composed of twin domains with one-, two-, and three-dimensional superstructures. The superstructure may have formed by ordering of $[Na_3Ca(SO_4)]^{3+}$ and $[(Na,K)_4(OH)]^{3+}$ clusters in the cubo-octahedral cages of the haüyne framework during an arrested phase transition from $P\bar{4}3n$ to $P23$ symmetry.

INTRODUCTION

Haüyne, nosean, and lazurite are sodalite-group minerals that occur in alkali-rich, silica-deficient volcanic rocks. A recent X-ray diffraction study of an isotropic haüyne sample indicates that the crystal has $P\bar{4}3n$ space-group symmetry and a disordered arrangement of $[Na_3Ca(SO_4)]^{3+}$ and $[CaK_2(OH)]^{3+}$ clusters (Hassan and Grundy, 1991). Although these framework silicates are commonly regarded as cubic, Voskoboinikova (1938) reported noncubic lazurite (a S- and SO_4^{2-}-containing sodalite-group mineral) from the contact zone of a pegmatite in Siberia and suggested that it is orthorhombic. Hogarth and Griffin (1976) also observed noncubic lazurite intergrown with optically isotropic lazurite. They found that extra lines (i.e., superlattice reflections) in powder X-ray diffraction patterns of anisotropic lazurite are related to the optical anisotropy.

Recent studies of haüyne and other sodalite-group minerals show that their disordered and average structures possess $P\bar{4}3n$ symmetry, but the true symmetry of each domain in modulated crystals is lower, possibly $P23$ (Hassan and Grundy, 1984, 1989; Hassan and Buseck, 1989a, 1989b). Some haüyne, nosean, and lazurite samples are characterized by complex superlattice reflections that indicate incommensurately modulated structures with multiple modulation directions (Ito and Sadanaga, 1966;

Taylor, 1967; Schultz, 1970; Morimoto, 1978; Tsuchiya and Takéuchi, 1985). High-resolution transmission electron microscopy (HRTEM) studies of haüyne and modulated nosean suggest that these modulations result from ordering of $[Na_3Ca(SO_4)]^{3+}$ and $[CaK_2(OH)]^{3+}$ clusters in haüyne and of $(Na_4SO_4)^{2+}$ and $(Na_4H_2O)^{4+}$ clusters in nosean (Hassan and Buseck, 1989a, 1989b).

In this paper, we describe selected-area electron diffraction (SAED) and HRTEM investigations of anisotropic haüyne exhibiting a well-defined superstructure in only one direction, isotropic haüyne with a three-dimensional superstructure, and isotropic haüyne without a superstructure.

EXPERIMENTAL METHODS AND CRYSTAL COMPOSITIONS

TEM studies were performed with a Philips EM420ST electron microscope operated at 120 keV and equipped with an EDAX energy-dispersive X-ray detector and Princeton Gamma-Tech analyzer. Thin specimens were prepared by Ar ion bombardment and coated with a thin layer of C. The sample we studied is a haüyne-bearing phonolite from volcanic neck- and vent-phase rocks of the Mesozoic alkali volcanic and subvolcanic complex in the area of Niang-niang Hill, Jiangsu Province, southeastern China (Tao et al., 1979). The euhedral, anisotropic haüyne crystals coexist with isotropic haüyne and crystallized from SiO_2-deficient phonolitic magma above 750 °C (Huang and Zhou, 1981). In cross-polarized light, the haüyne is clearly anisotropic but with very low bire-
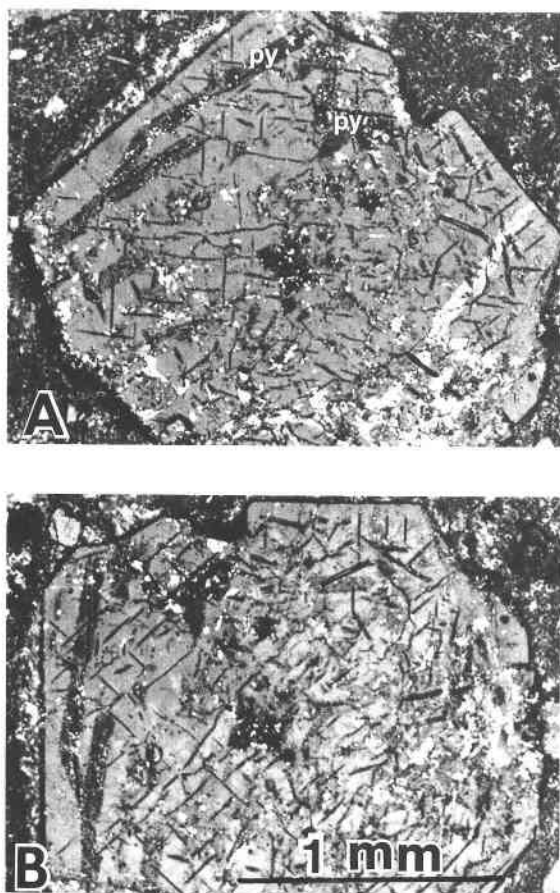

Fig. 1. Thin section of an anisotropic haüyne crystal from Niang-niang Hill, Jiangsu Province, China, cut nearly normal to [001] and displaying irregularly shaped domains (cross-polarized light with the gypsum plate inserted). (A) At extinction position. (B) Rotated counterclockwise, showing twin domains with different interference colors. The opaque minerals (py) within the haüyne crystal are pyrite.

TABLE 1. Chemical analyses and atomic proportions of isotropic and anisotropic haüyne

Analysis no.	1	2	3	4
Chemical analyses				
Na_2O	9.12	8.77	15.63	13.16
MgO	0.02	0.00	—	0.13
K_2O	0.11	0.10	0.82	5.10
CaO	5.33	6.19	7.44	9.16
TiO_2	0.00	0.00	0.06	0.02
MnO	0.02	0.01	—	0.04
FeO	0.00	0.04	1.14	0.05
Al_2O_3	30.06	30.09	25.59	28.35
SiO_2	34.63	34.39	34.80	30.82
SO_3	11.08	11.14	11.68	13.05
Cl	0.71	0.62	0.05	0.23
Total	91.14	91.35	97.21*	100.10
Atomic proportions based on 12(Si + Al)				
Na^+			5.59	4.77
K^+			0.19	1.22
Ca^{2+}			1.47	1.83
Mg^{2+}			—	0.04
Fe^{2+}			—	0.01
$\Sigma\ cc^{**}$			7.25	7.87
$^{[4]}Al$			5.57	6.24
Si			6.43	5.76
SO_4^{-2}			1.31	1.83
Cl^-			0.01	0.07
OH^-			0.52	—
H_2O			0.16	0.10

Note: analysis no. 1 is from anisotropic haüyne; analysis no. 2 is from isotropic haüyne coexisting with anisotropic haüyne; analysis no. 3 is from wet-chemical analysis of the mixture of anisotropic and isotropic haüyne; analysis no. 4 is from a sample of isotropic haüyne (USNM B17338) without a superstructure.
* 2.78% H_2O is not included.
** Total cations in the cubo-octahedral cage positions.

fringence (<0.001). With a gypsum plate inserted, however, twin domains are observed clearly (Fig. 1).

Electron microprobe analyses were carried out with a JEOL JXA-860 Superprobe using mineral standards. It was observed that both anisotropic and coexisting isotropic haüyne samples are very sensitive to the electron beam. They underwent very severe electron radiation damage and Na loss during microprobe analysis. Results show the compositions are distinctly low in Na (Table 1).

A wet-chemical analysis of a mixture of isotropic and anisotropic crystals reported by Huang and Zhou (1981) is listed in Table 1, together with results from microprobe analysis. The infrared spectrum shows bands from SO_4^{2-}, OH^-, and H_2O. Backscattering images show very small pyrite inclusions within haüyne crystals. Microprobe analyses of pyrite-free areas show very low Fe content, and analytical electron microscopy (AEM) analyses do not show any Fe at our detection limit (approximately 0.1 wt% Fe). Because of severe Na loss during micro-

probe analysis, we used wet-chemical analysis for calculation of the structural formula. All the Fe in the wet-chemical analysis (analysis no. 3 in Table 1) was therefore assumed to be present as FeS_2, and the requisite amount of S was also subtracted from the analysis. The unit cell was assumed to contain 12(Si + Al). A remaining S atom was assumed to be present as SO_4^{2-} in the cubo-octahedral cage position, and OH^- and H_2O were added to provide charge balance. The resulting structural formula is $(Na_{5.59}-Ca_{1.47}K_{0.19})_{\Sigma7.25}[(Si_{6.43}Al_{5.57})_{\Sigma12}O_{24}]\{(SO_4)_{1.31}(OH)_{0.52}Cl_{0.01}-(H_2O)_{0.16}\}$. If we use the results from microprobe analysis for the calculation based on 12(Si + Al), the haüyne formula is deficient in cation charges, which is obviously unreasonable.

Another isotropic haüyne for the study is a euhedral crystal from Monte Albani of Latium, Italy (USNM B17338). This haüyne sample contains more S (analysis no. 4 in Table 1) and is more stable under the electron beam. The calculated structural formula indicates that the cubo-octahedral positions in the haüyne structure are almost filled by SO_4^{2-} anions.

TEM OBSERVATIONS

Anisotropic haüyne

Figure 2A shows a [$\bar{1}10$] zone-axis SAED pattern from one anisotropic domain, with a series of superstructure

Fig. 2. (A) A [$\bar{1}$10] zone-axis SAED pattern of anisotropic haüyne showing very weak $h + k + l = 2n + 1$ reflections that violate $P\bar{4}3n$ symmetry, strong $h + k + l = 2n$ reflections, and a series of superstructure reflections with weak streaking along [110]. (B) Dark-field TEM image of anisotropic haüyne produced by imaging the 002 reflection and its nearby superstructure reflections, showing superstructure fringes and a superlattice dislocation (between two arrows). (C) HRTEM image of anisotropic haüyne corresponding to the orientation of A, showing a one-dimensional modulation along [110].

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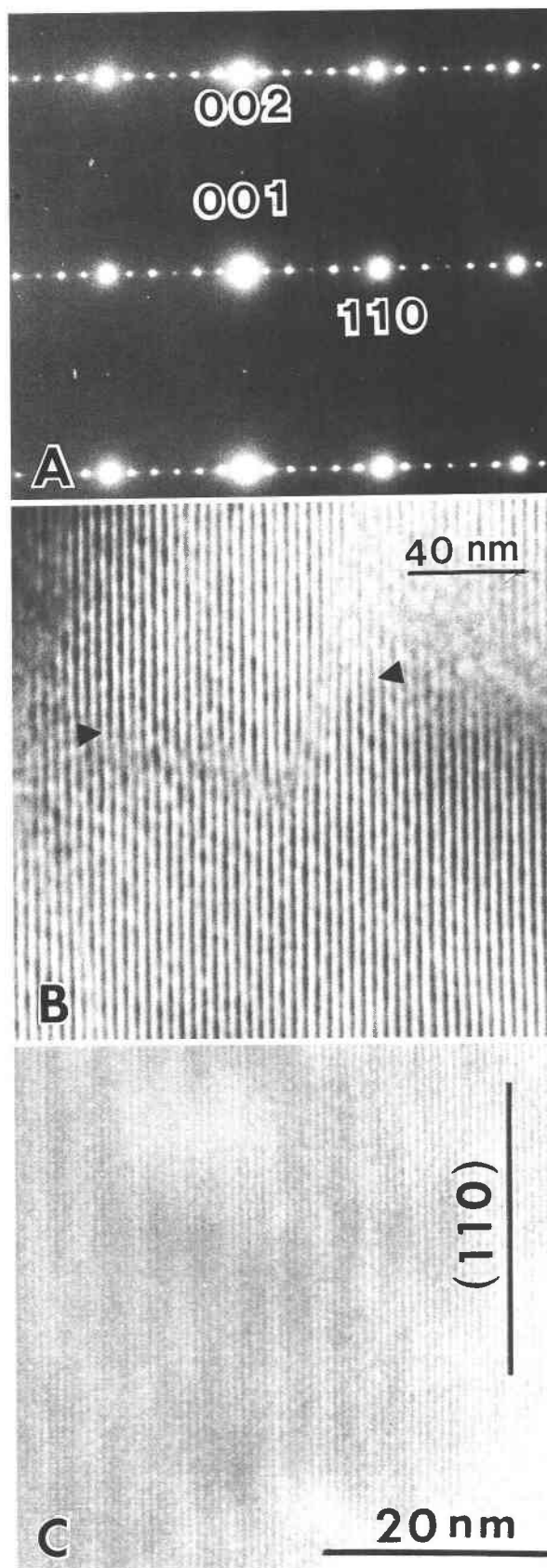
reflections along one of the ⟨110⟩ directions of the haüyne subcell. The cubic subcell lattice parameter measured from the diffraction pattern is $a = 0.910$ mm, and the modulation period indicated by the superstructure diffraction spots is $b_{sub} = 6d_{110sub}$, or 3.9 nm, where the subscript "sub" indicates the haüyne subcell, and "sup" indicates the supercell. Some very weak reflections with indices $h + k + l = 2n + 1$ are also present. These weak spots would represent violations of the n-glide planes in the ideal cubic space group $P\bar{4}3n$, suggesting that the local symmetry within the domains (i.e., if we neglect the superstructure) is $P23$, a maximum subgroup of $P\bar{4}3n$, as indicated by Hassan and Buseck (1989a). Figure 2B is a dark-field (DF) image produced by imaging a 002 reflection and its nearby superstructure reflections in the diffraction pattern of haüyne in Figure 2A, showing (110) superlattice fringes characteristic of a planar domain structure. Such images show occasional superlattice dislocations, such as the one that can be seen between the arrows in this figure by sighting along the fringes at a low angle. Areas near the superlattice dislocations experienced unusually rapid amorphization in the electron beam. Normal multiple-beam bright-field HRTEM images also show the one-dimensional superstructure (Fig. 2C), but the contrast from the modulation is weak.

SAED patterns from the [$\bar{1}$11] zone axis (Fig. 3A) also show the superstructure reflections along one of the ⟨110⟩ directions. This orientation also shows that the superstructure is one dimensional, because the superstructure spots occur along only one of the three ⟨110⟩ directions that are equivalent in the cubic crystal system. A dark-field image produced by imaging one main reflection and its nearby superstructure reflections shows one-dimensional superstructure fringes with a period of 3.9 nm ($=6d_{110sub}$) (Fig. 3B), and a corresponding bright-field HRTEM image (Fig. 3C) again reveals the structural modulation.

Isotropic haüyne

Optically isotropic haüyne possesses cubic symmetry, at least for the average structure. Electron diffraction patterns from the isotropic haüyne coexisting with the anisotropic haüyne show three-dimensional superstructure reflections (Fig. 4A). DF images produced by imaging one 110 reflection and its nearby superstructure reflections (Fig. 4B) show that the crystal is composed of domains
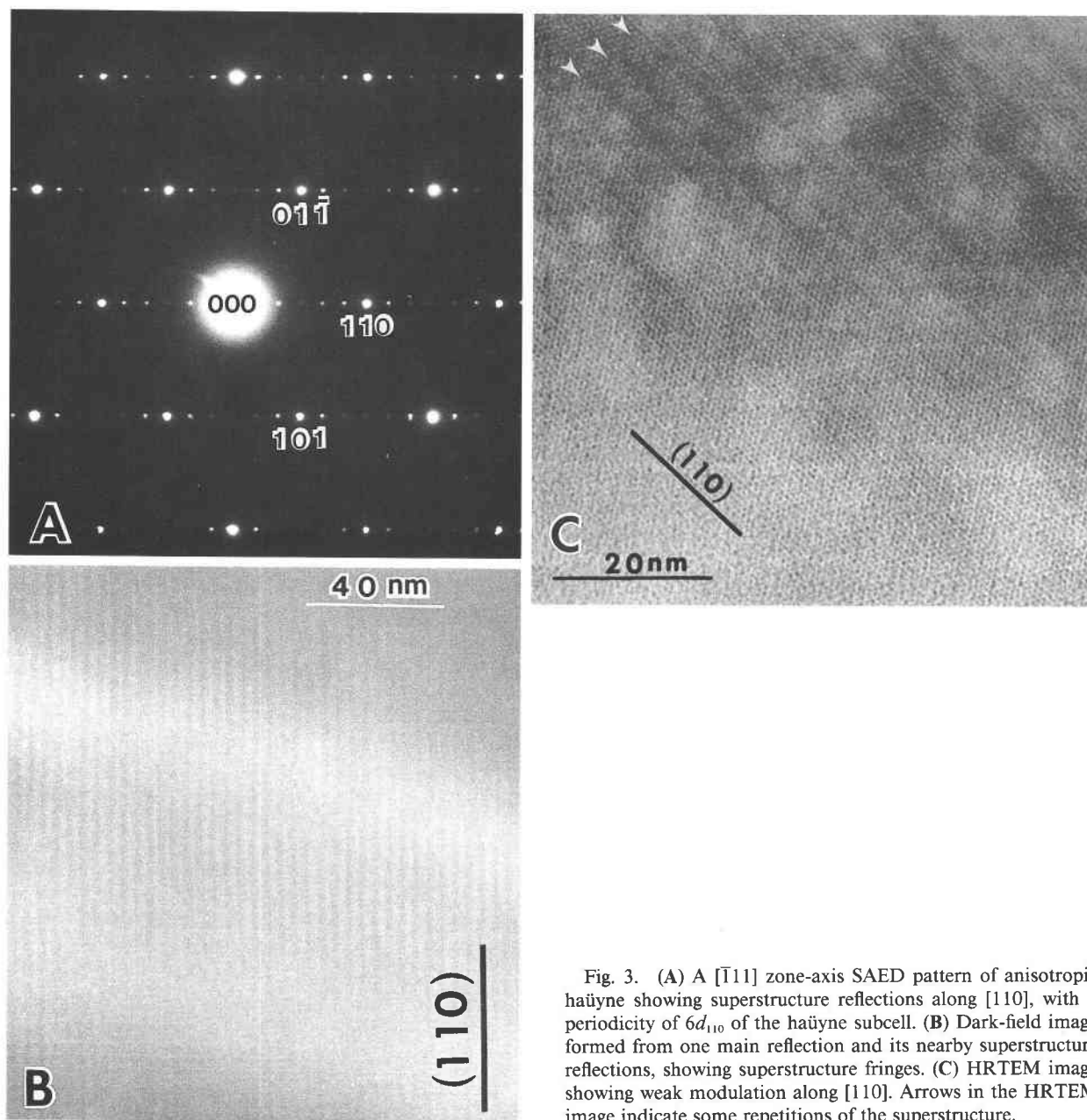
Fig. 3. **(A)** A [$\bar{1}$11] zone-axis SAED pattern of anisotropic haüyne showing superstructure reflections along [110], with a periodicity of $6d_{110}$ of the haüyne subcell. **(B)** Dark-field image formed from one main reflection and its nearby superstructure reflections, showing superstructure fringes. **(C)** HRTEM image showing weak modulation along [110]. Arrows in the HRTEM image indicate some repetitions of the superstructure.

with a superstructure having one-, two-, and three-dimensional modulations. A domain with a one- or two-dimensional superstructure does not have cubic symmetry, but crystals consisting of small domains in a twin relationship of this sort are isotropic and display average cubic symmetry. It is possible that superstructure reflections in Figure 4A could arise partly from the overlap of superstructural domains having one- and two-dimensional modulations. However, another isotropic haüyne sample (USNM B17338) shows no superstructure in its SAED pattern and HRTEM image (Fig. 5). A haüyne crystal without superlattice reflections (Fig. 5A) may have

a relatively disordered distribution of two types of clusters or only one type of anion in the cubo-octahedral cages, as described by Hassan and Grundy (1984, 1991), and it would have $P\bar{4}3n$ space-group symmetry. It can be seen from Table 1 that the cubo-octahedral cages in this isotropic haüyne are dominated by SO_4^{-2} anions.

DISCUSSIONS

A possible superstructure model for anisotropic haüyne

The electron diffraction patterns presented above indicate that the conditions for the presence of superstructure reflections occur at a multiple of $\frac{1}{6}$[110]*. The sim-

Fig. 4. (A) A [$\bar{1}$11] zone-axis SAED pattern of an isotropic haüyne crystal that coexists with anisotropic haüyne, showing superstructure reflections along three $\langle 110 \rangle$ directions with a periodicity of $6d_{110}$ of the haüyne subcell. (B) DF image formed from a 110 reflection and its nearby superstructure reflections, showing domains with one-, two-, and three-dimensional superstructures.

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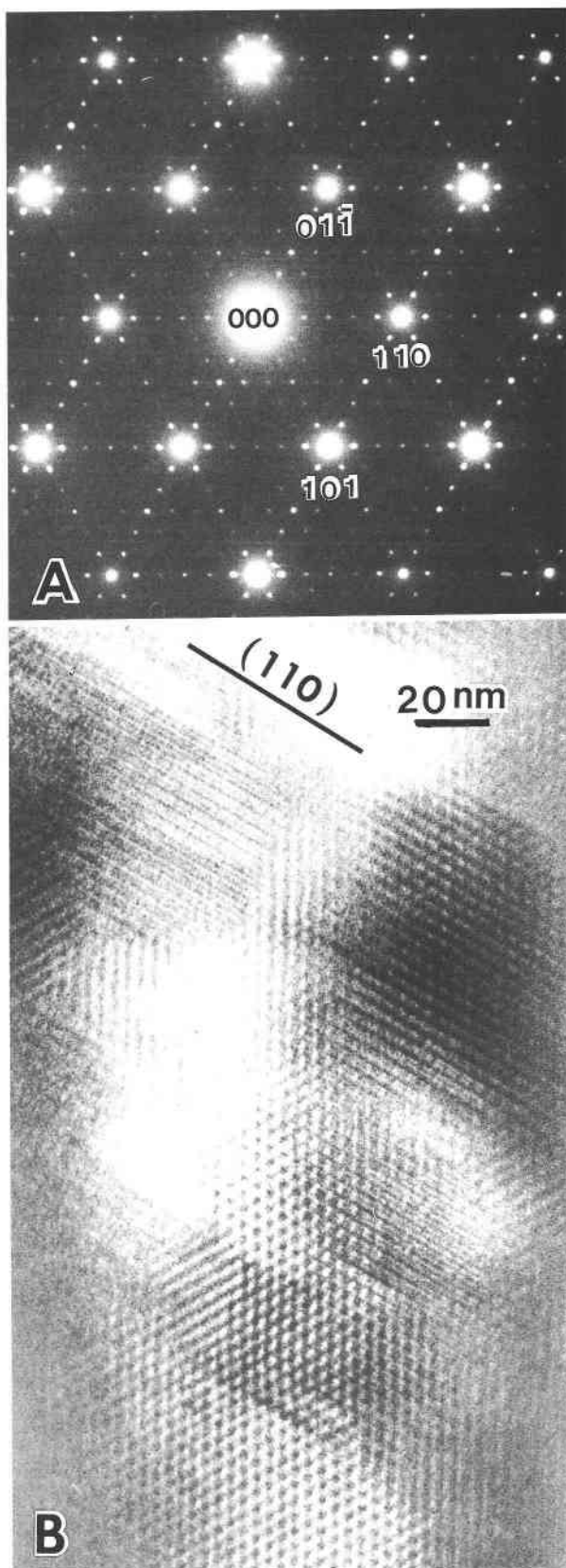
plest unit cell that can be chosen for this haüyne superstructure is primitive and metrically orthorhombic. The relationships among the parameters for this supercell and the cubic subcell are $a_{sup} = 2d_{\bar{1}10sub}$, $b_{sup} = 6d_{110sub}$, $c_{sup} = c_{sub}$, $\alpha = \beta = \gamma = 90°$, as illustrated in Figure 6.

A single-crystal X-ray diffraction study of an isotropic haüyne sample with weak streaking in the $\langle 110 \rangle$ directions shows that the crystal possesses a disordered distribution of $[Na_3Ca(SO_4)]^{3+}$ and $[CaK_2(OH)]^{3+}$ clusters in the cubo-octahedral cage positions and a random distribution of Na, Ca, and K cations in three sets of $8e$ positions with partial occupancies (Hassan and Grundy, 1991). The streaked reflections may be caused by local (or short-range) ordering of SO_4^{2-} and OH^- in the cage positions (Hassan and Grundy, 1991). Further ordering of the two kinds of anions in the cages may lead to a modulated structure with satellite reflections, as in a modulated nosean sample investigated by Hassan and Buseck (1989b). Although there have been different interpretations for the modulated structure in haüyne and nosean (Hassan and Buseck, 1989b; Tsuchiya and Takéuchi, 1985; Ito and Sadanaga, 1966), a possible model for the modulated structure of our anisotropic haüyne specimen can be derived from the disordered structure with $P\bar{4}3n$ symmetry by assuming ordering of $[Na_3Ca(SO_4)]^{3+}$ and $[(Na, K)_4-(OH)]^{3+}$ clusters in the 0,0,0 and ½,½,½ cubo-octahedral cages to form a one-dimensional superstructure, similar to the ordering proposed by Hassan and Buseck (1989a) for reduction from $P\bar{4}3n$ to $P23$ symmetry. From a cluster-disordered, $P\bar{4}3n$ haüyne structure (Hassan and Grundy, 1991), the ordering of $[Na_3Ca(SO_4)]^{3+}$ and $[(Na,K)_4(OH)]^{3+}$ clusters may produce a fine-scale domain structure with the neighboring domains in a translation-twin relationship (Fig. 6), similar to the twin domains in low-symmetry vesuvianite (Veblen and Wiechmann, 1991), instead of forming large, homogeneous domains. If these domains are arranged periodically in (110) layers, the result is a one-dimensional superstructure with comparatively low symmetry. The local symmetry of the layer domains is $P23$, a subgroup of $P\bar{4}3n$. In this structural model for anisotropic haüyne, each layer domain with thickness $3d_{110}$ locally possesses $P23$ symmetry and is related by (110) n-glide planes (Fig. 6). The maximum space-group symmetry for this proposed superstructure is Pn. The ordered arrangement of $[Na_3Ca(SO_4)]^{3+}$ and $[(Na, K)_4(OH)]^{3+}$ clusters leads to two different sets of O atoms, as in incommensurately modulated nosean (Hassan and Buseck, 1989b), even though the differences in O positions between the ordered struc-
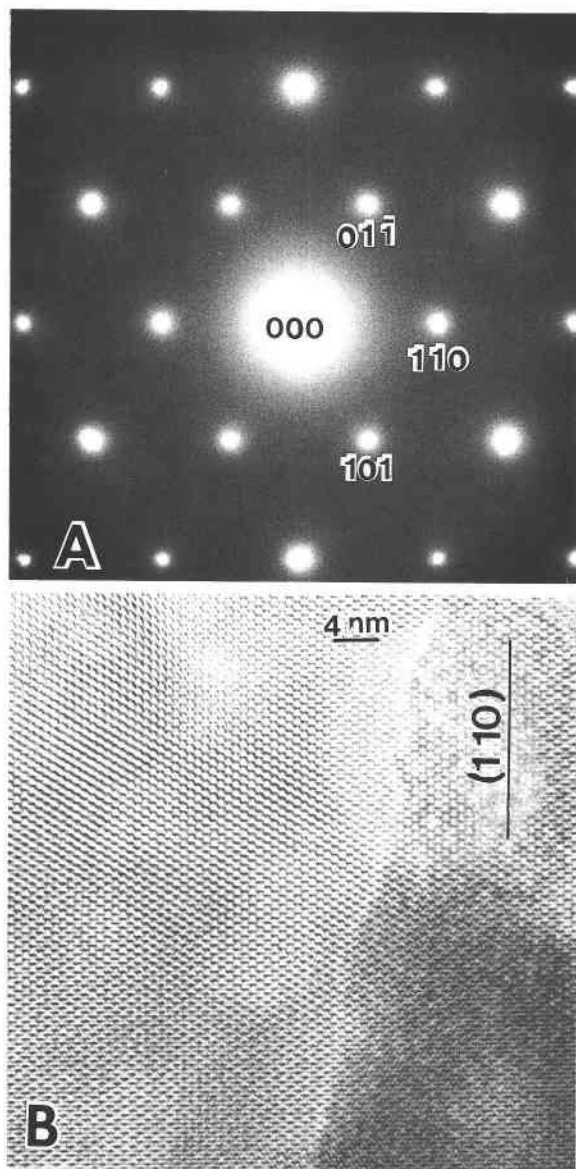
Fig. 5. (A) A [$\bar{1}11$] zone-axis SAED pattern from an euhedral, isotropic haüyne crystal from Monte Albani of Latium, Italy (USNM B17338), showing strong main reflections. (B) An HRTEM image of the haüyne without superstructure.

SO$_4^{-2}$ at 0,0,0 of subcell   SO$_4^{-2}$ at 1/2,1/2,1/2 of subcell

OH$^-$ at 0,0,0 of subcell   OH$^-$ at 1/2,1/2,1/2 of subcell

SO$_4^{-2}$ and OH$^-$ at the domain boundary positions

Fig. 6. A plausible structural model for the superstructure of anisotropic haüyne projected along c, showing an ordered distribution of SO$_4^{2+}$ and OH$^-$ anions in the centers of the cubo-octahedral cages. Each (110) layer domain has local $P23$ symmetry. The boundary positions of the layer domains have a disordered anion distribution and are n-glide plane positions of the superstructure. Haüyne subcells and a supercell are also outlined. Subscripts "sup" and "sub" represent supercell and subcell, respectively.

ture and the ideal cubic structure are presumably very small. For this anisotropic haüyne composition, there are about 70% [Na$_3$Ca(SO$_4$)]$^{3+}$ clusters and 30% [(Na,K)$_4$-(OH)]$^{3+}$ clusters in the cubo-octahedral cages. Clusters at the twin boundary positions are disordered in this model, and it is possible that these positions are mainly filled by [Na$_3$Ca(SO$_4$)]$^{3+}$ clusters.

Formation of optically anisotropic domains

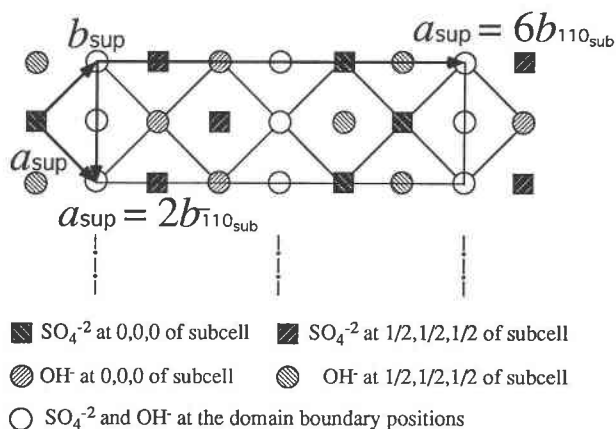Given the fine-scale domain structure observed in cross-polarized light, it seems likely that anisotropic, one-dimensionally modulated haüyne formed during a phase transition from the ideal, high-temperature $P\bar{4}3n$ structure by ordering of the clusters in the cubo-octahedral cages. If the ordered domains did, indeed, arise during a phase transition, such transformation twins obviously indicate that the anisotropic haüyne crystals grew above the phase-transition temperature. The crystallization temperature has been estimated to be above 750 °C (Huang and Zhou, 1981), suggesting that the phase transition occurs below this temperature.

The optical anisotropy observed in some lazurite samples (Voskoboinikova, 1938) may have an origin similar to that of anisotropic haüyne, and we suggest that such anisotropic lazurite also may have a one-dimensional or two-dimensional modulated structure. A heating experiment from anisotropic to isotropic lazurite (Hogarth and Griffin, 1976) verified that there is a phase transition from a modulated structure to the ideal cubic structure at approximately 530 °C. Some lazurite specimens show complex superstructure reflections in three dimensions, similar to those in some nosean and haüyne samples (Hassan et al., 1985), and these superstructures may be expected to disappear at higher temperatures.

It seems likely that all modulated structures in haüyne, nosean, and lazurite, with their different modulation periods and geometries, are metastable, intermediate states between disordered, high-temperature $P\bar{4}3n$ structures and fully ordered, low-temperature $P23$ structures, similar to the modulated structures observed in alkali feldspars (Xu and Veblen, 1993; Xu et al., 1994). The temperatures of the cluster-ordering phase transitions presumably are related to the ratios of the different cluster types, and it is likely that the ordering of clusters may occur in sodalite-group minerals containing two kinds of anions. If the

cubo-octahedral cages are fully occupied or dominated by one kind of anion (e.g., only Cl^- in sodalite and SO_4^{-2} in the isotropic haüyne without a superstructure), the ordering of clusters and the formation of a superstructure are not possible.

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