

# Electron spin resonance of diluted solid solutions of $\text{Gd}_2\text{O}_3$ in $\text{CeO}_2$

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## Abstract

Electron spin resonance spectra of  $\text{Gd}^{3+}$  in diluted solid solutions of  $\text{Gd}_2\text{O}_3$  in  $\text{CeO}_2$  have been studied at room temperature for Gd concentrations between 0.01 and 1.00 mol%. While in the case of  $\text{Mn}^{2+}:\text{CeO}_2$  samples, both the linewidth and the line intensity go through a maximum between 0.2 and 0.4% Mn and then start to decrease, in the case of  $\text{Gd}^{3+}:\text{CeO}_2$  samples the linewidth and the line intensity increase monotonically with the dopant concentration. This is taken as evidence that in  $\text{Gd}_2\text{O}_3\text{--CeO}_2$  diluted solid solutions there are no clustering effects similar to the ones observed in  $\text{Mn}:\text{CeO}_2$  solid solutions. It is not clear why clustering effects are present in  $\text{Mn}:\text{CeO}_2$  solid solutions and not in  $\text{Gd}:\text{CeO}_2$  solid solutions; however, it seems reasonable to assume that this is due to the fact that the ionic radius of  $\text{Mn}^{2+}$  (81 pm) is about 25% smaller than that of  $\text{Gd}^{3+}$  (107.8 pm). In any case, the fact that  $\text{Gd}:\text{CeO}_2$  solid solutions do not exhibit clustering effects means that ESR linewidth data can be used to estimate the concentration of Gd in  $\text{CeO}_2$  samples, as it is possible to do in several solid solutions of paramagnetic ions in ceramic materials. The results also suggest that the range of the exchange interaction between  $\text{Gd}^{3+}$  ions in  $\text{CeO}_2$  is about 0.89 nm.

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## 1. Introduction

In a recent investigation [1], the study of electron spin resonance spectra of  $\text{Mn}^{2+}$  showed significant clustering effects in  $\text{MnO}_2\text{--CeO}_2$  solid solutions. In the present work, we studied the electron spin resonance spectra of another S-state ion,  $\text{Gd}^{3+}$ , in  $\text{Gd}_2\text{O}_3\text{--CeO}_2$  solid solutions. This investigation is of particular interest because Gd-doped  $\text{CeO}_2$  has been proposed [2,3] as a material for intermediate temperature solid oxide fuel cells (IT-SOFCs).

## 2. Background

### 2.1. ESR of gadolinium-doped cerium oxide

ESR measurements in single-crystal gadolinium-doped cerium oxide [4] show that trivalent gadolinium ions substitutionally replace cerium ions in the lattice. The spectrum can be fitted to the Hamiltonian

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + B_4[O_4^0 + 5O_4^4] + B_6[O_6^0 - 21O_6^4] \quad (1)$$

with  $g = 1.991$ ,  $B_4 = 860 \times 10^{-4} \text{ cm}^{-1}$  and  $B_6 = 2.8 \text{ cm}^{-1}$ .

A recent investigation [5] has shown that this spectrum does not change significantly during heat treatment in gas mixtures such as  $\text{CO}/\text{CO}_2$ ,  $\text{N}_2$  and  $\text{Ar}/\text{H}_2$ , pointing to a very stable charge state.

### 2.2. ESR of dilute solid solutions

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

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Refs. [7,8] to take exchange interactions and clustering effects 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

$$\Delta H_{pp} = \Delta H_o + \Delta H_d = \Delta H_o + c_1 f_e. \quad (2)$$

- (iii) the intensity of the absorption line is

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

where  $\Delta H_o$  is the intrinsic linewidth,  $\Delta H_d$  is the dipolar broadening,  $c_1$  and  $c_2$  are constants and  $f_e$  is the concentration of isolated substitutional ions of the paramagnetic impurity, which can be expressed as

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

where  $f$  is the impurity concentration,  $z(r_c)$  the number of cation sites not included in a sphere of radius  $r_c$ ,  $r_c$  the effective range of the exchange interaction and  $p \geq 1$  is a “clustering factor” defined [9] as the ratio of the actual probability that a neighbor cationic site is occupied to the probability of occupation if the distribution were random. For a random solution,  $p = 1$ ; the larger the value of  $p$ , the stronger are the clustering effects.

### 3. Experimental procedure and results

#### 3.1. Sample preparation

The samples used in this study were prepared from high-purity  $\text{CeO}_2$  and  $\text{Gd}_2\text{O}_3$  powders by grinding them together and then firing the mixture for 24 h at 1200 °C in air. Actual Gd concentrations were determined by chemical analysis. Room-temperature X-ray diffraction patterns of the samples matched, within experimental error, the spectrum [10] of  $\text{CeO}_2$ . No other phases were detected.

#### 3.2. Magnetic resonance measurements

All magnetic resonance measurements were performed at room temperature and 9.5 GHz. The spectrum of a typical sample is shown in Fig. 1. All the lines can be identified as turning points of the Hamiltonian given by Eq. (1). In principle, linewidth and intensity data can be extracted from any of the lines in the powder spectrum. We chose the line indicated by an arrow in Fig. 1, that corresponds to the  $+3/2 \leftrightarrow +1/2$ ,  $\theta = 45^\circ$  transition, because it has a reasonable amplitude and is well separated from the other lines. The results are listed in Table 1.

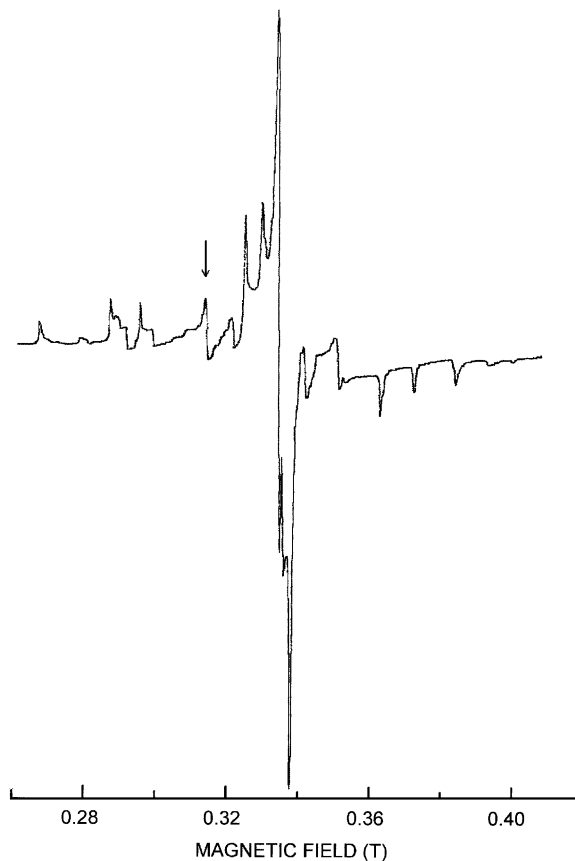


Fig. 1. ESR spectrum of a  $\text{CeO}_2$  sample doped with 0.01 mol% Gd. The arrow shows the line used to measure the linewidth and intensity of the spectrum.

Table 1

Peak-to-peak linewidth  $\Delta H_{pp}$  and line intensity  $I_R$  of the  $+3/2 \leftrightarrow +1/2$ ,  $\theta = 45^\circ$  ESR transition of  $\text{Gd}^{3+}$  in  $\text{CeO}_2$  for several Gd concentrations ( $T = 300$  K,  $\nu = 9.5$  GHz)

$f$ (mol%)	$\Delta H_{pp}$ (mT)	$I_R$ (a.u.)
0.01	0.55	9
0.10	0.97	31
0.20	1.28	54
0.40	1.72	100
0.60	2.00	126
0.80	2.25	146
1.00	2.38	166

### 4. Discussion and conclusions

The experimental data on the concentration dependence of the peak-to-peak linewidth  $\Delta H_{pp}$  and the relative intensity  $I_R$  of the  $\text{Gd}^{3+}$  spectrum are compared in Figs. 2 and 3 with similar data for  $\text{Mn}^{2+}$  in the same host lattice, taken from Ref. [1]. While in the case of  $\text{Mn}^{2+}:\text{CeO}_2$  samples both the linewidth and the line intensity go through a maximum between 0.2% and 0.4% Mn and then start to decrease, in the case of

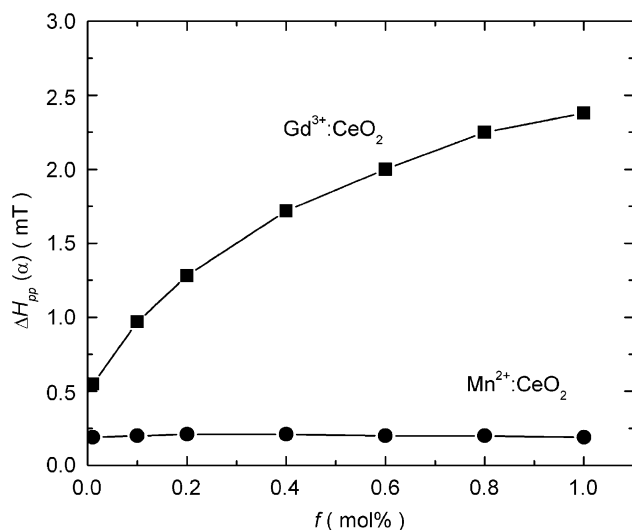


Fig. 2. Concentration dependence of the peak-to-peak linewidth of the spectrum,  $\Delta H_{pp}$ , in Gd- and Mn-doped  $\text{CeO}_2$ .

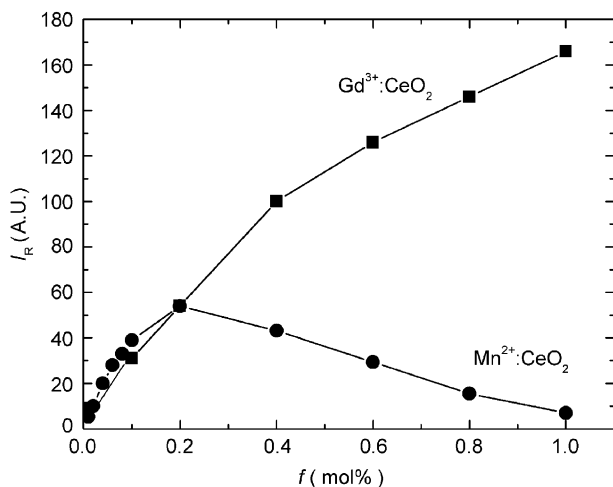


Fig. 3. Concentration dependence of the line intensity of the spectrum,  $I_R$ , in Gd- and Mn-doped  $\text{CeO}_2$ .

$\text{Gd}^{3+}:\text{CeO}_2$  samples the linewidth and the line intensity increase monotonically with the dopant concentration. This is taken as evidence that in  $\text{Gd}_2\text{O}_3\text{-CeO}_2$  diluted solid solutions there are no clustering effects similar to the ones observed in  $\text{Mn}:\text{CeO}_2$  [1],  $\text{Fe}:\text{MgO}$  [7,11] and  $\text{Fe}:\text{CaO}$  [12] solid solutions. The theoretical concentration dependence of the peak-to-peak linewidth  $\Delta H_{pp}$ , given by Eq. (2), is shown in Fig. 4 for  $p = 1$  (no clustering),  $\Delta H_0 = 0.55 \text{ mT}$  and 8 different ranges of the exchange interaction. Since the incorporation of trivalent metal ions in  $\text{CeO}_2$  is compensated via oxygen vacancies, the defect structure of  $\text{CeO}_{2-x}$  should in principle be taken into account in this analysis. However, the Gd concentrations used in this work (between 0.01 and 1.00 mol%) were so low that this effect can be neglected. The values of  $r_c$  and  $z(r_c)$  for the

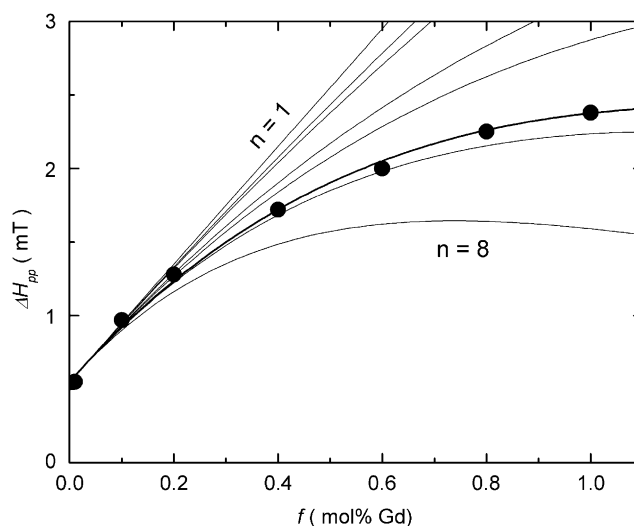


Fig. 4. Concentration dependence of the peak-to-peak linewidth,  $\Delta H_{pp}$ , in Gd-doped  $\text{CeO}_2$ . The circles are experimental points; the curves represent results of calculations for eight different ranges of the exchange interaction.

Table 2

Values of the effective range of the exchange interaction,  $r_c$ , and the number of cation sites not included in a sphere of radius  $r_c$ ,  $z(r_c)$ , for the first 8 coordinate spheres of the  $\text{CeO}_2$  lattice

$n$	$r_c$ (nm)	$z(r_c)$
1	0.000	0
2	0.383	12
3	0.541	18
4	0.663	42
5	0.765	54
6	0.886	78
7	0.937	86
8	1.012	134

first 8 coordinate spheres are listed in Table 2, where  $n$  is the number of the order of each coordinate sphere ( $n = 1$  includes no neighboring sites, and so on). The values of  $z(r_c)$  are those appropriate to the fcc lattice of  $\text{CeO}_2$ ; the values of  $r_c$  were calculated from the lattice constant at room temperature as measured by X-ray diffraction [10],  $a_0 = 0.54110 \text{ nm}$ . The experimental data are also shown in Fig. 4. The experimental data fit the theoretical curve  $n = 6$ , which corresponds, according to Table 2, to a range  $r_c = 0.886 \text{ nm}$  for the exchange interaction. Fig. 5 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  $p = 1$  and  $n = 6$ , or  $z(r_c) = 78$ . The agreement was found to be good.

In Fig. 6 we compare the concentration dependence of the dipolar broadening  $\Delta H_d$  of the  $\text{Gd}^{3+}$  spectrum in

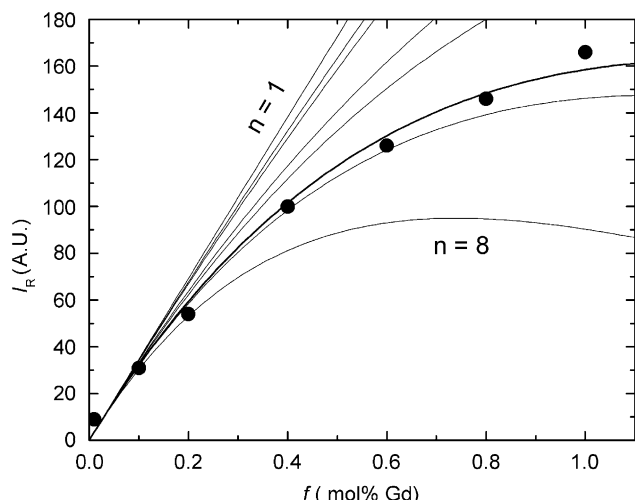


Fig. 5. Concentration dependence of the line intensity of the spectrum,  $I_R$ , in Gd-doped  $\text{CeO}_2$ . The circles are experimental points; the curves represent results of calculations for eight different ranges of the exchange interaction.

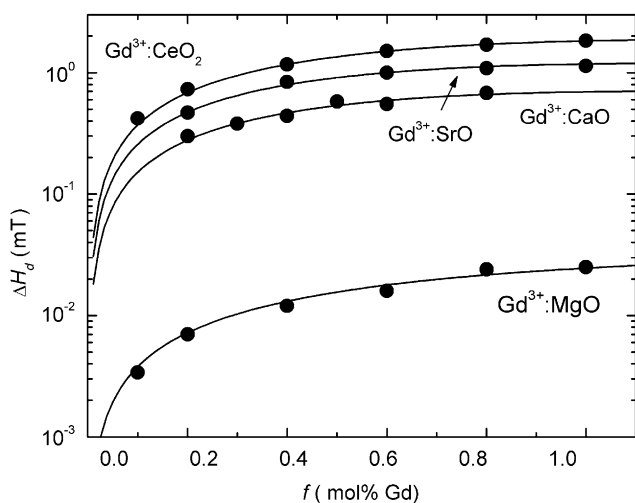


Fig. 6. Concentration dependence of the dipolar broadening of the spectra of  $\text{Gd}^{3+}$  in MgO, CaO, SrO and  $\text{CeO}_2$ . The curves are theoretical:  $\Delta H_d = c_1 f (1-f)^{z(r_c)}$  with  $c_1 = 4.5$ ,  $z(r_c) = 42$  (MgO),  $c_1 = 165$ ,  $z(r_c) = 86$  (CaO),  $c_1 = 280$ ,  $z(r_c) = 86$  (SrO) and  $c_1 = 400$ ,  $z(r_c) = 78$  ( $\text{CeO}_2$ ). MgO data are from [12], CaO data from [13] and SrO data from [14].

$\text{CeO}_2$  and in other three cubic host lattices, MgO [13], CaO [14] and SrO [15]. The faster increase of the linewidth with Gd concentration in  $\text{CeO}_2$  is not consistent with the fact that the lattice constant  $a_0$  in  $\text{CeO}_2$ , 0.541 nm [10], is larger than in the other three compounds. This is probably due to the fact that random lattice stresses broaden non-Kramers transitions such as the one investigated in the present work, as has been already observed in oxides such as MgO [16] and  $\text{Al}_2\text{O}_3$  [17,18].

It is not clear why clustering effects are present in Mn: $\text{CeO}_2$  solid solutions and not in Gd: $\text{CeO}_2$  solid solutions. However, it seems reasonable to assume that this is due to the fact that the ionic radius of  $\text{Mn}^{2+}$  (81 pm) is about 25% smaller than that of  $\text{Gd}^{3+}$  (107.8 pm) [19]. In any case, the fact that Gd: $\text{CeO}_2$  solid solutions do not exhibit clustering effects means that ESR linewidth data can be used to estimate the concentration of Gd in  $\text{CeO}_2$  samples, as it is possible to do in several solid solutions of paramagnetic ions in ceramic materials [20–23].

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