

Mössbauer Investigation of Eu^{3+} Site Occupancy and Eu-O Covalency in Y_2O_3 and Gd_2O_3 Nanocrystals

G. Concas, C. Muntoni, G. Spano, M. Bettinelli^a, and A. Speghini^a

Dipartimento di Fisica, Università di Cagliari and Istituto Nazionale per la Fisica della Materia, S.P. Monserrato-Sestu km 0.700, I-09042 Monserrato (Cagliari), Italy

^a Dipartimento Scientifico e Tecnologico, Università di Verona,

Ca' Vignal, Strada le Grazie, I-37134 Verona, Italy

Reprint requests to Dr. G. C.; Fax: +39 070 510171; E-mail: giorgio.concas@dsf.unica.it

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Samples of nanocrystalline $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ and $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ were examined by ^{151}Eu Mössbauer spectroscopy. The degree of covalency of the Eu-O bond has been studied. The spectrum of the cubic $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample has been resolved into 2 contributions due to europium in the C_{3i} and C_2 sites, for the first time in ^{151}Eu Mössbauer spectroscopy. The degree of covalency and the electric field gradient of the 2 sites has been compared. The occupancy, by the lanthanide ion, of the more and less symmetric sites in the cubic structure of $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ has been investigated and discussed.

Key words: Europium; Yttrium; Oxides; Nanocrystals; ^{151}Eu Mössbauer Spectroscopy.

1. Introduction

Lanthanide-doped yttrium and gadolinium oxides are important materials which find numerous applications in several fields. In particular, cubic Y_2O_3 and monoclinic Gd_2O_3 doped with Eu^{3+} are well-known luminescent materials [1, 2], whilst cubic $\text{Y}_{2-x}\text{Ln}_x\text{O}_3$ systems form an interesting class of diluted magnetic semiconductors [3], and yttria and rare earth oxide based catalysts find applications in the selective oxidation of ethane to ethene [4, 5].

In the case of the cubic host Y_2O_3 , the Y^{3+} ions are located in the two nonequivalent positions 24d (site symmetry C_2) and 8b (site symmetry C_{3i}) [6]. In principle, the luminescent and magnetic ion Eu^{3+} may replace Y^{3+} in a random or preferential way. The location of Eu^{3+} in these two sites in bulk cubic $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ was investigated by Grill and Schieber [7] by means of magnetic susceptibility measurements. The authors concluded the Eu^{3+} ions occupy preferentially the C_2 sites. On the other hand, more recently Antic et al. [8], on the basis of X-ray powder diffraction and magnetic susceptibility data, reported that in bulk cubic $\text{Y}_{2-x}\text{Eu}_x\text{O}_3$ the Eu^{3+} ions are randomly distributed between the two possible substitutional sites. In any case, these investigations have

been limited to bulk cubic yttria materials. It is interesting to investigate the distribution of the luminescent Eu^{3+} dopant ion in nanocrystalline cubic Y_2O_3 , which is characterized by interesting spectroscopic properties [9].

^{151}Eu Mössbauer spectroscopy represents a useful and sensitive tool to investigate structural questions about the lanthanide ion in europium containing materials [10 - 12]. In particular this spectroscopy can give information about the symmetry of the Eu site. It can also determine the relative abundance of europium atoms in different crystallographic sites, because the probability of resonant absorption by a single ^{151}Eu nucleus is approximately equal for trivalent ions in different sites of the same compound.

In this work we report on the estimation of the covalent component of the Eu-O bond in the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ and $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ nanocrystalline samples and the occupancy by the Eu^{3+} ions of the two available cation sites in the cubic structure of nanocrystalline $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$.

2. Experimental Procedure

Nanocrystalline Y_2O_3 and Gd_2O_3 powders doped with 10% Eu_2O_3 ($\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ and $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$)

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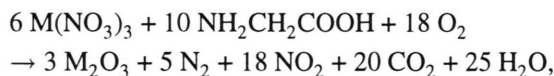
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were prepared by a propellant synthesis procedure [9, 13, 14], using an aqueous solution containing glycine NH_2CH_2COOH (Sigma, 99%), $Y(NO_3)_3 \cdot 6 H_2O$ or $Gd(NO_3)_3 \cdot 6 H_2O$ and $Eu(NO_3)_3 \cdot 6 H_2O$ (Aldrich, 99.9%) and the appropriate lanthanide nitrate (Aldrich, 99.9%). The reaction is:



where $M = Y$ or Ln . A glycine-to-metal nitrate molar ratio of 1.2:1 was employed to prepare the precursor solution. After combustion, the powders were fired for 1 h at 500 °C, in order to decompose the residual nitrate ions. Laser-excited Raman and FTIR spectra were measured on all the samples. Nitrate ions were found to be absent, but traces of OH and carbonate groups were detected.

Mössbauer absorption spectra were obtained using a standard transmission geometry, with a $^{151}SmF_3$ source of activity 3.7 GBq. A calibration was performed using a source of ^{57}Co in rhodium and a metallic iron foil (6 μm thick) as the absorber. The full width at half maximum (FWHM) of the crystalline absorption peak, determined with our source, was measured using $Cs_2NaEuCl_6$. The isomer shift of the samples was measured using EuS as reference material. In order to allow comparison with the literature data, the isomer shift values have been referred to EuF_3 by subtracting the measured shift of this compound (11.54 mm/s).

Measurements on the crystalline samples were carried out at room temperature on powders with an absorber thickness of 3.8 mg/cm² of Eu. The absorber was contained in a Plexiglas holder.

The gamma ray from ^{151}Eu is emitted during a transition from an excited state with spin 7/2 to the ground state with spin 5/2. If there is no threefold or fourfold symmetry axis passing through the nucleus, the asymmetry parameter η is non-zero. There are 12 allowed transitions, which give rise to 12 absorption lines. If there is a threefold or fourfold axis, only 8 transitions are allowed. In a system with two mutually perpendicular axes with threefold or higher symmetry (e. g. a site with cubic symmetry), the electric field gradient is zero and a single absorption line occurs [10].

The absorption spectra were analysed by fitting the data with lines of Lorentzian shape, allowing for the quadrupole interaction when present. We used the method for the analysis of pure quadrupole spectra proposed by Shenoy and Dunlap [15], with a value

of the quadrupole ratio $R = 1.312$ [16]. The thickness of the absorbers allows the use of a Lorentzian line shape, because the thin absorber approximation holds (thickness less than 6 mg/cm² of Eu) [17].

The quality of the fits was tested using the usual chi-squared (χ^2) test and a weighted form of the Durbin-Watson d statistics [18], that was recently introduced in the analysis of Mössbauer spectra [11]. The d value quantifies the serial correlation between adjacent least-squares residuals and is defined as

$$d = \sum_i [(\Delta_i/\sigma_i) - (\Delta_{i-1}/\sigma_{i-1})]^2 / \sum_i (\Delta_i/\sigma_i)^2, \quad (1)$$

where the sums are from 1 to N (the number of data points), Δ_i is the i th residual and σ_i indicates the standard deviation. The d parameter must be tested against the Q_d parameter defined as

$$Q_d = 2[(N-1)/(N-P) - 3.0902/(N+2)^{1/2}], \quad (2)$$

where P is the number of least-squares parameters. If $|d - 2|$ is smaller than $|Q_d - 2|$, then consecutive residuals are insignificantly correlated.

3. Results

The crystal structure of the samples under investigation was checked by powder X-ray diffraction [13, 14]. These measurements confirmed that all samples were single phase and that $Y_{1.8}Eu_{0.2}O_3$ and $Gd_{1.8}Eu_{0.2}O_3$ had been obtained as the cubic C [6] and the monoclinic B [19] polymorphs, respectively. Moreover, X-ray diffraction showed that the samples were nanocrystalline with sizes in the range 20 - 100 nm.

In addition, the luminescence spectra of nanocrystalline $Y_{1.8}Eu_{0.2}O_3$ and $Gd_{1.8}Eu_{0.2}O_3$ [20] are typical of the Eu^{3+} doped C-phase Y_2O_3 [9] and B-phase Gd_2O_3 [2].

The width of the crystalline, i.e. in an ordered environment, absorption peak for trivalent europium, determined with our source, has been measured using $Cs_2NaEuCl_6$, which contains Eu^{3+} in an octahedral site (cubic symmetry) [21]. In a site with cubic symmetry, the electric field gradient is zero and therefore there is a single absorption line [10]. The FWHM has been measured with an absorber thickness of 3.8 mg/cm² of Eu; this value corresponds to an effective thickness $t = 1$, when calculated using the recoilless fraction of the source, $f = 0.6$ [10]. The measured FWHM is 1.76 ± 0.01 mm/s with $t = 1$.

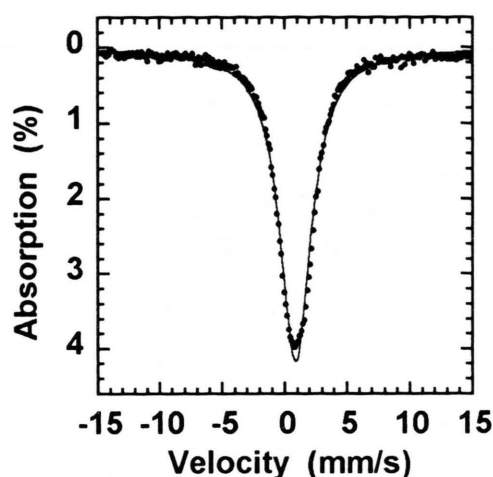


Fig. 1. Absorption spectrum of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample. Experimental data are reported as dots, the solid curve shows the fit with a single Lorentzian line.

The line width measured for other samples, with the same source, must be compared with the width measured for $\text{Cs}_2\text{NaEuCl}_6$ with the same effective thickness, i.e. approximately with the same superficial density of Eu. Widths measured with distinct sources of $^{151}\text{SmF}_3$ cannot be compared, because of the different features of the commercial sources [10].

We used EuS as reference material in the measurements of the isomer shift [22]. This compound has been chosen, following the suggestion in [22], instead of EuF_3 because it gives a single absorption line (europium in a site with cubic symmetry), while the fluoride has an unresolved quadrupole splitting. Moreover, any oxidation of the sulphide can be easily detected in the spectrum through a trivalent Eu peak, while the hydration of the fluoride is not detectable. The isomer shift of the anhydrous fluoride, referred to the sulphide, has been measured using commercial materials (Aldrich); its value was found to be 11.54 ± 0.01 mm/s.

The Mössbauer absorption spectrum of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ nanocrystalline sample is shown in Figure 1. The parameters obtained from the fit with a single line are given in Table 1; the solid curve in Fig. 1 shows the calculated data. The value of the isomer shift obtained from this fit represents an approximated average of the shift values of the two cation sites of the Y_2O_3 cubic structure. The FWHM of the peak (3.02 mm/s) is much larger than the crystalline

Table 1. Mössbauer parameters obtained by fitting the spectra. δ is the isomer shift with respect to EuF_3 , Γ is the FWHM, eQV_{zz} the quadrupole interaction parameter, η the asymmetry parameter and Area the relative area of the components. The d and Q_d Durbin-Watson parameter and the chi-squared parameter χ^2 are also reported. Statistical errors are given in parenthesis as errors on the last digit.

Sample	δ mm/s	Γ mm/s	eQV_{zz} mm/s	η	Area %	d	Q_d	χ^2
$\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ (Fit single Lor.)	1.05(1)	3.02(1)				0.4	1.6	4.7
$\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ (Fit single Lor.)	0.97(1)	2.87(1)				0.8	1.6	3.0
$\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$						1.8	1.7	1.0
Site C_{3i} :	1.23(3)	1.76	-5.5(5)		49(1)			
Site C_2 :	0.97(3)	1.76	-10.7(3)	1.0(1)	51(1)			

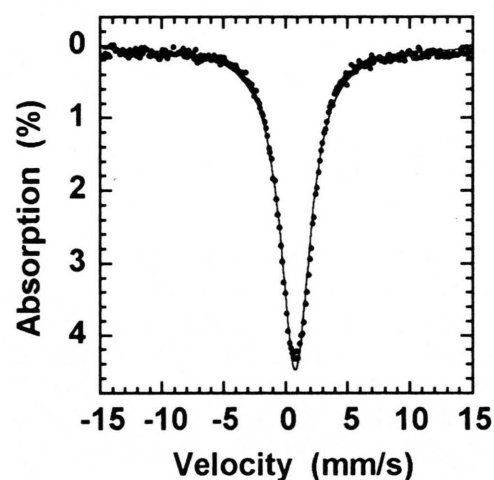


Fig. 2. Absorption spectrum of the $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample. Experimental data are reported as dots, the solid curve shows the fit with a single Lorentzian line.

width (1.76 mm/s); this width results from the unresolved quadrupole splitting and from the presence of two unresolved contributions due to the different sites. The value of the reduced chi-squared (4.7) shows that the fit is unsatisfactory.

Figure 2 shows the absorption spectrum of the $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ nanocrystalline sample. Table 1 shows the parameters given by a single line fit, while the calculated data are shown in Fig. 2 as solid curve. The isomer shift value can be considered an average value for the three cation sites of the monoclinic structure of Gd_2O_3 . The FWHM measured is due to unresolved quadrupole splitting and to the three contributions of the sites.

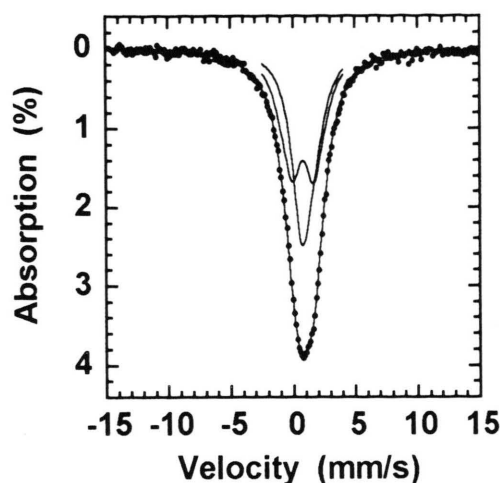


Fig. 3. Absorption spectrum of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample. Experimental data are reported as dots, the solid curves show the fit with 2 contributions and the contribution of each site.

The spectrum of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample has also been fitted using two contributions for the two sites. The 1st contribution is associated with the site with point symmetry C_{3i} ; the asymmetry parameter η has been fixed to zero (8 allowed transitions) because this site has a threefold symmetry axis. The 2nd contribution is associated with the C_2 site; the η parameter is free (12 allowed transitions). The FWHM of each component absorption line, corresponding to each allowed transition, has been fixed in the fit to the crystalline line width for effective thickness $t = 1$ (1.76 mm/s).

Figure 3 shows (outer curve) the data calculated by the fit with two contributions for $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$; the inner curves show the contribution of each site. Table 1 gives the best fit Mössbauer parameters and the control parameters; the reduced chi-squared is 1.0. The values of d and Q_d point out that the consecutive residuals are not correlated. Figure 4 shows the plots of the residuals of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ spectrum, as differences between experimental and calculated values, for the data with a Lorentzian line (Fig. 4a) and for the data with 2 contributions (Fig. 4b). The residuals of Fig. 4b are randomly distributed, therefore it is a good fit of the experimental spectrum.

It results that the relative area of the contribution due to the C_{3i} site is about equal, within the experimental error, to that due to the C_2 site (49% and 51% respectively).

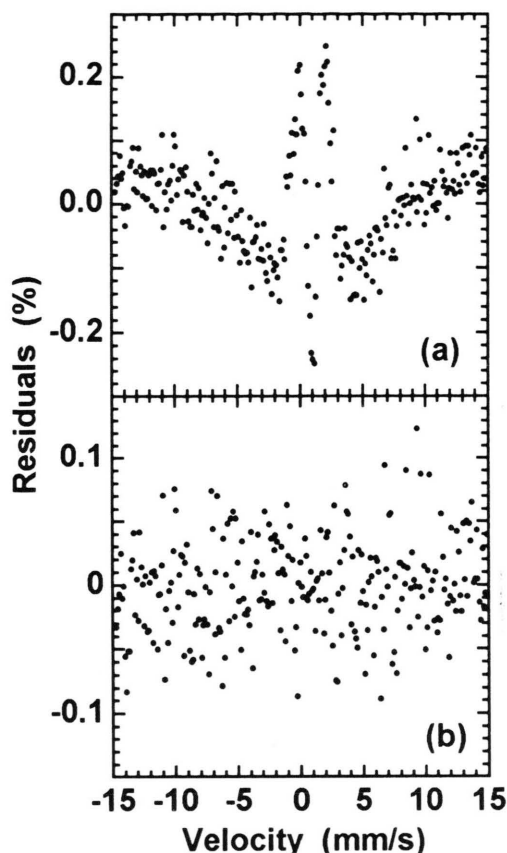


Fig. 4. Differences between experimental data and calculated values in the spectrum of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample analysed: (a) with a single Lorentzian line and (b) with 2 contributions.

Some trial fits of the spectrum of the $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ sample using 3 contributions, every one of them with its unresolved quadrupole splitting, gave no result because there are too many parameters to determine. Attempts of fitting the spectrum with 3 single Lorentzian lines gave a misleading result with unreasonable values of isomer shift, because the quadrupole splitting of the components is larger than the difference in the isomer shift for the 3 sites. This is the case also for a fit of the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{O}_3$ spectrum with 2 single Lorentzian lines. Therefore the fit reported in Table 1 must be considered the most meaningful procedure for the analysis of the $\text{Gd}_{1.8}\text{Eu}_{0.2}\text{O}_3$ spectrum presented here.

4. Discussion

The spectra of the nanocrystalline samples here investigated have values of the isomer shift corre-

sponding to an oxidation number +3; the values near to 1 mm/s point to a strong covalency of the Eu-O bond for both nanocrystalline hosts [10].

In the $Y_{1.8}Eu_{0.2}O_3$ sample, the C_{3i} site has a larger isomer shift than the C_2 site, the former site appearing to be characterised by a stronger covalent character. The axial component of the electric field gradient is much smaller in the more symmetric site because the value of the quadrupole interaction parameter is about half.

The europium dopant ion is distributed about equally between the C_{3i} and C_2 sites; therefore in nanocrystalline Y_2O_3 it occupies preferentially the C_{3i} sites, which are only 1/4 of the available sites.

In several studies carried out in the sixties, based on paramagnetic resonance spectroscopy, it has been claimed that trivalent lanthanide ions in cubic Y_2O_3 occupy both the C_2 and C_{3i} sites with nearly equal probability [23 - 25]. However, it has been shown more recently, using powder X-ray diffraction and magnetic susceptibility measurements [26], that several Ln^{3+} ions, such as Gd^{3+} [27] and Yb^{3+} [28], tend to occupy preferentially one of the two sites in bulk Y_2O_3 . In the case under investigation the dopant ion (Eu^{3+}) is characterised by an ionic radius for 6-fold co-ordination (0.950 Å) significantly different from that of Y^{3+} (0.892 Å) in the same conditions [29]. It is therefore conceivable that the substitution of Y^{3+} with Eu^{3+} occurs with some difficulty, and that one of the two sites, which are characterised by different Ln-O distances, is preferentially occupied. However, in a recent study it has been found that in bulk $Y_{2-x}Eu_xO_3$, on the basis of magnetic susceptibility data and X-ray diffraction, the two C_2 and C_{3i} sites are randomly occupied. At present we have no explanation for this difference, but we point out that the samples under investigation are nanosized and were obtained by a

propellant synthesis, which is intrinsically a non-equilibrium technique. It is therefore possible that the distribution of the Eu^{3+} ions in the present samples is different from that occurring in a bulk sample obtained by the conventional ceramic techniques [8]. On the other hand it has already found that the optical spectra of bulk and nanocrystalline $Y_{2-x}Nd_xO_3$ (the latter obtained by propellant synthesis) show several differences due to a different average co-ordination of Nd^{3+} in the two materials [30]. This behaviour is qualitatively similar to what is found here for $Y_{1.8}Eu_{0.2}O_3$. However, we point out that a Rietveld analysis of $Y_{1.8}Er_{0.2}O_3$ and $Y_{1.8}Nd_{0.2}O_3$ samples obtained by propellant synthesis gave no indication of a significant preferential occupation of different crystallographic positions, i.e. the lanthanide ions seem to be statistically distributed over both cationic sites, within the limit of the sensitivity of the X-ray diffraction [14]. This question will be the subject of further experimental work.

5. Conclusions

The mean isomer shift of the europium ion in the $Y_{1.8}Eu_{0.2}O_3$ and $Gd_{1.8}Eu_{0.2}O_3$ nanocrystalline samples indicates that the Eu-O bond has a strong covalent character. The relative area of the two contributions due to the Eu^{3+} ion in the C_{3i} and C_2 sites, in the spectrum of the $Y_{1.8}Eu_{0.2}O_3$ sample, show that half of the lanthanide ions is half in the more symmetric site and half in the less symmetric one, in spite of a ratio of 1:3 between the available sites.

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