

LOW-SPIN → 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 (Å)
3	6	Low	0.52 _s
2	4	High	0.57
3	6	High	0.61
2	6	Low	0.65
2	6	High	0.74 _s

$\text{Cr}^{3+}\text{V}^{5+}\text{O}_4$ 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