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E. S. R. OF Gd^{3+} IN La_2O_3 AND ITS SOLID SOLUTIONS WITH CeO_2

G. BACQUET, C. BOUYSSSET

Laboratoire de Physique des Solides (*)
118, route de Narbonne, 31077 Toulouse Cedex, France

and

D. HERNANDEZ

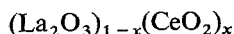
Laboratoire des Ultra-Réfractaires, B. P. 5, Odeillo, 66120 Font-Romeu, France

Résumé. — Les spectres de RPE des ions Gd^{3+} présents à l'état de traces dans La_2O_3 et $(La_2O_3)_{1-x}(CeO_2)_x$ sont caractéristiques d'une symétrie axiale suivant l'axe $\langle 111 \rangle$ et correspondent à un clivage en champ nul très important ($\sim 1,61 \text{ cm}^{-1}$). L'addition d'oxyde de cérium crée des distorsions aléatoires de la symétrie axiale. Par rapport aux spectres enregistrés avec La_2O_3 , cela se traduit par un fort élargissement de certaines raies de résonance.

Abstract. — In La_2O_3 and in its solid solutions with CeO_2 , the ESR spectra of Gd^{3+} ions present as traces in sites of $\langle 111 \rangle$ axial symmetry are characterized by a strong zero-field splitting ($\sim 1.61 \text{ cm}^{-1}$). With respect to the La_2O_3 patterns, the random distortions of the axial symmetry due to the introduction of Ceria, cause an important broadening of some lines.

1. Introduction. — The hexagonal modification of lanthanide oxides $A-Ln_2O_3$ belongs to the space group $P\bar{3}m1(D_{3d}^3)$. The character of such a structure is that the metallic atom, La in our case, is seven-fold coordinated with C_{3v} symmetry along the crystalline c axis (Fig. 1a). However, there are two types of oxygen atoms in this arrangement. One is inside a tetrahedron of lanthanum atoms, the other is six coordinated and is further remote from the metallic atoms than the former (about 2.70 Å versus 2.40 Å). Along the c axis (Fig. 1b) the structure is formed of a succession of slabs of a complex cation $(LaO)_n^{n+}$ consisting of OLa_4 tetrahedra edge-linked in a manner derived from the CaF_2 structure, separated by planes of oxygen anions [1]. This model implies a certain amount of covalent bonding inside the complex cation and the results of our previous experiments on Mn^{2+} doped La_2O_3 [2] are in good agreement with such considerations.

On the other hand by means of X-rays diffraction, Sibieude studied the evolution of the hexagonal modification of lanthanide oxides $A-Ln_2O_3$ by the addition of ThO_2 [3]. Intermediate phases having hexagonal or rhomboedral symmetries were found in the Ln_2O_3 rich domain. Their respective structures are deduced from $A-Ln_2O_3$ by stacking faults and are characterized by a great value of the c parameter. Such studies were also undertaken on the



system by Sibieude and coworkers [4, 5]. They showed that several intermediate phases resulting

(*) Associé au C. N. R. S.

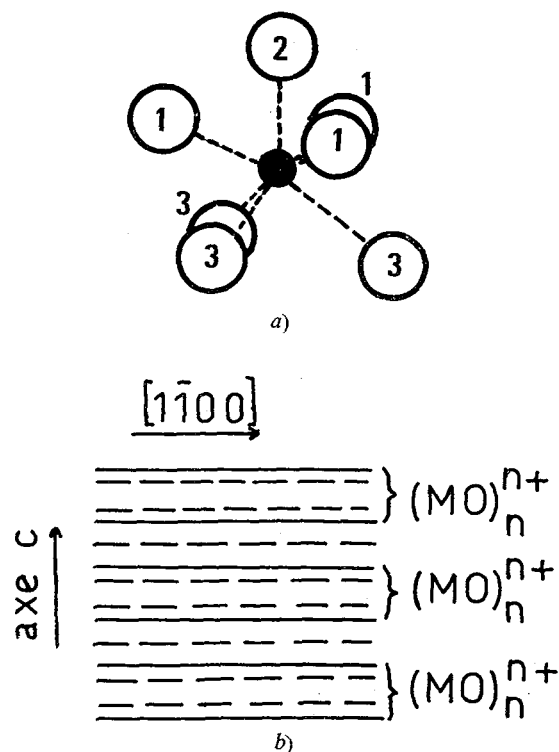


FIG. 1. — a) Lanthanum coordination polyhedron. The lanthanum-oxygen distances are : $o_1 = 2.39 \text{ Å}$, $o_2 = 2.48 \text{ Å}$, $o_3 = 2.68 \text{ Å}$. b) Schematic representation of the A-modification of lanthanide oxides after Caro [1].

from the addition of CeO_2 to La_2O_3 existed. They were observed in the range 5 to 35 mole % CeO_2 and their formation appears to be related to the method of synthesis used, i. e. co-fusion in air of

oxides followed by an oxidizing anneal at 1 550 °C. Tentative indexation schemes have been reported [4].

In the aim to obtain a better understanding of what happens in the La₂O₃-CeO₂ system with increasing amount of Ceria, we undertook in Toulouse an Electron Spin Resonance (ESR) study on Gd³⁺ doped single crystal (La₂O₃)_{1-x}(CeO₂)_x. We report here the results obtained with $x = 0.02$ and $x = 0.05$, and we compare them to those corresponding to Gd³⁺ doped La₂O₃ [6, 7].

2. Experiments and results. — 2.1 SAMPLES. —

The single crystals used in our experiments were obtained by one of us (D. Hernandez) with a solar furnace of the Laboratoire des Ultraréfractaires at Odeillo (France) using a slow cooling procedure, as described in [2]. They were conserved in quartz tubes sealed under vacuum to be preserved from moisture.

In the ESR experiments, the selected specimens were set at the centre of the cylindrical TE₀₁₁ resonant cavity of a conventional X-band ($\lambda = 3$ cm) spectrometer. Inside this cavity the crystal can be rotated about two perpendicular axes, thus permitting its perfect orientation in the static field.

2.2 Gd³⁺ DOPED La₂O₃. — The Gd³⁺ ion has an electronic configuration 4f⁷ with a ground state of ⁸S_{7/2}. When this ion is introduced in the axial crystal field of La₂O₃ the ground level is split in four Kramers doublets, the distance between the two extreme being equal to 1.61 cm⁻¹, value which is very large [6, 7].

The spectra we recorded at room temperature with the d. c. field respectively parallel and perpendicular to the crystalline *c* axis are shown in figure 2a. It is worthwhile to underline here that the linewidth values are included between 11 and 23 G. This is due to the extreme care we took to avoid the hydration of samples during our experiments. We checked recently [8] that one of the first effects of the hydration is to broaden the ESR lines. This can explain the values (from 50 to 70 G) observed in our first experiments [6].

The La₂O₃ : Gd³⁺ spectra were fitted to a spin Hamiltonian :

$$\mathcal{H}_S = g\mu_B \mathbf{H} \cdot \mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 O_4^3 + B_6^3 O_6^3 \quad (1)$$

with $S = 7/2$ and where the O_n^m are the Stevens' operator equivalents. The best computer fit was obtained with the constants quoted in table I the values of which very slightly differ from those we reported previously [6].

2.3 Gd³⁺ DOPED (La₂O₃)_{1-x}(CeO₂)_x. — Addition of CeO₂ introduces some striking modifications in the spectra, specially when the *c* axis is aligned with the static field as can be seen in the left part of figure 2.

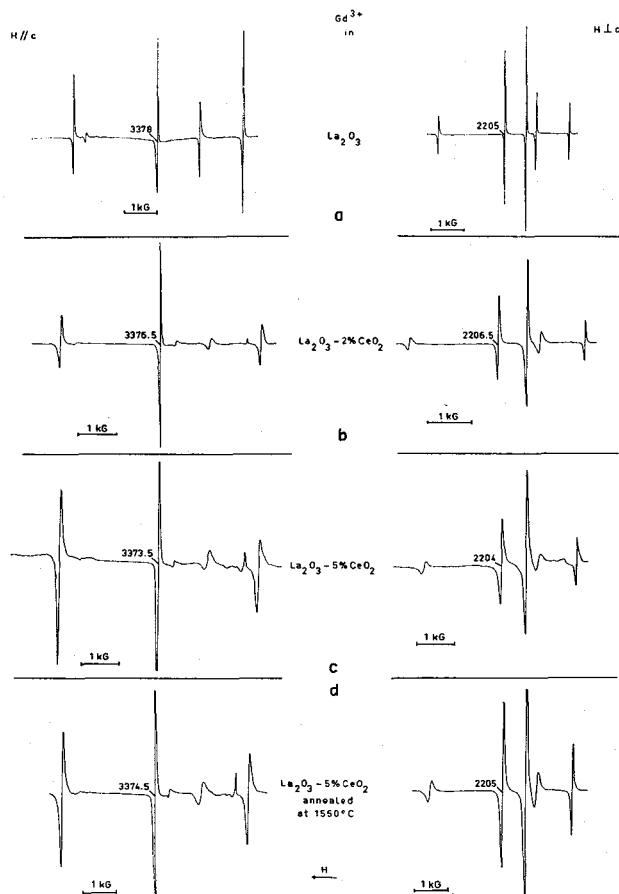


FIG. 2. — Room temperature spectra of Gd³⁺ ions in : a) La₂O₃ ; b) (La₂O₃)_{0.98}-(CeO₂)_{0.02} ; c) (La₂O₃)_{0.95}-(CeO₂)_{0.05} ; d) (La₂O₃)_{0.95}-(CeO₂)_{0.05} annealed during 4 hours at 1 550 °C in oxidizing atmosphere.

Now some lines are very broad (up to 85 G) and their intensity is much weaker than in La₂O₃. On the other hand, two lines appear in the low field region which correspond to $\Delta m_s > 1$ fine structure transitions. They become allowed by the existence of random deviations to the axial symmetry (due to the presence of Cerium atoms in different neighbour sites) which introduce variable amount of mixing in the eigenstates. The line ($| -3/2 \rangle \rightarrow | 3/2 \rangle$) located at about 1 140 G, very close to the crossing of the levels corresponding to $| +1/2 \rangle$ and $| -3/2 \rangle$ Gd³⁺ states in La₂O₃ (we use the high field notation for the eigenstates) is completely dissymmetrical looking like an absorption line. A possible explanation might be the following. In our solid solutions an extrarhombic distortion creates a repulsion between these two levels. For a given magnetic field value (and specially near the original crossing), the existing distortions have different strengths and directions, then each corresponding level is differently shifted in energy. In the diagram translating the situation in the crystal as a whole, the eight levels will be more or less spread out in energy. The most important effect arise in this magnetic field region where the above repulsion takes place.

TABLE I
Spin Hamiltonian parameters of Gd^{3+}

| Gyromagnetic factor | | La_2O_3 1.9918 ± 0.0003 | $(La_2O_3)_{0.98}(CeO_2)_{0.02}$ 1.9925 ± 0.003 | $(La_2O_3)_{0.95}(CeO_2)_{0.05}$ 1.9932 ± 0.0003 |
|---|-----|-----------------------------------|--|--|
| Second order constants B_2^m in $10^{-4} cm^{-1}$ | m | | | |
| | 0 | 440.3 ± 0.1 | 440.4 ± 0.1 | 440.4 ± 0.1 |
| | 2 | 0 | $-1.86 \pm 0.02 \leq \leq 1.86 \pm 0.02$ | $-4.65 \pm 0.02 \leq \leq 4.65 \pm 0.02$ |
| Forth order constants B_4^m in $10^{-4} cm^{-1}$ | 0 | 0.314 ± 0.002 | 0.313 ± 0.002 | 0.313 ± 0.002 |
| | 2 | 0 | $(1.86 \pm 0.02) \times 10^{-3} \geq \geq (-1.86 \pm 0.02) \times 10^{-3}$ | $(3.72 \pm 0.02) \times 10^{-3} \geq \geq (-3.72 \pm 0.02) \times 10^{-3}$ |
| | 3 | 6.56 ± 0.03 | 6.64 ± 0.03 | 6.64 ± 0.03 |
| Sixth order constants B_6^m in $10^{-4} cm^{-1}$ | 0 | $(1.53 \pm 0.03) \times 10^{-4}$ | $(2.47 \pm 0.03) \times 10^{-4}$ | $(2.47 \pm 0.03) \times 10^{-4}$ |
| | 3 | $(-0.60 \pm 0.03) \times 10^{-2}$ | $(-0.79 \pm 0.03) \times 10^{-4}$ | $(-0.70 \pm 0.03) \times 10^{-2}$ |

When H is perpendicular to the c axis the spectra are identical to that of $La_2O_3 : Gd^{3+}$ if we except the strong broadening (up to 100 G) and the consequent lower intensity of the second and fifth lines in the increasing fields sense.

The spectra were described by a spin Hamiltonian of the form (1) to which the terms $B_2^m O_2^2$ and $B_4^m O_4^2$ were added. The constants corresponding to the two studied solid solutions are given in table I. The zero field splittings obtained are as large as in the Gd^{3+} doped La_2O_3 case.

No fundamental differences are seen in the spectra

recorded with Gd^{3+} doped $(La_2O_3)_{0.95}(CeO_2)_{0.05}$ single crystals before and after heating at $1550^\circ C$ in oxidizing atmosphere during 4 hours (Fig. 2c and d). This can be understood considering the minor modifications existing in the La_2O_3 and $(La_2O_3)_{0.95}(CeO_2)_{0.05}$ X-ray diffraction patterns obtained with powdered samples [4] and shown in figure 3.

Further experiments are in progress on samples containing greater amounts of Cerium oxide and which are doped with either Gd^{3+} and Mn^{2+} .

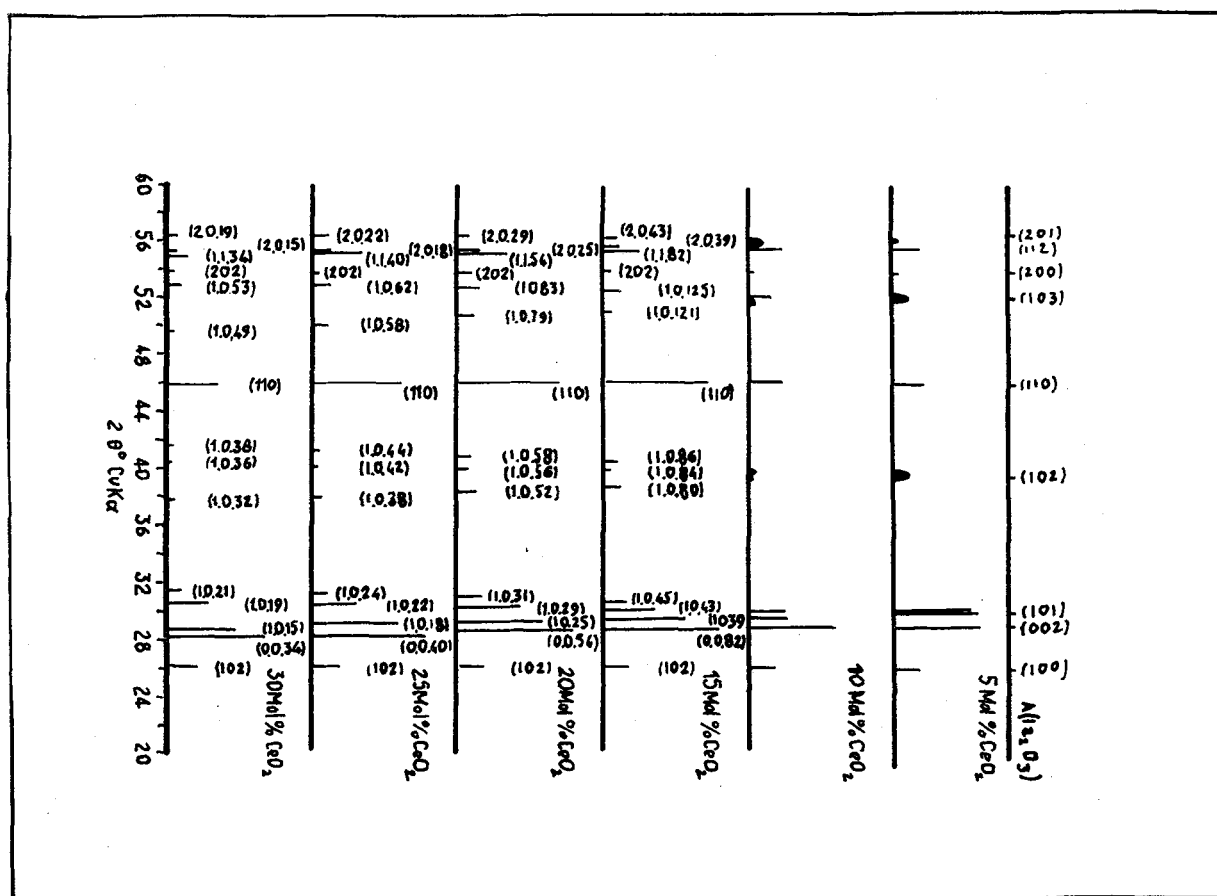


Fig. 3. — X-ray diffraction patterns obtained with powdered samples of $(La_2O_3)_{1-x}(CeO_2)_x$ after Sibieude *et al.* [4]. In the case of La_2O_3 only, the position of lines is indicated.

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