Hyperfine interactions at europium sites in oxide glasses

G. Concas, F. Congiu, and C. Muntoni

Dipartimento di Scienze Fisiche, Università and Unità Istituto Nazionale di Fisica della Materia di Cagliari,
via Ospedale 72, I-09124 Cagliari, Italy

M. Bettinelli and A. Speghini

Sezione di Chimica, Istituto Policattedra, Facoltà di Scienze Matematiche, Fisiche e Naturali, Università di Verona, Ca' Vignal,
Strada le Grazie, I-37134 Verona, Italy

The shape of the γ resonance absorption peak of the Eu^{3+} ion in a disordered structure was investigated in some phosphate, borate, and silicate glasses by using ^{151}Eu Mössbauer spectroscopy. The quality of the fits was tested by using the Durbin-Watson d statistics. The observed full width at half maximum of the peak was resolved in a contribution of the broadening and a contribution of the quadrupole splitting, due to the distortion of the Eu site compared to a cubic symmetry. The Eu-O bond was found to have a covalent admixture with $6s$ character. The axial component of the electric-field gradient at the Eu site was found to be correlated with the optical basicity of the glass.

I. INTRODUCTION

Glass materials containing rare-earth ions exhibit interesting technological applications for the production of optical devices, for example, laser glasses, fiber amplifiers, and up-conversion materials. ^{151}Eu Mössbauer spectroscopy represents a useful and sensitive tool to investigate the local structure around rare-earth ions in europium-containing glasses.

Some measurements on trivalent Eu in oxide glasses found absorption lines broader than that expected for Eu^{3+} in a site with cubic symmetry.[1–4] The separation of the contribution of the broadening to the observed peak width from the contribution of the unresolved quadrupole splitting is an open question in glasses containing Eu^{3+}. This problem has been treated for Eu^{2+} in amorphous $EuFe_2Si_2$, where the full width at half maximum (FWHM) of the absorption peak is around 7 mm/s;[5] the authors fitted the absorption peak using a convolution of Lorentzian multiplets, corresponding to a distribution of the quadrupole interaction (QI) parameter or to a distribution of the asymmetry parameter.

The aim of this work is to determine the size of the quadrupole interaction in glasses containing trivalent europium. The hyperfine parameters will be discussed in terms of electronic properties and bonding of the lanthanide ion. We studied the absorption spectra of Eu^{3+} in some phosphate, borate, and silicate glasses.

II. EXPERIMENTAL DETAILS

A strontium metaphosphate glass of composition $0.1Eu(PO_3)_3 \cdot 0.9Sr(PO_3)_2$ (labeled ESPO) was prepared by mixing appropriate quantities of $SrCO_3$, $(NH_4)_2HPO_4$ (both Carlo Erba RPE), and Eu_2O_3 (Aldrich 99.99%) in a sintered alumina crucible and melting the batch for 2 h at 1250 °C. The melt was cast in a brass mold and the obtained glass was annealed for 12 h at 450 °C. Glasses of compositions $0.1Eu(PO_3)_3 \cdot 0.9Zn(PO_3)_2$ (EZPO) and $0.1Eu(PO_3)_3 \cdot 0.9Pb(PO_3)_2$ (EPPO) were prepared as described elsewhere.[6] A zinc borate glass of composition $4ZnO \cdot 3B_2O_3$ doped with 2.5 mol % of Eu^{3+} (substituting for Zn^{2+}) (EZBO) was prepared by mixing appropriate quantities of ZnO, H_3BO_3 (both Carlo Erba RPE), and Eu_2O_3 in a platinum crucible and melting the batch at 1250 °C for 4 h. The melt was cast in a brass mold and the obtained glass was annealed for 12 h at 500 °C. A gel-derived monolithic silica glass nominally doped with 1% mol Eu^{3+} (ESO) was prepared following the procedure described by Campostrini *et al.*[7] The sample was heated for 48 h at 180 °C and left aging for 1 year. Finally, a multicomponent aluminosilicate glass of composition (by weight) SiO_2 =59%, MgO=8%, Al_2O_3=14%, SrO=10%, Li_2O=2%, Eu_2O_3=4.5%, Cs_2O=1.5%, ZnO=1% (ESMASO) was prepared following the procedure described for a scintillating glass for x-ray detection having the same composition, but in which Ce_2O_3 replaces Eu_2O_3.[8,9]

The Mössbauer absorption spectra were obtained in a standard transmission geometry, using a source of $^{151}SmF_3$ with activity 3.7 GBq. A calibration was performed using a source of ^{57}Co in rhodium and a natural iron foil as absorber. The FWHM of our ^{151}Sm source was measured on $Cs_2NaEuCl_6$, which contains Eu^{3+} in a cubic site;[10] the FWHM measured with an absorber of effective thickness $t=1$ is 1.76(1) mm/s (error is given in parentheses). The effective thicknesses are approximately calculated using the recoiless fraction of the source $f=0.6$; $t=1$ corresponds to a surface density of europium equal to 3.8 mg/cm^2. The isomer shift (IS) of the source was measured using anhydrous EuF_3; the values of isomer shift are referred to the fluoride.

The measurements on the oxide glasses were carried out at room temperature on powder samples with effective thickness $t=1$, except for the glasses EPPO and ESO. The thickness was 0.5 for EPPO in order to optimize the signal-to-noise ratio, and 0.1 for ESO because of the small quantity of sample available. The absorbers were contained in a Plexiglas holder. In our experimental conditions, we can use the thin absorber approximation in the analysis of the experimental data.[11,12]

The absorption spectra were tentatively analyzed by fitting the data using a single Lorentzian line shape, but the quality of the fit was very poor in various samples. These trial fits showed that it was necessary to fit the absorption spectra allowing for the quadrupole interaction; we used the method for the analysis of pure quadrupole spectra proposed by Shenoy and Dunlap,[13] with a value of the quadrupole ratio $R = 1.312$.[14]

It is of great importance to test the correctness of the fitting procedure; the use of a quadrupole multiplet of 12 lines with Lorentzian shape, corresponding to the 12 allowed transitions, is fully justified in crystalline materials in the thin absorber approximation.[12] In Eu^{3+}-containing glasses it must be verified if it is possible to use a single quadrupole multiplet or a convolution of quadrupole multiplets.[5,15]

The quality of the fits was tested using the usual χ^2 test and a weighted form of the Durbin-Watson d statistics, which was used in the Rietveld analysis of powder diffraction data.[16] The d value quantifies the serial correlation between adjacent least-squares residuals and is defined as

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

where N is the number of experimental data, Δ_i is the ith residual, and σ_i indicates the standard deviation. It is useful to test d against the parameter Q_d, 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.

III. RESULTS

In the absorption spectrum of the strontium metaphosphate glass the maximum resonant absorption, relative to the background, is 2.6% and the standard deviation of the data is 0.035%. Figure 1(a) shows the experimental data and a trial fit by a single Lorentzian line; Fig. 1(b) reports the difference between the experimental and the calculated data. The presence of structure in the plot of the difference clearly indicates that our spectrum deviates strongly from a single Lorentzian line shape. This visual evidence is confirmed by the parameters of the fit reported in Table I, with $\chi^2 = 2.58$, $d = 0.75$, and $Q_d = 1.64$; if $d < Q_d < 2$, successive values of the residuals tend to have the same sign, indicating a systematic deviation of the experimental data from the fitting curve.

The data were then tentatively fitted allowing for the quadrupolar interaction parameter (e^2QV_{zz}), but with the asymmetry parameter (η) fixed equal to zero; Fig. 2(a) shows this fit while Fig. 2(b) is the plot of the residuals. This fit is better than that reported in Fig. 1(a), but does not reproduce well the experimental data; the residuals have serial positive correlation, as can be seen from Fig. 2(b) and from the d and Q_d values reported in Table I.

The experimental spectrum was then satisfactorily fitted allowing for the complete quadrupolar interaction with a free asymmetry parameter; in this procedure all the parameters reported in Table II and the background were full free pa-
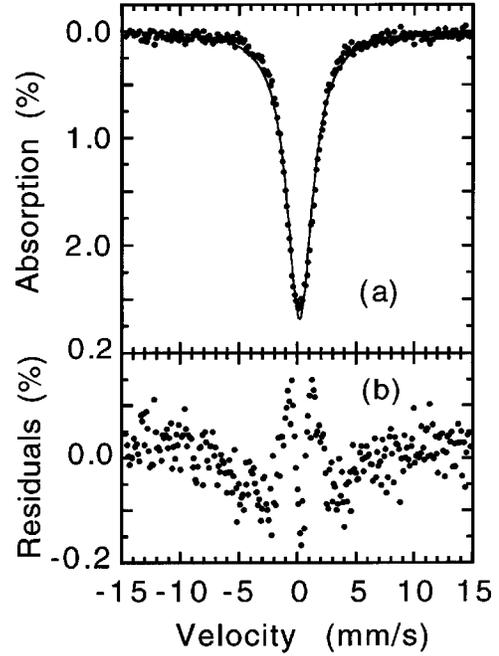
FIG. 1. (a) Absorption spectrum of the sample ESPO: The experimental data (dots) and the fit by a single Lorentzian curve (solid line) are shown. (b) Difference between experimental and calculated data.

rameters of the fit, without any constraint. The resulting calculated curve is shown in Fig. 3(a); the residuals are shown in Fig. 3(b). The lack of structure in the plot of the residuals demonstrates that this is the correct peak shape; the values of the control parameters reported in Table I confirm that this fit is fully satisfactory.

All the physical parameters resulting from this last fit are physically acceptable; the value of η lies between 0 and 1. The value of the FWHM of the Lorentzian component of the multiplet is 1.88 mm/s and is larger than the value of the FWHM measured in trivalent Eu in a cubic site.

Therefore the full width at half maximum of the absorp-

TABLE I. Control parameters relative to different fits. Fit 1, one Lorentzian curve; fit 2, quadrupole multiplet with asymmetry parameter equal to zero; fit 3, quadrupole multiplet with free parameters. d and Q_d are the Durbin-Watson parameter; χ^2 is the chi-squared parameter.

Sample	Fit	d	Q_d	χ^2
ESPO	1	0.8	1.6	2.6
	2	1.1	1.6	1.7
	3	1.7	1.7	1.1
EZPO	1	0.8	1.6	2.5
	2	1.2	1.6	1.7
	3	1.8	1.7	1.1
EZBO	1	1.0	1.6	2.2
	2	1.3	1.6	1.6
	3	1.8	1.7	1.1
ESMASO	1	0.5	1.6	4.6
	2	0.8	1.6	3.0
	3	1.7	1.7	1.4
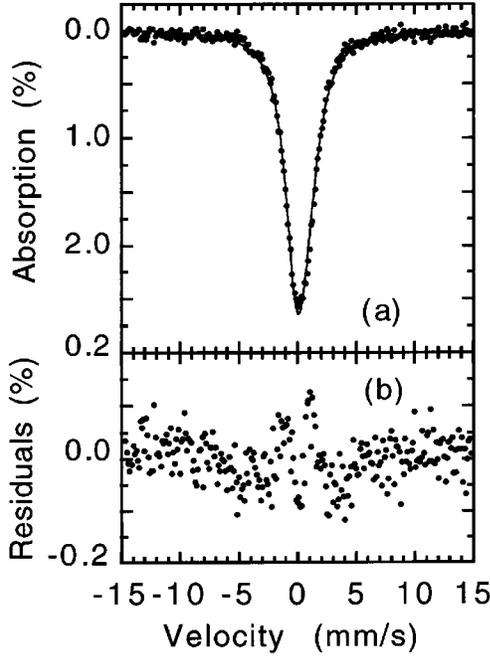
FIG. 2. (a) Absorption spectrum of the sample ESPO: The experimental data (dots) and the fit by a quadrupole multiplet with asymmetry parameter equal to zero (solid line) are shown. (b) Difference between experimental and calculated data.

FIG. 3. (a) Absorption spectrum of the sample ESPO: The experimental data (dots) and the fit with all free parameters (solid line) are shown. (b) Difference between experimental and calculated data.

tion peak ($\gamma_p = 2.67$ mm/s) can be interpreted: It is the result of the unresolved quadrupole interaction with $e^2QV_{zz} = -6.1$ mm/s and of the width of the Lorentzian component.

The use of a single quadrupole multiplet of Lorentzian components is based on fundamental arguments, because each transition corresponds to a Lorentzian absorption line in the thin absorber approximation.[11,12] The use of a convolution of quadrupole multiplets is justified only if a fit with a single multiplet shows a departure from the Lorentzian shape, because of the structural disorder of the glass;[15,17] this departure was not found in our glasses.

The absorption spectra of the other glasses are shown in Fig. 4, Fig. 5, and Fig. 6; the best fits are also shown for each sample. The parameters obtained by the fitting procedure are reported in Table II.

The spectra of the glasses EZPO, EZBO, and ESMASO are fitted satisfactorily only by accounting for the quadrupolar interaction with asymmetry parameter $\eta \neq 0$; the quality

of the trial fits was tested by the control parameters reported in Table I. It was not possible to resolve the quadrupole interaction in the glasses EPPO and ESO, beacause of the magnitude of the quadrupole splitting and of the signal-to-noise ratio.

The spectrum of the glass EPPO can be well fitted by a single Lorentzian line; the analysis allowing for the quadrupolar interaction does not improve significantly the fit. The peak width ($\gamma_p = 2.26$ mm/s) is the smallest of all of the samples, also accounting for the thickness broadening.[18] This peak width indicates that the quadrupole splitting corresponds to $|e^2QV_{zz}|$ less than 5 mm/s; this fact does not allow us to resolve the structure of the peak.

The spectrum of the glass ESO is rather noisy because of the small quantity of sample available. The fit by a single Lorentzian line is good; the FWHM of the absorption peak is compatible with a size of the quadrupolar interaction in the range found for the other samples.

TABLE II. Parameters obtained by fitting. δ is the isomer shift with respect to EuF$_3$, γ_p is the FWHM of the absorption peak, Γ is the FWHM of the Lorentzian components, e^2QV_{zz} is the quadrupole interaction parameter, η is the asymmetry parameter, and d, Q_d, and χ^2 are the Durbin-Watson and chi-squared parameters. Errors are given in parentheses.

Sample	δ (mm/s)	γ_p (mm/s)	Γ (mm/s)	e^2QV_{zz} (mm/s)	η	d	Q_d	χ^2
ESPO	0.36(2)	2.67(2)	1.88(2)	$-6.1(1)$	0.80(5)	1.7	1.7	1.1
EZPO	0.37(2)	2.48(2)	1.83(2)	$-5.3(1)$	0.83(6)	1.8	1.7	1.1
EPPO	0.29(2)	2.26(5)				1.8	1.6	1.1
EZBO	0.45(2)	2.76(2)	1.85(5)	$-6.6(1)$	0.83(6)	1.8	1.7	1.1
ESO	0.44(7)	2.4(2)				2.0	1.6	0.9
ESMASO	0.55(2)	3.11(2)	1.96(2)	$-7.8(1)$	0.81(3)	1.7	1.7	1.4
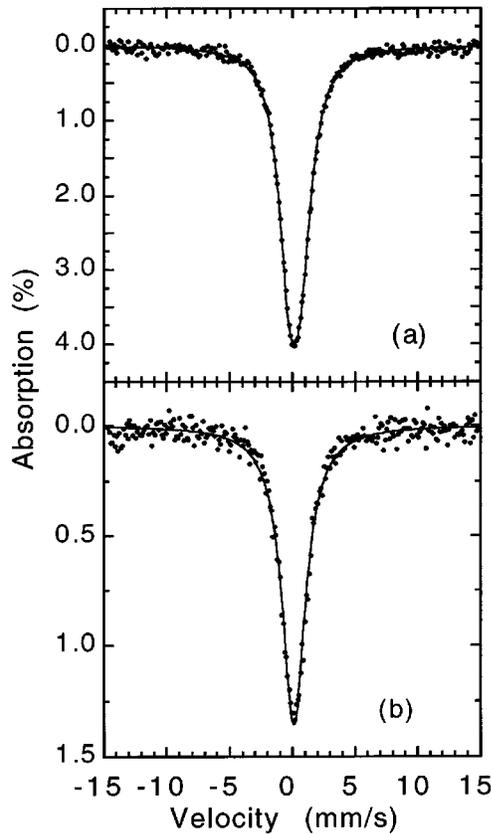
FIG. 4. Absorption spectra of the samples EZPO (a) and EPPO (b): The experimental data (dots) and the fit (solid line) are shown.

IV. DISCUSSION

All of the spectra show only one resonance peak with values of the isomer shift between 0.29 and 0.56 mm/s, corresponding to an oxidation number +3; there is no detectable presence of Eu^{2+}.

The phosphate glasses show the smallest values of isomer shift. The IS of most nonconducting compounds in the trivalent charge state deviates from the shift of the fluoride towards a higher electron density at the nucleus;[19] this applies also to the present oxide glasses. This fact is a consequence
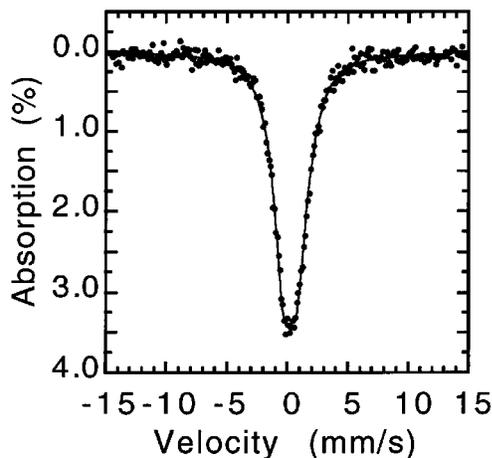
FIG. 5. Absorption spectrum of the samples EZBO: The experimental data (dots) and the fit (solid line) are shown.
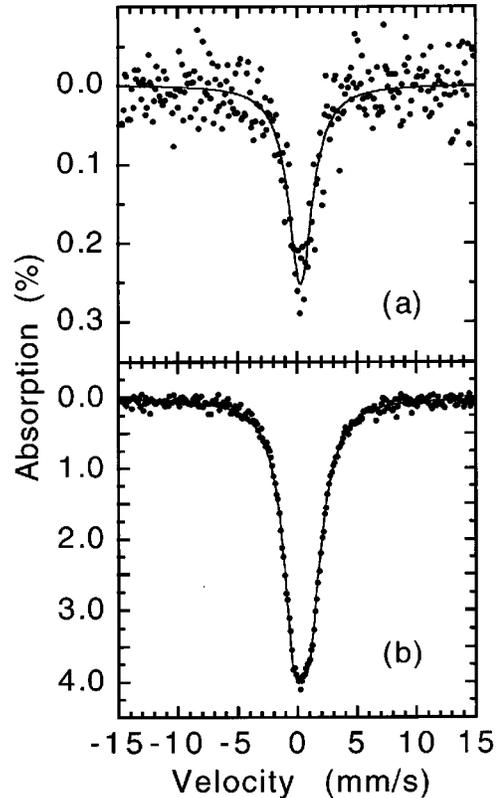
FIG. 6. Absorption spectra of the samples ESO (a) and ES-MASO (b): The experimental data (dots) and the fit (solid line) are shown.

of covalent admixtures to the bond, since the fluoride compound is considered to be the most ionic species.[19]

The electron density of Eu^{3+} at the nucleus, and therefore the isomer shift, increases by adding $6s$ electrons, while it decreases by adding $4f$ or $5d$ electrons, because of the screening. It is possible to estimate the charge transfer to the Eu^{3+} ion by using the optical basicity (Λ) concept proposed by Duffy and Ingram,[20,21] which measures the electron donation by the oxygen anions. It is defined as

$$\Lambda = \sum_{i=1}^{n} \frac{z_i r_i}{2\gamma_i}, \qquad (3)$$

where z_i is the oxidation number of the ith cation, γ_i is its basicity moderating parameter, r_i is the atomic ratio of the ith cation and of the oxygen, and the sum is extended over the number n of cation species.

Figure 7(a) shows the isomer shift of the oxide glasses versus the optical basicity, calculated using the parameters given by Duffy and Ingram;[20–22] the IS increases along with the optical basicity. This result agrees with the correlation found by Tanabe et al. in silicate and aluminate glasses.[2] Since the optical basicity measures the electron donation by the oxygen anions to the metal ion used as probe, i.e., the europium, the correlation that we found indicates that the charge transferred to the Eu^{3+} ion occupies mainly $6s$ orbitals. This result indicates that the phosphates have the smallest charge in the $6s$ orbitals in comparison with the other oxide glasses.
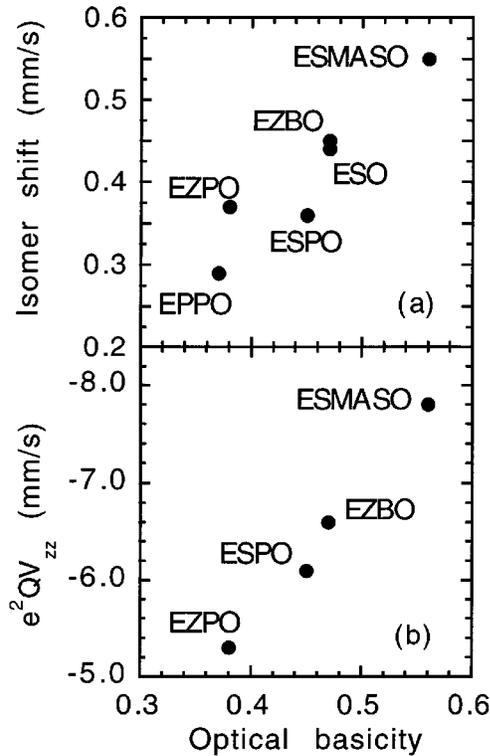
FIG. 7. (a) Isomer shift versus calculated optical basicity. (b) Quadrupole interaction parameter versus calculated optical basicity.

The QI parameter is expressed as e^2QV_{zz}, where e is the proton charge, Q is the quadrupole moment of the nucleus, and V_{zz} is the axial component of the electric field gradient (EFG); V_{zz} is given by the relation

$$V_{zz} = V_{zz}^{latt} + V_{zz}^{val}, \qquad (4)$$

where V_{zz}^{latt} is the lattice contribution and V_{zz}^{val} is the valence contribution. In Eu^{3+}, V_{zz}^{val} is due to a second-order $4f$ contribution;[23] in a large class of crystalline oxides, it is positive and equal, in absolute value, to about half V_{zz}^{latt}, which is negative.[23,24] Therefore the QI parameter is usually negative in the trivalent europium oxides; in particular values ranging from -5 to -8 mm/s are reported for most of the compounds.[23–25] In these cases values of the asymmetry parameter of around 0.8 are frequently found.[24,25]

In the oxides glasses studied here, the values of the parameter e^2QV_{zz} are negative and similar to those found in crystals; this fact suggests that the relative contribution of the two components to V_{zz} is not very different from that found in crystals.

A nonzero QI parameter indicates that there is a deviation of the Eu sites from the cubic symmetry; therefore it is related to the distortion of the sites. Moreover, the fact that the asymmetry parameter is different from zero indicates that there is no fourfold or threefold axis of simmetry passing through the Mössbauer nucleus.

Figure 7(b) shows that the QI parameter increases, in absolute value, along with the optical basicity; this correlation is confirmed in the case of lead phosphate glass, for which $|e^2QV_{zz}|$ is estimated to be less than 5 mm/s. This empirical

correlation can be due to an influence of a different degree of covalency of the Eu-O bond on the axial component of the EFG; it is consistent with the observation of an increase of V_{zz} on decreasing the minimum Eu-O distance in an isostructural series of oxides (pyrochlores).[23]

In the metaphosphate glasses the structure consists of long chains of PO_4 tetrahedra; in particular, the metal cations act as network modifiers linking complex phosphate chain and ring structures.[26] In a study of the optical spectroscopy of the metaphosphate glasses $Ba(PO_3)_2$, $Pb(PO_3)_2$, and $Zn(PO_3)_2$ doped with 2.5 mol % of $Eu(PO_3)_3$, the crystal field parameters (in C_{2v} symmetry) were obtained for the Eu^{3+} sites from the site-selective $^5D_0 \rightarrow {}^7F_J$ luminescence spectra at 77 K.[6] A comparison of the results for the different glasses showed that the magnitude of the crystal field parameter B_{20}, which is related to the QI parameter,[23,27,28] was smaller for lead metaphosphate than for the other glasses. Moreover, in the same study the asymmetry ratios AR, reflecting the average distortion of the Eu^{3+} sites,[29] were obtained from

$$AR = \frac{I(^5D_0 \rightarrow {}^7F_2)}{I(^5D_0 \rightarrow {}^7F_1)}, \qquad (5)$$

where I are the integrated intensities of the $^5D_0 \rightarrow {}^7F_2$ and the $^5D_0 \rightarrow {}^7F_1$ inhomogeneous emission bands. The lowest value of the asymmetry ratio AR was found for lead metaphosphate glass, indicating that in this glass the Eu^{3+} sites are on average less distorted than in the other metaphosphates.

The behavior of the B_{20} parameter could not be explained on the basis of the size of the modifier cations, and was attributed to the strong and directional nature of the Pb-O bond, which effectively reduces the crystal field at the doping ions, as already proposed for Nd^{3+}-doped lead phosphate glasses.[30] In the metaphosphate glasses considered in this study, the smallest value of the QI parameter was found for the glass EPPO; this observation qualitatively agrees with the results obtained from luminescence spectroscopy. The present results confirm that the presence of the Pb^{2+} ion as a network modifier strongly influences the properties of the Eu-O bond and the crystal field at the lanthanide sites in oxide glasses.

In the glasses ESPO, EZPO, EZBO, and ESMASO, it is possible to evaluate the true broadening of the Lorentzian component of the multiplets. This broadening results from local inhomogeneities of the hyperfine fields;[31] these can be due to stoichiometric inhomogeneities, impurities, and defects, also found in crystals,[32] or to the disordered structure of the glass.[15,17,33] The FWHM measured in our glasses must be compared with the FWHM measured in crystalline trivalent cubic Eu (in $Cs_2NaEuCl_6$) with the same effective absorber thickness ($t = 1$); the broadening ranges from 0.07 mm/s in the glass EZPO to 0.20 mm/s in the glass ESMASO.

The values of the width of the Lorentzian components are not directly comparable with that reported for Eu^{3+} in crystal oxides[24] because of the different linewidths of the various $^{151}SmF_3$ sources[25] and of the different absorber thickness used.[18] Nevertheless, the broadenings we found are not very different from those found in crystals; this fact indicates that

the disorder of the glass structure does not have a dramatic effect on the width in glasses containing Eu^{3+}. This observation agrees with the results found by Coey *et al.*[34] in fluorozirconate glasses, where the FWHM of the absorption peak of Eu^{3+}, which includes an unresolved quadrupole splitting, was found to be 2.10 mm/s.

V. CONCLUSIONS

In the oxide glasses we examined, the europium atom was found to have oxidation number +3. The bond is ionic with a small covalent admixture with $6s$ character.

The FWHM of the absorption peak results from the quadrupole interaction and from the broadening due to inhomogeneities of the hyperfine fields; these contributions are separated in most of the samples.

In the glasses ESPO, EZPO, EZBO, and ESMASO the europium ion is accommodated in sites distorted with respect to a cubic symmetry, with no threefold or fourfold simmetry axis. In the glasses EPPO and ESO the structure of the spectra is not resolved but the FWHM of the absorption peak is compatible with a distortion of the sites.

The broadening of the Lorentzian component of the peak is at maximum equal to 10% of the width. The axial component of the EFG was found to be correlated with the optical basicity of the glass.

[1] M. Taragin and J.C. Eisenstein, Phys. Rev. B **2**, 3490 (1970).

[2] S. Tanabe, K. Hirao, and N. Soga, J. Non-Cryst. Solids **113**, 178 (1989).

[3] S. Music, Z. Bajs, K. Furic, and V. Mohacek, J. Mater. Sci. Lett. **10**, 889 (1991).

[4] S. Tanabe, T. Hanada, T. Ohyagi, and N. Soga, Phys. Rev. B **48**, 10 591 (1993).

[5] J.A. Hodges, G. Jehanno, and J.M. Friedt, Hyperfine Interact. **27**, 365 (1986).

[6] J.A. Capobianco, P.P. Proulx, M. Bettinelli, and F. Negrisolo, Phys. Rev. B **42**, 5936 (1990).

[7] R. Campostrini, G. Carturan, M. Ferrari, M. Montagna, and O. Pilla, J. Mater. Res. **7**, 745 (1992).

[8] G. Zanella, R. Zannoni, R. Dall'Igna, B. Locardi, P. Polato, M. Bettinelli, and A. Marigo, Nucl. Instrum. Methods A **345**, 198 (1994).

[9] M. Bettinelli, G. Ingletto, P. Polato, G. Pozza, G. Zanella, and R. Zannoni, Phys. Chem. Glasses (to be published).

[10] L.R. Morss, M. Siegal, L. Stenger, and N. Edelstein, Inorg. Chem. **9**, 1771 (1970).

[11] S. Margulies and J.R. Ehrman, Nucl. Instrum. Methods **12**, 131 (1961).

[12] I. Nowik and I. Felner, Hyperfine Interact. **28**, 959 (1986).

[13] G.K. Shenoy and B.D. Dunlap, Nucl. Instrum. Methods **71**, 285 (1969).

[14] J.G. Stevens, in *CRC Handbook of Spectroscopy*, edited by J.W. Robinson (CRC Press, Boca Raton, 1981), Vol. III, p. 464.

[15] C. Wivel and S. Morup, J. Phys. E **14**, 605 (1981).

[16] R.J. Hill and H.D. Flack, J. Appl. Crystallogr. **20**, 356 (1987).

[17] G. Concas, F. Congiu, C. Muntoni, and G. Pinna, J. Phys. Chem. Solids **56**, 877 (1995).

[18] G.J. Perlow, in *Chemical Applications of Mössbauer Spectroscopy*, edited by V.I. Goldanskii and R.H. Herber (Academic Press, New York, 1968), p. 377.

[19] E.R. Bauminger, G.M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts*, edited by G.K. Shenoy and F.E. Wagner (North-Holland, Amsterdam, 1978), p. 661.

[20] J.A. Duffy and M.D. Ingram, J. Inorg. Nucl. Chem. **37**, 1203 (1975).

[21] J.A. Duffy and M.D. Ingram, J. Non-Cryst. Solids **21**, 373 (1976).

[22] J.A. Duffy, Chem. Br. **30**, 562 (1994).

[23] C.L. Chien and A.W. Sleight, Phys. Rev. B **18**, 2031 (1978).

[24] Z.M. Stadnik, G. Stroink, and T. Arakawa, Phys. Rev. B **44**, 12 552 (1991).

[25] F. Grandjean and G.J. Long, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, edited by G.J. Long and F. Grandjean (Plenum Press, New York, 1989), Vol. 3, p. 513.

[26] G. Cormier, J.A. Capobianco, and A. Monteil, J. Non-Cryst. Solids **168**, 115 (1994).

[27] J. Blok and D.A. Shirley, Phys. Rev. **143**, 278 (1966).

[28] R.G. Barnes, R.L. Mössbauer, E. Kankeleit, and J.M. Poindexter, Phys. Rev. **136**, A175 (1964).

[29] E.W.J.L. Oomen and A.M.A. Van Dongen, J. Non-Cryst. Solids **111**, 205 (1989).

[30] M.J. Weber, L.A. Boatner, and B.C. Sales, J. Non-Cryst. Solids **74**, 167 (1985).

[31] P. Gütlich, R. Link, and A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry* (Springer-Verlag, Berlin, 1978), p. 13.

[32] C. Janot, *L'Effect Mössbauer et ses Applications* (Masson & Cie, Paris, 1972), p. 115.

[33] M.P. Medda, G. Piccaluga, G. Pinna, M. Bettinelli, and G. Cormier, Z. Naturforsch. A **49**, 977 (1994).

[34] J.M.D. Coey, A. McEvoy, and M.W. Shafer, J. Non-Cryst. Solids **43**, 387 (1981).