Rhombic symmetry sites in Fe/TiO₂ powders

J. S. THORP, H. S. EGGLESTON
Department of Applied Physics and Electronics, University of Durham, Durham, UK

In previous papers [1, 2], Thorp and Eggleston have reported details of the EPR powder spectrum of iron-doped rutile. Here attention was given to the spectrum due to isolated Fe³⁺ ions in substitutional sites — the major spectrum observed — and it was shown that the general features and field values of the powder (obtained from a series of iron-doped pigment-like rutile powders) could be reasonably well simulated from computations made using single-crystal spin-Hamiltonian parameters together with the equivalent single-crystal linewidths. The experimental spectrum due to substitutional iron (as Fe³⁺) exhibits four main features in the first derivative plot, which is reproduced in Fig. 1a. Two of these, A and B, appear as spikes and two, E and H, as features with almost equal positive and negative portions, in good agreement with the theoretical powder spectrum, in Fig. 1b, computed using single-crystal spin-Hamiltonian parameters.

In the present work we have examined a range of iron-doped rutile powders (prepared at the Central Laboratories, Tioxide International Ltd, Stockton-on-Tees); in these, the respective total-iron contents, as determined by X-ray fluorescent analysis, ranged between about 35 ppm and 405 ppm. A typical experimental spectrum from these, recorded as first derivative plots at 9 GHz, is given in Fig. 1c. Here the important new aspect is the occurrence of feature C whose amplitude (like those of the substitutional Fe³⁺ features A, B, E and H) increases with increasing doping level. For the present purposes the features D, G and F, which are not dependent on the amount of iron present, may be ignored; they are due to defects and light-induced centres and have been discussed elsewhere [3, 4]. The g-value characterizing feature C is g = 4.30 and the first-derivative powder-lineshape is quite symmetrical with almost equal positive and negative portions; for a total iron concentration of 405 ppm the linewidth was about 10 mT (peak-to-peak).

A check was first made to ascertain whether feature C could represent any of the previously reported iron-associated centres. It may be noted here that the significant features in the Fe³⁺/TiO₂ powder spectrum occur at the same magnetic-field values as the single-crystal resonances when the magnetic field is aligned along the principal magnetic axis of the dopant ion. Consequently, to assist in characterizing the observed spectrum, a computer program was written [5] to give the values of the resonant field for transitions within the doublets for magnetic fields along the x, y or z axes. Inserting the parameters given by Anderson and Kollberg [6] for the three cases of a Fe³⁺ ion substitutional

![Figure 1](https://example.com/figure1.png)

Figure 1 ESR spectra of iron-doped rutile powders: (a) previous experimental spectrum from crushed single crystal; (b) computer simulation from single-crystal data; (c) experimental spectrum from present powders.
for Ti$^{4+}$, a Fe$^{3+}$ ion associated with a nearly interstitial proton and a Fe$^{3+}$ ion with a nearest neighbour O$^{2-}$ vacancy, respectively showed that none of these gave resonant-field values near that at which feature C was observed. However, it is known that iron ions in a rhombic symmetry exhibit, for the $3 \rightarrow 4$ transitions, a nearly isotropic absorption line. This was first pointed out by Castner et al. [7] to explain spectra observed in glasses and has since been observed for other rhombic sites. This isotropic spectrum arises when the two terms $E$ and $D$ in the spin Hamiltonian have the ratio $E/D = 1/3$ and this represents rhombic symmetry. The computed values of the principal values of resonant field as a function of $E$ are shown in Fig. 2; in these calculations, made for a frequency of 9.1 GHz, the value of the $D$ parameter was taken as that for rutile, i.e. $D = 20$ GHz. It can be seen that as $E$ approaches the value $D/3$ (i.e. $E = 6.6$ GHz in this instance) all the $(3 \rightarrow 4)$ transitions tend to occur at the same value of magnetic field corresponding to a $g$-value of $g = 4.28$. Small departures from the exact condition that $E = D/3$ would lead to a spread in the values of the resonant field with a consequent broadening of the powder spectrum. Computer simulation [5] of the powder lineshape to be expected if $E = D/3$ confirms that a feature with symmetrical shape and equal positive and negative portions should be obtained. It thus seems that an assignment of feature C to Fe$^{3+}$ in a rhombic symmetry site is well founded.

In considering possible causes for the lattice distortion it may be noted that analysis [5] showed that the crushed single crystal (which gave the spectrum of Fig. 1a) contained about 1500 ppm Fe but only about 0.002% alumina, whereas the doped-rutile powder (which also gave the rhombic symmetry site, Fig. 1c) contained only 670 ppm Fe and about 1.8% alumina. The addition of the iron dopant was

Figure 2 Dependence of resonance field on value of $E$-term; computed for $D = 20$ GHz, $v = 9.11$ GHz.

Figure 3 Comparison of profiles of $(521)$ peaks of rutile powders prepared in the same way, but (a) excluding iron and (b) with 500 ppm Fe CoK$_{a_1}$ radiation.