

LOW-SPIN $\rightarrow$ HIGH-SPIN STATE TRANSITION IN HIGH PRESSURE COBALT SESQUIOXIDE

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Co_2O_3 with the corundum structure was synthesized under high pressure. A refinement of the structure indicated that Co^{3+} is in the low-spin state. By annealing, this oxide transformed to a corundum structure with a larger volume indicating that the Co^{3+} is in the high spin state. The increase in volume was 6.7 per cent.

ALL TRIVALENT 3d transition metals form a sesquioxide with the corundum structure except cobalt, nickel and manganese. The former two elements are more stable as divalent cations.

CoO and NiO with the NaCl structure are the stable oxides. Another cobalt oxide is known, namely Co_3O_4 , which crystallizes with the normal spinel structure. In this oxide 2/3 of the cobalt ions are trivalent while the other third is divalent. It has been shown that the Co^{3+} ions in this compound are in the low spin state. Only a few cobalt compounds are known in which the cobalt ions are all trivalent, LiCoO_2 and CoF_3 are two examples. From the ionic radii of Co^{3+} and Co^{2+} with coordination number 6,¹ one could speculate that the transformation $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ should be favored by high pressures, especially if the Co^{3+} ions are in the low spin state (see Table 1). This note reports the high pressure synthesis of Co_2O_3 with the corundum structure.

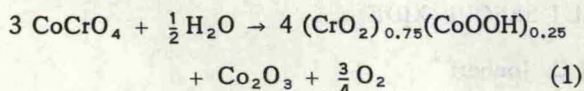
Two different syntheses were performed. In the first the starting material was $\text{Co}^{2+}\text{Cr}^{6+}\text{O}_4$. This double oxide has the orthorhombic

Table 1

Valence	Coord.	Spin	Radius ($\text{\AA}$)
3	6	Low	0.52 ₅
2	4	High	0.57
3	6	High	0.61
2	6	Low	0.65
2	6	High	0.74 ₅

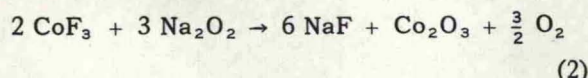
$\text{Cr}^{3+}\text{V}^{5+}\text{O}_4$ structure in which the Co^{2+} ions have octahedral coordination, while the smaller Cr^{6+} ions are tetrahedrally coordinated. The high pressure runs were done in a modified 'belt' apparatus. A platinum cylindrical cell was used as sample container. A standard heater assembly was used. The pressure was calibrated by measuring the resistance of bismuth and thallium wires at room temperature.² The temperature was calibrated by a Pt-Pt/10% Rh thermocouple. By applying a pressure of ≥ 90 kbar and 1000°C in the presence of a small amount of water, CoCrO_4 decomposes into Co_2O_3 with the corundum structure and a solid solution of CoOOH and CrO_2 with the

orthorhombic distortion of the rutile structure, as revealed by X-ray photographs of the quenched materials. The decomposition occurs according to the formula:



Under pressure Co_2O_3 transforms in the presence of water to a high pressure form of CoOOH , therefore different amounts of water affect the composition of the solid solution $(\text{CrO}_2)_x(\text{CoOOH})_{1-x}$ ³

The second synthesis was based on the following reaction:



The X-ray pattern of the quenched material of a run done at 80 kb and 850°C showed the same hexagonal pattern obtained in syntheses (1). Unfortunately some reduction took place and the quenched material contained some Co_3O_4 .

Table 2. Powder pattern of Co_2O_3 (low spin)

<i>hkl</i>	<i>d</i> ₀	<i>d</i> _c	<i>I</i> ₀
012	3.476	3.489	25
104	2.546	2.551	100
110	2.389	2.391	66
113	2.088	2.092	16
024	1.743	1.745	33
116	1.601	1.602	90
214	1.408	1.409	43
027	1.379	1.380	50
1010	1.236	1.236	48
119	1.233	1.233	15
220			
217	1.195	1.195	46
306	1.163	1.163	48

Table 2 gives the powder pattern of Co_2O_3 which was indexed on a hexagonal cell, $a = 4.782 \text{ \AA}$, $c = 12.96 \text{ \AA}$, $c/a = 2.710$, $V = 258.5 \text{ \AA}^3$. These values correspond to the material of synthesis (2). The X-ray powder photographs were taken using a Norelco camera of

114.6 mm dia. and filtered $\text{CrK}\alpha$ radiation. In general the synthesis (1) yielded lattice parameters which were slightly larger. A typical run gave $a = 4.790 \text{ \AA}$ and $c = 13.00 \text{ \AA}$. We believe that these larger values are due to a small percentage of substituted Cr. The pattern reported in Table 2 resembles closely that of $\alpha\text{-Al}_2\text{O}_3$ as far as the sequence of the *d*-spacings is concerned, but the intensities of the reflections are similar to those of V_2O_3 . This indicates that the radius of the Co^{3+} ions is very close to that of the Al^{3+} ions. Therefore the Co^{3+} ions must be in the low spin state. The reported ionic radius for the six coordinated Al^{3+} is $0.53 \text{ \AA}$, while that of the corresponding Co^{3+} in the low spin state is $0.52 \text{ \AA}$. On the other hand the arrangement of the structure of Co_2O_3 should be different from that of Al_2O_3 as the relative intensities indicate.

By annealing Co_2O_3 at 400°C for a half hour in air, this oxide transforms to a corundum structure with a different volume and *c/a* ratio. The new values are $a = 4.882 \text{ \AA}$, $c = 13.38 \text{ \AA}$, $c/a = 2.742$, $V = 276.2 \text{ \AA}^3$. The X-ray powder pattern is reported in Table 3. Since the unit cell volume and the *d*-spacings of this Co_2O_3 are nearly the same as those of $\alpha\text{-Fe}_2\text{O}_3$, the Co^{3+} ions must be in the high spin state. The oxide Co_2O_3 with Co^{3+} ions in the low spin state will be referred herein as Co_2O_3 (low spin) whereas that with Co^{3+} ions in the high spin state will be referred as Co_2O_3 (high spin). The transformation Co_2O_3 (low spin) → Co_2O_3 (high spin) is accompanied by an increase in volume $\Delta V/V(\text{low spin}) = 6.7$ per cent. These results seem to indicate that Co_2O_3 (high spin) is the cobalt sesquioxide stable at atmospheric pressure whereas Co_2O_3 (low spin) is the high pressure phase. This pressure-induced transformation involves only a change in the spin state of the cations. The coordination of the ions and their packing remain the same. The coordination-number of the cations remains six and for the anions it remains four, while the oxygen packing is nearly h.c.p. in both oxides.

Preliminary refinements of the two structures based on powder intensities gave the positional parameters and the interatomic distances reported in Table 4. The average Co—O distances are 1.90

Table 3. Powder pattern of Co_2O_3 (high spin)

<i>hkl</i>	d_0	d_c	I_0
012	3.571	3.574	24
104	2.620	2.624	61
110	2.440	2.441	50
113	2.139	2.141	21
024	1.788	1.787	24
116	1.647	1.647	100

Due to the short annealing time, the back-reflection lines were diffuse. Extended annealing times produced the reduction of Co_2O_3 to Co_3O_4 .

and 1.99 Å for Co_2O_3 (low spin) and (high spin) respectively. These values are in fairly good agreement with those calculated from Shannon and Prewitt ionic radii, 1.92 Å and 2.01 Å respectively. The oxygen octahedra in the two compounds seem to have different distortions. That of the Co_2O_3 (high spin) is similar to the one found in the other corundum structures. Instead, the distortion of the Co_2O_3 (low spin) seems quite unique. The Co—O distance toward the shared face is shorter than that toward the unshared face. The contrary is true for all the other corundum structures. The Co—Co distances across the shared face between two octahedra are quite short in both compounds. Relative to the ionic radii it is smaller in Co_2O_3 (high spin). Also the Co—Co distance across the shared edge is anomalously short in Co_2O_3 (high spin).

Due to the contamination of the samples from the by-products of both reactions we have been unable to measure physical properties such as resistivity and magnetic susceptibility.

In the last decade the transition metal sesquioxides with the corundum structure have been thoroughly studied because of their quite unique electrical and magnetic properties. As the number of *d*-electrons of the ions, n_d , increases the transition metal oxides go from a band metal behavior to a localized insulator behavior.⁴ Also the oxides with $n_d \geq 2$ are magnetically ordered at low temperatures whereas those with $n_d < 2$, such as Ti_2O_3 , have not been found to order at any temperature. The oxides with a large number of *d*-electrons, such as Cr_2O_3 and Fe_2O_3 are magnetic insulators. According to these general trends, Co_2O_3 (high spin) should be a magnetic insulator, whereas Co_2O_3 (low spin) a nonmagnetic insulator. In octahedral coordination the Co^{3+} ions in the low spin state have the configuration $t_{2g}^6 e_g^0$ which corresponds to a zero magnetic moment. The filled t_{2g} band would be compatible with the predicted insulator character of Co_2O_3 (low spin).⁵

From shock-wave experiments it has been shown that Fe_2O_3 (high spin) undergoes a phase transition from corundum to a denser phase.⁶ The data extrapolate to a zero-pressure density of 5.96 g/cm³ for the new phase, as compared

Table 4. Positional parameters

		Low Spin	High Spin
Z_{Co}		0.346 ± 0.002	0.346 ± 0.002
x_{O}		0.295 ± 0.013	0.344 ± 0.020
$R = \Sigma \Delta F / \Sigma F$		0.03	0.04
Interatomic distances in Co_2O_3			
Co—O	toward shared face	1.88 ± 0.06	2.12 ± 0.08
Co—O	toward unshared face	1.29 ± 0.04	1.86 ± 0.04
O—O	shared edge	2.60 ± 0.02	2.79 ± 0.07
O—O	shared face	2.44 ± 0.11	2.91 ± 0.17
O—O	unshared edge	2.74 ± 0.02	2.75 ± 0.03
O—O	unshared face	2.93 ± 0.06	2.77 ± 0.08
Co—Co	across face	2.49 ± 0.05	2.58 ± 0.06
Co—Co	across edge	2.78 ± 0.06	2.84 ± 0.08

with the value of 5.24 g/cm^3 observed for Fe_2O_3 with the corundum structure at zero pressure. Several explanations based on crystal chemical relationships have been offered for this transformation.^{7,8} The high spin-low spin transition found in Co_2O_3 offers another plausible one. The Fe^{3+} ion in the low spin state has an ionic radius of $0.55 \text{ \AA}$. From this value one can interpolate the molecular volume and the density

at zero pressure of Fe_2O_3 (low spin). The calculated density of this phase, $5.98 \pm 0.06 \text{ g/cm}^3$, seems to indicate that the transition observed by shock-wave in Fe_2O_3 is Fe_2O_3 (high spin) → Fe_2O_3 (low spin).

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REFERENCES

1. All the ionic radii quoted in this paper are from: SHANNON R.D. and PREWITT C.T., *Acta Crystallogr.* **B25**, 946 (1969), **B26**, 1046 (1970).
2. JEFFERY R.N., BARNETT J.D., VANFLEET H.B. and HALL H.T., *J. appl. Phys.* **37**, 3172 (1966).
3. CHENAVAS J., JOUBERT J.C. and MAREZIO M., to be published.
4. McWHAN D.B., MENTH A. and REMEIKA J.P., *J. Phys.* (in press).
5. RICE T.M., (private communication).
6. CLARK S.P., Ed. Handbook of Physical Constants, Rev. Ed., *Geol. Soc. Am. Mem.* **97**, 153 (1966).
7. REID A.F., and RINGWOOD A.E., *J. Geophys. Res.* **74**, 3238 (1969).
8. AHRENS T.J., ANDERSON D.L. and RINGWOOD A.E., *Rev. Geophys.* **7**, 667 (1969).

L'oxyde de cobalt Co_2O_3 a été synthétisé sous haute pression. Un affinement de la structure montre que l'ion Co^{3+} se trouve dans l'état 'low-spin'. Après recuit, cet oxyde se transforme en une nouvelle phase de structure corindon et de densité plus faible, contenant l'ion Co^{3+} dans l'état 'high spin'. L'augmentation de volume correspondant est de 6.7 pour cent.