ceptibility suggests that the band is narrow and has a high density of states. Further grounds for choosing between Mo–Mo and Mo–O–Mo* orbitals might come from a study of mobility values. However, to be meaningful, mobility values would need to be determined on single-crystal specimens.

Another parameter that would be valuable for defining the electronic states in the molybdenum bronzes is the electronic heat capacity and its implied information about density of states. $BaMoO_3$, with $d\chi/dT$ equal to zero, appears to represent a metal in which the two opposing effects contributing to $d\chi/dT$ just cancel each other out. These two effects are (I) variation with temperature of the width of the Fermi distribution and (II) variation with temperature of the Fermi energy itself. As remarked by Kriessman and Callen,[15] the alternation of sign(+, −, +, −, +) observed for $d\chi/dT$ in the sequence Ti, V, Cr, Mn, (Ru) matches the oscillation of magnetic susceptibility and electronic specific heat in these elements, presumably because of the sequence of maxima and minima in the density-of-states curve. At low temperatures, contribution (II) to $d\chi/dT$ is always negative, so contribution (I) must be positive for $BaMoO_3$. This would be the case if the Fermi energy in $BaMoO_3$ lies near a minimum in the density-of-states curve, as is true for titanium and presumably also for zirconium. Compared to metals in general, then, $BaMoO_3$ should show a moderately high electronic specific heat. Also if $BaMoO_3$ corresponds to electron-filling at a minimum in the density-of-states curve, a reduction in carrier density would move the Fermi level to higher density of states, thereby leading to a larger electronic specific heat and a larger magnetic susceptibility. These predictions might be open to experimental verification by systematic study of Brixner's series $SrMo_xZr_{1-x}O_3$ and $SrMo_xTi_{1-x}O_3$.[16] Both the conductivity and the Seebeck effect of these materials change so as to suggest that substitution of Zr or Ti for Mo reduces carrier density. Systematic substitution of Zr (or Ti) for Mo and study of the magnetic suceptibility and specific heat as a function of temperature would provide valuable data for defining a density-of-states curve.

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High-Pressure $NaAlO_2$, an α-$NaFeO_2$ Isotype

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Received July 28, 1967

The β form of sodium aluminate has been transformed at 110 kbars and 900° to a new high-pressure form isostructural with rhombohedral α-$NaFeO_2$. The increase in density from 2.74 to 3.61 g cm^{-1} corresponds to a change from tetrahedral to octahedral coordination for all atoms in the structure. The new phase has three molecules in a hexagonal unit cell with dimensions $a = 2.868 \pm 0.005$ Å and $c = 15.88 \pm 0.01$ Å. The space group is R3m, with sodium atoms in positions 3(a), aluminum atoms in 3(b), and oxygen atoms in 6(c) with atomic coordinates (0, 0, 0.228). Aluminum–oxygen distances are 1.92 ± 0.05 Å, and sodium–oxygen distances are 2.35 ± 0.05 Å. The present study confirms that this new form of sodium aluminate together with jadeite, $NaAlSi_2O_6$, are the products of dissociation of nepheline, $NaAlSiO_4$, at pressures in the region 100 to 200 kbars.

Polymorphic transformations of minerals are believed to be responsible for density increases in the upper mantle of the earth at depths of some several hundred kilometers.[1] We have recently shown[2] that synthetic potassium feldspar (sanidine), $KAlSi_3O_8$, transforms at 900° and 120 kbars to the dense hollandite structure, with randomly distributed six-coordinated aluminium and silicon. Various investigations have shown[3] that high pressures favor denser phases containing octahedral rather than tetrahedral aluminum. A recent example[4] is the transformation at high pressure of $NaAlGeO_4$, a low density analog of $NaAlSiO_4$ (nepheline), to the much denser calcium ferrite structure[5] with Al^{3+} and Ge^{4+} randomly distributed in octahedral positions.[4] $NaAlSiO_4$ should itself ultimately transform to the calcium ferrite structure, but at pressures as high as 250 kbars it was found[6] to disproportionate to jadeite and a new phase according to the proposed reaction

$$\underset{\text{(nepheline)}}{2NaAlSiO_4} \xrightarrow[250\ \text{kbars}]{900^\circ} \underset{\text{(jadeite)}}{NaAlSi_2O_6} + \underset{\text{(high-pressure form)}}{NaAlO_2}$$

The iron compound behaved similarly and gave $NaFeSi_2O_6$ (acmite, isomorphous with jadeite) plus a phase assumed to be $NaFeO_2$.

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TABLE I

HEXAGONAL LATTICE PARAMETERS[a] FOR HIGH-PRESSURE $NaAlO_2$, α-$NaFeO_2$, AND HIGH-PRESSURE $LiGaO_2$, SPACE GROUP $R\bar{3}m$, $Z = 3$

	a, Å	c, Å	Vol per formula unit, Å^3	
			α form	β form
α-$NaAlO_2$ (high pressure)[b]	2.868 ± 0.005	15.88 ± 0.01	37.7	49.6
α-$NaFeO_2$ (low temperature)[10,11]	3.019	15.934	42.2	54.4
α-$LiGaO_2$ (high pressure)[14]	2.9113 ± 0.003	14.466 ± 0.001	35.3	43.1

[a] Parameters obtained at 1 atm pressure. [b] This work.

TABLE II

POWDER DIFFRACTION DATA[a] FOR HIGH-PRESSURE $NaAlO_2$

h	k	l	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}	h	k	l	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}
0	0	3	5.290	5.293	20	18	0	2	4	1.185	1.185	10	9
0	0	6	2.645	2.647	15	7	2	0	5	...	1.157	0	0
1	0	1	...	2.454	0	0	1	1	9	...	1.113	0	0
0	1	2	2.370	2.371	10	6	1	0	13	...	1.096	0	0
1	0	4	2.103	2.106	100	95	0	2	7	...	1.090	0	1
0	1	5	1.955	1.957	4	2	0	0	15	...	1.059	0	1
0	0	9	1.762	1.764	2	1	2	0	8	1.053	1.053	2	4
1	0	7	1.674	1.675	5	5	0	1	14	1.032	1.032	4	3
0	1	8	1.550	1.551	20	19	0	2	10	0.9786	0.9784	1	2
1	1	0	1.432	1.434	20	48	1	1	12	0.9728	0.9727	4	4
1	1	3	1.385	1.385	1	2	2	0	11	0.9416	0.9416	1	1
1	0	10	1.338	1.338	5	5	2	1	1	...	0.9374	0	0
0	0	12	1.323	1.323	4	2	1	2	2	0.9317	0.9326	1	1
1	1	6	1.260	1.261	5	5	1	0	16	0.9218	0.9217	1	1
0	1	11	1.247	1.248	2	2	2	1	4	0.9133	0.9139	5	9
0	2	1	...	1.238	0	0	1	2	5	...	0.9005	0	0
2	0	2	1.225	1.227	1	1	0	0	18	0.8827	0.8822	2	1

[a] Taken at 1 atm pressure.

In a separate study we have now found that β-$NaAlO_2$, isostructural with β-$NaFeO_2$[7,8] and β-$LiGaO_2$,[9] when subjected to a pressure of 110 kbars at 900°, transforms from a distorted wurtzite structure with both metals in tetrahedral positions to the rhombohedral α-$NaFeO_2$ type[10,11] where they are octahedral. The calculated density increased from 2.74 to 3.61 g cm^{-1}.

In the powder pattern of the products from the reaction of $NaAlSiO_4$, the lines additional to those of jadeite[6] were identifiable as the strongest lines of the new high-pressure form of $NaAlO_2$, confirming that the given equation is correct. Similarly the strongest lines of α-$NaFeO_2$ could be recognized among those from the products of reaction of $NaFeSiO_4$.

Experimental Section

Low-pressure $NaAlO_2$ was prepared by heating a finely ground stoichiometric mixture of sodium oxalate and aluminum oxide at 1000° for 15 hr, after a preliminary heat at 600°. The transformation to the high-pressure phase was effected in a modified Bridgman anvil apparatus fitted with an internal heater.[12] A few milligrams of $NaAlO_2$, slightly moistened with water to promote reaction, was heated at 900° and about 110 kbars for approximately 3 min, and the samples were then cooled under pressure.

Powder diffraction data were obtained with a 114-mm Debye–Scherrer camera, using nickel-filtered Cu Kα radiation. Line separations were measured for both front and back angle reflections, and a small film shrinkage error was applied. After the powder pattern was indexed, lattice parameters (Table I) were obtained by use of a least-squares fitting program. An intensity series was obtained from multiple-film exposures by visual comparison with a calibrated scale, and strongest and weakest reflections were related by normalization to reflections of intermediate intensity.

The observed reflection condition for the hexagonal indices given in Table I, namely, $-h + k + l = 3n$, corresponded among others to the space group $D_{3d}{}^5$ ($R\bar{3}m$), and suggested that high-pressure $NaAlO_2$ was isostructural with α-$NaFeO_2$[10,11] and consequently one of the large series of $CsICl_2$ isotypes.[11] Sodium was therefore placed in position 3(a) of $R\bar{3}m$, with atomic coordinates 0, 0, 0; Al was placed in 3(b), 0, 0, $^1/_2$, and O was placed in 6(c) at $\pm(0, 0, u)$. Calculations with arbitrary values of u near 0.25 showed that structure factors were sensitive to the value of this parameter, and that, despite the limited number of reflections, refinement was possible. The powder intensities were therefore converted to structure factors by application of Lorentz polarization and multiplicity corrections. During least-squares structure factor refinement, temperature factors B for all atoms were fixed at 1 Å^2. A final R factor $100\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ of 22.7% was obtained for $u = 0.228 \pm 0.004$. Calculated structure factors were then converted to intensities, which when normalized to those observed gave an R factor $100\Sigma(I_o - I_c)/\Sigma I_o$ of 27%, Table II.

Scattering curves for Na^+ and Al^{3+} were taken from the "International Tables for X-ray Crystallography,"[13] and those for O^{2-} from Suzuki.[14] Structure factor calculations were based on the programs of Daly, Stephens, and Wheatley.[15]

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Results and Discussion

The powder diffraction data for high-pressure $NaAlO_2$ are given in Table II. The satisfactory agreement between observed and calculated intensities shows that the compound does indeed have the same structure as α-$NaFeO_2$.[10,11] This is a rhombohedral distortion of the NaCl structure type in which sodium ions and trivalent ions are ordered out into layers normal to the hexagonal c axis. The oxygen layers on either side of the metal layers allow octahedral coordination for each metal ion with all bond lengths equal. Viewed in the (110) projection, Figure 1, the structure is seen effectively to consist of infinite sheets of edge-shared aluminum–oxygen octahedra separated by layers of sodium atoms. The coordinate u gives the location of the oxygen planes up the hexagonal c axis, and for $u = {}^1/_4$, these planes would lie midway between those of sodium and aluminum. The refined value of u, 0.228 ± 0.004, shows the oxygen planes in fact to be closer to those of aluminum. The resulting Al–O octahedral distance of 1.92 ± 0.05 Å is close to that in $MgAl_2O_4$, 1.928 Å,[16] and to the average distance in Al_2O_3, 1.915 Å.[17] The octahedral Na–O distance of 2.35 ± 0.05 Å lies in the range usually found.[18]

Hexagonal lattice parameters for high-pressure $NaAlO_2$ are given in Table I, together with those for α-$NaFeO_2$ and high-pressure $LiGaO_2$, which has the same structure.[19] It is proposed, with Marezio and Remeika,[19] that the high-pressure forms should be denoted by α, as is their α-$NaFeO_2$ isotype. In the $NaFeO_2$ system the transformation of α-$NaFeO_2$ to the low-density β-$NaFeO_2$ form occurs[20] irreversibly at 750° at zero pressure, but it is evident from the formation of α-$NaFeO_2$ at 100 kbars and 900° as a consequence of $NaFeSiO_4$ disproportionation that the α form can be retained under pressure.

In the isomorphous series of orthorhombic compounds[7–9] β-$NaAlO_2$, β-$NaFeO_2$, and β-$LiGaO_2$, distortions from the hexagonal wurtzite structure are occasioned by the need to fit two kinds of metal atoms into the structure instead of one. Similarly the denser rhombohedral forms are a distortion along a trigonal axis of the sodium chloride structure,[11] and it is interesting that the undistorted wurtzite form of zinc oxide (zincite) transforms to undistorted NaCl type at 100 kbars.[21]

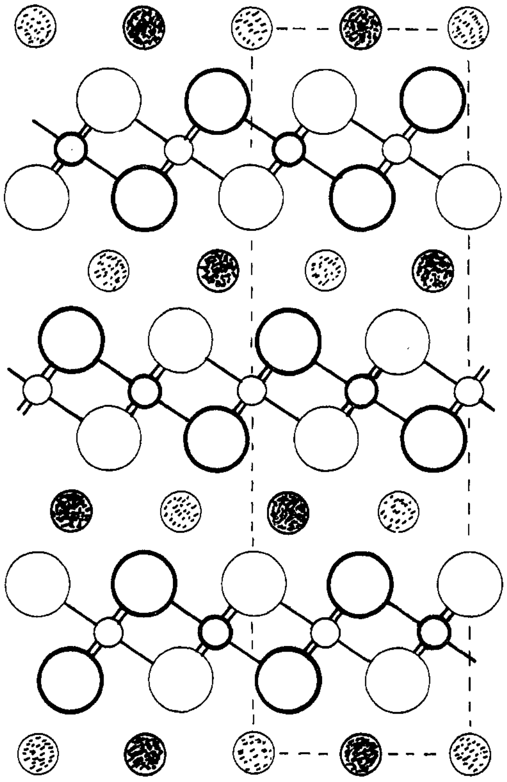

Figure 1.—Crystal structure of high-pressure $NaAlO_2$ projected on (110). Hexagonal c axis is vertical, horizontal repeat distance is $a_H\sqrt{3}$: Oxygen atoms, large circles; aluminum atoms, small circles; sodium atoms, shaded. Atoms represented with heavy outlines lie in a plane parallel to the page separated by a_H (2.868 Å) from those represented with light outlines.

At very high pressures ABO_2 compounds could generally be expected to adopt the 6:6 coordination of the distorted sodium chloride type, and Rooymans[22] has indeed mentioned this possibility for $NaAlO_2$ itself. Kordes and Petzoldt[23] in a study of the MgO–$LiCrO_2$ solid solution system have shown that rhombohedral $LiCrO_2$, which is isomorphous with α-$NaFeO_2$, can accommodate MgO up to the composition $2(MgO)_2 \cdot 3LiCrO_2$ and that above this ratio $LiCrO_2$ is accommodated in the cubic NaCl type MgO structure. In addition to an expected solid solution with α-$NaFeO_2$, it is therefore likely that at high pressures α-$NaAlO_2$ will show solid solution with any sodium chloride structure containing ions of a comparable size, and in particular with the geochemically important phases MgO, CaO, FeO, or ZnO.

Acknowledgments.—The authors are indebted to Dr. W. G. Mumme and to Dr. A. D. Wadsley for helpful discussions.

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