The α-FeOOH → α-Fe_2O_3 Transition and the Origin of Adsorbed Oxygen on Iron Oxides

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It has been found that an i.r. band observable at 1140 cm^{-1} on goethite, which undergoes several reversible splittings and shifts on dehydration of the sample, is the precursor of similar bands previously observed on haematite and assigned to adsorbed oxygen.

The existence of adsorbed or 'non-stoicheiometric' oxygen at the surface of iron oxides has been observed by various authors. Recently Al-Mashta *et al.*[1] reported a systematic spectroscopic approach to the characterization of the oxidic species present at the surface of α-Fe_2O_3 (haematite), produced by thermal decomposition of α-FeOOH (goethite). The observed species were divided into two spectral groups, termed A and B bands.

Work carried out in this laboratory on several samples of FeOOH revealed that most, if not all, of the oxidic species at the surface of haematite are derived from similar species pre-existing at the surface of the goethite phase. Figure 1 gives the i.r. spectra of a thin layer of FeOOH deposited on a silicon plate and treated *in vacuo* (residual pressure $<10^{-5}$ Torr) at various temperatures. A medium-strong band centred at 1140 cm^{-1} in the original sample [Figure 1(a)] is modified on evacuation up to 180 °C [Figure 1(b)]; the band is weaker and shifted slightly, new components being present on its high $\bar{\nu}$ side (A bands). When the temperature reaches 200 °C [Figure 1(d)], the goethite → haematite transition is complete, (monitored by the elimination of the strong bands at 915 and 790 cm^{-1}) and the spectrum in the 1400—800 cm^{-1} range exhibits weaker individual components, the pattern typical of 'oxygen-rich' Fe_2O_3.[1] These bands were produced with no intervention of O_2, and another experiment carried out in the presence of O_2 (in static conditions) did not result in any significant spectral differences.

Additional considerations are as follows:

i, Figure 1(b) shows that, after vacuum treatment at 180 °C, the transformation to α-Fe_2O_3 had already occurred to a small extent, as shown by the weakened bands at 915 and 790 cm^{-1} and by the appearance of a weak band of haematite at 530 cm^{-1}.[2] Nevertheless, the changes in the 1400—1000 cm^{-1} range are not ascribable to this partial phase transformation. Figure 2 shows that the transformation of the original 1140 cm^{-1} bands is gradual and starts long before the beginning of the phase transformation. Bands typical of the A region of the 'oxygen-rich' α-Fe_2O_3 are also produced step by step on α-FeOOH.

ii, The correlation between the original 1140 cm^{-1} band and the new components above 1200 cm^{-1} is reversible, and mainly ascribable to surface hydration. In fact Figure 1(c) shows that the original shape *and* intensity at 1140 cm^{-1} can be restored if water is allowed onto the outgassed sample. It was also observed that the destruction of the high $\bar{\nu}$ absorptions (1350, 1325, and 1250 cm^{-1}) begins with the slightest presence of water and is complete after equilibration with saturated water vapour. The restoration of the starting spectral pattern begins upon evacuation at ambient temperature, and is complete only after degassing at the original activation temperature, *i.e.*, after reaching the starting degree of hydration.

iii, Owing to the strong intrinsic mode at 915 cm^{-1} it is difficult to determine whether any band is present, on goethite, in the 1100—900 cm^{-1} range, where the B bands occur on haematite. However, no changes were observed in that range during the dehydration–rehydration cycles. It would appear that, during the phase transition, both A and B bands of haematite are produced by the transformation of the A band system existing on goethite, consistent with the decreased intensity in all bands visible on going from Figure 1(b) and (c) to Figure 1(d).

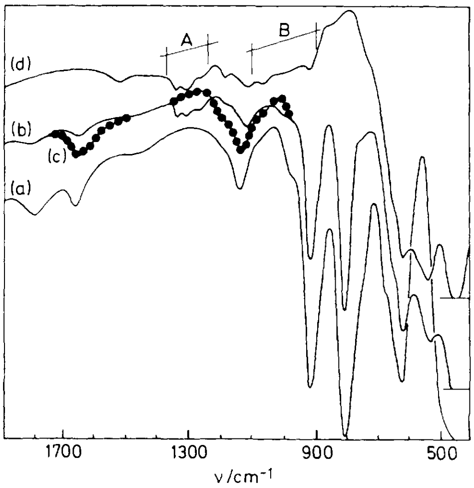

Figure 1. I.r. spectra of FeOOH: (a) sample in air; (b) treated *in vacuo* at 180 °C; (c) sample (b), equilibrated with water vapour at ambient temperature; (d) treated *in vacuo* at 200 °C. The letters A and B indicate the spectral regions where the corresponding oxidic species occur on α-Fe_2O_3 (ref. 1).

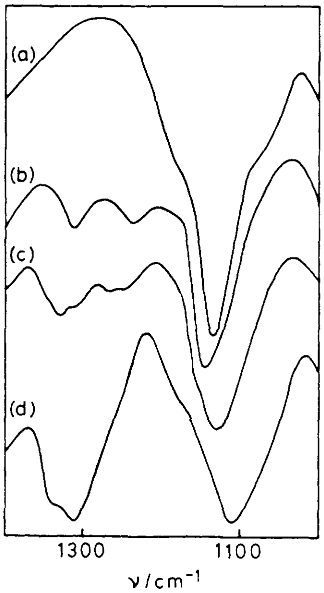

Figure 2. Detailed i.r. spectra of FeOOH (a) in air and after vacuum treatment at: (b) 100 °C; (c) 140 °C; and (d) 160 °C.

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