substance: MoO_3
property: defects

MoO_3 is not a line phase, maximum values of γ in $MoO_{3-\gamma}$ before a second phase appears are

$10^4\,\gamma$	1.4	T = 607ºC	in the range 607...739ºC	74Z
	1.6	T = 637ºC	γ is proportional to $p_{O2}^{-1/6}$	
	2.5	T = 670ºC		
	3.1	T = 691ºC		
	3.6	T = 714ºC		
	5.2	T = 739ºC		

There is some controversy over the nature of the defects. The thermogravimetry data [74Z] is consistent with doubly ionized O vacancies. However further reduction apparently gives rise to (301)-shear planes (Fig. 1). The O-vacancy model was further developed [68D, 78S1] and epr data reported by [68D] is consistent with a small concentration of singly ionized O vacancies. This has been queried by [69I] and [72S]. [69I] found no epr signal in air-grown MoO_3 but in Ar-grown crystals a signal corresponding to the localization of the electron on two different Mo-sites with hyperfine structure associated with a proton – the defect being Mo^{5+} – OH^- – Mo^{6+}. [72S] also found a 4d' signal associated with a proton provided the crystals were in an atmosphere containing traces of H_2. For Ar-grown crystals, or those reduced with H_2, a different epr signal is found but no evidence for O-vacancies. However the technically important colour centres in MoO_3 films [68D, 74T] are most naturally ascribed to Mo^{5+} localized near oxygen vacancies or OH^- ions.

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Fig. 1.

MoO_3. (a) Displacements of octahedra in MoO layers, (b) (301) shear planes through adjacent layers [78S2].