# Investigation of Structural Questions on Europium Compounds by Means of $^{151}$Eu Mössbauer Spectroscopy

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$^{151}$Eu Mössbauer spectroscopy permits the determination of the symmetry of the site in which Eu is accommodated. It has been shown that the $^{151}SmF_3$ source can be considered a monochromatic source. This source was used to measure the line width of $Eu^{3+}$ in a site with cubic symmetry, i. e. in a $Cs_2NaEuCl_6$ crystal. The isomer shift of commercial compounds used as standards (anhydrous $EuF_3$ and EuS) was also measured. In the case of $Cs_2NaEu(NO_2)_6$ hexanitritoelpasolite the trivalent europium ion is accommodated in a site with perfect cubic symmetry. In $Eu(PO_3)_3$ crystalline metaphosphate, the rare earth is located in a site which appears to be distorted with respect to cubic symmetry; this site has no threefold or fourfold symmetry axis.

*Key words:* Elpasolites; Oxides; $^{151}$Eu Mössbauer Spectroscopy.

## 1. Introduction

$^{151}$Eu Mössbauer spectroscopy represents a useful and sensitive tool to investigate the local structure around the lanthanide ion in europium containing materials [1 - 5]. In particular, a relation between the isomer shift and the co-ordination number of the Eu atom in crystalline oxides has been found by Tanabe et al. [6]. Moreover, a relation between the isomer shift and the optical basicity of the glass, as defined by Duffy [7], has been found by us in some europium doped oxide glasses [8 - 10].

However, $^{151}$Eu spectroscopy can give also direct information about the site symmetry of the lanthanide atom. In fact, 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 [11]. If there is no threefold or fourfold symmetry axis passing through the nucleus, the components of the electric field tensor along the principal axes are different and the asymmetry parameter $\eta$ is non-zero [12]. There are 12 allowed transitions which give 12 emission or absorption lines, if we consider the source or the absorber. If a threefold or fourfold axis is present, the asymmetry parameter is zero and 8 transitions are allowed. In a compound with two mutually perpendicular axes of threefold or higher symmetry (e. g. a site with cubic symmetry), the electric field gradient is zero and a single emission or absorption line is observed [11].

The resolution of the absorption spectrum in the components split by the quadrupole interaction is limited by different experimental factors. First of all, the best kind of source available ($^{151}SmF_3$) gives a line width much larger than the natural width of 1.33 mm/s [11]. The quadrupole splitting is usually smaller than the line width; therefore the components are not resolved and must be identified by the fitting procedure. The resolution of the absorption peak requires that the component lines have a Lorentzian shape; in some cases the knowledge of the line width is also required.

The aim of the present work is to investigate the symmetry of the lanthanide site in the $Cs_2NaEu(NO_2)_6$ and $Eu(PO_3)_3$ crystalline compounds. For this

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purpose we verified that the $^{151}SmF_3$ source can be considered as a monochromatic source; we measured also the line width of $Eu^{3+}$ in a site with cubic symmetry, using a $Cs_2NaEuCl_6$ crystal.

## 2. Experimental Procedure

The EuS and anhydrous $EuF_3$ compounds are commercially available materials. $Cs_2NaEuCl_6$ and $Cs_2NaEu(NO_2)_6$ single crystals were prepared as described in [13] and [14], respectively.

Crystalline $Eu(PO_3)_3$ was prepared by heat treating an intimate mixture of $Eu_2O_3$ (Aldrich 99.999%) and $(NH_4)_2HPO_4$ (Carlo Erba RPE). A 15% molar excess of the latter compound was used in order to compensate for $P_2O_5$ losses at high temperature. The mixture was heated for 1 h at 400 °C, 1 h at 700 °C and 1 h at 1000 °C; the resulting powder was ground and subsequently heated for 2.5 h at 1000 °C.

The crystalline europium metaphosphate was characterised by powder X-ray diffraction, as reported in [15].

The 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 $Cs_2NaEuCl_6$ which contains $Eu^{3+}$ in a site with cubic symmetry [16].

The isomer shift of the samples was measured using EuS as reference material; this compound is a better standard than $EuF_3$ [17]. The isomer shift of the anhydrous fluoride, referred to the sulphide, was also measured. The values of the isomer shift, measured with respect to EuS, have been related to the ones of $EuF_3$ by subtracting a fixed value, in order to allow comparison with the literature data.

The measurements on the compounds were carried out at room temperature on a powder sample with an absorber thickness of 3.8 mg/cm$^2$ of Eu, if not specified otherwise; this value corresponds to an effective thickness $t = 1$, when calculated using the recoilless fraction of the source, $f = 0.6$ [11].

The absorbers of EuS, $EuF_3$, $Cs_2NaEuCl_6$, and $Cs_2NaEu(NO_2)_6$ were prepared in a dry box under argon atmosphere, with $O_2$ less than 1 ppm and $H_2O$ less than 1 ppm. The absorbers were contained in a Plexiglas holder; the holder was sealed in the dry box with a vacuum grease.

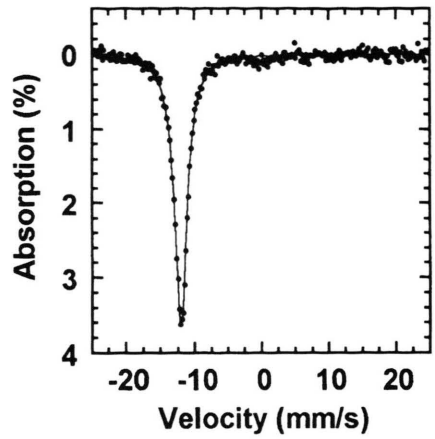


Fig. 1. Absorption spectrum of EuS. Experimental data are reported as dots and the solid curve shows the fit.

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 [18], with a value of the quadrupole ratio $R = 1.312$ [19]. The thickness of the absorbers permits the use of a Lorentzian line shape, because the thin absorber approximation can be used (thickness less than 6 mg/cm$^2$ of Eu) [20].

The quality of the fits was tested using the usual chi-squared ($\chi^2$) test and a weighted form of the Durbin-Watson $d$-statistics [21]. This statistics was used in the analysis of X-ray diffraction spectra with the Rietveld method [21]; it was recently introduced by us in the analysis of the Mössbauer spectra [8]. The $d$ value quantifies the serial correlation between adjacent least-squares residuals and is defined as

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

where the sums are from 1 to $N$ (the number of data points), $\Delta_i$ is the $i$th residual and $\sigma_i$ 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 consecutive residuals are insignificantly correlated, $d$ has a value nearer to 2 than $Q_d$.

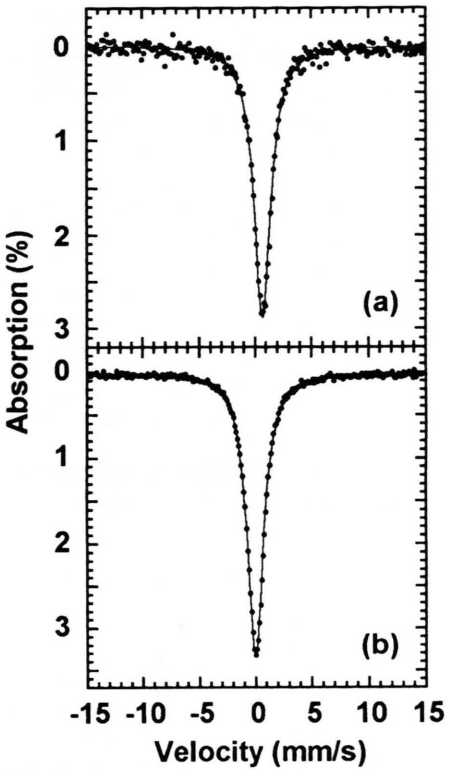


Fig. 2. Absorption spectra of: (a) $Cs_2NaEuCl_6$ and (b) $Cs_2NaEu(NO_2)_6$. Experimental data are reported as dots and the solid curve shows the fit.

## 3. Results

Figure 1 shows the spectrum of EuS, which we used as a reference material in the measurements of the isomer shift. This compound has been chosen, instead of $EuF_3$, following [17], because it gives a single absorption line (europium in a site of cubic symmetry), while the fluoride has an unresolved quadrupole splitting [22, 23]. 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 commercial anhydrous fluoride, referred to the sulphide, has been measured and its value was found to be (11.54±0.01) mm/s.

In Fig. 2 the absorption spectra of the $Cs_2NaEuCl_6$ crystal (Fig. 2a) and of the $Cs_2NaEu(NO_2)_6$ crystal (Fig. 2b) are shown.

The $Cs_2NaEuCl_6$ crystal contains $Eu^{3+}$ in an octahedral site (cubic symmetry) [16]. It permits to verify that the emission line of our source can be treated as

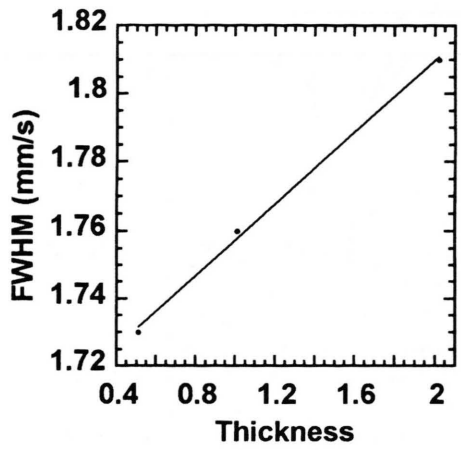


Fig. 3. Full width at half maximum with absorbers of $Cs_2NaEuCl_6$ of different thickness. Experimental data are reported as dots and the solid line shows a linear fit.

monochromatic (unsplit), because $Eu^{3+}$ in a site of cubic symmetry gives a single absorption line if the source is monochromatic [11]. The elpasolite crystal was used also in order to measure the line width of our source using the trivalent europium in a crystalline environment. The FWHM of the absorption peak has been measured with an absorber thickness of $t = 1$; the obtained value is (1.76±0.01) mm/s with $t = 1$.

The line width was also measured using absorbers of $Cs_2NaEuCl_6$ with effective thickness $t = 0.5$ and $t = 2$. The resulting FWHM are plotted in Fig. 3 as a function of the thickness $t$. The linear behaviour predicted by the theory is verified by our results [12, 24]. The FWHM at zero thickness, obtained by a linear fit, is $\Gamma = (1.70 \pm 0.01)$ mm/s.

The line width measured for other samples, with the same source, must be compared with the width measured for $Cs_2NaEuCl_6$ with the same effective thickness, i.e. approximately with the same superficial density of Eu. Widths measured with distinct sources of $^{151}SmF_3$ cannot be compared because of the different features of the commercial sources [11].

The spectrum of the $Cs_2NaEu(NO_2)_6$ crystal, shown in Fig. 2a, can be fitted using a single Lorentzian line; it points out the absence of a quadrupolar interaction. The line width is equal to that of $Cs_2NaEuCl_6$ with $t = 1$.

The spectrum of the anhydrous $EuF_3$ compound is shown in Fig. 4a. Due to the small value of the quadrupole interaction (QI) parameter, the spectrum

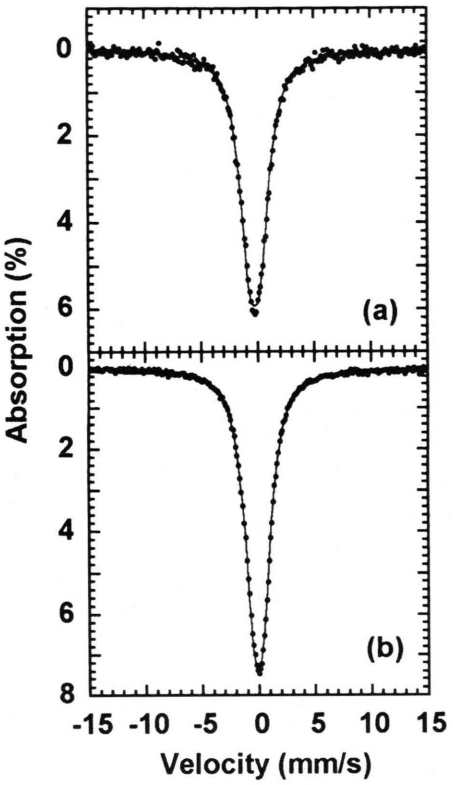


Fig. 4. Absorption spectra of: (a) $EuF_3$ and (b) $Eu(PO_3)_3$. Experimental data are reported as dots and the solid curve shows the fit.

of $EuF_3$ is usually fitted without considering the QI, even though the Eu site has a symmetry lower than cubic. The fit of the spectrum with a single Lorentzian line gives an unsatisfactory result ($\chi^2$ = 1.6), with a line width, (2.53±0.01) mm/s, much larger than 1.76 mm/s which is the value for our source at $t$ = 1. The spectrum can be well fitted only by a quadrupole multiplet of 12 absorption lines, by fixing the line width to 1.76 mm/s. The resulting parameters are reported in Table 1; the $\chi^2$ is 1.1. The small value of the QI parameter and the value of the asymmetry parameter close to 1 (which makes the absorption peak symmetrical) explain the difficulty in the resolution of the features of the spectrum.

Figure 4b shows the spectrum of the crystalline europium metaphosphate. In this sample, the fits without the quadrupole interaction or with a zero asymmetry parameter give $\chi^2$ values of 7 and 5, respectively. The spectrum can be reasonably fitted only by a quadrupole multiplet of 12 absorption lines. The resulting parameters are reported in Table 1; the $\chi^2$ is 1.5. The width of the Lorentzian components is (1.77±0.01) mm/s, equal to the width measured for $Cs_2NaEuCl_6$ (with $t$ = 1), within the experimental error.

Table 1. Mössbauer parameters obtained by fitting the spectra. $\delta$ is the isomer shift with respect to $EuF_3$, $\Gamma$ the FWHM, $eQV_{zz}$ the quadrupole interaction parameter and $\eta$ the asymmetry parameter. The $d$ and $Q_d$ Durbin-Watson parameters and the chi-squared parameter $\chi^2$ are also reported. Statistical errors are given in parenthesis as errors of the last digit.

| Compound | $\delta$ mm/s | $\Gamma$ mm/s | $eQV_{zz}$ mm/s | $\eta$ | $d$ | $Q_d$ | $\chi^2$ |
|---|---|---|---|---|---|---|---|
| EuS | −11.54(1) | 2.10(1) | | | 1.4 | 1.6 | 1.5 |
| $Cs_2NaEuCl_6$ | 0.93(1) | 1.76(1) | | | 2.0 | 1.6 | 1.2 |
| $Cs_2NaEu(NO_2)_6$ | 0.26(1) | 1.76(1) | | | 1.4 | 1.6 | 1.3 |
| $EuF_3$ | 0.00 | 1.76 fix. | −5.5(1) | 0.97(5) | 1.8 | 1.6 | 1.1 |
| $Eu(PO_3)_3$ | 0.21(1) | 1.77(1) | −4.50(5) | 1.0(1) | 1.4 | 1.6 | 1.5 |

## 4. Discussion

The spectra of the EuS and $Cs_2NaEuCl_6$ compounds, where Eu is in a site of cubic symmetry, show a single absorption line of Lorentzian shape; this indicates that our $SmF_3$ source can be considered monochromatic, i.e. the emission line can be considered unsplit. This fact permits the use of the Mössbauer effect in $^{151}Eu$ for the study of the site symmetry of the Eu atom in compounds whose crystallographic structure is not precisely known.

The anhydrous $EuF_3$ compound is very important because it is commonly used as reference for the values of isomer shift (IS) and it is considered the most ionic Eu compound. In this material, the Eu ions are located in sites of non-cubic symmetry, but the structure of the absorption peak has been resolved in this work for the first time. This was possible because the value of the FWHM of each component absorption line, split by the quadrupole interaction, has been fixed equal to the value measured for the crystalline $Eu^{3+}$ in $Cs_2NaEuCl_6$. The resolution of the spectrum of $EuF_3$ gives a better value of the shift of the fluoride referred to EuS; it was found IS = (11.54±0.01) mm/s. This value has been used in this work to convert the IS measured with respect to EuS into the IS referred to $EuF_3$; we suggest this procedure in order to take advantage of the use of EuS as IS standard in the experiments.

The analysis of the spectrum of the $Cs_2NaEu(NO_2)_6$ compound points out that the $Eu^{3+}$ ion is in a site with cubic symmetry, because there is no splitting due to the quadrupole interaction. This observation agrees with the published crystal structure for this material [14]. The narrow line width shows that the amount of disorder in this sample is extremely limited.

As for the crystalline europium metaphosphate, the quadrupole interaction indicates that there is a deviation of the $Eu^{3+}$ sites from cubic symmetry. Moreover, the non-zero asymmetry parameter indicates that the $Eu^{3+}$ site has a low symmetry (no threefold or fourfold axis passing through the Eu atom). The quadrupole interaction parameter is negative, as usual in the trivalent europium oxides. In general, the values reported for most of the compounds range from –4 to –8 mm/s. The values of the asymmetry parameter are in the range 0.8 - 1.0, in agreement with the results obtained for several crystalline oxides [2 - 5, 11].

## 5. Conclusions

The $^{151}$Eu Mössbauer spectroscopy permits to determine the symmetry of the Eu site, if the measurements are performed with a source that can be considered monochromatic (unsplit line).

The spectrum of the $Cs_2NaEu(NO_2)_6$ crystalline compound shows that the trivalent europium is accommodated in a site with cubic symmetry, with no splitting due to an electric field gradient.

In the $Eu(PO_3)_3$ crystalline metaphosphate, the rare earth is located at a site which is distorted with respect to cubic symmetry. This site has no threefold or fourfold symmetry axis because the components of the electric field gradient tensor along the principal axes are different.

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