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Emission spectra and local symmetry of the Eu^{3+} ion in polymer electrolytes

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The emission spectra of poli(ethylene oxide) (PEO) and poli(propylene oxide) (PPO) modified by different concentrations of europium bromide, PEO$_n$EuBr$_3$ ($n = 8,12,16,20,24,28,32,80$) and PPO$_n$EuBr$_3$ ($n = 32,80$), were recorded and the observed lines assigned to the intra $4f^{N=6}\ {}^5D_{0,1} \rightarrow {}^7F_{0-4}$ transitions. The corresponding Stark levels were identified for the ${}^7F_{0-4}$ and ${}^5D_0$ states. The luminescence of both these polymer complexes (presenting almost identical characteristics) is sufficiently intense to suggest their use as possible luminescence devices. The local coordination of a rare-earth ion in polymer electrolytes is attempted. We used a local-field interaction model, the polarization behavior of the ${}^5D_0 \rightarrow {}^7F_0$ transition, certain moment operators, and the allowed optical activity of the ${}^7F_{2,3,4}$ components for identifying the approximate local symmetry of Eu^{3+} to the C$_{2v}$ point group.

I. INTRODUCTION

Polymer electrolytes with monovalent and divalent cation salts have received considerable attention in the last two decades.[1] In spite of some recent results concerning basically the ionic conductivity of polymer electrolytes, modified by trivalent rare-earth (RE) cations,[2,3] their optical properties and the related local coordination have received very little attention up to now.[4–6] Because polymeric electrolytes in general present certain liquidlike features, with the polymer acting as an "immobile" solvent[7] the structural properties of these materials are predominantly determined by the local structure in the vicinity of the ions' salt. Following a previous work,[6] the present paper is a first attempt to determine the local coordination of an RE ion in polymer electrolytes by means of their luminescence characteristics. We used the emission spectra of poli(ethylene oxide) (PEO) and poli(propylene oxide) (PPO) doped with EuBr$_3$ [(PEO/PPO)$_n$EuBr$_3$] with n being the number of oxygen atoms in the polymeric chain per Eu^3+ cation, for investigating the local structure surrounding the europium ion. Emission spectra of (PEO/PPO)$_n$EuBr$_3$ were recorded for different concentrations of the salt and the observed lines were assigned to the ${}^5D_{0,1} \rightarrow {}^7F_{0-4}$ transitions (Table I; Sec. III). These lines, besides being well defined, are sharper than the corresponding lines identified for Eu^{3+} in glassy media,[8,9] with widths of the order of tens of cm^{-1} (Fig. 1). This seems to indicate that in PEO and PPO the number of different microscopic environments for the ion is smaller than the characteristic number associated with glasses; that is, the order of coordinated ligands in these polymer complexes seems to extend beyond the first-neighbor shell.

The emission spectra obtained indicate that, independently of the electrolytes phases, only one local symmetry occurs for the ion, and that this coordination may belong only to the triclinic, monoclinic, or orthorhombic crystallographic classes. More specifically, we show (Sec. V) that the possible site symmetries of the europium ion are restricted to the groups C_1, C_s, C_2 and C_{2v}. The results of the polarization behavior of the ${}^5D_0 \rightarrow {}^7F_0$ transition excluded the C_s point group (Sec. VI).

The interaction of the ion with its surrounding neighbors reproduces the connection between the observed energies and the local symmetry features of the PEO/PPO complexes. This interaction is expressed by a local-field Hamiltonian,[10] written in terms of a set of parameters which encompass all the dynamics, and which are directly related to the local symmetry characteristics of the ion in each complex. This model does not furnish, however, a unique correspondence between one definite point group and one given set of parameters. In fact, the model does not decide between two sets of dynamical parameters: a first set associated with the point group C_1, and a second one associated with the point groups C_2 and C_{2v} (Sec. IV).

We looked, therefore, for another method of connecting the observed energies with the symmetry-related dynamical parameters, which would permit a selection between the two possibilities C_1 and C_2, C_{2v}. This is accomplished by expressing both the observed transition energies and the dynamical parameters in terms of certain moment operators introduced by Leavitt.[11,12] Since this explicitly relates the observed energies with the local symmetry characteristics of the Eu^{3+} in the complexes, it will select, therefore, the set of parameters which best reproduces these energies; that this, it will select between the two cases C_1 and C_2, C_{2v}. The weaker and less well resolved sublevels of ${}^7F_{2,3,4}$ will be related to components without optical activity. This, in turn, will render possible the identification of the approximate Eu^{3+} local coordination in PEO and PPO electrolytes (Sec. VII).

II. EXPERIMENTAL

A. Materials

Polymer electrolytes of PEO (MW = 5×10^6, Aldrich) and PPO (Zeon Chemicals) with anhydrous europium bromide (Rare Earth Products) were prepared by the usual solvent casting technique. The yellowish-green solutions of $EuBr_3$ in ethanol were filtered and mixed with the PEO and PPO dissolved in isopropanol and acetonitrile. The $(PEO/PPO)_nEuBr_3$ solutions, with $n=8,12,16,20,24,28,32,80$ for PEO, and with $n=32,80$ for PPO, were cast into glass formers on Teflon plates and the residual solvent was removed by heating the resulting films for 48 h at 70 °C, under vacuum. The films were next vacuum-dried for several days and stored in an inert atmosphere dry-box. As expected, these europium electrolytes, with a heterogeneous salt distribution (analyzed by differential scanning calorimetry techniques, x-ray diffraction, and electronic and optical microscopy) reveal a complex morphology, characterized, in PEO complexes, by an admixture of crystalline and amorphous phases, and, in the two PPO electrolytes with low salt concentration, predominantly by amorphous regions.[13]

TABLE I. Luminescence emission for PEO_nEuBr_3 ($n=8,28,80$) and $PPO_{80}EuBr_3$.

		Energy (cm^{-1})/relative intensity[a]		
Transition	PEO_8	PEO_{28}	PEO_{80}	PPO_{80}
$^5D_0\rightarrow{}^7F_0$				
	17 254.8/3	17 266.7/14	17 254.8/4	17 262.2/24
$^5D_0\rightarrow{}^7F_1$				
	16 962.1/6	16 965.0/18	16 959.2/6	16 957.8/25
	16 874.8/7	16 887.6/22	16 859.1/6	16 889.0/26
	16 803.9/5	16 801.1/16	16 791.2/5	16 809.5/23
$^5D_0\rightarrow{}^7F_2$				
	16 326.5/32	16 326.5/62	16 329.2/28	16 326.5/69
	16 289.3/100	16 285.3/100	16 292.0/100	16 292.0/100
	16 245.6/14	16 206.1/35	16 173.4/9	16 189.1/28
	16 224.0/10	16 178.6/32	16 135.5/11	16 173.4/29
	16 131.6/10	16 130.3/24	16 119.9/10	16 131.6/25
$^5D_0\rightarrow{}^7F_3$				
	15 422.6/0	15 404.8/7	15 402.4/4	15 401.2/11
	15 408.3/1	15 384.6/8	15 350.4/4	15 391.7/11
	15 384.6/2	15 355.1/8	15 339.8/4	15 372.8/11
	15 370.4/1	15 337.4/7	15 322.0/3	15 351.6/11
	15 351.6/2	15 311.6/7	15 292.9/4	15 332.7/10
	15 313.9/1	15 298.7/7	15 276.5/3	15 306.9/10
	15 267.2/1	15 282.3/6	15 261.4/3	15 278.8/10
$^5D_0\rightarrow{}^7F_4$				
	14 559.2/1	14 529.6/9	14 534.9/4	14 513.8/10
	14 515.9/3	14 504.3/10	14 515.9/5	14 497.0/9
	14 484.4/2	14 473.9/10	14 484.4/4	14 476.0/10
	14 432.1/4	14 436.3/12	14 427.9/4	14 436.3/9
	14 413.4/3	14 415.5/13	14 376.1/4	14 413.4/10
	14 341.0/4	14 373.0/12	14 314.3/5	14 369.9/11
	14 316.4/4	14 332.8/16	14 294.9/5	14 316.4/20
	14 302.1/4	14 291.8/17	14 263.3/5	14 289.8/12
	14 225.7/13	14 220.6/15	14 225.7/12	14 222.6/17
$^5D_1\rightarrow{}^7F_3$				
	17 170.3/1	17 130.6/8	17 199.9/3	17 185.1/19
	17 129.2/1	17 117.4/8	17 126.2/3	17 158.1/19
	17 117.4/1	17 105.7/8	17 063.4/4	17 056.1/18
				17 012.6/6
$^5D_1\rightarrow{}^7F_4$				
	16 086.2/11	16 114.7/24	16 078.5/14	16 110.8/25
	16 064.3/16	16 069.4/22	16 069.4/17	16 087.5/23
	16 051.3/16	16 053.9/23	16 063.0/18	16 072.0/24
	16 041.1/12	16 047.5/23	16 052.7/16	16 061.7/24
	16 025.6/5	16 033.3/22	16 043.6/13	16 043.6/20

[a] Normalized in terms of the intensity of the $^5D_0\rightarrow{}^7F_2$ strongest peak.

B. Measurements

Emission spectra for $(PEO/PPO)_n EuBr_3$ were recorded, with a resolution of 0.05 nm, for several excitation wavelengths (predominantly 395 and 465 nm, which correspond to the two more intense lines in the excitation spectra), in the temperature range 13–310 K, using a KRATOS LH151N/1S 1000 W xenon arc lamp as the excitation source, a KRATOS GM-252 excitation monochromator, and a 1704 SPEX 1-m Czerny-Turner spectrometer coupled to an RCA C31034 photomultiplier.

Polarization experiments were performed at 13 K with the exciting light vertically polarized (**z** direction) and focused along a direction (**x** direction) normal to the plane of the electrolyte films. Using a second polarizer, the transitions ${}^5D_{0,1} \rightarrow {}^7F_{0-4}$ were recorded in a direction perpendicular to the **x** direction, for two normal orientations, one having the electric field of these transitions parallel to the **z** direction and the other having this field parallel to the xy plane.

III. THE EMISSION SPECTRA

The emission spectra of $(PEO/PPO)_n EuBr_3$ show a considerable number of lines between 570 and 710 nm, representing the transitions ${}^5D_{0,1} \rightarrow {}^7F_{0-4}$ between the first excited states and the ground multiplet of the Eu^{3+} ion. These spectra—which are dominated by the transitions to the ${}^7F_2$ manifold—present very well defined lines assigned to the ${}^5D_0 \rightarrow {}^7F_{0,1,2,4}$ transitions and less well defined weak ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_1 \rightarrow {}^7F_{3,4}$ transitions. The ${}^5D_0 \rightarrow {}^7F_{2,4}$ and ${}^5D_1 \rightarrow {}^7F_{3,4}$ transitions are of electric dipole (ED) nature (corresponding to a selection rule $\Delta J \leq 6$, $0 \leftrightarrow 0$ forbidden, or $\Delta J = 2,4,6$, if the initial state has $J = 0$); the ${}^5D_0 \rightarrow {}^7F_1$ is a magnetic dipole (MD) induced transition (for which $\Delta J = 0, \pm 1$, $0 \leftrightarrow 0$ forbidden).

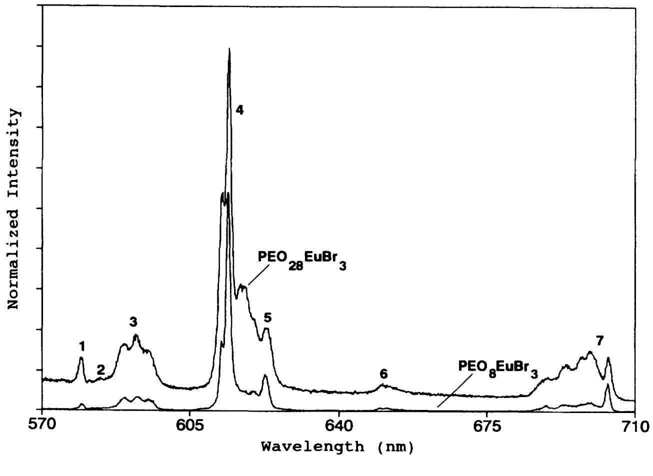

FIG. 1. Emission spectra ($\lambda_{exc} = 395$ nm) for PEO_8EuBr_3 and $PEO_{28}EuBr_3$ at 14 K. (1), (3), (4), (6), (7): ${}^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$; (2), (5): ${}^5D_1 \rightarrow {}^7F_{3,4}$. The emission intensities are proportional to the photon flux and are normalized relative to most intense ${}^5D_0 \rightarrow {}^7F_2$ peak.

As commonly occurs, the ${}^5D_1 \rightarrow {}^7F_{3,4}$ transitions were observed in the same wavelength region of the ${}^5D_0 \rightarrow {}^7F_{1,2}$ lines. As temperature increased from 13 to 310 K, the intensity of the lines was approximately reduced by an order of magnitude, but no significant variations were detected in the Stark energies. Similar results were obtained for the several excitation wavelengths used. In Table I, we present the energies and the relative intensities of the observed lines, normalized in terms of the intensity of the ${}^5D_0 \rightarrow {}^7F_2$ strongest peak, for $PEO_{8,28,80}EuBr_3$ and for $PPO_{80}EuBr_3$. Figure 1 shows the emission spectra ($\lambda_{exc} = 395$ nm), at 14 K, for PEO_8EuBr_3 and $PEO_{28}EuBr_3$. The energy superposition between the transitions ${}^5D_1 \rightarrow {}^7F_3 / {}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_1 \rightarrow {}^7F_4 / {}^5D_0 \rightarrow {}^7F_2$, gives place to a certain ambiguity in the identification of some of the local-field split com-

TABLE II. Observed ${}^7F_{0-4}$, ${}^5D_0$ Stark levels and the corresponding barycenters (cm^{-1}) for $PEO_n EuBr_3$ ($n = 8,28,80$) and $PPO_{80}EuBr_3$.

	Observed Stark energies			
Level	PEO_8	PEO_{28}	PEO_{80}	PPO_{80}
${}^7F_0$				
	0	0	0	0
${}^7F_1$				
	292.7	301.7	295.6	304.4
	380.0	379.1	395.7	373.2
	450.9	465.6	463.6	438.5
Barycenter	374.5	382.1	385.0	372.0
${}^7F_2$				
	928.3	940.2	925.6	935.7
	965.5	981.4	962.8	970.2
	1 009.2	1 060.6	1 081.4	1 073.1
	1 040.8	1 088.1	1 119.3	1 088.8
	1 123.2	1 136.4	1 134.9	1 130.6
Barycenter	1 013.4	1 041.3	1 044.8	1 039.7
${}^7F_3$				
	1 832.2	1 861.9	1 852.4	1 861.0
	1 846.5	1 882.1	1 904.4	1 870.5
	1 870.2	1 911.6	1 915.0	1 889.4
	1 884.4	1 929.3	1 933.8	1 910.6
	1 903.2	1 955.1	1 961.9	1 929.5
	1 940.9	1 968.0	1 978.3	1 955.3
	1 987.6	1 984.4	1 993.4	1 983.4
Barycenter	1 895.0	1 927.5	1 934.2	1 914.2
${}^7F_4$				
	2 695.6	2 737.1	2 719.9	2 748.4
	2 738.9	2 762.4	2 738.9	2 765.2
	2 770.4	2 792.8	2 770.4	2 786.2
	2 882.7	2 830.4	2 826.9	2 825.9
	2 841.4	2 851.2	2 878.7	2 848.8
	2 913.8	2 893.7	2 940.5	2 892.3
	2 938.4	2 933.9	2 959.9	2 945.8
	2 952.7	2 974.9	2 991.5	2 972.4
	3 039.1	3 056.1	3 039.1	3 049.96
Barycenter	2 857.0	2 870.3	2 874.0	2 870.5
${}^5D_0$				
	17 254.8	17 266.7	17 254.8	17 262.2

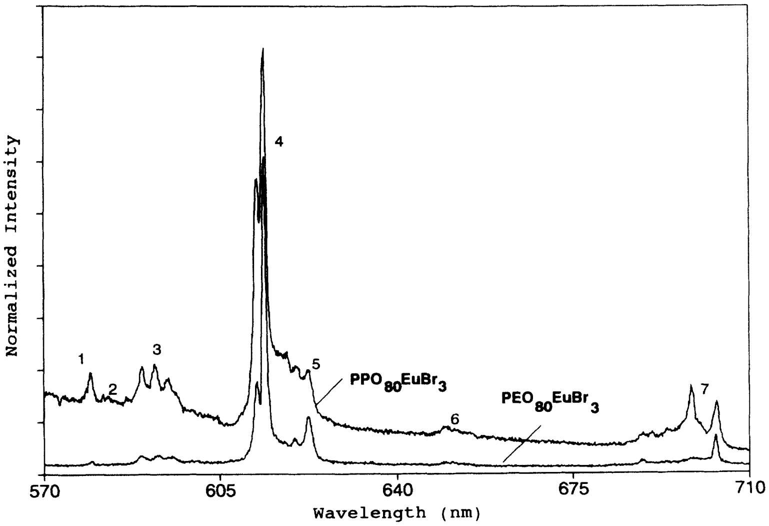

FIG. 2. Emission spectra ($\lambda_{exc}=395$nm) for $PEO_{80}EuBr_3$ and $PPO_{80}EuBr_3$ at 14 K. (1), (3), (4), (6), (7): $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$; (2), (5): $^5D_1 \rightarrow {}^7F_{3,4}$.

ponents of the $^7F_{1,2}$ states. This difficulty was resolved by comparing these transitions with the Eu^{3+} spectra in other matrices, and by analyzing the effects of the change in temperature and in ion concentration. The Stark levels of the $^7F_{0-4}$ and $^5D_0$ states, and the corresponding barycenter energies are indicated in Table II. Due to the weak intensity of the $^5D_0 \rightarrow {}^7F_3$ transition, the energies of some of the $^7F_3$ Stark components exhibit a non-negligible uncertainty; this is also the case for the weakest Stark levels of the $^7F_4$ multiplet. The number of Stark levels identified, in the range of n investigated, seems to be independent of the two polymer hosts and of the Eu^{3+} concentration. Figure 2 compares the emission spectra ($\lambda_{exc}=3950$ nm), at 14 K, for $PEO_{80}EuBr_3$ and $PPO_{80}EuBr_3$. In what follows, we will relate these observed transition energies to the local symmetry of the Eu^{3+} ion.

IV. LOCAL-FIELD MODEL

The energetic configuration structure of materials doped with an RE ion may be modeled by the superposition $H=H_0+V$, with H_0 representing the free ion Hamiltonian and with the spin Hamiltonian V describing the ion's interaction potential with the surrounding ligand neighbors, in terms of a local-field perturbation:[10,14]

$$V=\sum_i \sum_{k,q} B_q^k C_q^k(\theta_i,\phi_i)$$

$$=\sum_i \sum_{k,q} B_q^k \left[\frac{4\pi}{2k+1} \right]^{1/2} Y_q^k(\theta_i,\phi_i) \ , \quad -k \le q \le k \tag{1}$$

with the spherical coordinates (r_i,θ_i,ϕ_i) fixing the location of the ith electron, $(i=1,2,\ldots,N)$, and $Y_q^k(\theta_i,\phi_i)$ being the kth-order spherical harmonics. All the dynamics of this interaction are included in the phenomenological parameters B_q^k, which are determined, comparing, for each Stark component, the observed energies (Table II) with the eigenvalues of V. These dynamical parameters are responsible for the spherical symmetry breaking of the free ion levels and for their corresponding splitting to a maximum of $(2J+1)$ Stark components. This splitting depends on the crystallographic classes comprising the 32 symmetry point groups.[15]

The matrix elements of V between two different states of the $4f^N$ $(l=l'=3)$ configuration are expressed in terms of the matrix elements of Racah tensor operators U_q^k (Ref. 16) as

$$\langle f^N\alpha SLJJ_z|V|f^N\alpha' SL'J'J_z'\rangle = -7\sum_{k,q} B_q^k \begin{bmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{bmatrix} (-1)^{S+L'-J_z}[(2J+1)(2J'+1)]^{1/2}$$

$$\times \begin{bmatrix} J & k & J' \\ -J_z & q & J_z' \end{bmatrix} \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \langle f^N\alpha SL \| U^k \| f^N\alpha' SL'\rangle \ , \tag{2}$$

where

$$\begin{bmatrix} J & k & J' \\ -J_z & q & J_z' \end{bmatrix}$$

are 3-j symbols and

$$\begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix}$$

are 6-j symbols. The matrix elements of the complex (ion-surrounding ligands) interaction for each J_z level of a given multiplet $^{2S+1}L_J$, Eq. (2), are calculated taking into account the values of k (2,4,6) and of q, which characterize the local symmetry of the complex; that is, this calculation requires the knowledge of the symmetry group of the complex. Diagonalizing these matrix elements, the corresponding eigenvalues are expressed in terms of the allowed B_q^k's. Thus, for each symmetry point group, the

B_q^k's representing each ion-surrounding ligands interaction will be fixed by the best fitting between the observed energies and the calculated eigenvalues. Although there is no unique correspondence between a given set of B_q^k's and a given point group, the symmetry operations characteristic of the different point groups within each crystallographic class fix the different sets of nonzero B_q^k's (Tables 8 of Ref. 17). As we show in the next two sections, the determination of these symmetry related parameters was accomplished by taking into account the number of Stark components, the relative intensities of ED/MD transitions, and the polarization behavior of $^5D_0 \rightarrow {}^7F_0$.

V. EMISSION SPECTRA AND SITE SYMMETRIES

The existence of several phases in these europium electrolytes may raise the question of whether or not the local coordination of the Eu^{3+} ion may change with the electrolyte phase and/or with the polymer/salt ratio. The possible existence of more than one local coordination in RE complexes may be determined through the number of observed Stark levels.[18] In the electrolytes investigated, the number of lines identified in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions were 1, 3, and 5, respectively, and since the resolution of these transitions is always of the order of only 1 cm^{-1}, these lines cannot correspond to more than one transition.

When permitted by the local symmetry, the $^5D_0 \rightarrow {}^7F_0$ transition is characterized by only one Stark component (both states are nondegenerate), which is just what is observed. Since there is no other transition near this energy, two symmetry groups consistent with $^5D_0 \rightarrow {}^7F_0$ cannot exist. The question may be raised, however, whether different groups may coexist in such a way that $^5D_0 \rightarrow {}^7F_0$ can appear in only one of them. For each of those groups, the sum of the number of lines for $J=1$ and 2 cannot be larger than 3 and 5, respectively. From the number of Stark components characteristic of the seven crystallographic classes and from the selection rules associated with each of the 32 point groups,[19,20] these two conditions concerning the number of lines can only be satisfied if either (a) one cubic and one trigonal or hexagonal group coexist, or (b) there is only one point group belonging to the triclinic, monoclinic, or orthorhombic classes. The cubic symmetry does not split the $J=1$ level. Insofar as the hexagonal and trigonal classes are concerned, their two Stark energies, expressed by the eigenvalues of the local-field interaction, Eq. (2), involve only one of the dynamical parameters and are given by $-B_0^2/10$ and $B_0^2/5$. This makes the quotient of the absolute values of the corresponding two energies either 2 or $\frac{1}{2}$ (a pure number). Comparing the quotients of any two of the three energies measured for the $^7F_1$ level, we do not find neither of these two possibilities, which then prevents possibility (a). Usually (although not always), the different level degeneracies characteristic of the coexistence of more than one crystallographic site—possibility (a)—gives rise to different widths for the Stark components of a state.[21] The fact that the observed widths are approximately the same for all components of the two $^7F_{1,2}$ levels supports the choice of (b). That is, as was to be expected from the outset, the only coordination possibility for the Eu^{3+} ion in PEO and PPO is ascribed only to lower symmetry groups.

Although it seems improbable, the question might yet be put as to the existence of undetected lines either due to their very weak intensities, or because they are hidden under one given line. Both situations would generate a superposition of symmetries involving a number of lines greater than the one observed. The superpositions involving the tetragonal symmetry are excluded by the same argument used for the hexagonal and trigonal cases. Of the remaining superpositions, the ones associated with a cubic coordination are certainly not allowed by the PEO and PPO structures. Finally, the last possibility (coexistence of at least two groups of the triclinic, monoclinic, or orthorhombic classes) is prevented by the fact that the number of lines observed (3 for $J=1$ and 5 for $J=2$) is far from the numbers (6 and 10) required for this case.

On the other hand, if the RE ion admits more than one symmetry group, a change of excitation/emission energy,[22,23] or of temperature,[24,25] leads to a modification of the number of lines appearing in the emission/excitation spectra. For the several wavelengths utilized (395, 410, 465, and 535 nm) and in the range of temperature 13–310 K, the number of lines characteristic of the recorded spectra is always the same. All this suggests that only one local coordination occurs for the Eu^{3+} ion, independently of whether the ion is in a crystalline or in an amorphous phase. (This conclusion has already been suggested in the investigation of PEO electrolytes modified by europium salts.)[4]

Thus, the observed degeneracy in each of the $^7F_{0-4}$ levels indicates that the point group of the Eu^{3+} ion will belong to the triclinic class, comprising the groups C_1, and S_2 (or C_i), the monoclinic class, comprising the C_2, C_s, and C_{2h} groups, or the orthorhombic class, comprising the C_{2v}, D_2, and D_{2h} groups. The strong ED transitions observed between $^5D_0$ and the sublevels of $^7F_2$, with intensities far greater than the observed MD transition $^5D_0 \rightarrow {}^7F_1$ (Table I), imply that the symmetry group of Eu^{3+} in these PEO/PPO electrolytes does not have an inversion center. This excludes the S_2 (or C_i), C_{2h}, and D_{2h} groups and, hence, from the above eight possibilities, only the C_1, C_s, C_2, C_{2v}, and D_2 groups remain. The $^5D_0 \rightarrow {}^7F_{0,3}$ transitions are prohibited by the ED and MD selection rules (Sec. III). However, for C_s, $C_{1,2,3,4,6}$, and $C_{2v,4v,6v}$, group-theoretical selection rules permit the occurrence of these transitions with a predominantly ED nature,[26] which can be explained by J-mixing effects[27] and/or by third-order contributions of the spin-orbit interactions.[28] Therefore, the only possible local coordination of the europium ion in these PEO/PPO complexes seems to be C_1, C_s, C_2, or C_{2v} (as has been previously pointed out[6]).

VI. POLARIZATION EXPERIMENTS

Although ED transitions are strictly forbidden between intraconfigurations states, they are observed in RE salt complexes spectra due to the mixing of states of other configurations with opposite parity (essentially, the states of the $4f^{N-1}\,5d$ configuration). This admixture is essentially provoked by two odd-parity interactions, the odd terms of the local-field Hamiltonian V, and the term corresponding to the small vibrations of the complex. If the RE ion is at a center of inversion, the odd terms in V will vanish and only the term corresponding to the vibrations will contribute to the ED transitions. That is, as we already mentioned in the preceding section, the observed strong ED transitions in PEO/PPO electrolytes are associated with the absence of an inversion center, this being the case of the C_1, C_s, C_2, and C_{2v} point groups.

The electric dipole operator, $\mathbf{P}=-e\sum_i \mathbf{r}_i$ (summed over the N electrons of the RE ion) in the irreducible tensorial form of Racah,[10,17] written in terms of the Cartesian coordinates (x_i,y_i,z_i) of each electron is

$$P_\rho^1=-e\sum_i r_i C_\rho^1(x_i,y_i,z_i)\ , \tag{3}$$

where ρ represents the direction of polarization: $\rho=0$ gives the z_i components corresponding to the absorption or emission of π-polarized light (electric field, $\mathbf{E}$, parallel to $\mathbf{z}$), and $\rho=\pm 1$ represents the $x_i \pm y_i$ components, associated with the emission or absorption of σ-polarized light (direction of $\mathbf{E}$ parallel to the xy plane).

The ${}^5D_0 \rightarrow {}^7F_0$ transition is essentially due to the $k=1$, $q=0,\pm 1$ terms of the local-field Hamiltonian (the odd-parity vibrations of the polymer electrolytes are irrelevant). As we showed in Sec. V, the local symmetry of the Eu^{3+} ion in the PEO and PPO matrices must be C_1, C_s, C_2, or C_{2v}. The site symmetry of the last three cases implies that, for $k=1$, the C_s group admits only the $C_{\pm 1}^1$ terms, while C_2 and C_{2v} admit only the C_0^1 term (Table V of Ref. 29). Therefore, the intensity of the ED transition ${}^5D_0 \rightarrow {}^7F_0$ is strongly dependent on its state of polarization, and is expected to be much smaller for the π component, if the site group is C_s, and much smaller for the σ component, if the site symmetry is C_2 or C_{2v}.[9,28] For the PEO/PPO electrolytes investigated, the intensity of the ${}^5D_0 \rightarrow {}^7F_0$ transition was consistently larger for the π component; that is, the intensity measured along the exciting light direction, $\mathbf{x}$, was lower than the intensity for the polarization direction, $\mathbf{z}$. This precludes the site symmetry of Eu^{3+} being C_s, leaving, therefore, C_1, C_2, and C_{2v} as the only possible point groups. The selection rules of the ED and MD transitions, associated with the emission or absorption of π- and σ-polarized light, distinguish between these three groups.[30] However, as was to be expected, due to the heterogeneous distribution of the cation in the electrolytes, the polarization measures cannot make such a distinction.

VII. LOCAL COORDINATION OF Eu^{3+}

The number of nonzero B_q^k's distinguishes the site symmetry C_1 from C_2, C_{2v}. However, since the local-field model employed does not decide between these two possibilities, we looked for an independent method for relating the observed transition energies with the B_q^k's. This is provided by the moment operators introduced by Leavitt.[11,12] Accordingly, we define, for any configuration l^N, the second-order moment operator

$$\sigma^2(l^N\alpha SLJ)\equiv\frac{1}{2J+1}\sum_{J_z}\{E(l^N\alpha SLJJ_z)-E^0(l^N\alpha SLJ)\}^2\ , \tag{4}$$

where $E(l^N\alpha SLJJ_z)$ are the observed energies of each of the sublevels J_z and $E^0(l^N\alpha SLJ)$ are the mean energies (barycenters) of each state J of a multiplet ${}^{2S+1}L_J$. Treating the interaction as a first-order perturbation to the free ion (absence of J-mixing terms), the energy of each of the $2J+1$ Stark components of a given αLSJ multiplet is given by

$$E(l^N\alpha SLJJ_z)=E^0(l^N\alpha SLJ)+\langle l^N\alpha SLJJ_z|V|l^N\alpha SLJJ_z\rangle\ .$$

Therefore

$$\begin{aligned}\sigma^2(l^N\alpha SLJ)&=\frac{1}{2J+1}\sum_{k,q}(B_q^k)^2\frac{1}{2k+1}\langle f^N\alpha SLJ\|C^k\|f^N\alpha SLJ\rangle^2\\&=\sum_{k,q}(B_q^k)^2\frac{(2L+1)^2(2J+1)}{2k+1}\left[\begin{Bmatrix}J&J&k\\L&L&S\end{Bmatrix}\begin{bmatrix}L&k&L\\0&0&0\end{bmatrix}\right]^2\ .\end{aligned} \tag{5}$$

Using the B_q^k's determined from the perturbative Hamiltonian, Eq. (2), we calculate these second-order operators, σ_{cal}^2. Next, using Eq. (4), we determine the corresponding empirical values of these operators, σ_{obs}^2, directly in terms of the transition energies. These two independent methods of determining these moments will coincide only if the chosen set of parameters B_q^k of C_1 or C_2,C_{2v} will correspond to the observed energy differences.

The B_q^k's associated with those three point groups are B_0^2, B_2^2, B_0^4, B_2^4, B_4^4, B_0^6, B_2^6, B_4^6, B_6^6. Of these, the parameters B_q^6 could not be determined, as the only levels we took into account in our calculations were ${}^7F_{1,2}$. However, as we show below, the calculation of $B_q^{2,4}$ allowed the desired symmetry identification. The only symmetry existing in C_1 is the identity operator. The comparison of our spectra with other spectra of known symmetry higher than C_1 points to the Eu^{3+} local symmetry being also of higher order than this. The calculations of the B_q^k's were, therefore, performed for the C_2 and C_{2v} groups, and Table III includes the results for all the electrolytes investigated. The second-order moments, σ_{cal}^2, were then calculated taking these B_q^k values into Eq. (5). Independently of any symmetry arguments, the second-order moments σ_{obs}^2 may be determined directly from the observed

TABLE III. B_q^k's (cm^{-1}) for the polymer electrolytes PEO$_n$EuBr$_3$ ($n = 8,12,16,20,24,28,32$) and PPO$_{32,80}$EuBr$_3$.

	B_0^2	B_2^2	B_0^4	B_2^4	B_4^4
PEO$_8$EuBr$_3$	27.5	−322.7	808.9	155.3	−238.3
PEO$_{12}$EuBr$_3$	−15.5	328.8	349.8	−227.2	377.1
PEO$_{16}$EuBr$_3$	420.0	167.0	667.8	−54.5	−249.2
PEO$_{20}$EuBr$_3$	−10.5	351.7	415.0	344.9	−348.6
PEO$_{24}$EuBr$_3$	−433.5	−150.8	−884.3	−22.0	−96.8
PEO$_{28}$EuBr$_3$	417.5	−157.8	556.5	−579.2	−32.3
PEO$_{32}$EuBr$_3$	379.5	−163.9	938.3	−66.6	−347.9
PEO$_{80}$EuBr$_3$	53.5	342.7	−694.6	−337.9	635.7
PPO$_{32}$EuBr$_3$	−357.0	133.5	−1088.3	−1.7	−184.4
PPO$_{80}$EuBr$_3$	−338.0	133.5	−1087.5	−1.2	−150.9

energy levels $^7F_{1,2}$, Eq. (4). Table IV compares these two calculations. The fact that the values of σ^2 determined by the two methods coincide indicates that J-mixing effects can, in fact, be neglected and validates the suggestion mentioned above that the local symmetry of Eu^{3+} is indeed of higher order than C_1, and, therefore, either C_2 or C_{2v}.

The $^5D_0 \rightarrow {}^7F_{0-4}$ emissions are split into the maximum number of components 1,3,5,7,9, for the ligand field of C_2 or C_{2v}, although, for C_{2v}, optical activity is allowed only for one, three, four, six, and seven components (Table III of Ref. 31). We observed this maximum number of components (Sec. V), but some of the $^7F_{2,3,4}$ levels, besides being substantially weaker than the remaining (Table I), are also not well resolved [1 in $^7F_2$, 1–2(?) in $^7F_3$, and 2 in $^7F_4$, Fig. 1]. These ambiguous lines are usually related to components without optical activity and consequently, are associated with formally forbidden transitions of the group C_{2v}. Therefore, the local coordination of Eu^{3+} in PEO/PPO electrolytes appears to be approximately given by the C_{2v} symmetry. This identification does not exclude, however, the possibility of the overall site symmetry in the electrolytes investigated to be of lower order than C_{2v} (namely C_2).

VIII. CONCLUSIONS

In spite of their promising luminescence properties, trivalent RE polymer electrolytes had, until recently, received much less attention than the corresponding complexes modified by monovalent and divalent cation salts. In particular, the expected connection between their luminescence properties and the local structure surrounding the ion had not been determined up to now.

The emission spectra for (PEO/PPO)$_n$EuBr$_3$ were recorded for several doping ion concentrations and the observed transitions identified with $^5D_{0,1} \rightarrow {}^7F_{0-4}$. The general luminescence features of PEO and PPO electrolytes are not significantly altered by the two different polymer host matrices and by the ion's concentrations. The transitions $^5D_{0,1} \rightarrow {}^7F_{0-4}$ are sufficiently intense as to raise the possibility of these PEO and PPO complexes being used as luminescence devices (with essentially identical emission characteristics, notwithstanding their different morphologies). The observed lines are well defined and sharper than the corresponding ones for glasses, suggesting that the order of coordinated ligands seems to go beyond the first-neighbor shell.

This paper is an attempt to determine the local coordi-

TABLE IV. Values of σ^2_{calc} and σ^2_{obs} (cm^{-1}) for PEO$_n$EuBr$_3$ ($n = 8,12,16,20,24,28,32$) and PPO$_{32,80}$EuBr$_3$.

		$^7F_1$			$^7F_2$	
	σ^2_{calc}	σ^2_{obs}	%[a]	σ^2_{calc}	σ^2_{obs}	%[a]
PEO$_8$EuBr$_3$	4186.2	4180.5	+0.1	4472.2	4484.6	−0.3
PEO$_{12}$EuBr$_3$	4335.6	4329.2	+0.1	3424.5	3430.6	−0.2
PEO$_{16}$EuBr$_3$	4637.7	4643.6	−0.1	3713.6	3815.8	−2.8
PEO$_{20}$EuBr$_3$	4949.9	4955.8	−0.1	4205.4	4139.1	+1.6
PEO$_{24}$EuBR$_3$	4668.1	4663.3	+0.1	4620.7	4620.6	0
PEO$_{28}$EuBr$_3$	4482.2	4481.8	0	5188.1	5083.2	+2.0
PEO$_{32}$EuBr$_3$	3954.9	3954.9	0	5509.8	5519.3	−0.2
PEO$_{80}$EuBr$_3$	4755.0	4761.6	−0.1	7184.7	7188.1	−0.1
PPO$_{32}$EuBr$_3$	3261.9	3262.0	0	5670.6	5725.4	−1.0
PPO$_{80}$EuBr$_3$	2997.8	2997.8	0	5483.8	5487.1	−0.1

[a] Difference between σ^2_{calc} and σ^2_{obs}.

nation of Eu^{3+} in PEO and PPO electrolytes, based on the number of observed Stark components, on the relative intensities of the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ transitions, and on the polarization behavior of the $^5D_0 \rightarrow {}^7F_0$ transition. The number of local-field split components identified indicates that, independently of the electrolyte phases, only one local coordination occurs for the ion, and shows that this coordination is consistent with the C_s, C_1, C_2, or C_{2v} point groups. The polarization behavior of the $^5D_0 \rightarrow {}^7F_0$ transition is incompatible with the C_s point group.

The interaction of Eu^{3+} with its surrounding neighbors reproduces the connection, existing for the complexes, between the observed transition energies and the ion's local symmetry features. We expressed this interaction by a local-field Hamiltonian, written in terms of empirical parameters B_q^k, directly related to the local symmetry characteristics at each ion's neighbors. This model, however, does not distinguish the possibility C_1 from the possibility C_2 and C_{2v}. We were able to exclude C_1 by expressing the observed energies and the symmetry-related B_q^k's in terms of Leavitt's moment operators.

Some of the $^7F_{2,3,4}$ Stark components may be associated with transitions without optical activity. Thus, the local immediate neighborhood of the europium ion in PEO/PPO electrolytes seems to be approximately reproduced by the C_{2v} symmetry, which is consistent with an eightfold coordination for the bulk of Eu^{3+} (the commonest behavior for this ion in oxide-type media).

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[1] For a review see, for example, *Polymer Electrolyte Reviews 1 and 2,* edited by J. R. MacCallum and C. A. Vincent (Elsevier Applied Science, London, 1987 and 1989).

[2] P. G. Bruce, F. Krok, J. Nowinski, F. M. Gray, and C. A. Vincent, Mater. Sci. Forum **42**, 193 (1989); A. S. Reis Machado and L. Alcácer, *2nd International Symposium on Polymer Electrolytes,* edited by B. Scrosati (Elsevier Applied Science, London, 1990), p. 283.

[3] C. J. Silva and M. J. Smith, Solid State Ion. **58**, 269 (1992); **60**, 73 (1993); G. Petersen, L. M. Torell, S. Panero, B. Scrosati, C. J. Silva, and M. J. Smith, *ibid.* **60**, 55 (1993).

[4] Rokeya Huq and Gregory C. Farrington, *2nd International Symposium on Polymer Electrolytes* (Ref. 2), p. 281.

[5] Annika Bernson and Jan Lindgren, Solid State Ion. **60**, 31 (1993).

[6] L. D. Carlos, M. Assunção, T. M. Abrantes, and L. Alcácer, in *Solid State Ionics III,* edited by Gholam-Abbas Nazri, Jean-Marie Tarascon, and Michel Armand, MRS Symposia Proceedings No. 293 (Material Research Society, Pittsubrgh, PA, 1993), Vol. 293, p. 117.

[7] M. Armand and M. Gauthier, in *High Conductivity Solid Ionic Conductors,* edited by Takehiko Takahashi (World Scientific, Singapore, 1989), p. 114.

[8] C. Brecher and L. A. Riseberg, Phys. Rev. B **13**, 81 (1976); **22**, 2607 (1980).

[9] Goro Nishimura and Takashi Kushida, Phys. Rev. B **37**, 9075 (1988).

[10] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Wiley Interscience, New York, 1965).

[11] Richard P. Leavitt, J. Chem. Phys. **77**, 1661 (1982).

[12] Y. Y. Yeung and D. J. Newman, J. Chem. Phys. **84**, 4470 (1986).

[13] M. Puga, L. D. Carlos, and L. Alcácer (unpublished).

[14] S. Hufner, *Optical Spectra of Transparent Rare Earth Compounds* (Academic, New York, 1978).

[15] H. Bethe, Ann. Phys. (Leipzig) **3**, 133 (1929), translated as *Splitting of Terms in Crystals* (Consultants Bureau, New York, 1958); W. A. Runciman, Philos. Mag. (London) **8**, 1075 (1956).

[16] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943); **76**, 1352 (1949).

[17] C. A. Morrison, *Angular Momentum Theory Applied to Interactions in Solids,* Lecture Notes in Chemistry Vol. 47 (Springer-Verlag, Berlin, 1988), p. 84-85.

[18] See, for example, A. P. B. Sinha, in *Spectroscopy in Inorganic Chemistry,* edited by C. N. R. Rao and John R. Ferraro (Academic, New York, 1971), Vol. 14, p. 266.

[19] John H. Forsberg, Coord. Chem. Rev. **10**, 195 (1973).

[20] G. Vicentini (private communication).

[21] C. Brecher, J. Chem. Phys. **61**, 2297 (1974).

[22] A. Meijerink and G. Blasse, J. Phys.: Condens. Matter **2**, 3620 (1990).

[23] M. F. Hazenkamp, G. Blasse, and N. Sabbatini, J. Phys. Chem. **95**, 783 (1991).

[24] M. Faucher and P. Caro, J. Chem. Phys. **63**, 446 (1975).

[25] G. Huber, W. Lenth, J. Lieberts, and F. Lutz, J. Lumin. **16**, 353 (1978).

[26] S. P. Sinha and E. Butter, Mol. Phys. **16**, 285 (1969); P. Porcher and P. Caro, J. Lumin. **22**, 207 (1980).

[27] O. L. Malta, Mol. Phys. **42**, 65 (1981); O. L. Malta, W. M. Azevedo, E. A. Gouveia, and G. F. De Sá, J. Lumin. **26**, 337 (1982).

[28] M. C. Downer, D. K. Sardar, and G. W. Burdick, J. Chem. Phys. **89**, 1787 (1988); **91**, 1511 (1989).

[29] J. L. Prather, *Atomic Energy Levels in Crystals,* Natl. Bur. Stand. (U.S.) No. 19 (National Bureau of Standards, Washington, D.C., 1961).

[30] A. A. Kaplyanskii, Opt. i Spektrosk. **16**, 602 (1964).

[31] J. Dexpert-Ghys and M. Faucher, Phys. Rev. B **20**, 10 (1979).