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Influence of manganese concentration on the ESR spectrum of Mn^{4+} in rutile

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Abstract

Electron spin resonance spectra of manganese-doped rutile were studied at room temperature for Mn concentrations between 0.10 and 2.00 mol%. The results suggest that the range of the exchange interaction between Mn^{4+} ions is about 0.36 nm, much smaller than the ranges of the exchange interaction between Cr^{3+} and between Fe^{3+} ions, which are 0.59 and 0.55 nm, respectively.

Keywords: Manganese concentrations; Electron spin resonance; Rutile

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 for studying these transition metal impurities within the TiO_2 structure. In the present work, we investigated the effect of manganese concentration on the ESR spectrum of Mn^{4+} in polycrystalline rutile. The importance of this investigation is twofold. First, once the effects of manganese concentration on the spectrum are known, it becomes possible to use ESR results to measure, rapidly and non-destructively, small concentrations of Mn in commercial TiO_2; second, knowledge of the range of the exchange interaction between Mn^{4+} ions is essential for a better understanding of the magnetic properties of manganese-doped rutile.

2. Background

2.1. ESR of manganese-doped rutile

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

$$\mathcal{H} = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \quad (1)$$

with $g_x = 1.995$, $g_y = 1.9909$, $g_z = 1.9898$, $|D| = 12.23$ GHz, $|E| = 3.918$ GHz, $|A_x| = 217$ MHz, $|A_y| = 211.0$ MHz and $|A_z| = 218.1$ MHz [5].

2.2. ESR of dilute solid solutions

The theory of dipolar broadening in dilute solid solutions was developed in Ref. [6] and extended in Ref. [7] 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

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

and (iii) the intensity of the absorption line is

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

where 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

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

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

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

where ΔH_0 is the concentration-independent linewidth due to stresses in the crystal lattice [8].

3. Experimental procedure and results

3.1. Sample preparation

The manganese-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 Mn concentrations were determined by chemical analysis. The heat treatment in an oxidizing atmosphere was long enough to convert almost all the Mn ions to the tetravalent state, which is the most stable state in rutile [4,5]. The concentration of Mn ions at substitutional Ti sites was therefore assumed to be equal to the total Mn concentration.

3.2. Magnetic resonance measurements

All magnetic resonance measurements were performed at room temperature and 9.50 GHz. The spectra of typical samples in the field range from 0.09 to 0.15 T are shown in Figs. 1(a) and 2(a), where the two hyperfine sextets correspond to the $4 \rightarrow 3$ (z) and $2 \rightarrow 1$ (y) transitions [5]. Computer simulations of the powder spectra, such as those shown in Figs. 1(b) and 2(b), were used to determine the single-crystal linewidth from the experimental data. The results are listed in Table 1, along with line intensity data, obtained in the same simulations.

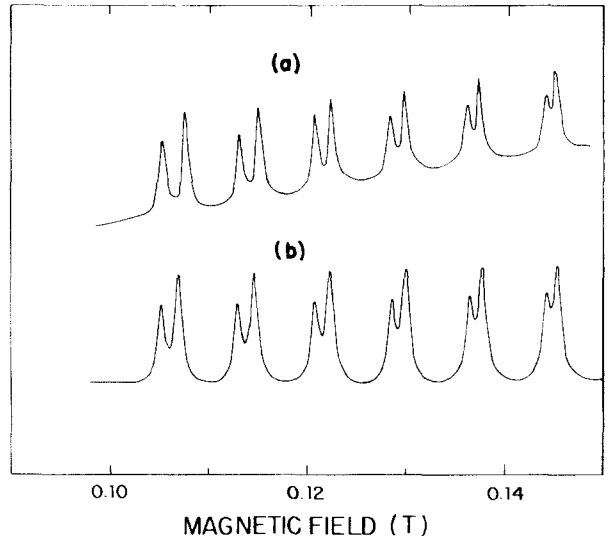

Fig. 1. (a) ESR spectrum of a rutile sample doped with 0.2 mol% Mn. (b) Computer simulation of the spectrum, using the spin Hamiltonian parameters given in the text and a single-crystal linewidth $\Delta H_{pp} = 1.45$ mT.

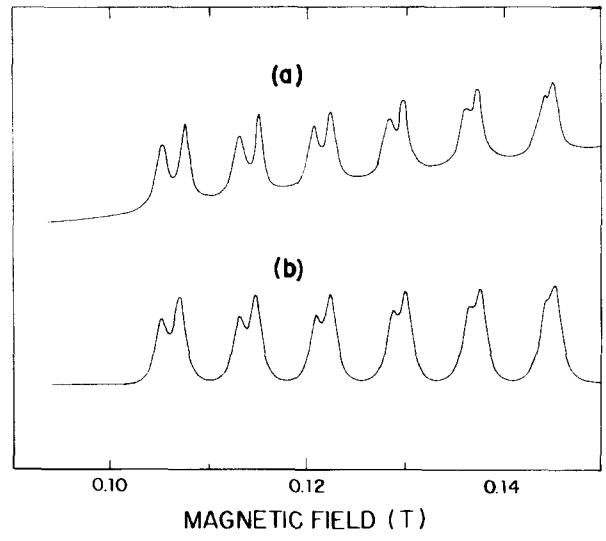

Fig. 2. (a) ESR spectrum of a rutile sample doped with 0.8 mol% Mn. (b) Computer simulation of the spectrum, using the spin Hamiltonian parameters given in the text and a single-crystal linewidth $\Delta H_{pp} = 2.25$ mT.

4. Discussion

The theoretical concentration dependence of the peak-to-peak linewidth, ΔH_{pp}, given by Eq. (5), is shown in Fig. 3 for $\Delta H_0 = 1.20$ mT and four different ranges of the exchange interaction. The values of r_c and $z(r_c)$ for the first four 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, and so on). The values of $z(r_c)$ are those appropriate to the tetragonal lattice of rutile [9]; the values of r_c were calculated from the lattice constants at room temperature as measured by X-ray diffraction [10], $a = 4.593\,659$ Å and $c = 2.958\,682$ Å. The experimental data are also shown in Fig. 3. The experimental results fit the theoretical curve for $n = 3$, which corresponds, according to Table 2, to a range $r_c = 0.36$ nm for the exchange interaction.

Fig. 4 shows the theoretical [Eq. (3)] and experimental (Table 1) 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 $n = 3$, or $z(r_c) = 10$. The agreement was found to be fair.

Table 1
Experimental results for the Mn^{4+}–TiO_2 system (T=300 K, ν=9.50 GHz)

f (mol%)	ΔH_{pp} (mT)	I_R
0.10	1.35	0.15
0.20	1.45	0.30
0.40	1.70	0.50
0.60	2.00	0.70
0.80	2.25	0.90
1.00	2.40	1.40
1.50	3.00	1.65
2.00	3.30	2.20

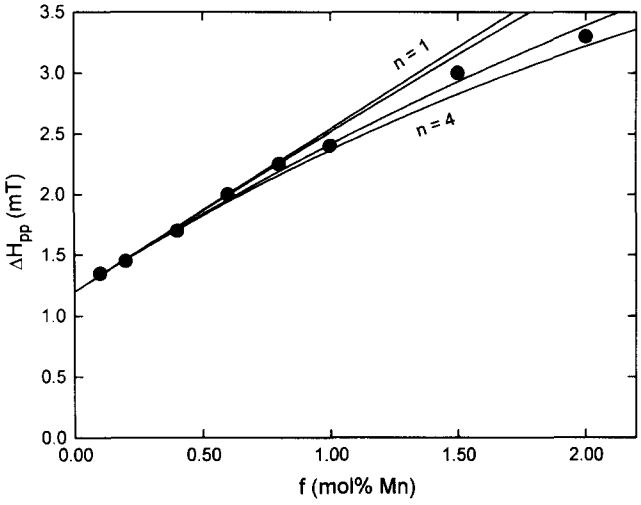

Fig. 3. Concentration dependence of the peak-to-peak linewidth, ΔH_{pp}, in Mn-doped rutile. The circles are experimental points; the curves represent results of calculations for four different ranges of the exchange interaction.

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

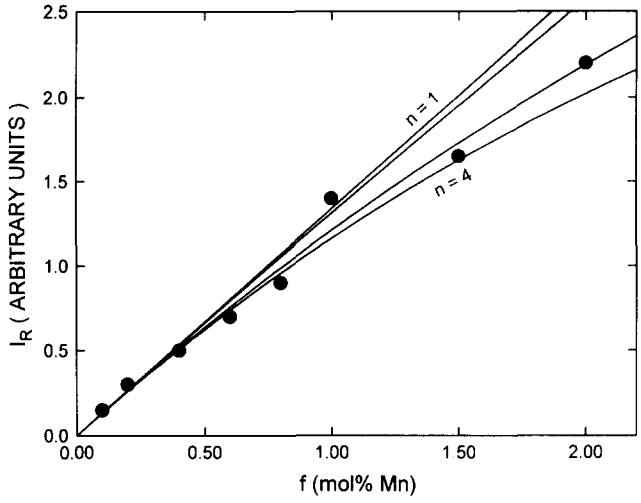

Fig. 4. Concentration dependence of the line intensity, I_R, in Mn-doped rutile. The circles are experimental points; the curves represent results of calculations for four different ranges of the exchange interaction.

The results suggest that the range of the exchange interaction between Mn^{4+} ions in Mn-doped rutile is 0.36 nm, much smaller than the range of the exchange interaction between Cr^{3+} ions, 0.59 nm [11], and between Fe^{3+} ions, 0.55 nm [12], in the same host lattice.

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