EPR spectra of Fe^{3+} and Cr^{3+} in powdered rutile

Rutile is widely used as a pigment in paints and consequently there is considerable interest in relating its technological properties to the defects and impurities contained in a typical pigment. While a considerable amount of work has been reported on single-crystal rutile there appears to have been little previous interest in powders, for example, the electron paramagnetic resonance (EPR) spectra of substitutional Fe^{3+} and Cr^{3+} ions in single crystals of rutile are well known e.g. [1–3] but there appears to have been no reported observation of Fe^{3+} or Cr^{3+} in powdered rutile. The powder spectra of Fe^{3+} and Cr^{3+} have now been observed and compared with computer-simulated spectra derived from published single crystal data. High sensitivity was necessary and a Varian V4500 X-band spectrometer with 100 kHz modulation fitted with an Oxford Instruments ESR-9 liquid helium cryostat was used. This enabled spectra to be recorded from room temperature to about 3.8 K. A heavily iron-doped single crystal (containing approximately 1.5% Fe) was first examined between 0.0 and 0.5 tesla and the 9 GHz spectrum was compared with published data; there was good agreement between the results. This sample was then crushed and the spectrum of the powdered material was recorded (Fig. 1a). The features A, B, C and D, correspond to the principle values of the $-\frac{1}{2} \rightarrow +\frac{1}{2}$ and $-\frac{3}{2} \rightarrow +\frac{3}{2}$ transitions and are not present in samples containing little or no iron; line E is due to an unknown centre. The $-\frac{5}{2} \rightarrow +\frac{5}{2}$ transition was not seen in single crystals or powders. Pigments which were known to contain iron as an impurity were examined and these four features were clearly visible and it was noticed that their amplitudes were related to the concentration of iron. Pigments containing Cr^{3+} were also examined and three features were visible (Fig. 2a) which were related to the Cr^{3+} ion. No spectra were seen at room temperature. At temperatures less than about 70 K other, as yet unidentified,

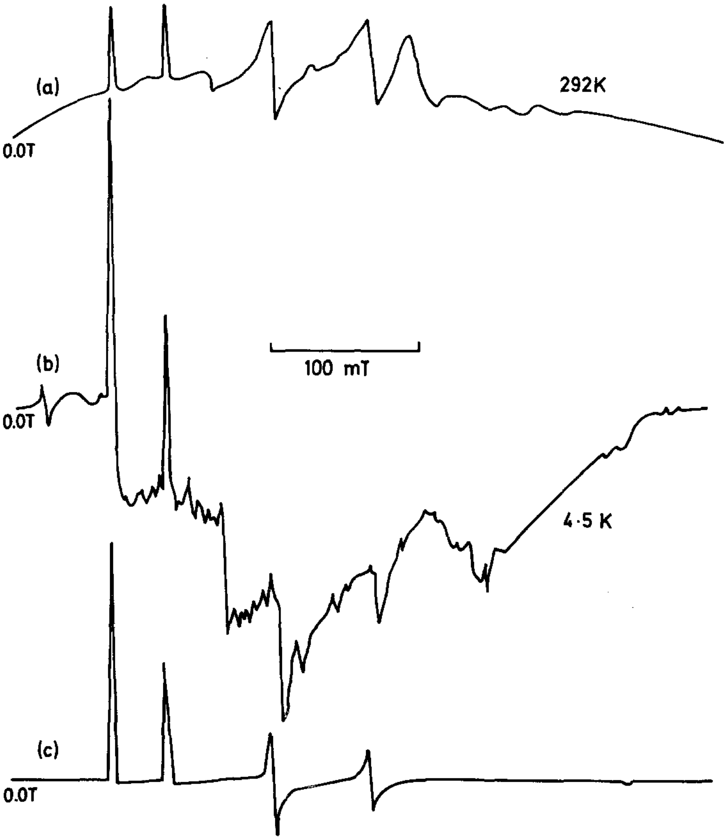

Figure 1 Experimental powder spectra of iron-doped rutile at (a) 292 K (b) 4.5 K and (c) the computed spectrum (9.1 GHz).

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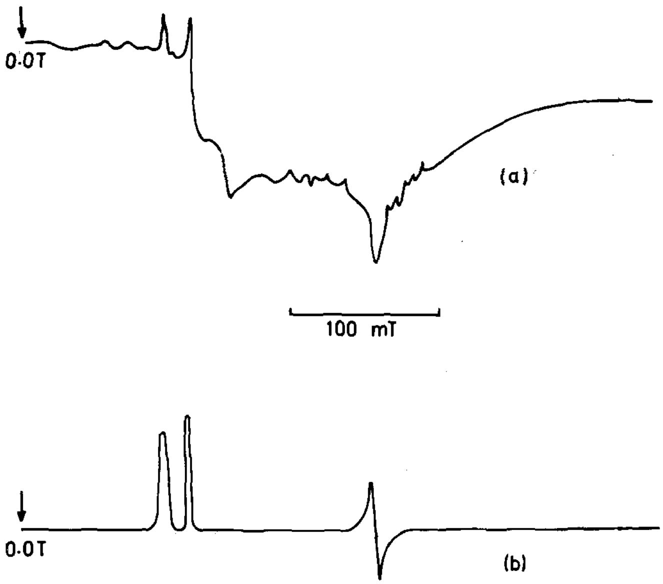

Figure 2 Powder spectra of chromium-doped rutile (a) experimental spectrum at 4.2 K and (b) the computed spectrum (9.1 GHz).

spectra could be seen (Fig. 1b). The computed iron spectra were compared with the room temperature results because then spectra due to other centres did not distort the iron lines.

To evaluate a powder spectrum the values of resonant field must be found for a variety of orientations of applied magnetic field thus simulating the effect of an assembly of randomly orientated crystallites. A completely rigorous computation of powder spectra would involve diagonalizing the spin Hamiltonian for many differing orientations of magnetic field, which would require large amounts of computer time, not only because of the need to diagonalize a 6 × 6 complex matrix several times for each direction, but because of the large number of orientations that would have to be chosen to obtain a reasonable signal-to-noise ratio. In the range under examination the powder spectrum of Fe^{3+}/TiO_2 would extend from about 0.08 to 0.5 T and if the spectrum were evaluated at only 800 points (i.e. 5.25×10^{-4} T) it would require about eight million orientations to be used to obtain a signal-to-noise ratio of about 100:1. A much simpler method was used which is fully described in reference [4].

There are only two observed transitions in Fe-doped rutile. These are the $-\frac{1}{2} \rightarrow +\frac{1}{2}$ and $-\frac{3}{2} \rightarrow +\frac{3}{2}$ and as there is a large zero-field splitting the spectrum can be simulated by two completely independent transitions each with an effective spin $S' = \frac{1}{2}$. This results in the use of effective g values for each transition and these are shown in Table I. (The use of effective g values has been reviewed by Pilbow [5].)

All these can be measured experimentally except for g_y for the $\pm\frac{3}{2}$ transition. In fact only the $\pm\frac{1}{2}$ transition is seen in this direction as the spacing for the $\pm\frac{3}{2}$ Kramers doublet grows to a maximum of about 8 GHz at a field of about 0.35 T and then decreases. The value chosen gave a reasonable approximation to the true behaviour in the field range $0 \rightarrow 0.5$ T. As the powder spectrum is spread over a wide range of field, account must be taken of the g^{-1} factor noted by Aasa and Vanngard [6]. They pointed out that as EPR is a field-swept technique, the transition probability is proportional to g^{-1} for a transition of effective spin $\frac{1}{2}$. The simulations with and without the g^{-1} factor both give good agreement with experiment as regards g values, but only the simulation with the g^{-1} correction (Fig. 1c) shows the correct amplitude of the observed features. In the simulations there is an additional small peak at about 0.42 T which was not seen experimentally though

TABLE I Effective values for Fe^{3+}/TiO_2

g	$\pm\frac{1}{2}$	$\pm\frac{3}{2}$
g_x	1.571	5.64
g_y	8.818	1.0
g_z	3.465	2.564

this could be due to the fact that its amplitude is comparable to the noise and so it would not be visible. The same procedure was adopted to simulate the Cr^{3+} spectra (Fig. 2b). The results are less clear because the effect of other lines is much larger in the Cr^{3+} samples but the Cr^{3+} spectra can be easily identified both from the effective g values and from the simulation procedure.

These experiments have opened the way for an EPR examination of the behaviour of rutile pigments rather than the single crystals. It has been reported by several authors [7, 8] that the method by which rutile is doped, and whether the impurity is present initially when the crystal is grown or subsequently doped, has an effect on the preferred site for the impurity. Work is continuing to identify the other observed features and also to find spectra of other ions, for example nickel and manganese, both of which can exist in different sites with different charge states in rutile.

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Reaction sintering of $ZnO–Al_2O_3$ mixtures

In previous work, attention has been focussed on reaction sintering [1], and more specifically on the system $ZrSiO_4–Al_2O_3$ which has been studied both by pressureless reaction sintering [2] and by reaction hot-pressing [3]. It has been shown that the $ZrSiO_4–Al_2O_3$ system densifies during the reaction process and one of the main results obtained has been that it is possible to correlate the densification kinetics with the reaction kinetics at least for the intermediate stage of the overall process.

The present work reports the results obtained by studying the pressureless reaction sintering of a system which expands during the reaction process, namely, the $ZnO–Al_2O_3$ system, in which ZnO and Al_2O_3 react in the solid to form a unique stable compound $ZnAl_2O_4$ of a normal spinel structure. An attempt is made to exploit the information provided by the co-existence of the solid-state chemical reaction and the expansion of the material in order to develop a model in which the kinetics of the reaction and the kinetics of the expansion are quantitatively correlated.

The kinetics of the solid-state reaction, as well as the mechanism of formation of $ZnAl_2O_4$, have been studied by various authors [4, 5]. From their work it has been concluded that, firstly, by using alumina grains with sizes larger than the ZnO grains, classical diffusional (Valensi–Carter) models can be applied to the results and, secondly, that the formation of zinc aluminate spinel proceeds through a three-step reaction sequence:

(a) the formation of a solid solution of zinc oxide in alumina oxide;

(b) the formation of a disordered spinel structure;

(c) the formation of the ordered spinel.

So it has been determined that the overall process can be seen as a one-way transfer [4, 6, 7] of ZnO to alumina grains.

The raw materials used (greater than 99.5 wt% purity) were ZnO and Al_2O_3 A15 SG, obtained from UCB, Belgium and from Alcoa, USA, respectively. The grain-size distributions of ZnO and Al_2O_3 were measured using a

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