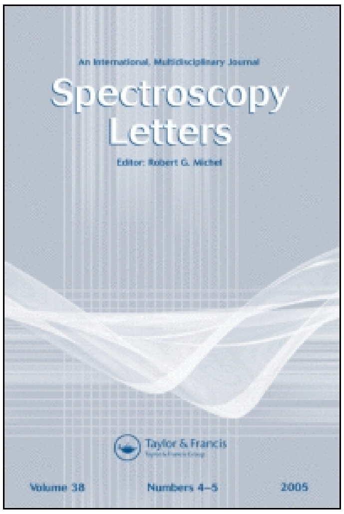

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Macroscopic Models for the Radiative Relaxation Lifetime of Luminescent Centers Embedded in Surrounding Media

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Abstract: Two macroscopic models for the dependence of the spontaneous emission rate of luminescent ions or nanoparticles embedded in dielectric media of various optical refractive indexes are presented. The available experimental results on the spontaneous emission rate (lifetime) are examined using the two models. A simple criterion for how to choose the proper model for a given system is summarized.

Keywords: Lorentz model, luminescent center, real-cavity model, refractive index, spontaneous emission rate

INTRODUCTION

Einstein demonstrated in 1917 that spontaneous emission always occurs for matter in excited states from consideration of the thermal equilibrium

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between the matter and the radiation field.[1] It was not until 1946 that Purcell[2] noticed that the spontaneous emission rate, such a fundamental property of matter, is not always constant for a given system, but can depend strongly on the environment. A lot of theoretical work has been carried out since 1970 to study the modification of spontaneous emission rate of luminescent centers in various environments. In particular, Yablonovitch et al.[3,4] showed theoretically that in photonic band gap materials, the spontaneous emission can be completed inhibited. Most of the theoretical work is based on the macroscopic Maxwell theory of the electric-magnetic field.

However, the fundamental problem of "the modification of spontaneous emission rate of luminescent center due to surrounding dielectrics" was only broadly studied theoretically and experimentally in the past decade and is still inconclusive.[5] According to electromagnetic theory, spontaneous emission rates depend not only on the density of states of photons but also on the ratio of local electric field to the macroscopic electric field. The well-known Lorentz model for the ratio of local electric field to the macroscopic field, which is also referred to as the virtual-cavity model, can be found in many famous textbooks.[6–8] Although the Lorentz model has been widely used in the calculation of spontaneous relaxation rate and oscillator strength, there was no systematic experimental study of the dependence of spontaneous emission rates on the refractive index until the 1980s.[9] More definitive experiments were carried out in the 1990s by several groups,[10–12] with results supporting a different model given by Glauber and Lewenstein,[13] which has also been referred to as the real-cavity model. Both the Lorentz model and the real-cavity model show monotonic increases of spontaneous emission rates with increasing refractive index n of the surrounding medium. The Taylor expansions of the rate formula for the two models with respect to $n - 1$ have the same zeroth-order and first-order terms but different second-order and higher-order terms. When n is larger (>1.5), then the differences between the two models are very substantial. There are also some other models[14] based on microscopic theory. Most of them are also close to the above two macroscopic models. More experimental studies have been carried out in the past few years.[15–18] In 1999–2001, Meltzer and co-workers[15] studied the radiative lifetime of Y_2O_3:Eu^{3+} embedded in media of various refractive index and claimed that the results support the Lorentz model. In 2003, Kumar and co-workers[17] published the radiative lifetime of Eu^{3+} in $PbO–B_2O_3$ binary glass with varying refractive index and claimed the lifetimes of embedded emitters should follow the real-cavity model. In 2004, Meijerink and co-workers[16] published the lifetimes of CdSe and CdTe quantum dots embedded in surrounding media of various refractive index. They claimed that the results should follow the microscopic model given by Crenshaw,[18] different from both the Lorentz model and the real-cavity model.

We believe that a lot of theoretical and experimental work will be necessary to completely solve the theoretical problem of the local-field effect on the spontaneous emission rates. In this paper, we examine the hypotheses underlying the two macroscopic models and show under which condition the two models should apply and then apply appropriate models to available experimental results. Finally, we comment on how to choose the proper model for a given system.

THE LORENTZ MODEL AND REAL-CAVITY MODEL

Local-Field Effect on the Spontaneous Relaxation Rate

According to quantum mechanics, the spontaneous emission rate γ of an isolated electric dipole luminescent emitter follows the Fermi golden rule

$$\gamma = \frac{2\pi}{\hbar} \langle |\mathbf{E}_{sp}^{loc} \cdot \boldsymbol{\mu}_{12}|^2 \rangle_{osc} \rho(\omega), \tag{1}$$

where $\langle \, \rangle_{osc}$ is the average of all the polarizations of the electromagnetic wave field with an angular velocity of $\omega = (E_2 - E_1)/\hbar$, $\bar{\mu}_{12}$ is the electric dipole matrix element between initial and final states, $\mathbf{E}_{sp}^{loc}$ is the local microscopic electric field at the position of the luminescent center for the calculation spontaneous relaxation, and $\rho(\omega)$ is the energy density of states of electromagnetic wave.

In general, $\mathbf{E}_{sp}^{loc}$ is different from the macroscopic electric-field $\mathbf{E}_{sp}^{mac}$. In microscopic isotropic media, the local electric field is proportional to the macroscopic electric field with a ratio $f = \mathbf{E}_{sp}^{loc}/\mathbf{E}_{sp}$ that depends on the local structure. The spontaneous emission rate in macroscopic isotropic media can be described as

$$\gamma(n) = \frac{4f^2 n\omega^3}{3\hbar c^3} |\boldsymbol{\mu}_{12}|^2 = \gamma_0 n f^2, \tag{2}$$

where $\gamma_0 = 4\omega^3/3\hbar c^3 |\boldsymbol{\mu}_{12}|^2$ is the spontaneous emission rate of luminescent center in a medium that has the refractive index of 1 (more detail can be found in Ref. 11), and n is the refractive index of the medium.

The Lorentz Model

The medium is not uniform at atomic-level size. Therefore, the local electric field $\mathbf{E}_{loc}$ at the luminescent center is different from the macroscopic electric field $\mathbf{E}_{mac}$ in the surrounding medium, which is just the average electric field. In the Lorentz model (also referred to as the virtual-cavity model), the medium is divided into two regions surrounding the luminescent

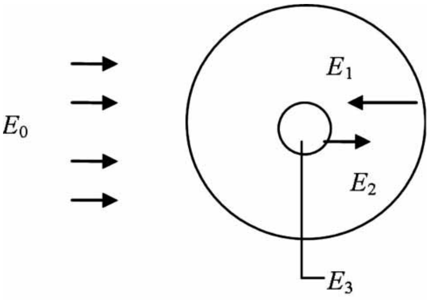

Figure 1. The Lorentz model. The luminescent center is placed in the medium without disturbing the medium. The local field at the luminescent center is the sum of the external field ($\mathbf{E}_0$), the field due to the polarization charge on the surface of the sample ($\mathbf{E}_1$), the field due to the polarization charge on the inner surface of the hypothetical sphere ($\mathbf{E}_2$), and the dipole within the hypothetical sphere ($\mathbf{E}_3$). The macroscopic field is the sum of the external field and the depolarization field ($\mathbf{E}_1$).

center. As shown in Figure 1, the region within the small sphere is treated microscopically as ions and molecules at given positions, and the region outside of the small sphere is treated macroscopically as a continuous medium. The local electric field at the luminescent center ($\mathbf{E}_{\text{loc}}$) and the macroscopic electric field ($\mathbf{E}_{\text{mac}}$) can then be calculated by following Kittel[7]

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3, \tag{3}$$

$$\mathbf{E}_{\text{mac}} = \mathbf{E}_0 + \mathbf{E}_1. \tag{4}$$

Here, $\mathbf{E}_0$ is the externally applied field, $\mathbf{E}_1$ is the depolarization field due to polarization charges on the outer surface of the medium, $\mathbf{E}_2$ is the Lorentz cavity field due to the polarization charges on the surface of the inner surface of the small sphere, and $\mathbf{E}_3$ is the field due to the electric dipoles of all the ions inside the small sphere.

If we choose spherical regions for the calculations, the depolarization field $\mathbf{E}_1$ and macroscopic polarization intensity P satisfy the equations below:

$$\mathbf{E}_1 = -\frac{\mathbf{P}}{3\varepsilon_0}, \tag{5}$$

$$\mathbf{P} = \varepsilon_0(\varepsilon - 1)\mathbf{E}_{\text{mac}}, \tag{6}$$

where the dielectric constant of the medium $\varepsilon = n^2$. $\mathbf{E}_2$ can be obtained in a calculation similar to that of $\mathbf{E}_1$ as

$$\mathbf{E}_2 = \frac{\mathbf{P}}{3\varepsilon_0}. \tag{7}$$

When the arrangement of ions inside of the small sphere has high symmetry or has a totally random distribution, then $\mathbf{E}_3$ (or the statistical average value of it) is 0. Therefore, the local electric field and macroscopic electric field are

$$\mathbf{E}_{\mathrm{loc}} = \mathbf{E}_0, \tag{8}$$

$$\mathbf{E}_{\mathrm{mac}} = \frac{3}{n^2+2}\mathbf{E}_0. \tag{9}$$

Then the ratio of local electric field to the macroscopic field is

$$f_{\mathrm{virtual}}(n) = \frac{|\mathbf{E}_{\mathrm{loc}}|}{|\mathbf{E}_{\mathrm{mac}}|} = \frac{n^2+2}{3} \tag{10}$$

The Real-Cavity Model

The real-cavity model assumes that the luminescent center expels the medium away from the space occupied by the center and creates a cavity in the medium,[5,13] as shown in Figure 2. In the original form of the real-cavity model, the cavity is assumed to be vacuum-like. The local electric field $\mathbf{E}_{\mathrm{loc}}$ at the luminescent center is the parallel electric field inside the vacuum cavity, and $\mathbf{E}_{\mathrm{mac}}$ is the electric far field outside the cavity (the average field in the medium). The relationship between the electric fields inside and outside the cavity can be described by Eq. (9) analogously with the following substitution: the $\mathbf{E}_{\mathrm{mac}}$ in Eq. (9) is substituted with $\mathbf{E}_{\mathrm{loc}}$ and the $\mathbf{E}_0$ in Eq. (9) is substituted with $\mathbf{E}_{\mathrm{mac}}$ in the real-cavity model, and at the same time, the refractive index n in Eq. (9), which is the ratio of the refractive index of the part inside of the sphere (n) to the index outside of the sphere (one), needs to be replaced with $1/n$, which is the ratio of the refractive index of the part inside of the real cavity

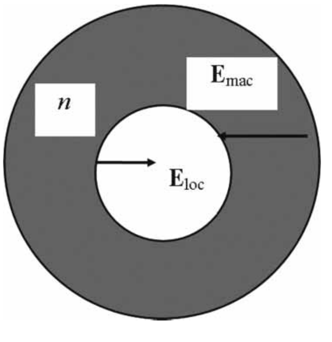

Figure 2. The real-cavity model. The luminescent center expels the medium away from the space occupied by it and makes a cavity of the medium. The refractive indexes of the medium and the cavity are n and 1, respectively for the original real-cavity model. The local field is the field in the cavity, and the macroscopic field is the average field in the medium outside of the cavity.

(one) to the index of the medium outside of the real cavity (n). So the ratio of electric fields for the real-cavity model is

$$f_{\text{real}}(n) = \frac{E_{\text{loc}}}{E_{\text{mac}}} = \frac{3}{(1/\text{n})^2 + 2} = \frac{3n^2}{1 + 2n^2}. \tag{11}$$

It is apparent that f factor is different for the Lorentz model and the real-cavity model. Therefore, the dependence of the spontaneous emission rate on the refractive index is decided by the model applicable to the particular case. The two models of spontaneous emission rate are also named as the Lorentz model (the virtual-cavity model) and the real-cavity model.

REINTERPRETATION OF EXPERIMENTAL RESULTS

The spontaneous emission rate is an important parameter for luminescent materials. There are a lot of data published on this parameter but only a few systematic studies of the dependence of the spontaneous emission rate on the refractive index. They fall into three categories: 1) the luminescent ions replace host cations with very small electronic polarizabilities, where the introduction of luminescent ions has little effect on the surrounding medium; 2) the luminescent ions replace host ions with large electronic polarizabilities, so that the introduction of luminescent ions effectively expels the medium from the place occupied by the luminescent ion and creates a hole in the medium; 3) the luminescent centers are nanometer particles containing luminescent ions or semiconductor quantum dots, where the medium is expelled away from the space occupied by the luminescent centers. According to the underlying assumption of the Lorentz model and the real-cavity model, case 1 is close to the Lorentz model, and in cases 2 and 3 the real-cavity model is applicable. In fact, in most experimental studies, the results obey the real-cavity model. In the following, we revisit the experimental results and the interpretations for all three cases.

The Spontaneous Emission Rates of $5d$–$4f$ Transitions of Ce^{3+} Ions in Hosts of Various Refractive Index

There is only one valence electron in the trivalent cerium ion, which occupies $5d$ and $4f$ orbitals in the initial and final states, respectively, of the optical transition.[20] The emission from the lowest states $5d_1$ of the $5d$ shell contains two adjacent bands, which correspond with the transitions to two states $4f_j$ ($j = 5/2$ and $7/2$) that originate from the spin-orbit splitting of $4f$ states.[20] The transitions are electric dipole allowed with approximately fixed electric dipole strength proportional to $(2j + 1)$. The total spontaneous emission rates $1/\tau_{5d_1}$

(in unit of s^{-1}) for $5d_1$ can be given as follows[21]

$$\frac{1}{\tau_{5d_1}} = 4.34 \times 10^{-4} \langle 5d|r|4f \rangle^2 \chi(n) \overline{\tilde{v}^3}, \tag{12}$$

where the function of refractive index $\chi(n) = nf^2$ depends on whether the Lorentz model or the real-cavity model is used, the radial integral $\langle 5d|\mathrm{r}|4f \rangle$ is in unit of nm, the wavenumber $\tilde{v}$ is in unit of cm^{-11}, and the overbar on $\overline{\tilde{v}^3}$ indicates the average of $\tilde{v}^3$ weighted by the electric dipole strength. From Eq. (12) we can obtain the experimental values for $\langle 5d|\mathrm{r}|4f \rangle^2 \chi$ for samples of different refractive index. Because $\langle 5d|\mathrm{r}|4f \rangle$ can be considered approximately constant in different hosts, we can fit the experimental $\langle 5d|\mathrm{r}|4f \rangle^2 \chi$ values with different models to determine the dependence on the refractive index and see which model fits best. Detailed analysis can be found in Ref. 21, which showed that the experimental results fit the Lorentz model much better than the real-cavity model and give the value for the radial integral $\langle 5d|\mathrm{r}|4f \rangle = 0.0281$ nm.

The Spontaneous Emission Rates of (Sub)Nanometer Particles Embedded in Media

Most of the experimental work on emission rates is in this category. The results in Refs. 11 and 12 are representative, where Eu^{3+}-hfa-topo or $Eu(hod)_3$ luminescent clusters of sub-nanometer size were embedded in solvents of various refractive index. Because those clusters are solid Eu^{3+}–ligand complexes, with very small polarizabilities, they can be treated as emitters of fixed electric dipole moment that expel the medium from the space occupied. Thus the real-cavity model should be applicable. This has been confirmed by detailed analysis of the experimental results.[11,12]

Special care is required in the case where the polarizability of the nanoparticle is not negligibly small, so that the effect of the polarization of the nanoparticles on the surrounding medium needs to be taken into consideration. In this case, the space occupied by the nanoparticle cannot be treated as a vacuum cavity but a cavity with medium of refractive index n_{particle}. The ratio of electric field for this case can be obtained from Eq. (11) by replacing the n there with $n_{\mathrm{r}} = n/n_{\mathrm{particle}}$, that is,

$$f_{\mathrm{real}}(n_r) = \frac{E_{\mathrm{cavity}}}{E_{\mathrm{mac}}} = \frac{3n_r^2}{1 + 2n_r^2}. \tag{13}$$

According to Eq. (2), the spontaneous emission rates in this case are proportional to $f^2_{\mathrm{real}}(n\mathrm{r})\, n_{\mathrm{r}}$, with a coefficient that is no longer γ_0. This coefficient cannot depend on the refractive index n but may depend on the refractive index n_{particle}. By setting $n_{\mathrm{r}}=1$ to obtain the coefficient, we finally obtain the dependence of the spontaneous emission rate on the refractive index n

of the surrounding medium through $n_r = n/n_{particle}$ as

$$\begin{aligned}\gamma(n) &= \gamma(n_{particle}) n_r f_{real}^2(n_r) \\ &= \gamma(n_{particle}) \frac{9n_r^5}{(1+2n_r^2)^2}.\end{aligned} \tag{14}$$

This equation is more general than the real-cavity model, because by setting $n_{particle}=1$ we recover the real-cavity model. Equation (14) has been used in Refs. 22 and 23 to calculate the radiative lifetime (the inverse of spontaneous emission rate) of Y_2O_3:Eu^{3+} nanoparticles embedded in hosts of various refractive index and theoretical results were obtained that agree with measurements.

The Spontaneous Emission Rate of 4*f*–4*f* Transitions of Eu^{3+} Ions Doped in Binary Glass

Kumar et al.[17] measured the radiative relaxation lifetime of the $^5D_0$ energy level of Eu^{3+} ions doped in xPbO + $(1-x)$ B_2O_3 ($x = 0.3$ to 1.0) binary glass with refractive index $n = 1.7$ to 2.2. The measurements were found to follow the real-cavity model. However, the interpretation presented in the paper[17] completely rules out the applicability of the Lorentz model in any case of dopants in a host material, including the case of Ce^{3+} ions in various hosts. In fact, Ref. 23 has given a more reliable interpretation based on the fact that Eu^{3+} ions actually substitute Pb^{2+} ions of very high polarizabilities and form stable ion–ligand clusters. The cluster composed of Eu^{3+} ions and O^{2-} ions has a substantially smaller polarizability compared with that of the Pb^{2+} ion and creates a real cavity in the surrounding medium. Therefore, the real cavity can describe the measured radiative lifetimes very well.

CONCLUSIONS

We have analyzed the dependence of the spontaneous emission rates (radiative lifetimes) of isolated emitters on the refractive index of the surrounding medium by presenting the derivations of the two models and their applications in interpretation experimental results. We conclude the following: 1) Unlike the conclusion given in several publications that the local field effect should follow a certain model (either the Lorentz model or the real-cavity model), actually the local field effect follows different models in different cases. 2) In the case of cations with small polarizabilities, such as rare-earth ions, doped as luminescent ions in a host, the local field effect follows the Lorentz model when the replaced ions have small polarizabilities and follows approximately the real-cavity model when the replaced ions have large polarizabilities. 3) In the case of nanometer particles acting as luminescent centers in surrounding medium, the local effect follows the real-cavity model, but in general the refractive index involved in the model should be the relative refractive index of the medium against that of the nanoparticles, and the refractive index of the nanoparticles may be substantially different from 1 for some cases.

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