Table 3. Powder pattern of Co_2O_3 (high spin)

hkl	d_o	d_c	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 back-reflection lines were diffuse. Extended annealing times produced the reduction of Co_2O_3 to Co_3O_4.

and 1.99Å 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/cm³ 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 Å. 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 ± 0.06 g/cm³, 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.