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The Crystal Structures of Orthorhombic $SmAlO_3$ and of Trigonal $NdAlO_3$

M. MAREZIO, P. D. DERNIER, AND J. P. REMEIKA

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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The structures of $NdAlO_3$ and $SmAlO_3$ have been refined with high precision from single crystal X-ray data. Both compounds have the perovskite-like arrangement. In the trigonal $NdAlO_3$ (space group $R\bar{3}c$) the neodymium atoms have coordination number 12, the average Nd–O distance being 2.660 Å. The aluminum atoms are surrounded by a trigonally distorted octahedron, with an average Al–O distance of 1.896 Å. In the orthorhombic $SmAlO_3$, the samarium atoms are surrounded by 12-oxygen polyhedra but the coordination is slightly less than 12. The average Sm–O distance is 2.658 Å. Our results indicate that with the orthorhombic → trigonal transition, the distortion of the rare earth polyhedron decreases, whereas that of the aluminum octahedron increases slightly. The overall distortion of the structure decreases. A comparison of the $SmAlO_3$ structure with that of its iron counterpart shows that the distortion from the ideal cubic perovskite structure is quite different. Therefore, the two compounds cannot be considered truly isostructural.

Introduction

Among the ABO_3 perovskite-like compounds with A = rare earth (RE) and B = Al, Fe, Ga, V, Cr, Rh, the rare earth orthoaluminates are unique in that they are not isostructural across the series. Although all the $REAlO_3$ have the perovskite-like arrangement, $LaAlO_3$, $CeAlO_3$, $PrAlO_3$, and $NdAlO_3$ have trigonal symmetry at room temperature (*1*, *2*), whereas the members from Sm to Yb have the orthorhombic symmetry (*1*, *3*, *4*). The smaller rare earth orthoaluminates are difficult to synthesize and $LuAlO_3$ has never been prepared. For instance, if one prepares single crystals of these compounds by using the flux method (*5*), the ABO_3 compound is obtained from La through Tb. A mixture of the ABO_3 and of the garnet $A_3B_5O_{12}$ is obtained for Dy, whereas only the garnet phase is obtained from Ho to Lu. In 1961, Schneider, Roth, and Waring reported some crystal data on the smaller rate earth orthoaluminates (*3*). They were able to prepare powder samples of $HoAlO_3$, $ErAlO_3$, and $TmAlO_3$, but always as mixtures with the respective garnet. Subsequently, Garton and Wanklyn reported the synthesis of single crystals of the rare earth orthoaluminates (*4*). By dissolving an equimolar mixture of the oxides in PbO flux at 1260°C and by cooling the solution at 50°C/hr, they were able to synthesize single crystals of Dy, Ho, Er, Tm, and Yb orthoaluminates. The last two samples were not pure, but mixed with the respective garnet phase. They failed to get $LuAlO_3$ with the perovskite-like structure. In a different experiment we were unsuccessful in preparing solid solutions of $RE(Al_{1-x}Fe_x)O_3$. Unless x was small one always obtains two phases, the orthoaluminate containing a small amount of Fe^{3+} and the orthoferrite containing a small amount of Al^{3+}. All these observations led us to believe that even though the rare earth orthoaluminates from Sm to Yb have the perovskite-like arrangement isostructural with the orthoferrites, their structures should be somewhat different from their iron counterparts. This paper reports the refinements of the trigonal $NdAlO_3$ and of the orthorhombic $SmAlO_3$ from single crystal data. We thought that by determining the structure of a trigonal member and an orthorhombic member, one could have a better understanding of the crystal chemistry of the rare earth orthoaluminates.

Crystal Data

Single crystals of the rare earth orthoaluminates were grown from a flux consisting of PbO and B_2O_3 (*5*). At room temperature, $LaAlO_3$, $CeAlO_3$,

$PrAlO_3$, and $NdAlO_3$ are trigonal. Their structure was first reported in the space group $R\bar{3}m$ with six formula units per unit cell (hexagonal axes[1]) (*1*). In 1965, de Rango, Tsoucaris, and Zelwer showed from single crystal X-ray and neutron data that the correct space group for $LaAlO_3$ was either $R\bar{3}c$ or $R3c$ (*6*). The same conclusion was reached independently by Derighetti et al. from resonance measurements (*7*). These space groups are also consistent with the X-ray powder data reported in (*1*) if the two very weak reflections appearing in the powder pattern are indexed as the 113 and the 211, rather than the 113 and/or 021 and the 211 and/or 205. By using several single crystals of $NdAlO_3$ we observed that the 113 and the 211 reflections had measurable intensities whereas the 021 and the 205 always had zero intensity. Our refinement of the $NdAlO_3$ structure was done on a highly twinned crystal; therefore we could not reach any decision based on experimental data concerning the center of symmetry. On the other hand, the orthorhombic distortion of the perovskite structure has been shown to be centrosymmetric based on single crystal X-ray data (*8*). The undistorted cubic perovskite structure is also centrosymmetric; therefore it seems logical to assume that the trigonal distortion belongs to the space group $R\bar{3}c$. In this space group the 6 rare earth atoms are in the special positions $(6a) \pm (00\tfrac{1}{4}) + \mathrm{Rh}$, the 6 aluminum atoms in the special positions $(6b)\ (000;\ 00\tfrac{1}{2}) + \mathrm{Rh}$ and the 18 oxygen atoms in the special positions $(18e) \pm (x,0,\tfrac{1}{4};\ 0,x,\tfrac{1}{4};\ \bar{x},\bar{x},\tfrac{1}{4}) + \mathrm{Rh}$. The lattice parameters of $NdAlO_3$ were measured from an X-ray powder film taken with a Guinier camera. A KCl internal standard and $\mathrm{Cu}K\alpha_1$ (1.5405) were used. The lattice parameters were refined by least squares. They are: $a = 5.322 \pm 0.002$ Å and $c = 12.916 \pm 0.005$ Å. These values are in good agreement with those reported by Geller and Bala (*1*).

The rare earth orthoaluminates (from Sm to Yb) crystallize in the orthorhombic space group Pbnm with four molecules per unit cell. The 4 rare earth atoms are in the special positions $(4c)\ (x,y,\tfrac{1}{4})$, and 4 Al atoms in the special positions $(4b)\ (0,\tfrac{1}{2},0)$; four of the twelve oxygen atoms are in the special positions $(4c)\ (x,y,\tfrac{1}{4})$ and the remaining eight in the general positions. The lattice parameters for $SmAlO_3$, $a = 5.2912 \pm 0.0002$, $b = 5.2904 \pm 0.0002$ and $c = 7.4740 \pm 0.0002$ Å, were measured by a simplified version of Bond's method (*9*, *10*). This was necessary as the three parameters a, b and $c/(2)^{1/2}$ for $SmAlO_3$ are almost identical.

Twinning

In general, the rare earth orthoaluminates grow as multidomain crystals with the domain walls parallel with the pseudocube faces. The domains are easily observed optically with transmitted polarized light. Each one contains one orientation of the pseudocubic cell. In the trigonal crystals, four orientations are possible. In fact, at the cubic → trigonal transformation each of the four threefold axes of the cubic structure can become the threefold axis of the trigonal structure. In $LaAlO_3$, which has the least distorted trigonal perovskite structure, the domains are finite in all three directions. In $PrAlO_3$, the domains are finite in two directions and extend to the limit of the crystal in the other direction. In $NdAlO_3$ the domains are finite in one direction and extend to the limit of the crystal in the other two directions. If one applies light pressure on one of these polydomain crystals in a general crystallographic direction, the number of domains increases. The pressure causes a random reorientation of the pseudocubic cell. In 1967, Fay and Brandle (*11*) reported that by applying pressure along one of the [111] pseudocubic directions, one can detwin single crystals of $LaAlO_3$. With the cubic → trigonal transformation one of the (111) planes becomes the (003) and the other three (101)'s. Since the d-spacing of the (006) planes in $LaAlO_3$ is 2.185 Å and for the (202) it is 2.190 Å, by applying pressure along a [111] pseudocubic direction, one compels this direction to be the threefold axis of the trigonal structure.

The polydomain $SmAlO_3$ crystals are similar to those of $NdAlO_3$. The domain walls are parallel to the pseudocubic cell and they extend to the limit of the crystal in two directions and have finite length in the third direction. Each domain corresponds to an orientation of the pseudocubic cell. Also, for $SmAlO_3$ the number of domains increases by applying a light pressure along a general crystallographic direction. In a typical crystal batch one can frequently choose several single domain crystals of $SmAlO_3$, whereas all the trigonal orthoaluminate crystals we examined were polydomain. Therefore the crystal structure of $SmAlO_3$ was refined from single crystal data whereas $NdAlO_3$ was refined from polytwin crystal data. It should be pointed out that the twinning found in $LaFeO_3$ (*8*) occurs as a rotation of 90° around the c^* axis, such that along a^* there is a certain percentage of b^* and vice versa, whereas c^* is uniquely determined. Although we did not take any data on a twinned $SmAlO_3$ crystal, this type of twinning could also hold for $SmAlO_3$.

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[1] Unless otherwise noted, the hexagonal cell is always to be assumed.

In other words, the c^* axis would be coincident in every domain whereas the a^* and b^* axes could alternately interchange from one domain to the next.

Experimental

In the case of $NdAlO_3$ the X-ray intensity measurements were taken manually with a G.E. XRD-5 diffractometer. A scintillation counter and a decade scalar were used as the detection system. Single Zr-filtered MoK radiation was used with an 8° take-off angle. The sample was a polydomain parallelepiped of dimensions 0.276 × 0.188 × 0.293 mm with the domain walls parallel to the face 0.276 × 0.293. The faces of the parallelpiped were parallel to the pseudocubic (100), (010), and (001) faces. The crystal was oriented with the domain walls parallel to the φ axis of the goniostat. In order to measure intensities belonging only to the external domain, it was necessary to limit the measurements to those planes whose normals made an angle $<10°$ with the normal to the face of the parallelepiped. A further restriction was that the 2θ angle had to be $>40°$. Once a reflection was acquired, each angle was then maximized by hand and the intensity measured at the maximum. The background was taken $\pm 2°$ of 2θ off the peak maximum. Later the background intensities were averaged and subtracted from the maximum value to yield a net intensity. The intensities of those reflections whose 2θ angle exceeded 80° were adjusted for α_1–α_2 separation. This was done by measuring the $K\beta$ intensity for each reflection and normalizing the high angle data. The $K\alpha$ intensities were then converted to structure factors by applying the Lorentz-polarization and absorption corrections. The absorption factors were calculated numerically by a program written by C. T. Prewitt (*12*) modified in order to use the numerical integration method of Gauss.

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS OF $NdAlO_3$

	x	y	z	B (Å^2)
Nd	0.0	0.0	0.25	0.34(2)
Al	0.0	0.0	0.0	0.22(2)
O	0.5516(9)	0.0	0.25	0.48(3)

TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $NdAlO_3$

$h\ k\ l$	F_o	F_c
0 4 8	220.1	220.8
0 5 10	124.5	125.9
0 6 12	136.9	132.4
0 7 14	93.1	92.3
0 8 16	86.6	83.0
0 9 18	65.5	65.3
0 10 20	53.7	55.7
1 6 16	100.0	100.3
1 5 14	86.0	85.8
−1 7 10	89.6	90.0
−1 8 12	100.2	97.9
−1 7 13	8.9	8.7
−1 6 11	17.4	17.5
−1 5 9	15.6	16.5
0 6 18	80.2	78.6
−2 8 14	78.3	75.1
1 7 18	58.7	59.9
−1 9 14	61.7	61.5

The intensity data for $SmAlO_3$ were obtained by using the same G.E. diffractometer, but in the fully automatic mode. The integrated intensities were obtained by using the stationary crystal-stationary counter technique. The specimen was a sphere of radius $R = 0.015$ cm ($\mu R = 4.28$) ground from a single-domain crystal. It was oriented with the [111] axis along the φ axis of the goniostat. All possible reflections in the upper hemisphere within the 2θ range 20°–75° were measured. The background was

TABLE 3

FINAL POSITIONAL AND THERMAL PARAMETERS OF $SmAlO_3$

	Sm	Al	O(1)	O(2)
x	−0.00501(4)	0.0	0.0644(8)	−0.2766(6)
y	0.02402(7)	0.5	0.4903(11)	0.2770(6)
z	0.25	0.0	0.25	0.0335(6)
β_{11}	0.00428(13)	0.0035(6)	0.0075(12)	0.0049(6)
β_{22}	0.00473(17)	0.0049(4)	0.0079(13)	0.0051(7)
β_{33}	0.00243(7)	0.0017(3)	0.0025(6)	0.0044(4)
β_{12}	−0.00027(8)	−0.0001(3)	0.0028(11)	−0.0006(8)
β_{13}	0.0	0.0000(2)	0.0	0.0006(6)
β_{23}	0.0	0.0001(1)	0.0	−0.0001(5)

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SMALO3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	8	143.7	138.3	1	5	9	50.9	50.5	3	3	3	62.2	63.2	4	6	0	62.2	61.6	8	3	5	13.5	13.0
0	0	10	87.3	84.5	1	5	10	54.4	54.8	3	3	4	89.8	89.6	4	6	1	66.3	65.7	6	3	7	18.4	17.9
0	0	12	77.2	78.1	1	6	2	13.9	13.6	3	3	5	44.7	45.7	4	6	2	42.8	43.4	6	4	0	76.9	76.5
0	2	3	56.3	57.0	1	7	0	25.4	24.8	3	3	6	109.8	110.2	4	6	3	68.1	68.1	6	4	1	50.3	48.4
0	2	5	35.7	35.4	1	7	1	76.8	79.0	3	3	7	47.3	48.0	4	6	4	57.4	57.5	6	4	2	56.4	57.3
0	2	6	121.9	118.1	1	7	2	54.2	53.2	3	3	8	62.2	63.6	4	6	5	53.2	53.5	6	4	3	50.5	48.9
0	2	7	39.6	39.2	1	7	3	73.3	74.8	3	3	9	32.5	32.0	4	6	6	33.8	34.4	6	4	4	70.7	71.2
0	2	8	132.1	127.8	1	7	4	23.8	23.5	3	3	10	73.6	74.9	4	6	8	45.0	46.5	6	4	5	41.7	40.3
0	2	9	25.0	24.2	1	7	5	67.3	69.0	3	3	12	42.2	41.5	4	8	0	34.4	32.6	6	4	6	45.6	45.8
0	2	10	68.0	68.0	1	7	6	41.7	42.9	3	4	2	17.0	17.4	4	8	2	14.1	12.6	6	4	8	57.4	57.2
0	2	11	25.3	23.5	1	7	8	18.9	19.7	3	5	0	53.0	54.4	4	8	4	30.0	29.3	6	5	1	13.6	13.7
0	2	12	85.6	82.1	1	8	0	12.2	12.0	3	5	1	74.8	76.7	5	0	1	14.2	14.7	6	5	2	15.3	14.5
0	4	1	83.7	83.5	1	9	2	20.0	17.3	3	5	2	100.7	98.0	5	0	9	13.8	12.8	6	5	5	16.6	15.5
0	4	2	88.4	86.5	2	0	6	123.1	120.8	3	5	3	67.2	69.2	5	1	0	106.0	106.3	6	6	0	53.9	52.8
0	4	3	66.4	67.0	2	0	8	133.8	130.6	3	5	4	50.1	51.0	5	1	3	26.2	24.0	6	6	1	57.5	55.6
0	4	5	71.6	74.2	2	0	10	69.1	70.1	3	5	5	65.3	67.4	5	1	6	108.2	112.3	8	6	2	27.6	27.7
0	4	6	72.9	75.4	2	0	12	85.5	83.9	3	5	6	74.5	76.2	5	1	7	21.2	20.7	6	6	4	47.8	47.6
0	4	7	44.7	47.7	2	1	3	22.2	21.4	3	5	7	53.3	53.0	5	1	8	65.9	69.1	6	6	6	24.9	25.4
0	4	8	91.6	93.8	2	1	5	17.8	18.3	3	5	8	41.3	41.9	5	1	10	74.9	77.5	7	0	1	17.1	17.5
0	4	9	50.2	50.7	2	2	1	52.7	53.0	3	5	10	49.6	51.0	5	2	3	15.4	16.0	7	0	3	19.7	20.2
0	4	10	56.3	57.0	2	2	3	40.2	40.8	3	6	0	17.8	18.4	5	2	7	14.4	14.5	7	0	5	14.0	12.7
0	4	12	55.7	56.5	2	2	5	41.9	44.9	3	6	4	13.5	13.6	5	3	0	76.9	77.7	7	1	0	73.4	76.5
0	6	0	83.8	81.6	2	2	6	98.3	97.6	3	7	0	31.1	31.6	5	3	1	49.8	49.4	7	1	2	103.0	105.6
0	6	1	76.5	78.6	2	2	7	28.6	28.1	3	7	1	69.2	70.8	5	3	2	124.0	121.4	7	1	4	67.8	70.5
0	6	2	58.5	59.6	2	2	8	115.6	115.9	3	7	2	45.9	45.2	5	3	3	40.4	39.9	7	1	5	21.2	18.6
0	6	3	81.5	83.0	2	2	9	29.5	29.2	3	7	3	66.8	69.0	5	3	4	70.1	71.7	7	1	6	84.8	86.5
0	6	4	74.8	75.2	2	2	10	72.3	71.5	3	7	4	27.4	27.8	5	3	5	46.3	46.7	7	1	8	55.0	56.2
0	6	5	59.8	61.3	2	2	11	20.5	19.1	3	7	5	59.9	61.0	5	3	6	93.7	95.0	7	2	1	16.9	17.5
0	6	6	42.9	45.6	2	2	12	68.9	68.2	3	7	6	39.8	39.8	5	3	7	29.0	29.1	7	2	3	14.0	13.5
0	6	7	67.9	67.7	2	3	0	12.2	11.3	3	7	8	19.4	19.9	5	3	8	55.8	57.4	7	2	5	17.1	17.6
0	6	8	56.0	59.3	2	3	1	17.2	17.2	4	0	2	104.5	99.7	5	3	10	61.6	64.3	7	3	0	68.0	69.2
0	6	10	29.5	30.4	2	3	3	17.3	18.2	4	0	6	84.5	87.2	5	4	0	16.7	16.7	7	3	1	34.1	32.7
0	8	0	45.7	43.1	2	4	1	73.1	72.6	4	0	8	99.5	104.2	5	4	4	13.1	13.3	7	3	2	81.6	83.2
0	8	1	67.1	70.5	2	4	2	107.6	105.9	4	0	10	65.2	65.4	5	5	0	59.9	59.9	7	3	3	38.1	37.4
0	8	2	19.3	17.8	2	4	3	75.6	76.5	4	0	12	62.2	63.2	5	5	1	59.9	59.2	7	3	4	62.0	62.1
0	8	3	59.5	60.5	2	4	4	120.6	116.3	4	1	0	16.0	17.0	5	5	2	73.5	73.1	7	3	5	26.2	24.2
0	8	4	37.6	38.5	2	4	5	53.8	54.7	4	1	1	26.8	28.5	5	5	3	60.7	60.3	7	3	6	72.3	71.8
0	8	6	16.8	16.6	2	4	6	72.0	75.1	4	1	2	10.0	10.2	5	5	4	52.2	52.8	7	3	8	47.2	46.8
1	0	5	21.1	22.0	2	4	7	58.4	59.3	4	1	3	26.3	27.8	5	5	5	49.2	48.7	7	4	2	12.9	12.9
1	0	7	15.1	16.0	2	4	8	87.9	89.0	4	1	5	20.3	21.0	5	5	6	63.1	63.5	7	4	3	13.0	13.3
1	1	5	20.8	20.2	2	4	9	39.3	38.9	4	1	7	19.4	19.7	5	5	8	38.0	38.3	7	5	0	38.0	37.4
1	1	7	21.8	21.5	2	4	10	48.1	47.7	4	1	9	13.7	14.1	5	6	2	16.8	16.7	7	5	2	67.2	66.9
1	1	8	82.2	82.5	2	6	0	90.5	88.6	4	1	11	13.6	12.7	5	7	0	21.9	20.2	7	5	4	36.9	36.6
1	1	9	15.7	13.2	2	6	1	79.1	79.3	4.	2	1	40.2	38.8	5	7	2	50.1	49.1	8	0	0	81.3	85.3
1	1	10	94.5	94.2	2	6	2	41.5	43.1	4	2	2	119.6	116.1	5	7	4	20.4	20.6	8	0	2	55.5	56.9
1	1	11	13.6	12.8	2	6	3	67.0	67.6	4	2	3	40.3	40.1	6	0	0	111.7	111.9	8	0	4	74.5	76.9
1	1	12	54.0	52.6	2	6	4	75.6	77.4	4	2	4	132.2	126.6	6	0	2	85.6	87.9	8	0	6	48.6	50.1
1	2	3	18.5	16.6	2	6	5	73.4	73.6	4	2	5	30.0	29.7	6	0	4	100.8	103.0	8	1	0	11.9	12.2
1	2	5	17.9	18.3	2	6	6	37.9	39.4	4	2	6	80.5	83.6	6	0	6	65.3	68.7	8	1	1	18.3	18.1
1	2	7	14.0	14.2	2	6	7	50.1	50.9	4	2	7	30.4	30.8	6	0	8	75.0	80.7	8	1	3	18.8	18.5
1	3	1	77.7	76.8	2	6	8	52.5	54.5	4	2	8	92.6	97.0	6	0	10	45.2	46.7	8	1	5	15.1	15.1
1	3	3	65.2	66.9	2	6	10	31.5	31.6	4	2	9	22.0	21.1	6	1	1	23.9	24.2	8	1	7	16.2	15.6
1	3	4	94.5	91.1	2	8	0	36.4	36.0	4	2	10	52.9	53.6	6	1	2	12.2	13.1	8	2	0	71.7	74.0
1	3	5	58.9	61.3	2	8	1	63.1	64.2	4	3	1	22.4	23.3	6	1	3	20.5	21.4	8	2	1	23.7	21.6
1	3	6	123.6	121.2	2	8	2	21.7	19.5	4	3	2	14.8	14.5	6	1	5	21.4	21.6	8	2	2	54.4	55.2
1	3	7	45.5	46.9	2	8	3	67.1	67.8	4	3	3	16.9	17.7	6	1	7	15.2	16.2	8	2	3	23.4	21.2
1	3	8	66.1	66.4	2	8	4	34.6	33.6	4	3	5	21.6	21.4	6	1	9	16.3	15.8	8	2	4	67.5	68.7
1	3	9	41.8	40.7	2	8	6	16.4	15.9	4	3	9	15.3	15.0	6	2	0	115.0	115.2	8	2	6	45.9	45.9
1	3	10	77.5	78.3	3	0	7	16.2	15.5	4	4	1	64.6	64.6	6	2	1	32.8	30.4	8	3	1	15.1	15.8
1	3	11	32.5	30.6	3	1	1	31.1	28.7	4	4	2	63.7	63.3	6	2	2	66.2	67.4	8	3	5	17.0	16.3
1	3	12	44.7	44.0	3	1	3	19.5	16.4	4	4	3	56.5	55.4	6	2	3	29.5	27.2	8	4	0	59.0	60.4
1	4	0	18.7	18.4	3	1	4	112.2	109.6	4	4	4	104.9	104.2	6	2	4	98.7	101.3	8	4	2	37.0	38.5
1	4	4	10.3	10.5	3	1	5	27.7	27.8	4	4	5	58.9	58.5	6	2	5	28.9	27.3	8	4	4	54.2	54.8
1	5	0	63.9	64.1	3	1	7	12.3	10.3	4	4	6	56.2	57.0	6	2	6	57.8	59.9	9	0	1	20.6	20.1
1	5	1	84.5	85.9	3	1	8	76.6	78.4	4	4	7	42.6	41.5	6	2	7	22.3	20.9	9	0	3	18.7	18.6
1	5	2	102.4	98.7	3	1	9	18.8	17.8	4	4	8	71.1	72.4	6	2	8	70.1	72.5	9	1	0	55.8	57.2
1	5	3	80.3	82.2	3	1	10	87.1	88.1	4	4	9	43.7	42.1	6	2	10	45.7	46.4	9	1	2	70.1	71.1
1	5	4	54.8	57.1	3	1	12	53.0	51.6	4	4	10	45.5	44.6	6	3	0	16.2	16.7	9	1	4	52.5	52.6
1	5	5	69.6	70.9	3	2	0	15.9	14.5	4	5	0	13.1	12.8	6	3	1	17.9	18.1	9	2	1	18.3	18.0
1	5	6	77.8	79.4	3	2	5	15.0	15.5	4	5	3	16.9	16.5	6	3	3	20.6	20.8	9	2	3	17.9	18.0
1	5	7	60.6	63.0	3	3	0	111.7	104.5	4	5	7	15.3	14.4	6	3	4	13.5	12.2	8	3	0	43.5	43.1
1	5	8	41.8	42.5	3	3	1	60.1	60.8															

measured ±2° of 2θ off the peak maximum and the average value was subtracted from the maximum value. Those reflections for which the peak maximum was not at least twice as much as the background were regarded as unobserved. This criterion gave a total of 365 observed reflections. The Lorentz, polarization and absorption corrections were applied in order to convert the integrated intensities into structure factors.

Refinements

The refinements of the two structures were carried out with the refinement program of C. T. Prewitt, where the function minimized is $\Sigma w||F_o| - |F_c||^2$. In the case of $NdAlO_3$ each structure factor with $\ell = 2n$ was weighted by $w = 1/\sigma^2$ with $\sigma = 1/5\ F/F_{ox}$, where F is the total structure factor and F_{ox} is the oxygen contribution. The 3 reflections with $\ell =$

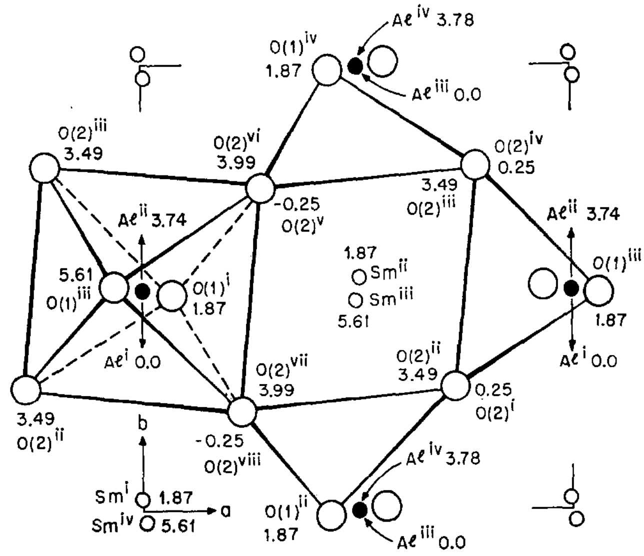

FIG. 1. A projection of the $SmAlO_3$ structure on the *ab* plane. The heights of the atoms are given in Å.

$2n+1$, namely, for which $F = F_{ox}$, were assigned $\sigma = 1.0$. In the case of $SmAlO_3$ for each reflection $\sigma = 2.5$, when $|F| \leqslant 25$, and $\sigma = 0.1\ |F|$, when $|F| > 25$. The atomic scattering tables (for neutral atoms) and real and imaginary anomalous dispersion coefficients were taken from the values reported by Cromer and Waber (*13*) and by Cromer (*14*), respectively. The secondary extinction correction was applied and its coefficient was refined with the positional and thermal parameters. In the case of $SmAlO_3$, 8 reflections for which the correction was greater than 25% of the structure factor value, were assigned zero weight in the refinement. In the case of $NdAlO_3$, one scale factor, the secondary extinction coefficient, one positional, and 3 temperature parameters were refined. Complete convergence was attained after 4 cycles. The final cycle gave $R = 0.016$, $wR = 0.012$, and S (standard deviation of an observation of unit weight) $= 0.68$, resulting in the positional and thermal parameters shown in Table 1. The degree of agreement between observed and calculated structure factors is shown in Table 2, where F_c represents the calculated structure factors per unit cell. In the case of $SmAlO_3$, at first one scale factor, the extinction coefficient, 7 positional parameters, and 4 thermal isotropic parameters were

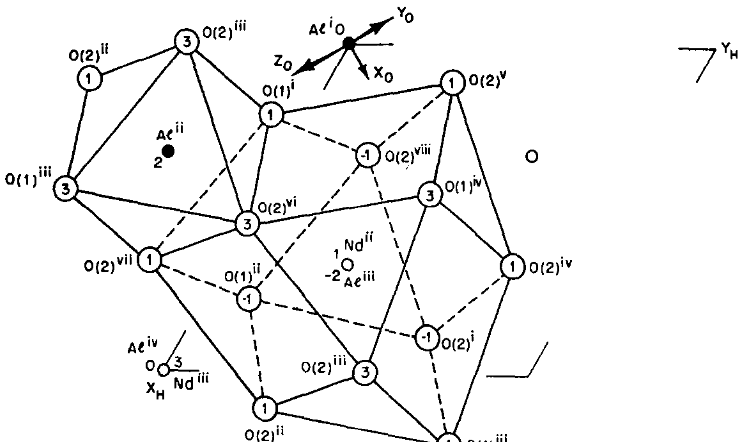

FIG. 2. A projection of the $NdAlO_3$ structure on the hexagonal basal plane. The heights of the atoms are given as the number of twelfths above or below this plane. The pseudo-orthorhombic axes are denoted x_0, y_0, and z_0

refined. The starting values for the positional and thermal parameters were the values found for $SmFeO_3$. After 4 cycles, the anisotropic temperature factors were introduced. The final indices were $R = 0.024$, $wR = 0.037$, and $S = 0.80$. The final positional and thermal parameters are reported in Table 3. A comparison between observed and calculated structure factors is shown in Table 4.

Discussion

$SmAlO_3$ is the last member of the orthorhombic perovskite compounds before they assume a trigonal symmetry. As the distortion of the perovskite arrangement decreases the rare earth approaches the position $00\frac{1}{4}$, the 0(1) approaches $0\frac{1}{2}\frac{1}{4}$ and 0(2) approaches $\frac{1}{4}\frac{1}{4}0$. When these conditions are satisfied and $a_{or} = b_{or} = c_{or}/(2)^{1/2}$, the structure becomes cubic. The two structures are related by the matrix

$$\begin{pmatrix} \vec{a}_c \\ \vec{b}_c \\ \vec{c}_c \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \vec{a}_{or} \\ \vec{b}_{or} \\ \vec{c}_{or} \end{pmatrix}.$$

The atoms do not move from the orthorhombic positions to the cubic ones directly. They move in such a way that the structure first assumes a trigonal symmetry. The orthorhombic to trigonal transformation occurs when the rare earth falls into the $00\frac{1}{4}$ position, the oxygen coordinates are related by

$$0(1)\begin{cases} x = -(\frac{1}{2} + 2\delta), \\ y = 0, \\ z = \frac{1}{4}, \end{cases} \qquad 0(2)\begin{cases} x = \frac{1}{2} - \delta, \\ y = \delta, \\ z = -(\frac{1}{4} + \delta), \end{cases}$$

and the angle between the two directions $[1\bar{1}1]$ and $[11\bar{1}]$ is 120°. The orientation of the trigonal cell with respect to the orthorhombic one is given by the matrix

$$\begin{pmatrix} \vec{a}_{tr} \\ \vec{b}_{tr} \\ \vec{c}_{tr} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ 0 & 2 & 1 \end{pmatrix} \begin{pmatrix} \vec{a}_{or} \\ \vec{b}_{or} \\ \vec{c}_{or} \end{pmatrix}.$$

The trigonal structure becomes cubic when the x coordinate of the oxygen atom and c/a ratio become $\frac{1}{2}$ and $\sqrt{6}$, respectively. The matrix relating the cubic and trigonal structures is

$$\begin{pmatrix} \vec{a}_c \\ \vec{b}_c \\ \vec{c}_c \end{pmatrix} = \begin{pmatrix} \frac{1}{3} & \frac{2}{3} & \frac{1}{6} \\ -\frac{2}{3} & -\frac{1}{3} & \frac{1}{6} \\ \frac{1}{3} & -\frac{1}{3} & \frac{1}{6} \end{pmatrix} \begin{pmatrix} \vec{a}_{tr} \\ \vec{b}_{tr} \\ \vec{c}_{tr} \end{pmatrix}.$$

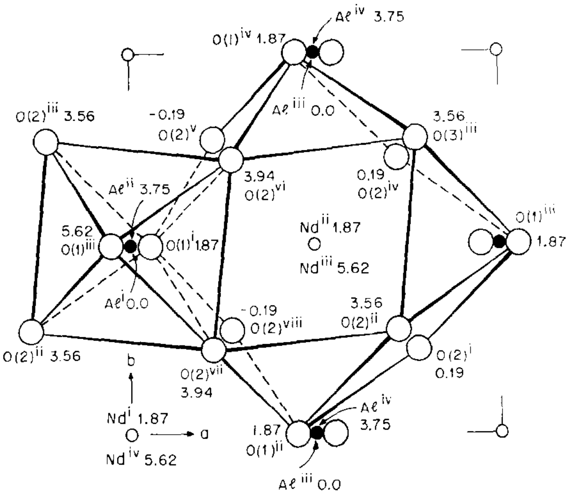

FIG. 3. A projection of a portion of the $NdAlO_3$ structure on the pseudo-orthorhombic *ab* plane. The heights with respect to this plane are given in Å.

Because of the choice of the origin for the orthorhombic cell, a shift of $(0\frac{1}{2}0)$ must be applied to the positional parameters on transforming from the orthorhombic structure to either the trigonal or the cubic one.

Figure 1 represents a projection of the $SmAlO_3$ structure on the *ab* plane. Figure 2 represents a projection of an equivalent portion of the $NdAlO_3$ structure on the hexagonal basal plane. Figure 3 represents a projection of the same portion of the $NdAlO_3$ structure on the pseudo-orthorhombic *ab* plane. Corresponding atoms in the three figures

TABLE 5

AL-OCTAHEDRON

	$NdAlO_3$	$SmAlO_3$
Al^{ii}–O(1)^{i}	1.896(1)	1.900(1)
Al^{ii}–O(2)^{vi}	1.896(1)	1.899(3)
Al^{ii}–O(2)^{vii}	1.896(1)	1.897(3)
O(1)^{i}–O(2)^{vii}	2.703(2)	2.683(6)
O(1)^{i}–O(2)^{vi}	2.659(1)	2.696(6)
O(1)^{i}–O(2)^{ii}	2.703(2)	2.674(5)
O(1)^{i}–O(2)^{iii}	2.659(1)	2.690(4)
O(2)^{vi}–O(2)^{vii}	2.659(1)	2.660(1)
O(2)^{vi}–O(2)^{iii}	2.703(2)	2.708(2)
O(1)^{i}–Al^{ii}–O(2)^{vii}	89.1(1)	89.8(2)
O(1)^{i}–Al^{ii}–O(2)^{vi}	89.9(1)	89.5(2)
O(2)^{vii}–Al^{ii}–O(2)^{vi}	89.1(1)	88.9(1)
Al–O average	1.896	1.899
O–O average	2.681	2.685

TABLE 6

RARE EARTH-POLYHEDRON

	Trigonal		Orthorhombic	
	$NdAlO_3$	$SmAlO_3$	$NdFeO_3$	$SmFeO_3$
$\mathrm{RE^{ii}{-}O(1)^{i}}$	2.387(5)	2.338(6)	2.343	2.310
$\mathrm{RE{-}O(1)^{ii}}$	2.659(1)	2.847(6)	3.244	3.329
$\mathrm{RE{-}O(1)^{iii}}$	2.935(5)	2.965(5)	3.172	3.177
$\mathrm{RE{-}O(1)^{iv}}$	2.659(1)	2.494(6)	4.444	2.391
$\mathrm{RE{-}O(2)^{i}}$	2.659(1)	2.380(4)	2.380	2.342
$\mathrm{RE{-}O(2)^{ii}}$	2.387(5)	2.380(4)	2.380	2.342
$\mathrm{RE{-}O(2)^{iii}}$	2.659(1)	2.545(4)	2.603	2.573
$\mathrm{RE{-}O(2)^{iv}}$	2.387(5)	2.545(4)	2.603	2.573
$\mathrm{RE{-}O(2)^{v}}$	2.935(5)	2.657(4)	2.730	2.706
$\mathrm{RE{-}O(2)^{vi}}$	2.659(1)	2.657(4)	2.730	2.706
$\mathrm{RE{-}O(2)^{vii}}$	2.935(5)	3.041(4)	3.424	3.487
$\mathrm{RE{-}O(2)^{viii}}$	2.659(1)	3.041(4)	3.424	3.487
Average	2.660	2.658	2.790	2.785
$\mathrm{O(1)^{i}{-}RE^{ii}{-}O(1)^{iv}}$	84.1(1)	85.9(2)		
$\mathrm{O(1)^{iv}{-}RE^{ii}{-}O(1)^{iii}}$	95.9(1)	101.9(2)		
$\mathrm{O(1)^{iii}{-}RE^{ii}{-}O(1)^{ii}}$	95.9(1)	94.0(2)		
$\mathrm{O(1)^{ii}{-}RE^{ii}{-}O(1)^{i}}$	84.1(1)	78.2(2)		
$\mathrm{O(2)^{v}{-}RE^{ii}{-}O(2)^{vi}}$	95.9(1)	105.8(2)		
$\mathrm{O(2)^{i}{-}RE^{ii}{-}O(2)^{ii}}$	84.1(1)	85.7(2)		
$\mathrm{O(2)^{i}{-}RE^{ii}{-}O(2)^{v}}$	95.9(1)	84.0(1)		
$\mathrm{O(2)^{vii}{-}RE^{ii}{-}O(2)^{viii}}$	95.9(1)	96.3(1)		
$\mathrm{O(2)^{iii}{-}RE^{ii}{-}O(2)^{iv}}$	84.1(1)	88.3(1)		
$\mathrm{O(2)^{iii}{-}RE^{ii}{-}O(2)^{vii}}$	95.9(1)	79.0(2)		
$\mathrm{O(2)^{vi}{-}RE^{ii}{-}O(2)^{vii}}$	56.5(1)	55.2(1)		
$\mathrm{O(2)^{vii}{-}RE^{ii}{-}O(2)^{ii}}$	60.0(1)	58.4(1)		
$\mathrm{O(2)^{ii}{-}RE^{ii}{-}O(2)^{iii}}$	63.3(1)	65.3(1)		
$\mathrm{O(2)^{iii}{-}RE^{ii}{-}O(2)^{vi}}$	61.1(1)	62.7(1)		
$\mathrm{O(1)^{i}{-}RE^{ii}{-}O(2)^{vii}}$	60.0(1)	58.1(1)		
$\mathrm{O(2)^{vii}{-}RE^{ii}{-}O(1)^{ii}}$	56.5(1)	54.4(1)		
$\mathrm{O(1)^{ii}{-}RE^{ii}{-}O(2)^{ii}}$	63.3(1)	61.2(1)		
$\mathrm{O(2)^{ii}{-}RE^{ii}{-}O(1)^{iii}}$	60.0(1)	58.8(1)		
$\mathrm{O(1)^{iii}{-}RE^{ii}{-}O(2)^{iii}}$	56.5(1)	57.8(1)		
$\mathrm{O(2)^{iii}{-}RE^{ii}{-}O(1)^{iv}}$	61.1(1)	64.1(1)		
$\mathrm{O(1)^{iv}{-}RE^{ii}{-}O(2)^{vi}}$	61.1(1)	62.7(1)		
$\mathrm{O(2)^{vi}{-}RE^{ii}{-}O(1)^{i}}$	63.3(3)	65.0(1)		

have been given identical superscripts. One can observe that a significant shift in the positional parameters is required to transform from the orthorhombic to the trigonal structure and from the trigonal to the cubic structure.

The interatomic distances and angles and their standard deviations are given in Tables 5, 6 and 7. In the trigonal $NdAlO_3$, the aluminum atoms are surrounded by 6 equidistant oxygen atoms forming a trigonally distorted octahedron. There are therefore two types of O–O distances, one at 2.659 Å and the other at 2.703 Å. The Al–O distance is 1.896 Å. The neodymium atoms are surrounded by 12 oxygen atoms of which 3 are at 2.387, 6 at 2.659 Å, and 3 at 2.935 Å, the average being 2.660 Å. These values indicate that it would be a good approximation to assume that the neodymium atoms are 12-coordinated as in the undistorted cubic perovskite. Assuming a value of 1.40 Å for a 6-coordinated O^{2-} (*15*), one can deduce an ionic radius of 1.26Å for 12-coordinated Nd^{3+}. In Table 6 the Nd–O distances in $NdFeO_3$, which has the orthorhombic arrangement of the perovskite structure, are shown for comparison. Their average is 2.790 Å. This larger value indicates that some of the oxygen atoms are not first nearest neighbors.

TABLE 7

DISTANCES AND ANGLES BETWEEN POLYHEDRA

	$NdAlO_3$	$SmAlO_3$
RE^{ii}–Al^{i}	3.256	3.263
RE^{ii}–Al^{iv}	3.229	3.343
RE^{ii}–Al^{iii}	3.229	3.136
RE^{ii}–Al^{ii}	3.256	3.220
Al^{ii}–$\mathrm{O(1)}^{i}$–Al^{i}	163.4(1)	159.1(3)
Al^{ii}–$\mathrm{O(2)}^{vii}$–Al^{iv}	163.4(1)	160.5(3)
Al^{ii}–$\mathrm{O(1)}^{i}$–RE^{i}	89.6(1)	90.0(1)
Al^{ii}–$\mathrm{O(1)}^{i}$–RE^{ii}	98.3(1)	100.2(1)
Al^{iv}–$\mathrm{O(2)}^{vi}$–RE^{ii}	88.7(1)	85.3(1)
Al^{ii}–$\mathrm{O(2)}^{vi}$–RE^{ii}	89.6(1)	90.0(1)
Al^{iv}–$\mathrm{O(2)}^{iii}$–RE^{ii}	88.7(1)	88.6(1)
Al^{ii}–$\mathrm{O(2)}^{iii}$–RE^{ii}	89.6(1)	91.7(1)
Al^{iv}–$\mathrm{O(2)}^{vii}$–RE^{iv}	98.3(1)	97.1(2)
Al^{iv}–$\mathrm{O(2)}^{ii}$–RE^{ii}	98.3(1)	102.2(2)

In the orthorhombic $SmAlO_3$, the distortion of the aluminum octahedron is slightly less than that of the aluminum octahedron in trigonal $NdAlO_3$. The six Al–O distances differ within one standard deviation and the 12 O–O distances vary from 2.660 to 2.708 Å. The average Al–O distance is 1.899 Å. On the other hand, the 12-oxygen polyhedron around the samarium atoms is much more distorted than the polyhedron around the Nd atoms in $NdAlO_3$. The Sm–O distances range continuously from 2.338 to 3.041 Å, the average being 2.658 Å. This value is essentially the same as the average Nd–O distance in $NdAlO_3$ (2.660 Å). If the coordination number of the rare earth atoms were the same in both compounds, one would expect an average Sm–O distance about 1% smaller than the average Nd–O distance. Therefore the coordination number of the Sm atoms in $SmAlO_3$ must be somewhat smaller than 12.

It is of interest to compare the structure of $SmAlO_3$ with that of $SmFeO_3$. The Sm–O distances in this latter compound are reported in Table 6. The average Sm–O distance in $SmFeO_3$ is 2.785 Å, which is 15% larger than the value found in $SmAlO_3$. On going from the orthoferrite to the orthoaluminate, the four shortest Sm–O distances increase, while the remaining eight decrease. It is because of this unusual variation of the individual distances that the Sm atoms have different coordination number, 8 in $SmFeO_3$ and ~12 in $SmAlO_3$. These results seem to indicate that $SmAlO_3$ and $SmFeO_3$ should not be considered truly isostructural compounds.

If one defines an index of distortion of the iron or aluminum octahedron as the standard deviation calculated from the average of the 12 O–O distances, this index decreases from 1.2×10^{-3} for $LuFeO_3$ to 0.55×10^{-3} for $LaFeO_3$ (*16*, *17*). The values for $SmAlO_3$ and $NdAlO_3$ are 0.40×10^{-3} and 0.58×10^{-3}, respectively. The relatively small variation of this parameter indicates that both iron and aluminum octahedra are insensitive to the distortion of the overall structure. Furthermore, since this parameter is small even for $LuFeO_3$, both the iron and aluminum octahedra behave as nearly rigid entities. Contrary to this, the rare earth polyhedra absorb the majority of the distortion of the structure. Because of the rigidity of the B-ion octahedra, solid solutions $RE(Fe_{1-x}Al_x)O_3$ are difficult to synthesize.

It is interesting to note that the index of distortion of the aluminum octahedron defined above is a smaller value for $SmAlO_3$ as compared to $NdAlO_3$. One would expect the contrary since the $NdAlO_3$ structure is less distorted than that of $SmAlO_3$. By defining an index of distortion for the rare earth polyhedron as the standard deviation calculated from the average of the 12 Re–O distances, one obtains a value of 0.64×10^{-2} for $SmAlO_3$ and 0.51×10^{-2} for $NdAlO_3$. Because of the small decrease in the distortion of the rare earth and the change in symmetry, the aluminum octahedron in $NdAlO_3$ is forced to assume a slightly more distorted configuration. It is quite likely that both indices of distortion will decrease on proceeding to the remaining trigonal members of the orthoaluminate series.

The high coordination of the rare earth atoms in the orthoaluminates explains why it is difficult to synthesize the smaller rare earth orthoaluminates. In oxide compounds at normal pressure, the smaller rare earth atoms usually have coordination number 8. Since in the orthoaluminates their coordination should be somewhat larger, these compounds are difficult to synthesize at normal pressure. Therefore their synthesis should be done under pressure, where one would probably avoid the formation of the garnet phase.

We conclude that one should not attempt to derive ionic radii of the rare earth ions from the orthorhombic perovskite-like compounds. Our studies (*16*, *17*) indicate that a continuous change of the coordination number occurs across the series leading to erroneous values.

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