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LOW-SPIN \rightarrow HIGH-SPIN STATE TRANSITION IN Co₂O₃

Table 3. Powder pattern of Co₂O₃ (high spin)

hkl	do	do	-I o
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 backreflection lines were diffuse. Extended annealing times produced the reduction of Co_2O_3 to Co_3O_4 .

and 1.99Å for Co2O3 (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 Co₂O₃ (high spin) is similar to the one found in the other corundum structures. Instead, the distortion of the Co₂O₃(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 Co2O3(high spin). Also the Co-Co distance across the shared edge is anomalously short in Co₂O₃ (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.

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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 $n_d \ge 2$ are magnetically ordered at low temperatures whereas those with $n_d < 2$, such as Ti₂O₃, 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, Co₂O₃ (high spin) should be a magnetic insulator, whereas Co_2O_3 (low spin) a nonmagnetic insulator. In octahedral coordination the Co3+ ions in the low spin state have the configuration $t_{20}^{6}e_{a}^{0}$ which corresponds to a zero magnetic moment. The filled t_{2g} band would be compatible with the predicted insulator character of Co2O3(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 _c		0.346 ± 0.002	0.346 ± 0.002
xo		0.295 ± 0.013	0.344 ± 0.020
$R = \Sigma \Delta F / \Sigma F$		0.03	0.04
	Interatomic distanc	es in Co ₂ O 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
0-0	shared edge	2.60 ± 0.02	2.79 ± 0.07
0-0	shared face	2.44 ± 0.11	2.91 ± 0.17
0-0	unshared edge	2.74 ± 0.02	2.75 ± 0.03
0-0	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

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