

THE CRYSTAL STRUCTURE OF NORDITE AND
ITS RELATIONSHIP TO MELILITE AND
DATOLITE-GADOLINITE

V. V. BAKAKIN, N. V. BELOV, S. V. BORISOV, AND
L. P. SOLOVYEVA, *Institute of Inorganic Chemistry,*
Novosibirsk, U.S.S.R.

ABSTRACT

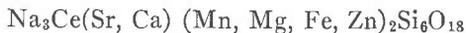
The crystal structure of nordite, $a=14.27\pm 0.03$, $b=5.16\pm 0.01$, $c=19.45\pm 0.15$; $Pcca$, $Z=4 \times (\text{La}_{2.1}\text{Ce}_{1.7}\text{Ca}_{0.2})(\text{Sr}_{2.1}\text{Ca}_{1.9})\text{Na}_2(\text{Na}_{0.8}\text{Mn}_{0.2})(\text{Zn}_{1.5}\text{Mg}_{1.3}\text{Fe}^{2+}_{0.7}\text{Mn}_{0.5})(\text{Si}_{5.85}\text{Fe}^{3+}_{0.15})\text{O}_{17}$ has been solved on the basis of a three-dimensional Patterson function. The refinement with 1335 independent photographic reflections gave $R_{hkl}=0.122$.

The structure consists of compact layers of RE, (Sr, Ca) and Na square antiprisms and Na, Mn octahedra which are connected along the b -axis by a new kind of $\text{T}_7\text{O}_{17.0000}$ flat net of tetrahedra formed by four-, five- and eight-rings. The structure of nordite is closely related to the structures of melilite and datolite-gadolinite, and can be considered as an unusual combination of both.

INTRODUCTION

The complex rare earth silicate nordite was discovered by V. I. Gerasimovsky in 1935 (Gerasimovsky, 1941). It has recently been found that nordite is present in a number of sodalite-syenites and pegmatites in the Lovozerski alkaline massif (Kola Peninsula). The samples for our investigation were kindly supplied by E. I. Semenov who urged a comprehensive study of nordite.

The chemical analysis for nordite by M. E. Kasakova (Semenov, 1961) gave (in weight percent): SiO_2 45.07; Ce_2O_3 9.38; Ln_2O_3 11.52; Fe_2O_3 1.15; FeO 2.12; MnO 3.29; MgO 1.66; ZnO 3.90; CaO 3.74; SrO 7.11; BaO 0.35; ThO_2 0.26; Na_2O 11.20; Σ 100.75. The formula derived from this analysis by E. I. Semenov was



or in a simplified form $\text{Na}_3\text{CeSrMn}_2\text{Si}_6\text{O}_{18}$. This is the fourth variant, differing from those given previously by V. I. Gerasimovsky (1941), A. G. Betekhtin (1950), and A. N. Winchell and H. Winchell (1951); it is in rather good agreement with the unit-cell volume from the original X-ray investigation of S. V. Borisov (E. I. Semenov, 1961), and has been included without reservation in the textbooks of A. S. Povarennykh (1966), H. Strunz (1966), and K. A. Vlasov (1964). In the course of our study, however, both the isomorphic groupings and the distribution of components contained in them had to be altered in this formula.

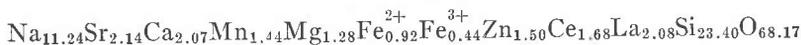
EXPERIMENTAL

A small crystal of nordite for the X-ray analysis was selected from metamict samples; it was treated for 10 hours at $\sim 800^\circ\text{C}$, after which it was cut into a sphere ~ 0.3 mm in diameter. The parameters of the orthorhombic unit cell were taken from the X-ray rotation and Weissenberg films on which a period $c = 19.45 \text{ \AA}$, not previously revealed, appeared very clearly; it doubled almost exactly the old $c' = 9.9 \text{ \AA}$. Two other periods were close to those given by S.V. Borisov (see above) after transposition of the a and b axes: $a = 14.27 \pm 0.03$; $b = 5.16 \pm 0.01$; $c = 19.45 \pm 0.15 \text{ \AA}$. The absences on the layer lines (Mo-radiation) were: for $h0l$ $l = 2n + 1$; for $0kl$ $l = 2n + 1$; and for hkl $h = 2n + 1$. In addition, one could observe along the (001) rows absences not represented in the tables, *i.e.* reflections with $l = 4n$. In the whole set of $F(hkl)$ the number of reflections with odd l is very small. The space group $Pcca$ was unambiguously established from the absences with a sharply expressed pseudo-period $c' = c/2$.

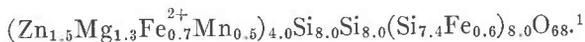
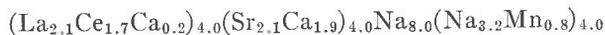
The intensities were estimated using a $\sqrt[4]{2}$ blackening scale with LP -factor taken into account. 1335 independent non-zero reflections were recorded on six layer lines (along b), and 105 reflections on $hk0$ (along c).

STRUCTURE ANALYSIS

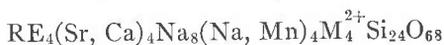
The structure analysis was principally based on a three-dimensional Patterson function. In the identification of maxima the precise data for the contents of the unit cell with the aforementioned parameters (experimental density $\rho = 3.48 \text{ g/cm}^3$ (Semenov, 1961)) played an important role:



Since in the $Pcca$ group only 8-fold and 4-fold positions are permitted, a preliminary distribution revealed (in accordance with generally accepted isomorphous associations):



Associating (Ce, La, Ca) with RE, Ca with Sr, and placing (Zn, Mg, Fe, Mn) into M^{2+} we obtain the working formula:



The analysis of the Patterson function revealed three sets of relatively heavy maxima corresponding to $4(d)$ positions on 2-fold axes. In order to differentiate between three groups: RE, (Sr, Ca) and M^{2+} , use was made of optimal values of the R -factor (of the order of 0.30–0.40 at that stage) with due allowance for reasonable thermal coefficients. The coordinates of identified maxima were used for the minimization of a

¹ Detailed refinement of the structure has been carried out; the given cation distribution and all interatomic distances remain unchanged.

three-dimensional Patterson distribution, which led to the location of three sets of intermediate Si atoms in general 8-fold positions. In order to decipher the framework of anions and locate the Na and (Na, Mn) cations, the projection of the electron density σ was constructed on which O(1), O(2), O(5), O(6), O(7), Na and (Na, Mn) appeared clearly. The remaining O atoms were found as a result of a crystal-chemical (geometrical) analysis. 40 coordinate parameters and 17 isotropic-thermal parameters of a model of the structure (17 basic atoms) were refined to $R_{hkl}=0.122$ for the entire set of 1335 F_{hkl} .

TABLE 1. NORDITE. ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS AND ESTIMATED STANDARD DEVIATIONS

| Atom | x/a | y/b | z/c | $B(\text{\AA}^2)$ |
|----------|-------------|-------------|--------------|-------------------|
| TR | 0.2500 | 0 | 0.3194 | 0.39 (3) |
| (Sr, Ca) | 0.2500 | 0 | 0.0217 (2) | 0.06 (5) |
| M^{2+} | 0.2500 | 0.5000 | 0.1687 (3) | 0.91 (7) |
| Si(1) | 0.0980 (7) | 0.4542 (23) | 0.0623 (4) | 0.61 (14) |
| Si(2) | 0.1019 (7) | 0.5433 (23) | 0.2747 (4) | 0.46 (13) |
| Si(3) | 0.1116 (5) | 0.5516 (17) | -0.0819 (4) | 0.31 (11) |
| (Na, Mn) | 0 | 0 | 0 | 2.05 (36) |
| Na | 0.0696 (10) | 0.0125 (81) | 0.1693 (8) | 2.10 (26) |
| O(1) | 0.9955 (16) | 0.3389 (53) | 0.0811 (14) | 0.84 (10) |
| O(2) | 0.1701 (18) | 0.2995 (71) | 0.1101 (12) | 0.70 (10) |
| O(3) | 0.1172 (18) | 0.3537 (59) | -0.0131 (12) | 1.49 (46) |
| O(4) | 0.1019 (16) | 0.7640 (68) | 0.0672 (12) | 1.64 (45) |
| O(5) | 0 | 0.6366 (96) | 0.2500 | 1.28 (58) |
| O(6) | 0.1783 (18) | 0.7090 (69) | 0.2321 (12) | 0.83 (33) |
| O(7) | 0.1221 (19) | 0.6503 (58) | 0.3532 (13) | 1.00 (37) |
| O(8) | 0.1178 (18) | 0.2392 (58) | 0.2714 (12) | 1.26 (40) |
| O(9) | 0.1857 (15) | 0.2226 (58) | 0.4173 (14) | 1.11 (33) |

The final coordinates and individual isotropic-thermal vibration parameters and the standard deviations for all independent parameters are presented in Table 1. The effective atomic amplitudes of cations were calculated in accordance with the indicated isomorphous groupings for nonionized atoms.

DISCUSSION OF THE STRUCTURE

Description of the Nordite Structure. Figure 1 shows the atomic asymmetric unit of the nordite structure projected along the b -axis. The independent atom coordinates from Table 1 and their equivalents, which enter into coordination polyhedra, are appropriately marked. As one can see from the y coordinates (Table 1) all large cations of RE, (Sr,

Ca), Na and (Na, Mn) occur at one level $0 \leq y/b \leq 0.01$ in the (010) plane between two layers of O atoms at the levels $0.24 \leq y/b \leq 0.35$ and $(-0.36) \leq y/b \leq (-0.22)$. To a first approximation the coordination polyhedra around RE, (Sr, Ca) and Na are square antiprisms (twisted cubes), which are eight-corner polyhedra characteristic for these cations in a number of structures, whereas those around (Na, Mn) atoms are octahedra. The polyhedra are linked to form a compact layer by sharing 4 or 5 side (oblique) edges, and one face in the case of Na. The characteristic features of this layer are the quadrangular openings of two

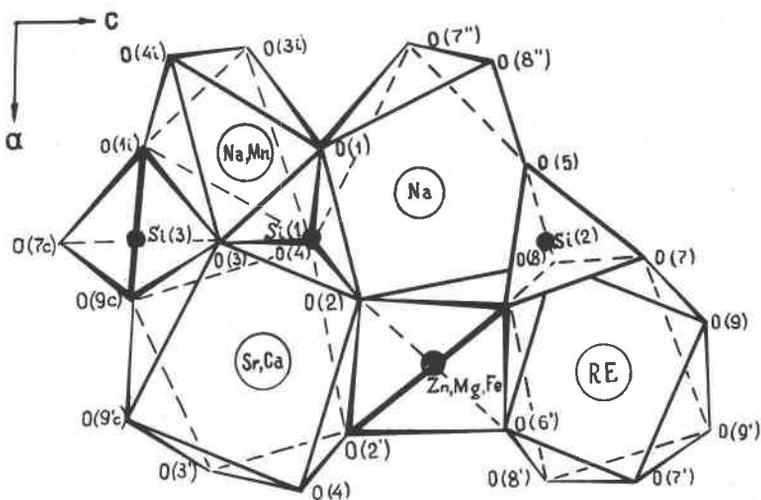


FIG. 1. Asymmetric unit of the nordite cell. The atoms related by a glide plane, center of inversion and two kinds of two-fold axes are denoted by the indices c , i , $'$, $''$.

types and tetrahedral pits between the triplets of polyhedra. These pits of two crystallographic types are oriented in opposite directions. This layer—the cationic basis of the structure of nordite—is shown in Figure 2c. Such layers, translationally repeated along b , are connected at the levels $0.45 \leq y/b \leq 0.55$ by Si and (Zn, Mg, Fe, Mn) atoms, all being tetrahedrally coordinated by O atoms. The Si tetrahedra are found in three orientations with respect to the (010) layer, one of these sharply differing. Si(1) and Si(2) are perched above the mentioned tetrahedral pits and share three or one common O vertices with the layer of cations in accordance with their direct or opposite orientation. The Si(3) tetrahedra are situated over the quadrangular openings between RE-, (Sr, Ca)- and Na-antiprisms and the Na, Mn-octahedron. The crossing edges of Si(3)-tetrahedra pertain to different layers of cations.

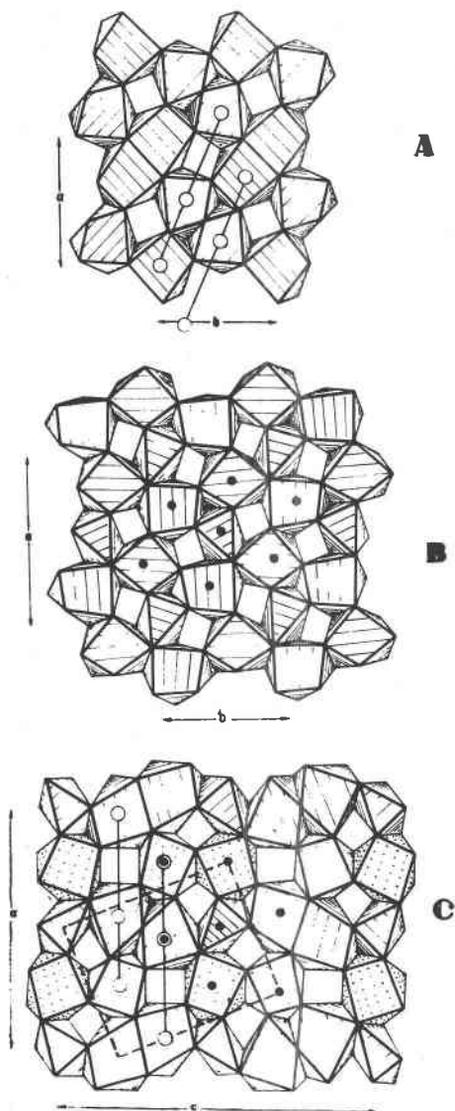


FIG. 2. Layers of the *A*-eight-corner polyhedra and *B*-octahedra in the structure types of: A. mellite; B. gadolinite; C. nordite. In Fig. 2a and 2c the mellite units of the same type are indicated by light circles, whereas those for gadolinite by black circles in Fig. 2b and 2c. The gadolinite subcell inside the nordite layer is shown by dotted lines. In Fig. 2c the shading of polyhedra corresponds to: Na (lines), (Sr, Ca) and RE (points).

Three kinds of Si tetrahedra can be distinguished by their orientation, being of the "face"-, "vertex"- and "edge"-type. (Zn, Mg, Fe, Mn) tetrahedra, or more precisely, those which are arranged over the larger openings, all are of the "edge" orientation. All Si tetrahedra have one "free" corner and three which bridge to neighboring tetrahedra. The vertices of the edge Si tetrahedra are common to three Si tetrahedra of the face and vertex type in the ratio 2:1 or 1:2; the face and vertex tetrahedra are connected to two Si tetrahedra and one (Zn, Mg, Fe, Mn) tetrahedron, the latter having only bridging vertices. The shared corners result in the appearance of a continuous approximately flat net of tetrahedra (Fig. 3c) with four-, five- and eight-membered rings in the ratio 1:2:1; its composition is given as $[(\text{Zn, Mg, Fe, Mn})\text{Si}_6\text{O}_{17}]_{\infty}^{8-}$. We can easily isolate within this net a $[\text{Si}_6\text{O}_{17}]_{\infty}^{10-}$ ribbon responsible for the elongation of the mineral along the *c*-axis, and speak of "the second polymorphic modification" of the xonotlite ribbon in which the four-rings (symmetry $2/m$) are linked together by the diorthogroups in the oblique (diagonal) manner. If, however, the Si and other tetrahedral cations play the same role in the architectural whole, it is difficult to isolate the silicon-oxygen motif. Besides, if account is taken of the periodicity of anions along the axis, the nordite silicon-oxygen ribbon must be given a more complicated formula, *i.e.* $[\text{Si}_{12}\text{O}_{34}]_{\infty}^{20-}$. The concrete analysis of the structure of nordite, when compared to related structures (see below), compels us to include in the infinite anion radical the M^{2+} tetrahedra. We then speak of a two-storied layer structure of nordite. Figure 4 demonstrates how the tetrahedral net and polyhedral layer in nordite are joined.

The structure of nordite is closely connected with the structures of the melilite and datolite-gadolinite groups, and may be considered as an unusual combination of both.

Description of the Melilite Structure Type. The structure type of melilite comprises more than twenty natural and synthetic compounds with a formula $A_2T_3X_7$, where A stands for Na, Ca, Sr, Pb, Y, RE; $T = \text{Be, Mg, Zn, Fe, Mn, B, Al, Ga, Si}$; $X = \text{O, OH, F}$. Their cells are tetragonal or pseudotetragonal with $a = 7.3\text{--}8.0$ and $c = 4.8\text{--}5.3$ Å. A structural study was carried out for hardyssonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (Warren and Trautz, 1930); gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (Raaz, 1930); melilite, $(\text{Ca, Na})_2(\text{Mg, Al})(\text{Si, Al})_2\text{O}_7$ (Warren, 1930); and $(\text{Ca}_{1.7}\text{Na}_{0.2}\text{K}_{0.1})(\text{Mg}_{0.5}\text{Al}_{0.4})\text{Si}_2\text{O}_7$ (Smith, 1953); leucophanite, $\text{CaNaBeSi}_2\text{O}_6\text{F}$ (Cannillo *et al.*, 1967); meliphanite, $\text{Ca}_{1.37}\text{Na}_{0.63}\text{Be}(\text{Si}_{1.87}\text{Al}_{0.13})\text{O}_{6.25}\text{F}_{0.75}$ (Dal Negro *et al.*, 1967); Ga-gehlenite (Korczak and Raaz, 1967); and $\text{Y}_2\text{SiBe}_2\text{O}_7$ (Bartram, 1969). The polyhedra around the A-cations can be described as eight-corner square antiprisms, their A-X distances within the limits 2.32–3.03 Å. The real

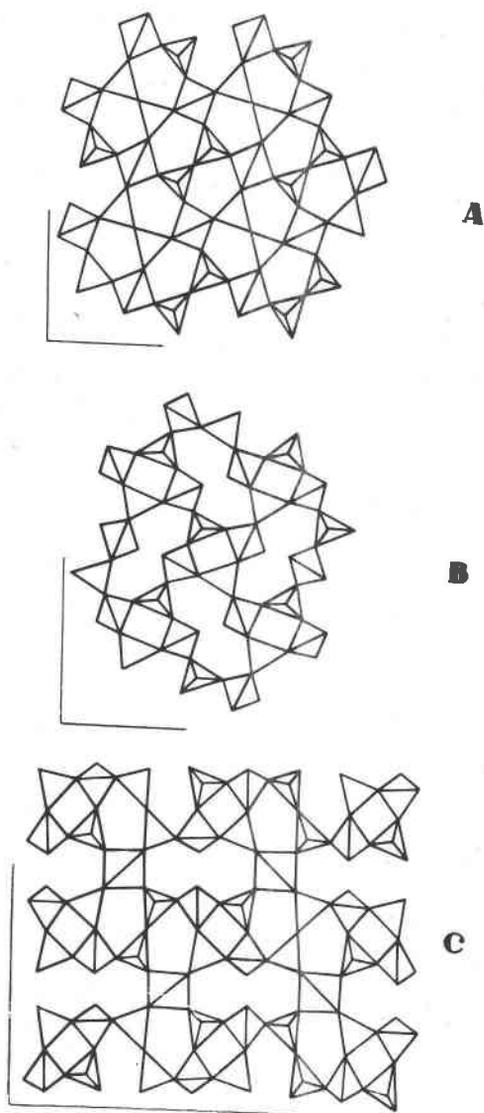


FIG. 3. Nets of tetrahedra in the structure types of: A. melilite
B. gadolinite; C. nordite.

coordination number is, as a rule, reduced to 6 or 7. The four common edges plus one face connect the polyhedra perpendicularly to $[001]$ into a continuous layer (Fig. 2a) with empty tetrahedra in the face- and vertex-type positions, and a cluster of four empty tetrahedra around the

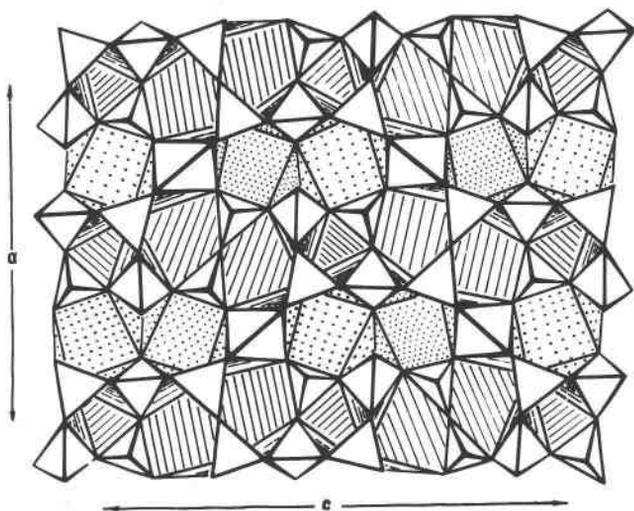


FIG. 4. Crystal structure of nordite projected on (010). The lower layer is the one of *A*- and *B*-polyhedra from Fig. 2c, the upper layer is the net of tetrahedra from Fig. 3c.

fifth central tetrahedron in edge position between them. The *A*-polyhedra and empty tetrahedra complete the layer in the ratio of $A:T=2:7$. This "heavy" layer of the structure of melilite is inhabited only by *A*-cations. The second layer is, geometrically, a true mirror reflection on the first one; it is subdivided into the same polyhedra, whereas all octagons remain empty, and only three tetrahedral vacancies out of seven are occupied: the central one in the cluster between the quadruples of *A*-cations and two between the triplets of *A*-cations in opposite (*i.e.* face and vertex) orientations. The tetrahedra are collected into a characteristic net with five-rings (Fig. 3a) in which all corners of the edge type tetrahedra are shared, while only three corners are shared by the remaining types. It should be noted, however, that the individual pattern of *T*-atom distribution over the tetrahedra in the net may be either of the same kind with regard to the atoms in all tetrahedra, as for example Al in $(Ca, Sr) RE Al_3O_7$ (Toropov and Ismatov, 1968; Toropov *et al.*, 1968), or differentiated into Zn or (Al, Mg) tetrahedra (of the edge-type) and Si double tetrahedra, as in hardystonite and melilite, or Be and Si tetrahedra plus a net with 16-membered rings of the Si tetrahedra, as in meliphanite, or Si tetrahedra and Be double tetrahedra in $Y_2SiBe_2O_7$. But the characteristic feature for the structure type of melilite still remains a continuous pack of tetrahedra linked together by corners, which in our case results in a net with five-rings.

Description of the Datolite-Gadolinite Structure Type. The structure type of datolite-gadolinite includes up to twenty natural and synthetic compounds (Ito, 1967). Its general formula is $A_2BT_4X_{10}$, where $A = \text{Ca, Y, RE}$; $B = \text{Fe}^{3+}, \text{Ga, Mg, Ni, Co, Zn, Mn, Cu, Cd}$; $T = \text{Be, B, Si, P}$; $X = \text{O, OH, F}$. The cell is monoclinic (pseudo-orthorhombic) with $a = 9.7\text{--}10.2 \text{ \AA}$, $b = 7.5\text{--}7.8 \text{ \AA}$, $c = 4.7\text{--}4.9 \text{ \AA}$; $\beta \sim 90^\circ$. A structure study has been carried out for datolite, $\text{Ca}_2\text{B}_2\text{Si}_2\text{O}_8(\text{OH})_2$ (Pavlov and Belov, 1959; Pant and Cruickshank, 1967), herderite, $\text{Ca}_2\text{Be}_2\text{P}_2\text{O}_8(\text{OH, F})_2$ (Pavlov and Belov, 1959), and gadolinite, $\text{Y}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$ (Pavlov and Belov, 1959). In the square antiprisms around the A -cations the distances $A\text{--}X$ are within the limits $2.3\text{--}2.7 \text{ \AA}$. The B -polyhedra are octahedra, those positions remaining empty in datolite and herderite. The polyhedra are connected by side edges into a layer (Fig. 2b). As in melilite, A -polyhedra have 5 neighbors of two kinds: $3A$ and $2B$, while octahedra of smaller size are surrounded by four A -polyhedra. The layer in gadolinite is more "skeletal" than in melilite and has more "windows" in accordance with an increased ratio of the quadruples of polyhedra, linked through their edges to the triplets (1:2 in melilite and 1:1 in gadolinite). However, the relative mean density of the layer in gadolinite is found to increase steadily: the specific area per one A -cation in melilite is 15 \AA^2 , while in gadolinite it is equal to 12.5 \AA^2 (per one A, B -cation). The increased openness as compared with melilite is the result of a somewhat different plan of the layer with a larger number of clusters of tetrahedral vacancies. Thus, in melilite the formula of the layer is $A_6T_{6+(5 \times 3)} = A_6T_{21}$ when reduced to the sum of polyhedral vacancies, whereas in gadolinite it is $A_4B_2T_{4+(5 \times 4)} = A_4B_2T_{24}$. The first number in the index indicates the vacancies between the triplets; the parentheses indicate clusters of vacancies between the quadruples. In other words, in gadolinite the total number of T -vacancies is increased on account of cluster-type vacancies. In the two-layered structure of gadolinite the first layer is occupied only by A (and B) cations, the second "mirror equivalent" by T -cations filling eight vacancies out of 24: four of the vertex-face type, and four of the edge-type, these being central in the cluster. The tetrahedra of each type having three common vertices with T -tetrahedra of another type, share their fourth vertex with only the functions of the A, B -polyhedra, thus forming a continuous two-dimensional net with four- and eight-rings (Fig. 3b). In this net the equal numbers of tetrahedra of two kinds alternate, and are filled in the ordered manner with two kinds of T atoms in three compounds whose structures are known. This led to considering heavier tetrahedra as "isolated," and calling the respective minerals orthophosphates (herderite) or orthosilicates (datolite, gadolinite). However, some real compositions (bakerite) as well as local charge balances of some

hypothetical examples point to the possibility in this particular case, as in melilite, of a statistical distribution of T atoms upon the uniform net of type $T_4^{3+}X_{10}$ and even (formally) of the $T_4^{4+}X_{10}$ type. Therefore, we are permitted to consider the tetrahedral datolite-gadolinite net as a single whole without isolating the different kinds of its tetrahedra.

Relationship of the Nordite to Datolite-Gadolinite and Melilite Structures.
In the comparative analysis of the structure of nordite and that of gadolinite it is convenient to proceed from a characteristic group of cation

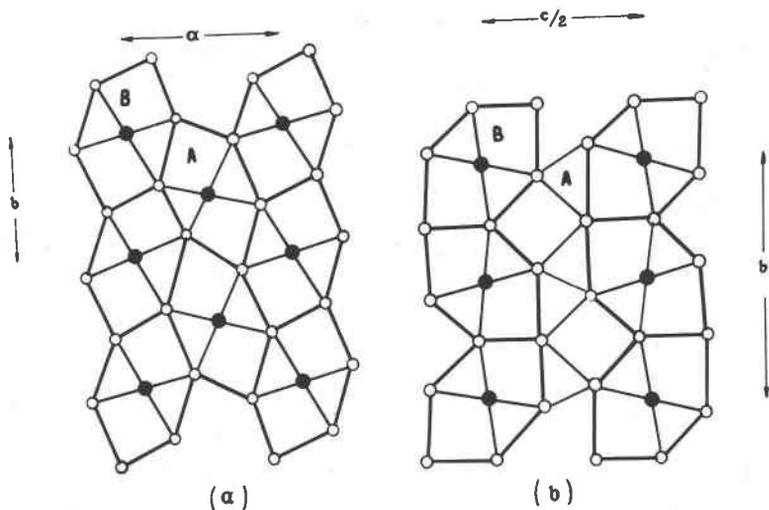


FIG. 5. Scheme for the packing of identical "cation units" (shown by thick lines) in the structures of A. gadolinite B. nordite. The coordination bonds of cations inside and outside the units are shown by thin lines.

polyhedra around the B -octahedron, *i.e.* two pairs of A -polyhedra substituted by the first one and forming a "butterfly" (see Solovyeva and Bakakin, 1968) and supplemented by two A -polyhedra to a ring in the form of an elongated hexagon. This latter is indicated in Figures 2b and 2c by black circles. Such hexagons in two orientations with respect to the axis of elongation completely fill the layer in gadolinite, their six sides being common to six neighboring hexagons (Fig. 5a). The formula of an isolated hexagon is BA_6 but each A -corner is common to three rings, making the formula of this unit $OA_{6/3} = OA_2$. In nordite the analogous hexagonal units, each sharing only two opposite sides, are packed in wavy parallel ribbons extended along the a -axis with openings between them (Fig. 5b). Neighboring ribbons are quite identical in their cation "core" but, with regard to O atoms, the hexagons are "antisymmetrical" in

projection, being related by a "black-white" translation which, as usual, is equal to half of the true one. This fact creates a $c' = c/2$ pseudo-period. The cation composition of the ribbon unit is $BA_{\frac{1}{2}+2} = BA_4$, which depicts the "nordite" character of the former. There are no additional A (and B) cations in the openings. The edges of ribbons are formed by only A cations: their relative disposition and joining follow the principle characteristic for the melilite group with not only shared octagonal edges, but also with one shared face in addition. In Figures 2a and 2c the areas common to nordite and melilite are indicated by circles. The "gadolinite" ($z=0$ and 0.50) and "melilite" ($z=0.25$ and 0.75) zones designated in the polyhedral layer of nordite, stand out in the tetrahedral layer as distinctly as in the cation one. These zones may be described as belts of four- and eight-rings which are interlayered by intermediate belts of five-rings. Thus, judging from their qualitative (dimensional) characteristics, the building units in nordite— A , B , T , X -groups—are the same as in melilite and gadolinite. The following intermediate ratios hold: $B:A$ and $(A+B):T$ (the corresponding ratios in melilite-nordite-gadolinite) are $0:2=0$, $1:4=0.25$, $1:2=0.5$ and $2:3=0.66$, $5:7=0.71$, $3:4=0.75$. It is interesting to observe that the over-all formula for nordite represents the arithmetical sum of the formulae for melilite and gadolinite: $A_2T_3X_7 + BA_2T_4X_{10} = BA_4T_7X_{17}$. We can write down this expression in a more concrete manner, for example, by substituting $(Na RE)^{4+}$ for $(Ca_2)^{4+}$ in melilite, and $(Na(Sr, Ca)NaSi_2)^{12+}$ for $(Fe^{2+}Y_2Be_2)^{12+}$ in gadolinite, obtaining the complete formula of nordite. The polyhedral formula of nordite is also of the same additive character. Each of the two layers in the structure of nordite consists of the following numbers of A , B , T blocks: $A_4BT_{4+(5 \times 3)} = A_4BT_{19}$ which is A_2T_{2+5} (melilite) + $A_2BT_{2+(5 \times 2)}$ (gadolinite). With reference to some metrical relationships nordite can be considered as a mineral intermediate between melilite and gadolinite. Thus, the specific area per one A , B -cation is 13.6 \AA^2 against 12.5 \AA^2 and 15 \AA^2 in melilite and gadolinite respectively. By superposing the common unit in the structures of nordite and gadolinite—the A -hexagon—we can conditionally separate in nordite the "gadolinite" subcell as shown in Figure 2c, in which part of B and A cations are transposed. The b -axis of gadolinite coincides with the $[301]$ direction in nordite; in this case $[301]_{(n)} \approx 6b_{(g)}$ or $b_{(g)} \approx \frac{1}{6}[301]_{(n)}$. The following values for Fe^{3+} , Ca , La -gadolinite (Ito, 1967) correspond to the last expression: 7.75 and 7.9 \AA . The a -axis of gadolinite corresponds to $[102]$ in nordite when $a_{(g)} = \frac{1}{4}[102]_{(n)}$ ($10.15 \text{ \AA} \approx 10.35$). The melilite zone dissected along $[250]$, is extended in nordite along the a -axis, taking into account that $a_{(n)} \approx \frac{1}{3}[250]_{(n)}$ ($14.3 \text{ \AA} \approx 14.05 \text{ \AA}$).

The structure of nordite considered as a derivative of the structures of melilite and gadolinite, together with these latter form a special group or

family of two-layered structures in which layers of cations alternate with the layers of tetrahedral anion radicals infinite in two dimensions, *i.e.* flat nets. In contrast to silicon-oxygen nets in micas, the melilite-gadolinite nets and that of nordite have two of their surfaces identical; they are squeezed from both sides by the layers densely filled with cations, and share with them all their O including the bridging O between *T* atoms. The resulting disproportion in the distribution of the valence strengths, makes it impossible to obtain the ideal balance on the basis of formal schemes; as a consequence, there appears a compensational range in the interatomic distances accompanied with alteration of the form of polyhedra, and even the change of the coordination number of isomorphous cations of isotypic series. The same reason accounts for the decrease of the *T-X-T* angles, as shown for datolite (Pant and Cruickshank, 1967).

Some Details of the Nordite Structure. The most important interatomic distances in nordite (Table 2) calculated from the coordinates given in Table 1 should be considered in the light of the preceding discussion. The valence balance is given in Table 3; it should be noted that these balances have been calculated without correction for the difference in the interatomic distances inside some polyhedra; therefore, the sum of valency bonds on O atoms varies over a wide range, and only the balance sums for O(2) and O(6) are more or less normal. O(4), O(8), O(9), *i.e.* the "free" vertices of three kinds of Si-tetrahedra, are "undersaturated" by 18–22 percent, O(1), O(3), O(5), O(7) are "oversaturated" by 14–21 percent, these being the bridges between the same Si-tetrahedra. The formal arithmetical mean contributions from large cations are insufficient to balance the first three undersaturated O and they appear as "excess" contributions for four bridging O with their valency balance already satisfied. It follows from Table 2 that a compromise is to be sought in nonequivalent contributions. The difference between the free and bridge Si-O bonds in the Si(3)-tetrahedron (of the edge-type) is striking: 1.57 and 1.68 Å against a mean of 1.63. These figures practically repeat those found for Si-tetrahedra in datolite (Pant and Cruickshank, 1967) where the difference is 0.12 Å = 1.68 – 1.56 against a mean of 1.64 Å.

The oxygen edges of Si-tetrahedra common to other polyhedra are, as usual, noticeably shorter, their average length being 2.54 Å (against 2.67 for those not shared). The minimal scatter in the O-O values is observed for the edge-type Si(3) tetrahedra linked with other polyhedra only via shared corners. The other edge-type tetrahedron—(Zn, Mg, Fe, Mn)—is also slightly distorted. Its O(2) and O(6) corners do not suffer any severe deviations as far as the valency balance is concerned, and the equal distances $M^{2+}-O$ agree well with the average observed distances

TABLE 2. INTERATOMIC DISTANCES (Å)^a AND ANGLES AT OXYGEN ATOMS (DEGREES) IN NORDITE

| | | | |
|----------------------------|-----------------------------------|------------------------------------|-------|
| <i>Si(1)—tetrahedron</i> | | <i>Si(2)—tetrahedron</i> | |
| Si(1)—O(3) | 1.58 | Si(2)—O(8) | 1.58 |
| Si(1)—O(2) | 1.60 | Si(2)—O(5) | 1.61 |
| Si(1)—O(4) | 1.60 | Si(2)—O(6) | 1.61 |
| Si(1)—O(1) | 1.62 | Si(2)—O(7) | 1.65 |
| mean | 1.60 | mean | 1.61 |
| O(1)—O(3) | 2.52° | O(6)—O(7) | 2.51° |
| O(2)—O(3) | 2.53° | O(5)—O(6) | 2.59° |
| O(1)—O(2) | 2.56° | O(7)—O(8) | 2.65 |
| O(3)—O(4) | 2.64 | O(5)—O(7) | 2.66 |
| O(1)—O(4) | 2.68 | O(5)—O(8) | 2.68 |
| O(2)—O(4) | 2.71 | O(6)—O(8) | 2.68 |
| <i>Si(3)—tetrahedron</i> | | <i>M²⁺—tetrahedron</i> | |
| Si(3)—O(9c) | 1.57 | ^b M ²⁺ —O(2) | 1.91 |
| Si(3)—O(1i) | 1.63 | ^b M ²⁺ —O(6) | 1.93 |
| Si(3)—O(7c) | 1.64 | O(6)—O(6') | 2.97 |
| Si(3)—O(3) | 1.68 | O(2)—O(2') | 3.08 |
| mean | 1.63 | ^b O(2)—O(6) | 3.18 |
| | | ^b O(2)—O(6') | 3.21 |
| <i>O(3)—O(7c)</i> | | <i>Na, Mn—octahedron</i> | |
| O(3)—O(7c) | 2.60 | ^b Na, Mn—O(4) | 2.30 |
| O(1i)—O(3) | 2.61 | ^b Na, Mn—O(1) | 2.35 |
| O(1i)—O(7c) | 2.65 | ^b Na, Mn—O(3) | 2.49 |
| O(1i)—O(9c) | 2.65 | ^b O(1)—O(3) | 2.52 |
| O(7c)—O(9c) | 2.69 | ^b O(1)—O(4i) | 3.25 |
| O(3)—O(9c) | 2.75 | ^b O(1)—O(4) | 3.34 |
| <i>RE—polyhedron</i> | | ^b O(1)—O(4i) | 3.35 |
| ^b RE—O(9) | 2.41 | ^b O(3)—O(4) | 3.42 |
| ^b RE—O(8) | 2.44 | ^b O(1)—O(3i) | 4.13 |
| ^b RE—O(6) | 2.48 | <i>Sr, Ca—polyhedron</i> | |
| ^b RE—O(7) | 2.65 | ^b Sr, Ca—O(9c) | 2.51 |
| ^b O(6)—O(7) | 2.51° | ^b Sr, Ca—O(2) | 2.58 |
| O(9)—O(9') | 2.94 | ^b Sr, Ca—O(4) | 2.59 |
| ^b O(6)—O(8) | 2.96 | ^b Sr, Ca—O(3) | 2.71 |
| ^b O(8)—O(9) | 3.00 | ^b O(2)—O(3) | 2.53° |
| ^b O(6)—O(8') | 3.02 | O(9c)—O(9c') | 2.94 |
| ^b O(7)—O(9') | 3.08 | ^b O(2)—O(4) | 3.04 |
| ^b O(7)—O(9) | 3.33 | ^b O(4)—O(9c) | 3.16 |
| ^b O(7)—O(8) | 3.42 | ^b O(3)—O(9c') | 3.19 |
| O(6)—O(6') | 3.63 | ^b O(2)—O(4') | 3.37 |
| <i>Na—polyhedron</i> | | ^b O(3)—O(9c) | 3.41 |
| Na—O(2) | 2.36 | ^b O(3)—O(4) | 3.42 |
| Na—O(8'') | 2.40 | O(2)—O(2') | 3.83 |
| Na—O(4) | 2.41 | O(6)—O(8) | 2.96 |
| Na—O(8) | 2.47 | O(2)—O(4) | 3.04 |
| Na—O(6) | 2.52 | O(2)—O(8) | 3.24 |
| Na—O(1) | 2.63 | O(1)—O(4) | 3.34 |
| Na—O(5) | 2.68 | O(1)—O(8'') | 3.40 |
| Na—O(7'') | 3.39 | O(4)—O(6) | 3.40 |
| O(1)—O(2) | 2.56° | O(7'')—O(8'') | 3.42 |
| O(5)—O(6) | 2.59° | O(8)—O(8'') | 3.46 |
| O(5)—O(7'') | 2.66 | ^b O(5)—O(8) | 3.55 |
| | | O(4)—O(7'') | 3.60 |
| | | O(2)—O(6) | 3.86 |
| | | O(1)—O(7'') | 4.13 |
| Si(2)—O(6)—M ²⁺ | 113.2; Si(1)—O(2)—M ²⁺ | 177.8; | |
| Si(2)—O(7)—Si(3) | 118.7; Si(1)—O(3)—Si(3) | 122.5; | |
| Si(1)—O(1)—Si(3i) | 135.7; Si(2)—O(5)—Si(2) | 143.7 | |

^a Estimated standard errors: 0.03Å for RE—O, Si—O, (Sr, Ca)—O, and M²⁺—O; 0.04Å for O—O.

^b Twice.

^c Edges shared between Si-tetrahedron and A, B-polyhedra (excluded O(7) at Na-polyhedron).

TABLE 3. VALENCE BALANCE IN NORDITE

| | Si(1) | Si(2) | Si(3) | M^{2+} | RE | Sr, Ca | Na | Na, Mn | Σ |
|------|-------|-------|-------|----------|-----|--------|-------|--------|----------|
| O(1) | 1.0 | — | 1.0 | — | — | — | 1/7 | 1/6 | 2.31 |
| O(2) | 1.0 | — | — | 2/4 | — | 2/8 | 1/7 | — | 1.89 |
| O(3) | 1.0 | — | 1.0 | — | — | 2/8 | — | 1/6 | 2.42 |
| O(4) | 1.0 | — | — | — | — | 2/8 | 1/7 | 1/6 | 1.56 |
| O(5) | — | 2×1.0 | — | — | — | — | 2×1/7 | — | 2.28 |
| O(6) | — | 1.0 | — | 2/4 | 3/8 | — | 1/7 | — | 2.01 |
| O(7) | — | 1.0 | 1.0 | — | 3/8 | — | — | — | 2.37 |
| O(8) | — | 1.0 | — | — | 3/8 | — | 2×1/7 | — | 1.65 |
| O(9) | — | — | 1.0 | — | 3/8 | 2/8 | — | — | 1.62 |

for the given cations in tetrahedral coordination. The shortest edge of the M^{2+} -tetrahedron is the one facing RE, the next facing (Sr, Ca) $^{2+}$, and the two longer edges facing Na $^{1+}$. The edges of maximum length are diagonal in projection.

The mean value for the $T-O-T$ angle is 125° (if M^{2+} is not taken into account, it equals 130°). This value is noticeably smaller than the values usually encountered in silicates, but it is in excellent agreement with the Si-O-B angle in datolite (Pant and Cruickshank, 1967).

In a centrosymmetric elongated (Na, Mn)-octahedron two edges common to Si(1)-tetrahedra force its equatorial cross-section into a rectangle ($2.52 \times 4.13 \text{ \AA}^2$). The meridional edges are 3.25–3.42 Å. A mean cation-anion distance (2.38 Å), less than average Na-O octahedral distances, agrees with the proposed substitution by Mn, (Na $_{0.8}$ Mn $_{0.2}$).

For the RE-polyhedron which is nearly a tetragonal antiprism the edge of its base that is common to the Si(2) tetrahedron deforms the square into a trapezium with one side shortened. Two oblique edges common to Sr, Ca- and Na-polyhedra are also shortened. The Sr, Ca-antiprism is closely related after allowing for an appropriate scaling.

We take the eight-corner figure—and octagon (although its eighth corner is outside the standard range) as a “primary” polyhedron around Na, departing from the relationship between this polyhedron and other polyhedra in the melilite-gadolinite-nordite family. This “primary” polyhedron is shown in our drawings. The analogous picture, which we may call transitional with respect to our case, can be observed in leucophanite (Cannillo *et al.*, 1967) where the Na,Ca-O distances monotonically extend from 2.35 to 3.03 Å. The Na-octagon is less symmetrical. One of its “lids” is also shaped like a trapezium, while the Si double tetrahedra are fitted to the other shaping it into a “di-delta.” When calculating the valency balance (Table 3) we used the coordination number seven. The “secondary” Na-polyhedron, with O(7) excluded (the most

oversaturated and displaced at a distance of 3.39 Å), may be described as a distorted trigonal prism with a square pyramid attached to one of its side faces.

REFERENCES

- BARTRAM, S. F. (1969) Crystal structure of $Y_2SiBe_2O_7$. *Acta Crystallogr.* **B25**, 791–795.
- BETEKHTIN, A. G. (1960) *Mineralogy*. Gosgeolizdat, Moscow [in Russian].
- CANNILLO, E., G. GIUSSEPPETTI AND V. TAZZOLI (1967) The crystal structure of leucophanite. *Acta Crystallogr.* **23**, 255–259.
- DAL NEGRO, A., G. ROSSI, AND L. UNGARETTI (1967). The crystal structure of melilite. *Acta Crystallogr.* **23**, 260–264.
- GERASIMOVSKY, V. I. (1941) Nordite—a new mineral of Lovozerski tundras. *Dokl. Akad. Nauk SSSR*, **32**, 496–498 [in Russian].
- ITO, Y. (1967) Synthesis of calciogadolinite. *Amer. Mineral.* **52**, 1523–1527.
- KORCZAK, P., AND F. RAAZ (1967) Verfeinerung der Kristallstruktur von Gehlenit unter Zugrundelegung des Gallium-Gehlenites. *Oesterr. Akad. Wiss., Math.-Naturwiss. Kl. Anz.* **104**, 383–387.
- PANT, A. K., AND D. W. J. CRUICKSHANK (1967) A reconsideration of the structure of datolite, $CaBSiO_4(OH)$. *Z. Kristallogr.* **125**, 286–297.
- PAVLOV, P. V., AND N. V. BELOV (1959) The structures of herderite, datolite and gadolinite determined by direct methods. *Kristallografiya* **4**, 324–340 [in Russian].
- RAAZ, F. (1930) The fine structure of gehlenite. A contribution to the knowledge of melilite. *Oesterr. Akad. Wiss. Math.-Naturwiss. Kl. Sitz. Abt. I*, **139**, 645.
- POVARENNYKH, A. S. (1966) *Crystal Chemical Classification of Mineral Species*. Naukova Dumka, Kiev [in Russian].
- SEMENOV, E. I. (1961) New data on nordite. *Tr. Mineral. Muz. Akad. Nauk SSSR*, **11**, 199–201 [in Russian].
- SMITH, J. V. (1953) Reexamination of the crystal structure of melilite. *Amer. Mineral.* **38**, 643–661.
- SOLOVYEVA, AND V. V. BAKAKIN (1968) The crystal structure of borcarite $Ca_4MgB_4O_{16}(OH)_6(CO_3)_2$. *Dokl. Akad. Nauk SSSR*, **180**, 1453–1456 [in Russian, transl. *Dokl. Earth Sci. Sec.* **180**].
- STRUNZ, H. (1966) *Mineralogische Tabellen*. 4. ed Geest and Portig Leipzig.
- TOROPOV, N. A., AND A. A. ISMATOV (1968) Strontium melilite and its derivatives. *Dokl. Akad. Nauk SSSR*, **180**, 889–891 [in Russian].
- , N. V. MARGOLIS, AND A. A. ISMATOV (1968) A new group of rare-earth silicates—the melilites and their derivatives. *Dokl. Akad. Nauk SSSR*, **179**, 610–613 [in Russian; transl. *Dokl. Earth Sci. Sec.* **179**].
- VLASOV, K. A. (Editor) (1964) *Geochemistry and mineralogy of rare elements and genetic types of their deposits. Vol. 2. The mineralogy of rare elements*. Nauka, Moscow [in Russian].
- WARREN, B. E. (1930) The structure of melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$. *Z. Kristallogr.* **74**, 131–139.
- , AND O. R. TRAUTZ (1930) The structure of hardystnite $Ca_2ZnSi_2O_7$. *Z. Kristallogr.* **75**, 525–530.
- WINCHELL, A. N., AND H. WINCHELL (1951) *Elements of Optical Mineralogy. An Introduction to Microscopic Petrography*. John Wiley and Sons, New York.

Manuscript received, October 21, 1969; accepted for publication, March 24, 1970.