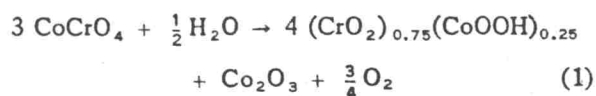
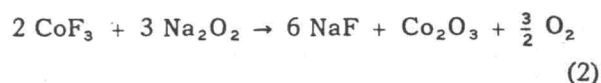


orthorhombic distortion of the rutile structure, as revealed by X-ray photographs of the quenched materials. The decomposition occurs according to the formula:



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 $(\text{CrO}_2)_x(\text{CoOOH})_{1-x}$.

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>	d_o	d_c	I_o
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) $\rightarrow$ 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