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# Influence of iron concentration on the electron spin resonance spectrum of $Fe^{3+}$ in rutile

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## Abstract

Electron spin resonance spectra of iron-doped rutile were studied at room temperature for iron concentrations between 0.03 and 1.00 mol%. The results suggest that the range of the exchange interaction between $Fe^{3+}$ ions is about 0.55 nm.

## 1. Introduction

Rutile ($TiO_2$) is a ceramic material with many industrial applications whose properties can be changed significantly by the presence of transition elements such as iron, chromium and manganese [1–3]. Electron spin resonance (ESR) spectroscopy is a convenient method of studying these transition-metal impurities within the $TiO_2$ structure. In the present work we investigated the effect of iron concentration on the ESR spectrum of $Fe^{3+}$ in polycrystalline rutile. The importance of this investigation is twofold. First, once the effects of iron concentration on the spectrum are known, it is possible to use ESR results to measure, rapidly and non-destructively, small concentrations of iron in commercial $TiO_2$; second, knowledge of the range of the exchange interaction between $Fe^{3+}$ ions is essential for a better understanding of the magnetic properties of iron-doped rutile.

## 2. Background

### 2.1. Electron spin resonance of iron-doped rutile

Analysis of the ESR spectrum in single-crystal iron-doped rutile [4, 5] shows that trivalent iron atoms substitutionally replace titanium ions in the lattice. The spectrum can be fitted to the Hamiltonian

$$\begin{aligned}\mathscr{H} = {} & g\beta \boldsymbol{H}\cdot\boldsymbol{S} + D[S_z{}^2 - (1/3)S(S+1)] + E(S_x{}^2 - S_y{}^2)\\ & + (a/6)[S_x{}^4 + S_y{}^4 + S_z{}^4 - (1/5)S(S+1)(3S^2+3S-1)]\\ & + (F/180)[35S_z{}^4 - 30S(S+1)S_z{}^2 + 25S_z{}^2 - 6S(S+1)\\ & + 3S^2(S+1)^2] \qquad (1)\end{aligned}$$

with $g = 2.00$, $D = 20.12$ GHz, $E = 2.19$ GHz, $a = 1.08$ GHz, $F = 0.51$ GHz [5].

The spectrum of iron-doped rutile powder has been investigated [3, 6]; the peaks in the powder spectrum corresponding to the $Fe^{3+}$ ion are easily identified as the turning points of the Hamiltonian (1) (see Section 3.2). The results suggest that when lightly doped $TiO_2$ is heat treated at high temperatures (above 900 °C), essentially all the iron atoms are converted to substitutional $Fe^{3+}$ ions.

### 2.2. Electron spin resonance of dilute solid solutions

The theory of dipolar broadening in dilute solid solutions was developed in ref. 7 and extended in ref. 8, to take exchange interactions into account. Its main results can be summarized as follows:

(i) the lineshape is a truncated Lorentzian;

(ii) the peak-to-peak first derivative linewidth may be expressed as

$$\Delta H_{pp} = c_1 f_e \qquad (2)$$

(iii) the intensity of the absorption line is

$$I = c_2 f_e \qquad (3)$$

Here $c_1$ and $c_2$ are constants and $f_e$ is the concentration of substitutional ions of the paramagnetic impurity not coupled by the exchange interaction, which can be expressed as

$$f_e = f(1-f)^{z(r_c)} \qquad (4)$$

where $f$ is the impurity concentration, $z(r_c)$ the number of cation sites not included in a sphere of radius $r_c$, and $r_c$ the effective range of the exchange interaction.

Although the theory was developed assuming that the spin energy states are degenerate, it can be applied

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to the case of fine splitting of electronic levels, provided that eqn. (2) is replaced by

$$\Delta H_{pp} = \Delta H_0 + c_1 f_e = \Delta H_0 + c_1 f(1-f)^{z(r_c)} \qquad (5)$$

where $\Delta H_0$ is the concentration-independent linewidth due to stresses in the crystal lattice [9].

## 3. Experimental procedure and results

### 3.1. Sample preparation

The chromium-doped samples used in this work were prepared from pure oxides by grinding them together and then firing the mixture for 16 h at 1100 °C in air. Actual iron concentrations were determined by chemical analysis. The heat treatment in an oxidizing atmosphere was long enough to convert almost all the iron ions to the trivalent state, which is the most stable state in rutile [3]. The concentration of iron ions at substitutional titanium sites was therefore assumed to be equal to the total iron concentration.

### 3.2. Magnetic resonance measurements

All magnetic resonance measurements were performed at room temperature and 9.50 GHz. The spectrum of a typical sample is shown in Fig. 1, where the lines are labelled according to the convention used in ref. 5. In principle, single-crystal linewidth data can be extracted from any of the lines in the powder spectrum. The most convenient for this purpose, however, is the $1/2 \rightarrow -1/2(x)$ line observed at magnetic fields near 0.2 T. Computer simulations of the powder spectrum (unpublished) show that the field difference between the positive and negative peaks of this line, $H_p - H_n$, is directly proportional to the single-crystal linewidth over a wide range of linewidth. In other words, we have

$$\Delta H_{pp} = c(H_p - H_n) \qquad (6)$$

where $\Delta H_{pp}$ is the single-crystal linewidth.

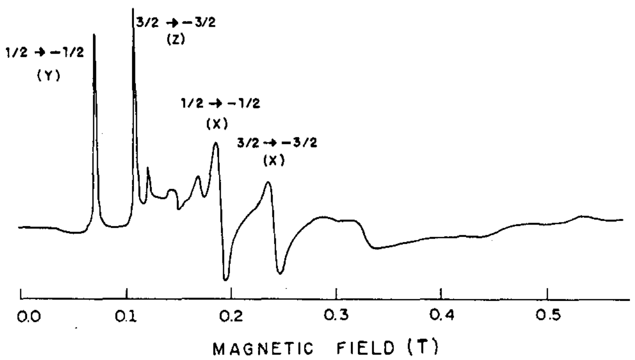

Fig. 1. ESR spectrum of a rutile sample doped with 0.2 mol% iron.

The constant $c$ in eqn. (6) can be determined by comparing the spectra of single crystals and powders doped with the same concentration of iron ions. Comparing one of our samples with Carter's single crystals [4], known to contain 0.03 mol% iron, we found that $c = 0.283$. The experimental results obtained by applying eqn. (6) to our data with $c = 0.283$ are listed in Table 1, along with the line intensity data, obtained from the expression $I = A\Delta H_{pp}^2$, where $A$ is the line amplitude.

## 4. Discussion

The theoretical concentration dependence of the peak-to-peak linewidth $\Delta H_{pp}$ given by eqn. (5) is shown in Fig. 2 for $\Delta H_0 = 1.80$ mT and nine different ranges of the exchange interaction. The values of $r_c$ and $z(r_c)$ for the first nine coordinate spheres are listed in Table 2, where $n$ is the number of the order of each coordinate sphere ($n = 1$ includes no neighbouring sites, $n = 2$ includes the nearest-neighbour sites, and so on). The values of $z(r_c)$ are those appropriate to the tetragonal lattice of rutile [10]; the values of $r_c$ were calculated

TABLE 1. Experimental results for the $Fe^{3+}$ $TiO_2$ system ($T = 300$ K, $\nu = 9.50$ GHz)

| $f$(mol%) | $\Delta H_{pp}$ (mT) | $I_R$ |
|---|---|---|
| 0.03 | 1.84 | 0.05 |
| 0.10 | 1.93 | 0.15 |
| 0.20 | 2.06 | 0.25 |
| 0.40 | 2.27 | 0.50 |
| 0.60 | 2.47 | 0.65 |
| 0.80 | 2.65 | 0.83 |
| 1.00 | 2.80 | 1.00 |

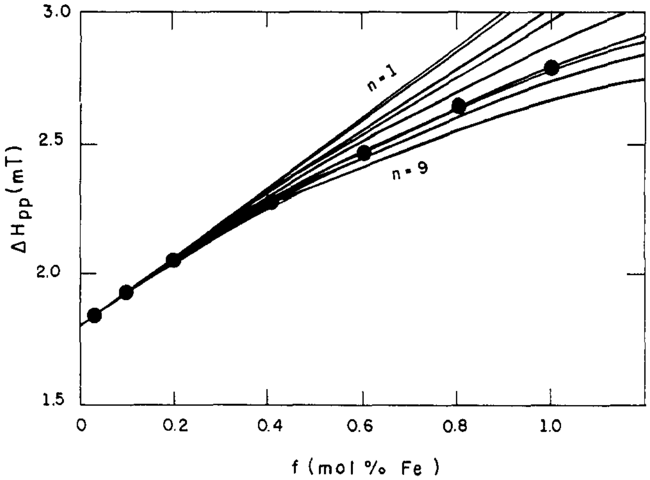

Fig. 2. Concentration dependence of the peak-to-peak linewidth $\Delta H_{pp}$ in iron-doped rutile. The dots are experimental points; the curves represent results of calculations for nine different ranges of the exchange interaction.

TABLE 2. Values of $r_c$ and $z(r_c)$ for rutile

| $n$ | $r_c$ (nm) | $z(r_c)$ |
|---|---|---|
| 1 | 0.00 | 0 |
| 2 | 0.30 | 2 |
| 3 | 0.36 | 10 |
| 4 | 0.46 | 14 |
| 5 | 0.54 | 22 |
| 6 | 0.55 | 30 |
| 7 | 0.59 | 32 |
| 8 | 0.65 | 36 |
| 9 | 0.71 | 44 |

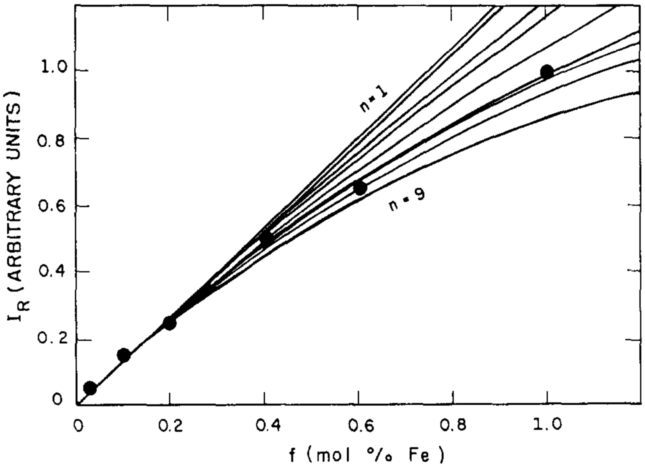

Fig. 3. Concentration dependence of the line intensity $I_R$ in iron-doped rutile. The dots are experimental points; the curves represent results of calculations for nine different ranges of the exchange interaction.

from the lattice constants at room temperature as measured by X-ray diffraction [11], $a = 4.593659$ Å and $c = 2.958682$ Å. The experimental data are also shown in Fig. 2. The experimental results closely fit the theoretical curve for $n = 6$, which corresponds, according to Table 2, to a range $r_c = 0.55$ nm for the exchange interaction.

Figure 3 shows the theoretical (eqn. (3)) and experimental (Table 2) intensity data. The vertical scale is arbitrary and was chosen so as to provide the best fit of the experimental points to the theoretical curve for $n = 6$, or $z(r_c) = 30$. The agreement was found to be fair.

The results suggest that the range of the exchange interaction between $Fe^{3+}$ ions in iron-doped rutile is 0.55 nm, slightly smaller than the range of the exchange interaction between $Cr^{3+}$ ions in the same host lattice [12] and of the same order of magnitude as in the Cr:MgO [8] and Gd:$CaF_2$ [13] systems.

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