

Crystal structure and isothermal compression of Fe_2O_3 , Cr_2O_3 , and V_2O_3 to 50 kbars

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Crystal structure and isothermal compression of Fe_2O_3 , Cr_2O_3 , and V_2O_3 to 50 kbars

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Crystal structures of several of the corundum-type oxides have been determined at pressures to 50 kbars. All materials have linear compression within the pressure range and precision of the techniques used. Compression of Cr_2O_3 and Al_2O_3 is essentially isotropic (c/a remains constant), Fe_2O_3 has a slightly anisotropic compression, with c/a decreasing slightly with pressure, and V_2O_3 is very anisotropic, with the a axis nearly three times more compressible than c . Similar differences are observed in the structural parameters. Aluminum, iron, and chromium sesquioxides simply scale, whereas atomic positions in V_2O_3 approach an ideal HCP arrangement with increasing pressure. The differences in structural variation with pressure for these "isostructural" compounds emphasize the difficulty in using simple bonding parameters to predict details of crystal structures under nonambient conditions.

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I. INTRODUCTION

Corundum-type oxides have been extensively investigated because of their importance in mineralogical and other solid-state systems. The high-pressure behavior of these materials is of special interest because of the widespread use of ruby as an internal pressure standard.¹ Static compression measurements of corundum-type compounds $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , and V_2O_3 by Sato and Akimoto² demonstrated that significant differences exist in the magnitudes and ratios of axial compression in these isostructural rhombohedral compounds. The present study is a report of high-pressure crystal structures and compression of $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , and V_2O_3 , determined with a modified diamond-anvil cell of Merrill and Bassett.³ Combined with previously reported high-pressure structure information on ruby,⁴ these data may be used to compare bond compression and polyhedral distortion in these several corundum isomorphs.

II. EXPERIMENTAL

Synthetic single crystals of hematite, $\alpha\text{-Fe}_2\text{O}_3$, were obtained from the sample used by Blake *et al.*⁵ that was synthesized by G. P. Espinosa of North American Rockwell Corporation. Single crystals of synthetic karelianite (V_2O_3) and eskolaite (Cr_2O_3) were kindly provided by John White, Smithsonian Institution (National Museum of Natural History Nos. 137007 and 739S, respectively).

Room-pressure data collections on the three transition-metal sesquioxides were performed on equant crystals, approximately 80 μm in diameter. The intensities of all reflections in one quadrant ($h \geq 0$ and $l \geq 0$) and $\sin \theta / \lambda < 0.7$ were measured with a four-circle diffractometer system,⁶ and lattice parameters were refined from the diffractometer angles of at least 12 centered reflections. Intensities were measured by a constant-precision procedure in which the background counting time and scan rate were dynamically adjusted such that the ratio of the intensity to the standard deviation calculated from counting statistics was of the order of 100.

Data were collected at high pressure on crystals approximately $100 \times 100 \times 30 \mu\text{m}$, mounted in opposed-anvil diamond cells of the type designed by Merrill and Bassett³ and modified by Hazen and Finger⁷ and Finger and King.⁸ Metal gaskets of Inconel 750X (International Nickel Co.), approximately 250 μm thick with 300- μm -diam holes, were used. Ruby crystals of 10- μm maximum dimension were included in the mount to serve as an internal pressure standard. Pressure was determined from the shift of the R_1 fluorescence line,¹ with a wavelength shift of 27.5 kbars/nm. The estimated precision of the pressure determination is approximately 0.5 kbars. Distance from the single crystals to the gasket wall was large enough to prevent shielding of x rays by the gasket. A 4:1 volume mixture of methanol:ethanol was used as the pressure-transmitting fluid in all experiments because this liquid retains low viscosity up to pressure above 100 kbars.⁹ The crystals were "cemented" to the face of one diamond anvil with a thin smear of the alcohol insoluble fraction of petroleum jelly.

Lattice constants of crystals at high pressure were determined from 12 to 20 reflections, corrected for errors in crystal centering and diffractometer alignment by the method of Hamilton,¹⁰ as modified by King and Finger.¹¹ The apparent position of the diffracted radiation for each reflection is measured in eight different settings, four at positive 2θ and four at negative 2θ . Significant shear stress leads to lattice strain and deviations from expected dimensionality,⁴ therefore, each set of data was refined without constraint, and the resulting "triclinic" cell was checked for agreement with the rhombohedral symmetry of corundum-type materials ($a = b$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$). These conditions are satisfied within two estimated standard deviations for all compounds at all pressures studied (Table I), and it is assumed, therefore, that conditions were hydrostatic.

High-pressure intensity data were collected for all accessible reflections with $\sin \theta / \lambda < 0.7$ using Nb-filtered MoK_α radiation and the constant precision intensity tech-

TABLE I. Unit-cell parameters refined without constraint and c/a ratios for R_2O_3 structures.

| | Pressure (kbars) | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | V (Å ³) | c/a |
|--------------------------------|---------------------|------------------------|-----------|-------------|--------------|-------------|--------------|-----------------------|-------|
| Fe ₂ O ₃ | 0.001 | 5.0347(4) ^a | 5.0344(5) | 13.7473(15) | 90.002(8) | 90.004(8) | 120.001(5) | 301.76(5) | 2.731 |
| | 15.4(5) | 5.0248(4) | 5.0251(5) | 13.7163(9) | 90.001(7) | 89.995(6) | 119.993(5) | 300.02(4) | 2.729 |
| | 31.4(5) | 5.0142(6) | 5.0144(8) | 13.6733(14) | 90.001(10) | 90.000(9) | 120.001(8) | 297.73(6) | 2.727 |
| | 41.6(5) | 5.0079(3) | 5.0081(4) | 13.6467(9) | 89.999(8) | 90.003(5) | 120.003(4) | 296.40(3) | 2.725 |
| | 43.9(5) | 5.0065(3) | 5.0068(5) | 13.6411(4) | 90.008(6) | 89.995(4) | 120.002(5) | 296.12(4) | 2.725 |
| Cr ₂ O ₃ | 52.4(5) | 5.0016(4) | 5.0024(9) | 13.6202(6) | 89.99(1) | 89.998(6) | 120.01(6) | 295.09(6) | 2.723 |
| | 0.001 | 4.9507(4) | 4.9514(4) | 13.5656(7) | 89.997(6) | 90.004(6) | 120.000(4) | 287.98(3) | 2.740 |
| | 18.6(5) | 4.9372(4) | 4.9370(3) | 13.530(1) | 90.004(6) | 90.007(8) | 119.999(5) | 285.62(4) | 2.740 |
| | 40.6(5) | 4.9230(4) | 4.9235(3) | 13.4953(8) | 90.009(5) | 89.990(6) | 119.991(4) | 283.31(3) | 2.741 |
| | 56.8(5) | 4.9128(2) | 4.9128(2) | 13.4689(6) | 90.005(3) | 89.997(4) | 120.002(2) | 281.52(2) | 2.742 |
| V ₂ O ₃ | 0.001 | 4.9519(3) | 4.9523(3) | 14.0024(8) | 89.998(5) | 90.003(5) | 120.005(3) | 297.36(3) | 2.828 |
| | 18.3(5) | 4.9322(3) | 4.9323(3) | 13.991(1) | 90.010(7) | 89.995(8) | 120.002(3) | 294.75(3) | 2.837 |
| | 28.3(5) | 4.9199(3) | 4.9198(3) | 13.9787(8) | 89.998(6) | 90.004(6) | 119.998(4) | 293.03(3) | 2.841 |
| | 47(1) | 4.9018(2) | 4.9019(2) | 13.969(4) | 90.000(10) | 89.996(9) | 120.001(3) | 290.67(9) | 2.850 |

^aParenthesized figures represent esd 's of least units cited.

nique described above. Two operational procedures unique to high-pressure intensity experiments, described in detail by Finger and King,⁸ were employed. The fixed- ϕ mode of data collection was used to maximize reflection accessibility and minimize attenuation by the diamond cell, and a correction was made for x-ray absorption by the diamond and beryllium components of the pressure cell, as described by Finger and Hazen.⁴

All intensity data were corrected for absorption by the crystal, and a parameter required for secondary extinction calculations¹² was computed. For each data set the average structure factor was calculated for reflections related by symmetry. No systematic deviations from the ideal symmetry or violations of the R -centered lattice were observed.

Least-squares refinement of the structural parameters was performed using program RFINE¹³ with neutral scatter-

ing factors from Cromer and Mann¹⁴ and the anomalous scattering coefficients of Cromer and Liberman.¹⁵ Each data set was converged with isotropic temperature factors and an isotropic correction for secondary extinction. The temperature factors for Fe₂O₃ and Cr₂O₃ were converted to anisotropic form, but vibrations were essentially isotropic. Refinement conditions and refined parameters are given in Table II.

Previous studies of the crystal structures of these materials include α -Fe₂O₃ by Blake *et al.*,^{5,16} Cr₂O₃ by Newnham and de Haan,¹⁷ and V₂O₃ by Newnham and de Haan,¹⁷ Derrier,¹⁸ and Robinson.¹⁹ The present study agrees with the results of Blake *et al.*,⁵ who used the same synthetic hematite although the experimental procedures were different. Data of Newnham and de Haan¹⁷ for Cr₂O₃ and this study are also in agreement.

TABLE II. Refinement conditions and refined parameters for R_2O_3 structures.

| | μ_t (cm ⁻¹) | Pressure (kbar) | Crystal No. | Weighted R (%) ^a | R (%) ^b | Number of obs. | Z_M | X_0 | B_M (Å ²) | B_0 (Å) | $r^* \times 10^{-5}$ ^c |
|--------------------------------|-----------------------------|--------------------|----------------|----------------------------------|----------------------|-------------------|-------------|------------|-------------------------|-----------|-----------------------------------|
| Fe ₂ O ₃ | 140.7 | 0.001 | 1 | 2.6 | 1.9 | 93 | 0.35534(6) | 0.3056(9) | 0.32(3) | 0.40(7) | 4.2(3) |
| | | 15.4(5) | 2 | 2.0 | 2.5 | 47 | 0.35539(11) | 0.3065(14) | 0.37(5) | 0.48(12) | 3.0(4) |
| | | 31.4(5) | 2 | 2.4 | 3.7 | 50 | 0.35517(12) | 0.3051(14) | 0.56(6) | 0.51(12) | 6.1(8) |
| | | 41.6(5) | 2 | 2.6 | 5.1 | 47 | 0.3551(2) | 0.304(2) | 0.58(8) | 0.8(2) | 6.2(10) |
| | | 43.9(5) | 3 | 1.8 | 4.2 | 65 | 0.3554(1) | 0.3043(20) | 0.30(6) | 0.51(17) | 7.5(9) |
| Cr ₂ O ₃ | 107.1 | 52.4(5) | 3 | 3.1 | 4.4 | 60 | 0.3552(2) | 0.3108(26) | 0.46(8) | 0.22(22) | 2.4(6) |
| | | 0.001 | 1 | 2.0 | 2.2 | 147 | 0.34766(3) | 0.3051(4) | 0.25(1) | 0.28(3) | 1.96(11) |
| | | 18.6(5) | 1 | 2.8 | 4.4 | 82 | 0.3475(2) | 0.3059(18) | 0.53(6) | 0.41(12) | 3.6(4) |
| | | 40.6(5) | 1 | 3.1 | 4.1 | 66 | 0.3477(2) | 0.3022(22) | 0.41(6) | 0.33(15) | 2.6(4) |
| | | 56.8(5) | 1 | 2.4 | 4.0 | 63 | 0.3475(2) | 0.3019(16) | 0.38(5) | 0.08(12) | 2.1(2) |
| V ₂ O ₃ | 114.4 | 0.001 | 1 | 1.3 | 2.4 | 147 | 0.34766(4) | 0.3049(4) | 0.31(1) | 0.51(3) | 2.2(8) |
| | | 18.3(5) | 2 | 1.6 | 3.0 | 47 | 0.3454(2) | 0.3118(11) | 0.47(4) | 0.69(8) | 14(1) |
| | | 28.3(5) | 1 | 3.9 | 5.8 | 52 | 0.3447(5) | 0.3135(26) | 0.6(1) | 0.4(2) | 10(2) |
| | | 47(1) | 2 | 3.4 | 5.2 | 42 | 0.3462(5) | 0.3217(36) | 0.2(1) | 0.7(2) | 8(2) |

^aWeighted $R = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$.^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.^c r^* is secondary extinction coefficient.

Several studies of V_2O_3 structure¹⁷⁻²⁰ are at variance, apparently due to small differences in sample stoichiometry. Vanadium sesquioxide cannot be grown as a stoichiometric phase unless oxygen fugacity is carefully controlled during synthesis. Nakahira *et al.*²¹ demonstrated large systematic variations in lattice parameters and transition behavior as a function of nonstoichiometry. Unit-cell parameters of karelianite under room conditions from the present study (Table I) correspond to a composition of approximately $V_2O_{3.01}$. The value of Z_M in the present study (0.34766) at 1 atm is larger than the value of 0.3463 observed in previous studies¹⁷⁻¹⁹ for V_2O_3 and is similar to the value reported for Cr-doped V_2O_3 ^{18,19}; however, a qualitative analysis with an energy dispersive x-ray detector did not show any metallic impurities at the 0.1% level of sensitivity for this experiment.

III. RESULTS

A. Linear compressibilities

Each of the materials studied compresses linearly within the precision of the measurements and the pressure range. There is qualitative agreement with the results of Sato and Akimoto² and quantitative agreement within 5% except for the c -axis compression of V_2O_3 , for which their compressibility is significantly greater than that of the present study. McWhan and Remeika,²⁰ on the other hand, obtained a *negative* c -axis compression. The composition of their apparently nonstoichiometric sample was $V_2O_{3.02}$, based on reported cell dimensions.²¹ Sato and Akimoto did not report their room-pressure unit-cell parameters, and meaningful comparison with that V_2O_3 sample is thus not possible. As noted above, small variations in V_2O_3 composition have large effects on the physical properties of this compound. In all three studies, however, the c axis of V_2O_3 is the least compressible, and the a axis the most compressible, of all directions in any of the R_2O_3 compounds measured.

The lattices of Cr_2O_3 and Al_2O_3 compress in a manner that is essentially isotropic as shown by the nearly constant values for c/a in Table I and in the data of Finger and Hazen.⁴ If the rhombohedral cell were used, the interaxial angle of the cell would remain constant and the axial length would change. In α - Fe_2O_3 , compression is only slightly anisotropic, with c approximately 25% more compressible than a (c/a decreases slightly with P). In V_2O_3 , on the other hand, the compression data noted above indicate a significant increase in c/a caused by anisotropic deformation of the lattice with a nearly three times more compressible than c in $V_2O_{3.01}$. A similar anisotropic compression has been noted for Ti_2O_3 .²⁰

B. Bulk moduli

Volume-pressure data for the R_2O_3 compounds (Table I) have been used to determine bulk moduli from the first-order Birch-Murnaghan equation of state. If the pressure derivative of the bulk modulus, K'_0 , is assumed to be 4.0, then calculated bulk moduli for α - Fe_2O_3 , Cr_2O_3 , and V_2O_3 are 2.25(4), 2.38(4), and 1.95(6) Mbars, respectively, compared with the values of 2.31(10), 2.31(5), and 1.75(3) determined by Sato and Akimoto.² McWhan and Remeika²⁰ mea-

sured bulk moduli of 2.14 and 1.86 Mbars for V_2O_3 and Ti_2O_3 , respectively, and Finger and Hazen⁴ determined K_0 and α - Al_2O_3 as 2.39 Mbars. The discrepancies in the bulk moduli of V_2O_3 are due to the differences in measured c -axis compressibility.

Sato and Akimoto² noted a slight discontinuity in unit-cell volume versus pressure at 30 kbars in α - Fe_2O_3 . They attributed this break to the Morin transition, and a 20% decrease in bulk modulus was reported across this transition. No such discontinuity was observed in this study of α - Fe_2O_3 to 52.4 kbars, and cell dimensions and compressibilities closely match those of Sato and Akimoto below the transition pressure. Significant differences in Fe_2O_3 compressibility and transition behavior may be due to impurities and crystallization history,²² which would explain the absence of the Morin transition in our sample.

C. High-pressure crystal structures

Oxides of the R_2O_3 corundum type have space group D_{3d}^6 ($R\bar{3}c$) with R at (0,0, z) and oxygen at (x ,0, $\frac{1}{4}$) with an R -centered cell. Cations are six-coordinated and occupy two-thirds of the octahedral sites in the nearly ideal hexagonal close-packed (HCP) oxygen array. In an ideal HCP corundum both z_R and x_0 are $\frac{1}{3}$, and $c/a = 2.833$. Thus, three parameters are sufficient to define deviations of the corundum-type structure from ideality.

In α - Fe_2O_3 and Cr_2O_3 , as well as α - Al_2O_3 ,⁴ the two variable positional parameters, $z_R = 0.35$ and $x_0 = 0.31$, and the unit-cell ratio c/a are virtually unchanged over the pressure range studied. Structural variations in these three sesquioxides are thus approximately isotropic, with all interatomic distances compressing at similar rates and interatomic angles constant (Tables III and IV). Bulk moduli of component octahedra are similar to those of the oxides, and distortion indices of the R^{3+} octahedra do not change significantly with pressure.

Vanadium oxide, on the other hand, responds anisotropically to changes in pressure, with V and O approaching the ideal HCP corundum structure at high pressure. Both oxygen x and vanadium z parameters become closer to $\frac{1}{3}$, and the c/a ratio, though it increases with P , is similar to the ideal 2.833 value throughout the pressure range studied. The changes in V_2O_3 with pressure thus may not be represented as a simple scaling of the structure as in other R_2O_3 compounds. The four distinct O-O distances (Table V), for example, converge to approximately 2.8 Å at high pressure, with longer O-O bonds compressing and shorter O-O bonds expanding toward a common value. As oxygens more closely approximate an HCP array, the octahedral distortions, as measured by quadratic elongation and angle variance,²³ also decrease. It is possible that the high-pressure results for this sample may be affected by the factor or factors that cause the anomalous results at room pressure.

D. Comparison of high- T and high- P structures

High-temperature behavior of V_2O_3 ¹⁹ mirrors the high-pressure results and thus provides an example of the "inverse relationship"²⁴ that exists between high-tempera-

TABLE III. Selected interatomic distances (Å), angles (°), octahedral volume (Å³), and distortion indices for Fe₂O₃.

| Parameter | Room <i>P</i> | 15.4 kbars | 31.4 kbars | 41.6 kbars | 43.9 kbars | 52.4 kbars |
|---|---------------|------------|------------|------------|------------|------------|
| <i>M</i> – O ₁ [3] | 2.113(3) | 2.112(5) | 2.100(5) | 2.090(3) | 2.094(7) | 2.114(10) |
| <i>M</i> – O ₅ [3] | 1.944(2) | 1.938(4) | 1.938(4) | 1.940(6) | 1.936(5) | 1.919(6) |
| O ₁ – O ₂ [2] | 2.665(7) | 2.667(12) | 2.650(12) | 2.635(20) | 2.638(17) | 2.693(22) |
| O ₁ – O ₃ [4] | 3.035(4) | 3.025(7) | 3.025(7) | 3.028(11) | 3.025(10) | 2.990(12) |
| O ₁ – O ₄ [2] | 2.770(2) | 2.766(3) | 2.756(3) | 2.748(4) | 2.749(4) | 2.758(6) |
| O ₁ – O ₅ [4] | 2.884(1) | 2.877(2) | 2.871(2) | 2.869(4) | 2.867(4) | 2.852(4) |
| <i>M</i> – <i>M</i> (shared edge [3]) | 2.969(1) | 2.964(1) | 2.956(1) | 2.952(1) | 2.952(1) | 2.949(1) |
| <i>M</i> – <i>M</i> (shared face [1]) | 2.896(2) | 2.891(3) | 2.876(3) | 2.869(5) | 2.875(4) | 2.865(5) |
| O ₁ – <i>M</i> – O ₂ [3] | 78.2(1) | 78.3(2) | 78.3(2) | 78.1(3) | 78.1(3) | 79.1(4) |
| O ₁ – <i>M</i> – O ₃ [6] | 85.0(1) | 86.0(1) | 86.0(1) | 85.9(1) | 85.9(1) | 86.2(1) |
| O ₄ – <i>M</i> – O ₆ [3] | 102.6(1) | 102.6(1) | 102.6(1) | 102.6(1) | 102.7(1) | 102.4(1) |
| O ₁ – <i>M</i> – O ₁ [3] | 90.5(1) | 90.4(1) | 90.6(1) | 90.7(2) | 90.6(2) | 89.9(3) |
| O ₁ – <i>M</i> ₁ – O ₆ [3] | 162.1(1) | 162.2(2) | 162.2(2) | 162.1(4) | 161.9(3) | 163.0(4) |
| Quad. elon. (Ref. 23) | 1.0265 | 1.0264 | 1.0263 | 1.0264 | 1.0269 | 1.025 |
| Angle variance (Ref. 23) | 85.61 | 84.79 | 85.3 | 86.4 | 87.6 | 78.0 |
| Fe oct. vol. ^a | 10.73 | 10.68 | 10.58 | 10.51 | 10.51 | 10.58 |

^aOctahedral volume is the volume of the polyhedron with vertices at the six oxygens nearest the metal ion.

ture and high-pressure structural responses of many simple compounds. With increasing temperature, both variable positional parameters diverge from the ideal value of $\frac{1}{3}$, and the axial ratio c/a decreases. Distortions from ideal HCP geometry thus increase with temperature and decrease with pressure.

The inverse relationship is also apparent in the thermal expansion versus compression of Al₂O₃ and Fe₂O₃.²⁵ In α -Al₂O₃ the c axis varies approximately 10% more than a both on heating and compression; in α -Fe₂O₃ the a axis compressibility and thermal expansivity are both greater than those of c . There are no published high-temperature structures of the sesquioxides of Al, Fe, or Cr. If these materials are assumed to conform to the inverse relationship, then no significant change in positional parameters is anticipated with increasing temperature.

High-temperature structural data on Ti₂O₃, which also has the corundum structure, were reported by Rice and Robinson²⁶ and may be used to predict possible high-pressure behavior of this material. As in V₂O₃, the two variable positional parameters diverge from the ideal of $\frac{1}{3}$ with increasing temperature. Unlike V₂O₃, however, the a axis of Ti₂O₃ contracts and the c axis expands with temperature, resulting in a large increase in c/a , convergent to the ideal 2.833 value. It is known that c/a decreases for Ti₂O₃ under compression,²⁰ and if the inverse relationship obtains, it is predicted that both variable positional parameters will converge on the $\frac{1}{3}$ value characteristic of HCP.

The profound differences in P - T response of the five corundum-type sesquioxides appear to be due to differences in the electronic structure of the R^{3+} cations. Both V₂O₃ (d^2 configuration) and Ti₂O₃ (d^1 configuration), for example,

TABLE IV. Selected interatomic distances (Å), angles (°), octahedral volume (Å³), and distortion indices for Cr₂O₃.

| Parameter | Room <i>P</i> | 18.6 kbars | 40.6 kbars | 56.8 kbars |
|--|---------------|------------|------------|------------|
| <i>M</i> – O ₁ [3] | 2.009(2) | 2.006(7) | 1.988(8) | 1.981(6) |
| <i>M</i> – O ₅ [3] | 1.962(1) | 1.956(4) | 1.958(6) | 1.956(4) |
| O ₁ – O ₂ [2] | 2.617(3) | 2.615(15) | 2.577(15) | 2.569(13) |
| O ₁ – O ₃ [4] | 2.987(2) | 2.975(3) | 2.984(10) | 2.979(8) |
| O ₁ – O ₄ [2] | 2.7300(8) | 2.724(4) | 2.710(4) | 2.704(3) |
| O ₁ – O ₅ [4] | 2.8435(7) | 2.835(3) | 2.833(4) | 2.828(3) |
| <i>M</i> – <i>M</i> (shared edge [3]) | 2.8848(3) | 2.8763(6) | 2.8690(3) | 2.8619(7) |
| <i>M</i> – <i>M</i> (shared face [1]) | 2.6486(10) | 2.640(4) | 2.638(5) | 2.626(5) |
| O ₁ – <i>M</i> – O ₂ [3] | 81.26(6) | 81.4(3) | 80.8(3) | 80.9(2) |
| O ₁ – <i>M</i> – O ₃ [6] | 86.84(1) | 86.9(1) | 86.7(1) | 86.8(1) |
| O ₄ – <i>M</i> – O ₆ [3] | 99.12(2) | 99.0(1) | 99.3(1) | 99.2(1) |
| O ₁ – <i>M</i> – O ₄ [3] | 91.44(4) | 91.4(2) | 91.8(2) | 91.8(2) |
| O ₁ – <i>M</i> – O ₆ [3] | 166.84(6) | 167.0(3) | 166.3(4) | 166.4(3) |
| Cr oct. vol. | 10.23 | 10.16 | 10.06 | 9.96 |
| Quad. elon. | 1.014 | 1.013 | 1.014 | 1.014 |
| Angle variance | 46.8 | 45.6 | 50.4 | 49.6 |

TABLE V. Selected interatomic distances (Å), angles (°), octahedral volume (Å³), and distortion indices for V₂O₃.

| Parameter | Room <i>P</i> | 18.3 kbars | 28.3 kbars | 47 kbars |
|--|---------------|------------|------------|-----------|
| <i>M</i> – O ₁ [3] | 2.037(2) | 2.036(4) | 2.033(10) | 2.072(13) |
| <i>M</i> – O ₅ [3] | 1.978(1) | 1.971(3) | 1.967(7) | 1.932(8) |
| O ₁ – O ₂ [2] | 2.615(4) | 2.664(9) | 2.672(22) | 2.731(31) |
| O ₁ – O ₃ [4] | 2.988(2) | 2.944(5) | 2.928(12) | 2.881(16) |
| O ₁ – O ₄ [2] | 2.790(1) | 2.799(2) | 2.799(6) | 2.814(6) |
| O ₁ – O ₅ [4] | 2.902(1) | 2.886(2) | 2.879(4) | 2.861(5) |
| <i>M</i> – <i>M</i> (shared edge [3]) | 2.887(1) | 2.868(1) | 2.858(2) | 2.853(2) |
| <i>M</i> – <i>M</i> (shared face [1]) | 2.735(1) | 2.669(6) | 2.649(14) | 2.689(14) |
| O ₁ – <i>M</i> – O ₂ [3] | 79.9(1) | 81.7(2) | 82.2(4) | 82.5(6) |
| O ₁ – <i>M</i> – O ₃ [6] | 88.1(1) | 88.6(1) | 88.8(1) | 89.2(1) |
| O ₄ – <i>M</i> – O ₆ [3] | 98.2(1) | 96.7(1) | 96.2(3) | 96.4(3) |
| O ₁ – <i>M</i> – O ₄ [3] | 92.6(1) | 92.1(1) | 92.0(3) | 91.1(4) |
| O ₁ – <i>M</i> – O ₆ [3] | 166.7(1) | 169.2(2) | 169.8(5) | 170.1(6) |
| Quad. elon. | 1.014 | 1.009 | 1.008 | 1.009 |
| Angle variance | 49.0 | 32.6 | 28.8 | 27.1 |
| V oct. vol. | 10.6 | 10.6 | 10.5 | 10.6 |

have high-temperature semiconductor-to-metallic transitions resulting from “delocalization of *d* electrons and an overlap of the *d*-electron energy levels of the two (face-sharing) cations.”²⁷ Metal-metal second-nearest-neighbor interactions may thus dominate some bond-distance variations with pressure in these transition metal compounds. Lesser degrees of metal-metal overlap are anticipated in oxides of Al and Fe³⁺ (high-spin *d*⁵ configuration).

Hazen and Finger²⁸ demonstrated an empirical bulk modulus-volume relationship for cation polyhedra. In the majority of compounds studied at high pressure the mean cation-anion bond compression within a polyhedron is given by:

$$\bar{\beta} = \frac{0.044d^3}{S^2z_cz_a} \text{ Mbar}^{-1},$$

where *d* is the mean cation-anion distance, *z_c* and *z_a* are cation and anion formal charges, respectively, and *S*² is an empirical ionicity term defined as 0.5 for all oxygen-based polyhedra. An important exception to this relationship is the CsCl-type structure in which second-nearest-neighbor interactions are important due to short cation-cation and anion-anion bonds. The corundum-type oxides, in which polyhedral compressibilities are greater than predicted by this equation (especially for V₂O₃), may also be influenced by second-nearest-neighbor metal-metal interactions.

IV. SUMMARY

Although the sesquioxides of Al, Cr, Fe, Ti, and V are isostructural, details of structure variations with temperature and pressure are quite different. Two of these materials, Al₂O₃ and Cr₂O₃, simply scale with changes in pressure; the three variables *z_R*, *x*₀, and *c/a* are essentially constant. Hematite, Fe₂O₃, is similar, with only a slight decrease in *c/a* at high pressure. By contrast, the structure of V₂O₃ approaches an ideal HCP configuration with increasing pressure or decreasing temperature. In addition, on the basis of high-temperature data only,²⁰ Ti₂O₃ has yet another behavior. The complexities of the high-pressure structural changes in R₂O₃

compounds thus illustrate the potential difficulty in attempting to predict structures at elevated temperature or pressure from nearest-neighbor electrostatic bonding parameters alone. Furthermore, analogies between temperature, pressure, and composition²⁹ must be used with caution when compounds with substituting cations of greatly differing electronic structure are considered.

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