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Photo-sensitive ESR spectra in Fe/TiO_2 powders

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Using a 9 GHz spectrometer, changes in the amplitude of the Fe^{3+} feature in the ESR spectra of a series of pigment-like iron-doped rutile powders have been monitored during and after optical irradiation. The doping levels ranged from 30 to 670 ppm Fe. The measurements were conducted using filtered radiation from a mercury lamp as the optical source and were made at temperatures within the range 4 to 300 K. In contrast to the previously reported situation in iron-doped single-crystal rutile it was found that the Fe^{3+} concentration was only affected by light of wavelength greater than 700 nm. The results are discussed in terms of the deep impurity level system proposed by Mizushima *et al.* [4] and it is suggested that, for powders, the more distorted nature of the lattice introduces a broad set of defect states in the band gap.

1. Introduction

The considerable interest in rutile pigments arises partly through their use in a wide variety of technologies such as those involving plastics, rubber leather or soap and not least, owing to rutile's superior qualities as regards excellent light scattering coupled with minimal light absorption [1] or because of its use in the manufacture of paints. In the latter application, where degradation during use is a matter for concern, it appears that in some paint degradation processes the pigment particles can act as catalysts for decomposition of the organic binder and there is some evidence that the addition of transition metal ions as dopants gives an increase in durability. Consequently, it is important to characterize these defect centres and to examine their photo-electron behaviour. For the most part thermally stimulated conductivity [2] and thermoluminescent [3] techniques have been used for this but some alternative approaches have been reported [4–6] which emphasize the advantages magnetic resonance techniques have in providing information on the origin and identity of each trapping centre as well as the more usual trapping parameters such as trap density, capture cross-section and ionization energy. As regards trapping centres in iron-doped rutile, however, the only literature references to photo-sensitive ESR studies apparently refer to single-crystal material. Consequently, the present work was undertaken in an attempt to establish whether the photo-electronic properties of iron-doped pigment-like rutile powders, (which from the industrial point of view are the most appropriate form of the material), were the same as those for bulk single crystals of the same composition.

2. Impurity levels in single crystal Fe/TiO_2

The deep impurity levels of some iron group impurities in rutile have been examined by Mizushima *et al.* [4] using two different magnetic resonance methods. The first method relied on moving the Fermi level and looking for changes in valence state while the second involved irradiating crystals with monochromatic radiation of energy less than the band gap and monitoring any resultant valence changes. In the interpretation of their data, Mizushima *et al.* used a model based mainly on the semi-empirical theoretical calculation first made by Allen [7] and consequently, the validity of the energy level diagram they suggest is limited by the exactness of the assumptions made in Allen's calculation.

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2.1. Theoretical determination of energy levels

It is helpful first to summarize Allen's method, an appraisal of which has been given in more detail by Eggleston [8]. When an electron is taken from an impurity ion and put into the conduction band the configuration of that ion changes from, say, d^n to d^{n-1}. Consequently, to find the depth of the impurity below the conduction band it is necessary to find the difference between these two levels. Using the approximations of crystal field theory, equations for the configuration energies (tabulated for transition metal ions by Griffith [9]) can be written down; these involve on the one hand quantities representing the electrostatic terms which split the degeneracy of the d-electrons and the crystal field splittings (which may be estimated experimentally from optical measurements on crystals) and on the other contributions due to the core and spherically symmetrical part of the crystal potential together with the Racah parameters originating from electrostatic interactions within the d-shell, all of which are more difficult to determine. For some materials, for example ZnS, sufficient experimental data exists for the values of the required parameters to be estimated with fair accuracy. This unfortunately does not apply to rutile; here the only reliable experimental result in doped TiO_2 is for the crystal field splitting, $\Delta = 17\,500\,cm^{-1}$, for the Cr^{3+} ion. Consequently, Mizushima *et al.* have through necessity made a series of approximations and estimates based on the few results known for other oxides. Allen gives a range of error of about 0.7 eV for some levels even in a situation where the parameters are quite well known so that it is to be expected that for doped rutile (where there is a great lack of basic information) the results, which are reproduced in Fig. 1, could be in error by a considerably larger amount.

2.2. Experimental determination of energy levels

2.2.1. Lithium doping

Lithium atoms in interstitial sites in rutile make shallow donors and consequently, these can supply electrons with a resulting rise in the Fermi level. The valence states of the impurity ions can be detected using ESR methods and, as the energy of the Fermi level is related to the lithium concentration, the Fermi level can be swept up to the conduction band. It is important to notice that the exact relationship between the energy of the Fermi level and the lithium concentration is not known; the information obtainable is, therefore, limited but nevertheless the method has been used by Misushima *et al.* and gave the data shown in Fig. 2.

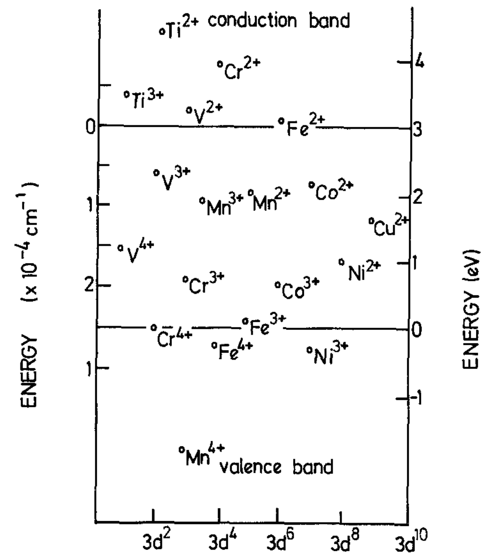

Figure 1 Previously proposed energies of impurity ions in rutile (after Mizushima *et al.* [4]).

2.2.2. Photo-sensitive ESR measurements

Measurements of the effect of optical irradiation of the ESR spectrum provide an alternative exper-

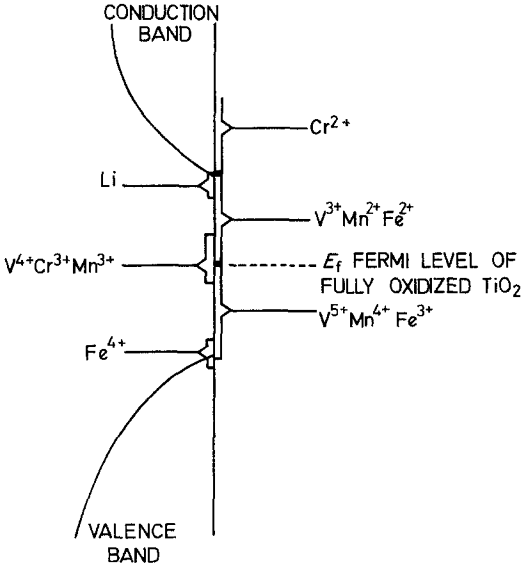

Figure 2 Energy levels of transition metal ions in TiO_2 as determined by the Li-doping method (after Mizushima *et al.* [4]).

TABLE I Analytical data for Fe/TiO_2 powders examined (a) Impurity levels in undoped rutile powder

Major impurities		Minor impurities			
Constituent	Concentration (wt %)	Constituent	Concentration (ppm)	Constituent	Concentration (ppm)
Al_2O_3	1.80	CaO	< 20	Pb	< 10
SiO_2	0.03	ZnO	< 20	K_2O	20
P_2O_5	0.03	Fe	< 10	Nb_2O_5	< 10
SO_3	0.03	Sn	< 20	Sb_2O_3	< 20
		ZrO_2	< 20	Cl	< 50

(b) Doping level determinations

Sample reference	Intended iron concentration (ppm)	Measured iron concentration (ppm)
1	10	30
2	50	60
3	100	100
4	150	110
5	250	170
6	500	290
7	1000	670

imental method for determining the position of paramagnetic impurities in the band gap. In this way Mizushima *et al.* monitored the ESR signals from V^{4+}, Cr^{3+}, Fe^{3+} and Mn^{4+} and, by plotting the changes in signal amplitude as functions of the wavelength of the monochromatic light used for irradiation, deduced the energy level scheme shown in Fig. 3; the amplitude of a given *g*-value ESR signal gives a direct measure of the number of ions of a particular dopant in the same valency state and localized environment so that by finding the energies of the light required to increase or decrease the concentration of a particular ion estimates of the respective depths of the ions below the conduction band could be made. Figs. 1 and 3 show that there was about 1 eV difference in the estimates for the position of the Mn^{3+} level. Two other features are important. Firstly, analysis of the ESR results revealed two sets of states: one (E_1) was centred at 2 eV below E_c and appeared to be due to surface states while the other (E_2) was attributed to bulk defect states (possibly cation vacancies) probably introduced by the doping technique used. Secondly, comparison of Figs. 1 and 3 shows that the energy level scheme derived from the experimental data departs significantly from the theoretical model.

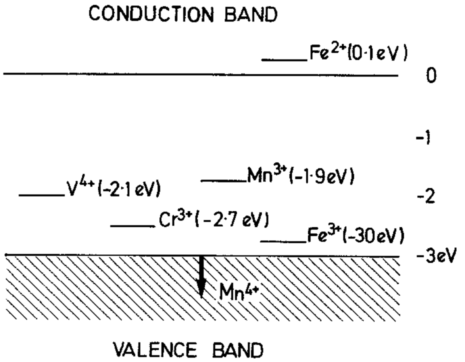

Figure 3 Location of M^{m+}:$3d^n$ levels in TiO_2 as determined by photosensitive ESR spectra (after Mizushima *et al.* [4]).

3. Experimental techniques

3.1. Preparation of powders

All the pigment-like powders studied here were made by Tioxide International Ltd (Central Laboratories) using the chloride process. In brief, this consisted of the formation of titanium tetrachloride by heating mineral rutile in chlorine, purification of the tetrachloride and its subsequent oxidation (at between 1200 and 1600° C in oxygen) to form undoped rutile powder; during manufacture small amounts of alumina were added to promote the formation of the rutile rather than the anatase phase and all the samples contained at least 99.9% of the rutile phase. Various levels of iron doping were introduced as follows. Initially, a solution of ferric chloride was mixed with the undoped powder (in the proportions 100 solution to 20 g TiO_2 powder), the concentration of the solution being chosen to give the required iron dopant concentration; next, the mixture was dried and finally heated for 12 h at 600° C. The doped powders were analysed by both X-ray fluorescent and mass spectroscopic techniques; analytical data are given in Table I, and this shows that the preparative techniques enabled a range of powders containing between about 30 and 670 ppm Fe to be made, there being no other paramagnetic impurities present above trace level.

3.2. ESR and irradiation techniques

All the electron spin resonance observations were taken using a Varian V4502-15 9 GHz specrometer

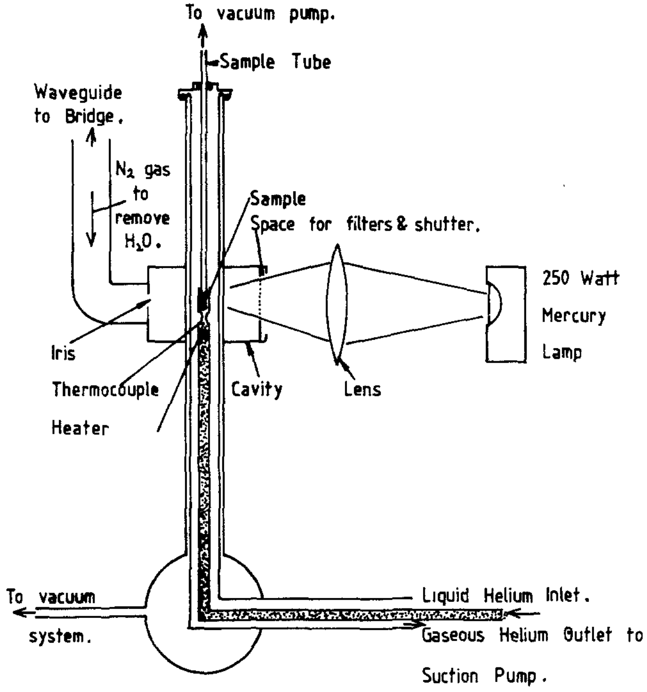

Figure 4 ESR cryostat and optical irradiation facilities.

which was fitted with an Oxford Instruments ESR 9 liquid helium cryostat and DTC2 temperature controller which enabled measurements to be made at selected temperatures between 3.8 and 300 K. The spectrometer was used in a conventional manner [8, 10] to give output spectra in first derivative form. The ESR 9 is a continuous flow cryostat. Liquid helium is sucked from its containing dewar through a flexible syphon into a stainless steel feed capilliary which takes coolant through the body of the cryostat to the bottom of the sample, Fig. 4. Cold helium gas then flows over a heater and thermocouple before reaching the sample, after which it exhausts through an annular space round the feed capilliary to cool the syphon. A diaphragm pump is used to avoid contamination of the helium gas. The temperature can be adjusted by alteration of either the heater current or gas flow rate and could be controlled to within ± 0.1 K.

To provide the irradiation facilities, the end wall of the microwave cavity was slotted to give 50% transmittance for optical radiation without appreciable degradation of the 9 GHz Q-factor. Light from a 250 W mercury lamp, focused by a lens on the sample, was used as the optical irradiation source. Filters and a shutter could be placed in front of the cavity if required. Silica tubes (Spectrosil) of 2 mm bore, were used as specimen holders as these did not contribute any ESR signals; one end of a specimen tube was sealed and, after insertion of the powder, the other was attached to a vacuum system so as to prevent solidification of residual gas in the tube. It was found that, at the doping levels examined, about 0.5 g powder was sufficient to give adequate signal-to-noise ratios in the ESR powder spectra.

4. Results

Monitoring the ESR spectra during and after optical irradiation revealed two main effects, namely the production of a light-induced centre with a g-value near $g = 2.00$ and changes in the amplitude of the feature of at $g = 8.18$ due to substitutional Fe^{3+}. Some details of the light-induced centre, which appears to have previously been unreported and which will be discussed in a separate publication, have been given by Eggleston [8]; here we are concerned primarily with the effects produced by optical irradiation on the Fe^{3+} spectrum, the amplitude of which was light-dependent at low temperatures.

4.1. Unfiltered radiation

The initial measurements were made with no filter. When the specimens were irradiated at temperatures below about 40 K the amplitude of the feature in the ESR powder spectrum due to substitutional Fe^{3+} decreased. An example is given in Fig. 5 from which it can be inferred that, since the ESR linewidth did not change, the number of Fe^{3+} ions

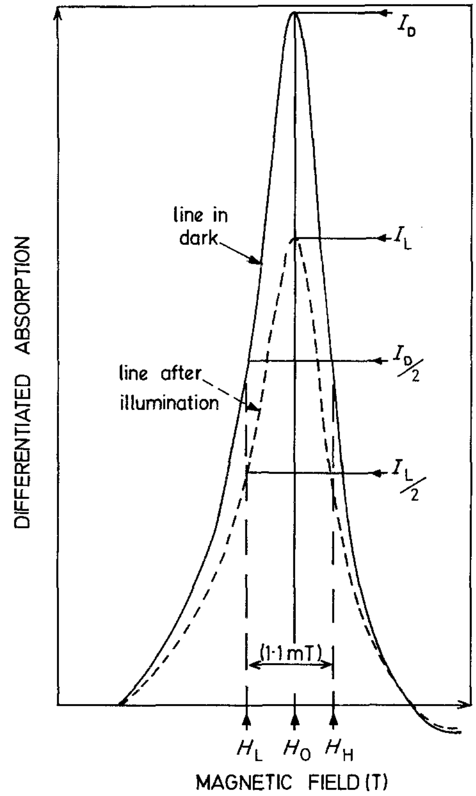

Figure 5 Effect of light on the Fe^{3+} substitutional feature; specimen 7, 15 K; $H_0 = 0.0793$ T $(H_H - H_L) = 1.1$ mT.

in this type of site had decreased. This experiment was repeated at a variety of temperatures between 5 K (the lowest temperature which could readily be obtained with the circulating gas cryogenic system) and 40 K and these results are shown in Fig. 6. Here the vertical axis shows the change in the number of the Fe^{3+} ions expressed as the ratio (I_L/I_D) where I_L and I_D are the line intensities in light-irradiation and dark conditions, respectively. No changes in line amplitude resulting from irradiation were seen at temperatures above 40 K. As Fig. 6 demonstrates, there is close agreement between samples containing 290 and 670 ppm Fe and for both samples the most marked change occurred near 10 K. When the irradiating light was removed the signal amplitude was restored to its original pre-irradiation value.

4.2. Filtered radiation

The next experiment was to observe the effect of varying the wavelength of the illuminating light in the same temperature range. For this a different method of recording the ESR spectrum was adopted. Instead of sweeping the magnetic field through a field range, it was carefully set at the value corresponding to the peak of the Fe^{3+} feature so that changes in the amplitude of the line could be continuously monitored. Fig. 7 shows the effect of several filters. At first the specimen was in the dark and then a shutter was opened causing the signal amplitude to decrease to the level marked [1]; various filters were then introduced in turn and the shutter finally shut to check any drift in the dark signal amplitude level. The introduction of either 350 or 400 nm band pass filters had virtually the same effect as closing the shutter. Chemical actinometry [11] of a similar lamp system suggests that these filters could reduce the number of incident photons to approximately 10 and 5% of the initial flux. However, since any changes of greater than 5% could have been detected in this experiment the overall conclusion is that overall

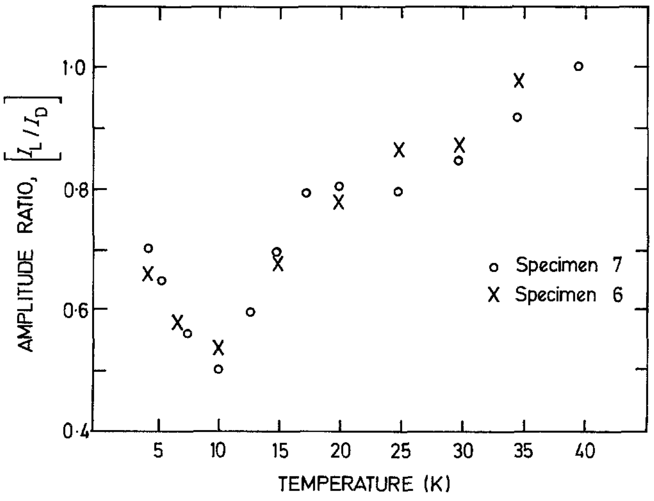

Figure 6 Change in amplitude of the Fe^{3+} feature with illumination.

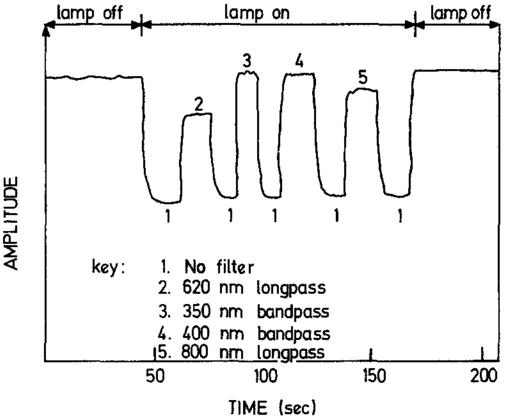

Figure 7 Effect of filter on amplitude of Fe^{3+} feature during optical irradiation.

these experiments showed that the light of bandgap energy (i.e. of wavelength equal to or greater than 400 nm) had no effect on the line amplitude but that the light of lower temperature energy did cause changes.

4.3. Recovery rates

A third set of measurements were made on the Fe^{3+} ESR lines. The previous data showed that when the illumination ceased the amplitude of the Fe^{3+} feature increased again. In this group of experiments the rate at which the line regained its original amplitude after irradiation with light of a given wavelength was monitored and plotted as a graph of log $(I_D - I_t)$ against time where, as previously, I_D is the amplitude of the line in dark conditions and I_t represents the intensity at a time, t, after stopping the illumination. An example is given in Fig. 8a. If it is assumed that the recovery back to the original line amplitude is exponential it can be characterized by a relaxation time, t, defined by the relation

$$I_t = I_D - (I_D - I_L) \exp^{-t/\tau} \qquad (1)$$

where I_L is the equilibrium signal amplitude under irradiation. Rewriting Equation 1 as

$$\ln \frac{(I_D - I_t)}{(I_D - I_L)} = -\frac{t}{\tau} \ ,$$

shows that, on the assumption of single exponential recovery, plotting ln $(I_D - I_t)$ against t should give a straight line of slope $(-1/\tau)$. The values of τ were calculated and one of the results, for specimen 7, is given in Fig. 8b for temperatures above 5 K. It was not possible to obtain data above about 20 K because the changes in amplitude then become comparable to noise. The main feature revealed is that τ increases with temperature.

5. Discussion

Most of the previously reported studies have been concerned only with single-crystal material (e.g. Faughan and Kiss [12], Mizushima *et al.* [4]). These authors all report changes in the iron spectra at 77 K but their results are somewhat different; thus Mizushima *et al.* show the Fe^{3+} spectrum is most affected by light of about 3 eV (i.e. greater energy than the band gap of rutile), while Faughan reports changes in amplitude of the Fe^{3+} lines by using light of 400 nm wavelength. In a more recent study, Hodgskiss reported observing amplitude changes at temperatures up to 200 K [13]; Hodgskiss *et al.* [6] also made some measurements on nominally pure pigment-like rutile powders but did not specifically examine iron-doped material. A summary of some previous results is given in Table II, which also contrasts the main features then found with those observed in the present study.

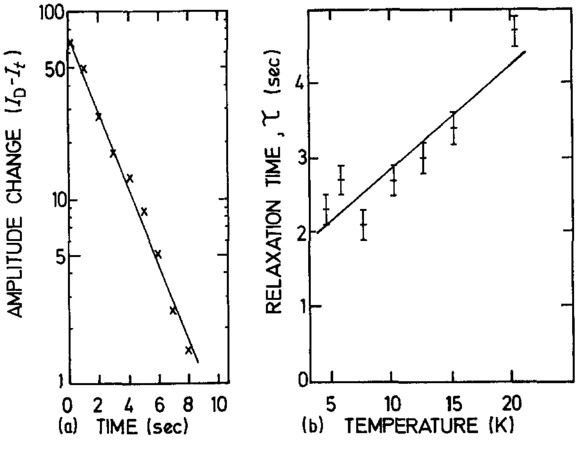

Figure 8 Recovery of Fe^{3+} feature after irradiation (specimen 7): (a) typical recovery data; (b) variation of relaxation time with temperature.

TABLE II Comparison of results of optically irradiating Fe^{3+}:TiO_2

	Faughan and Kiss [12]	Mizushima *et al.* [4]	Hodgskiss *et al.* [5, 6, 10, 13]	Present work
Type of sample examined	Single crystal Doped with Fe and Mo	Oxidized single crystal Doped with iron	Single crystal Doped with Fe, Ni, Cr and Mn	Pigment-like powders Doped with Fe
Wavelengths used to alter population	400 nm	400-850 nm Maximum change at wavelength > 400 nm	400 nm Hg lamp with Cu_2SO_4 solution and filter	$\lambda < 700$ nm No change with $\lambda = 400$ or 350 nm
Temperature at which effects were observed	77 K Not seen at room temperature No comment about other temperatures	77 K No comments about other temperatures	4.2 K to 230 K Fe^{3+} concentration reduced over entire range of temperature	4.2 K to 40 K No changes observed above 40 K
Residual effect on Fe^{3+} population after illumination ceased	No comment made	Yes	Yes	No

In order to provide a background against which to interpret the differences in behaviour observed with powders, it is useful to summarize first the explanations given by Muzushima *et al.* [4]. According to these authors, there exist in the band gap of rutile two sets of levels, E_1 and E_2, which are related respectively to surface states and to defects in the bulk of the crystal (Fig. 9). The Fe^{3+}:d^5 level is mostly occupied at equilibrium as it is just above the valence band but the Fe^{2+} level is close enough to E_c to be accessible as is also the Fe^{4+}:d^4 level. Thus a photo-excitation between one isolated Fe^{3+} ion and another would create both a Fe^{2+} ion and a Fe^{4+} ion as a result of the reaction

$$2Fe^{3+} + h\nu \rightarrow Fe^{2+} + Fe^{4+}\,.$$

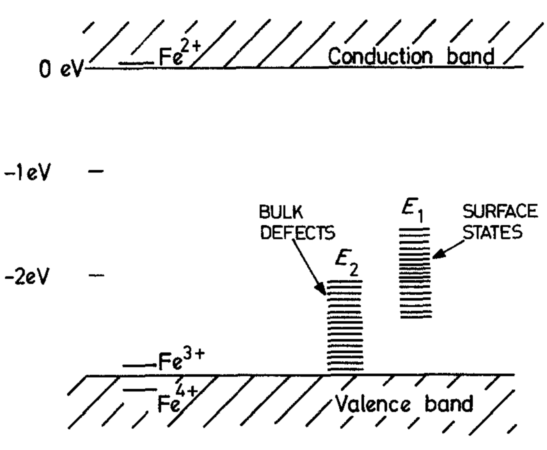

Figure 9 Energy level diagram of Fe:TiO_2 according to Mizushima *et al.* [4].

Although excitations can occur from E_1 to the conduction band for $\lambda < 700$ nm only wavelengths having $\lambda < 650$ nm affect the population of the Fe^{3+} level; this suggests that the Fe^{2+} level is just above the conduction band as shown. Light of wavelength $\lambda < 650$ nm excites electrons from E_1 to the Fe^{2+} level following

$$e^- + h\nu + Fe^{3+} \rightarrow Fe^{2+}\,.$$

When the incident energy $h\nu$ becomes equal to the energy difference $[E_c - E(Fe^{3+})]$ a sharp reduction in the intensity of the line due to the Fe^{3+} ion is seen because of direct excitations to the conduction band described by

$$2Fe^{3+} + h\nu \rightarrow Fe^{4+} + Fe^{2+}\,.$$

The powder samples discussed here show contradictory behaviour in that light of wavelength, $\lambda < 700$ nm produced no change and, in fact, the Fe^{3+} concentration was only affected by light having $\lambda > 700$ nm. One reason for the absence of any reduction in Fe^{3+} concentration during irraditiation with light of $\lambda < 700$ nm could be that any electrons excited to the conduction band are trapped at sites other than the Fe^{2+} levels. If there were a large number of traps just below the conduction band these would trap electrons before they could convert a neighbouring Fe^{3+} ion to a Fe^{2+} ion. There is some evidence for the existence of such a level because a separate ESR signal is generated by light of wavelength about 400 nm [8] and so transitions requiring this amount of energy do occur; also, as these samples are in an oxidized state, they are likely to have very low conductivity so there is only a small probability of the excited electrons travelling far enough to be trapped Fe^{2+} states. An explanation is still required, however, for the reduction in Fe^{3+} concentration at wavelengths exceeding 700 nm. There is evidence [8] from the analysis of the linewidth of the Fe^{3+} ESR powder spectrum (which will be reported separately) that the doped rutile crystallites forming the powders are strained. This strain could lead to more states in the band gap. Excitations of less than band gap energy could then excite electrons from a Fe^{3+} ion to a higher level and so lead to an increase in the Fe^{4+} concentrations in the process

$$Fe^{3+} + h\nu \rightarrow Fe^{4+} + e^- .$$

After the irradiation ceases, these electrons are retrapped at the Fe^{3+} level restoring the number of Fe^{3+} ions. It should be emphasized that the behaviour of pigment-like rutile powders may be considerably different from those of single crystals of equivalent composition but that this can be explained by the increased number of states in the band gap coupled with the more distorted nature of the crystal lattice in powders.

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