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Abstract
The Lamb shift observed by analysing the antiresonances in the absorption spectra of Cr^{3+}-doped glass systems has been studied. A discrepancy in the sign of the experimentally measured shifts and theoretical predictions is found. The experimental behaviour can be explained if we assume a site dependence of coupling between ^2E and $^4T_2$ levels. The proposed model yields positive values for shifts in accordance with the experimental results.

1. Introduction

The anomalous features which appear in the absorption spectra ($^4A_2 \rightarrow \,^4T_2$ transition) of Cr^{3+}-doped glasses have been analysed in terms of Fano antiresonances based on the interaction between the sharp levels (^2E and $^2T_1$) and the level continuum ($^4T_2$) [1, 2]. In this theory, the coupling of a discrete state of energy E_0 with a set of states of different energies which form a continuum gives an energy displacement of the discrete state. The resonance energy E_R calculated from the ratio $R(E)$ of the experimental absorption profile to the background spectra is slightly shifted compared with the energy of the unperturbed sharp absorption line (E_0). The difference $\Delta E = E_R - E_0$, which represents the displacement of the sharp level due to the coupling with the continuum, is an analogue to the Lamb shift and can be calculated by stationary perturbation theory [1]. The first direct observation of this shift was made by Lempicki *et al* [3] in several Cr^{3+}-doped oxide glasses as a result of the inhomogeneous broadening in glass. There exists an independent method for analysing the observed antiresonance profiles, which is the Fano theory adapted by Sturge *et al* [4]. In this formulation the Lamb shift is given by $\Delta E = W^2 G_1(E_0)$, where W is the matrix element for the interaction between the electronic wavefunctions of the discrete level and the continuum, which in the case of Cr^{3+} ions would be a spin–orbit coupling. $G_1(E_0)$ is the Hilbert transform of the absorption profile of the background spectrum $G_2(E)$:

$$G_1(E_0) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{G_2(E)}{E_0 - E}\, dE. \tag{1}$$

The background spectrum, $G_2(E)$, is the absorption band without antiresonance effect and is determined by fitting the optical absorption band to an appropriate function in the regions away from the antiresonance. We regard Fano's relation $R(E)$ to be written as [4]

$$R(E) = 1 + \rho^2 \frac{(q^2 + 2q\varepsilon - 1)}{1 + \varepsilon^2} \tag{2}$$

where ε is given by

$$\varepsilon = \frac{(E - E_0 - \Delta E)}{\Gamma + \gamma} = \frac{(E - E_0 - W^2 G_1(E_0))}{\Gamma + W^2 G_2(E_0)} \tag{3}$$

and the resonance line parameter q is defined as

$$q = \frac{G_1(E_0)}{G_2(E_0)}. \tag{4}$$

In the last expressions, we have expressly written $G_1(E_0)$ or $G_2(E_0)$ to indicate that the functions are calculated at E_0 according to the usual Fano formulation. ρ^2 determines the fraction of band states that take part in the interference processes and Γ represents the width related to processes with a coupling different from the spin–orbit one (electron–phonon interactions) [1, 2, 4].

In the last few years, many studies of Fano antiresonances in the absorption spectra of different optical materials have been reported in the literature [5–10]. However, a study of the 'Lamb shift' related to the antiresonances has not yet been made. Table 1 contains a summary of the ^2E antiresonance parameters collected in a variety of Cr^{3+}-doped glasses in which ΔE can be determined experimentally [3, 10–13]. The value of ΔE is calculated as $E_R - E_0$, where E_R is the resonance energy taken from the analysis of the antiresonance profiles while E_0 is derived from experimental $^2E \rightarrow {}^4A_2$ emission peak (R line) originating from a small fraction of sites for which ^2E is the lowest excited state. We see that the proportionality between q and ΔE, $\Delta E = q[W^2 G_2(E_0)]$, which can be inferred from equations (3) and (4), is not satisfied in these glasses. While the shifts are positive, the q values are negative. A positive value of ΔE implies that background absorption spectrum $G_2(E)$ must peak below E_0 if the coupling W is taken to be constant (see equation (1)). However, the peak of the background absorption spectra (E_{abs}) in these glasses is near to or above E_0 ($E_{\mathrm{abs}} \approx E_0$, $E_{\mathrm{abs}} > E_0$). Although the choice of the background is critical for the calculation of $R(E)$ and numerical values of E_R may be in doubt, the relative position of level E_0 (R line: $^2E \rightarrow {}^4A_2$ transition) and the ^2E antiresonance assures the positive values of ΔE. This discrepancy in the sign of q and ΔE can also be observed in the antiresonances of Cr^{3+}-doped disordered crystals [14, 15]. In contrast to this behaviour, we find that an analysis of the antiresonance profile of Cr^{4+}-doped crystals [5] suggests a positive value of ΔE for a positive value of q.

A recently published paper [16] suggests that Fano's equation calculated with $G_1(E)$ and $G_2(E)$ functions fixed at energy E_0 should not be used to interpret the anomalous features which appear in the absorption spectra profile of metal compounds and that this formulation should only be applied to slowly varying background spectra. Therefore, equation (2) should be used by taking coefficients ε and q to be energy dependent, that is $G_1(E)$ and $G_2(E)$ functions not evaluated at E_0:

$$\varepsilon = \frac{(E - E_0 - \Delta E)}{\Gamma + \gamma} = \frac{(E - E_0 - W^2 G_1(E))}{\Gamma + W^2 G_2(E)} \tag{5}$$

$$q = \frac{G_1(E)}{G_2(E)}. \tag{6}$$

Due to the dependence of γ on energy ($\gamma = W^2 G_2(E)$), it must be noticed that in this case the ρ^2 parameter would also be energy dependent because it is defined as a function of the ratio

Table 1. Summary of ^2E antiresonance parameters corresponding to several Cr^{3+}-doped glasses calculated by using the Fano formulation. E_R is the resonance energy, E_0 is the energy of the transition to the unperturbed state ($^2E \rightarrow {}^4A_2$ transition, R line) and $\Delta E = E_R - E_0$ is the 'Lamb shift'. q is a parameter which describes the shape of the resonance profile. E_{abs} is the peak of the background absorption spectrum.

Glass	E_R (cm^{-1})	E_0 (cm^{-1})	ΔE (cm^{-1})	q	
$74P_2O_5$–$26Al_2O_3$ [3]	14 793 ($T = 7$ K)	14 662 ($T = 7$ K)	+131	0	$E_0 \approx E_{abs}$
$67P_2O_5$–$33Na_2O$ [3]	14 800 ($T = 7$ K)	14 640 ($T = 7$ K)	+160	-0.2	$E_0 < E_{abs}$
$74SiO_2$–$13Na_2O$–$13CaO$ [3]	14 780 ($T = 7$ K)	14 580 ($T = 7$ K)	+200	-0.2	$E_0 < E_{abs}$
LiO_2–$2SiO_2$ [10]	14 734 ($T = 13$ K)	14 580 ($T = 13$ K)	+154	-0.56	$E_0 < E_{abs}$
$73SiO_2$–$14Na_2CO_3$–$13CaCO_3$ [11]	14 760 ($T = 4.2$ K)	14 600 ($T = 4.2$ K)	+160	negative[a]	$E_0 < E_{abs}$
BIGaZYT [12, 13]	15 245 ($T = 77$ K)	15 152 ($T = 4.2$ K)	+93	-0.105	$E_0 < E_{abs}$
ZBLA [12]	15 199 ($T = 77$ K)	—[b]	+47[c]	-0.085	$E_0 < E_{abs}$

[a] Not calculated. Since $E_0 < E_{abs}$, its value would be negative.
[b] Not observed.
[c] Assuming R line as in BIGaZYT glass.

$\gamma/\Gamma + \gamma$ [4]. For the case studied, we shall see that the variation of $G_1(E)$ and $G_2(E)$ functions with energy will not change the $R(E)$ profile near the dip position. Therefore, if this energy dependence were considered, the discrepancy in the sign of the Lamb shift would still remain.

The purpose of this work is to explain the discrepancy found in the sign of ΔE by taking into account the inhomogeneous broadening in glasses. Indeed, the possibility of measuring the ΔE shifts is a consequence of disorder being inherent to glasses. In a previous work [12], the authors also noticed the dependence of ΔE on glass inhomogeneity. By analysing the antiresonances of Cr^{3+}-doped fluoride glass excitation spectra at 4.2 K, a pronounced blue shift of E_R with decreasing emission wavelength (λ_{em}) and increasing time after excitation was observed. This behaviour was related to glass inhomogeneity and this shift was shown to depend on the inhomogeneous broadening related to the Cr^{3+} ion site distribution. In this paper we propose a model which takes into account a site dependence of coupling between ^2E and $^4T_2$ levels in order to explain the experimentally measured shifts and yields positive values for them.

2. Results and discussion

As was commented in the introduction, the inhomogeneous broadening related to the ion site distribution in glasses will be regarded to explain the obtained ΔE values. The Cr^{3+} ions in a glass occupy a range of crystal field sites, and there is a spread of luminescent $^4T_2$ energy levels among them. We shall introduce the effects of site to site disorder in the $^4A_2 \rightarrow {}^4T_2$ transition by supposing that the distribution of $^4T_2$ energy levels among the ions is described by a distribution function $F(\xi)$. The variable ξ represents the crystal field splitting, that is, the electronic separation between the $^4A_2$ and $^4T_2$ levels. A normalized Gaussian distribution
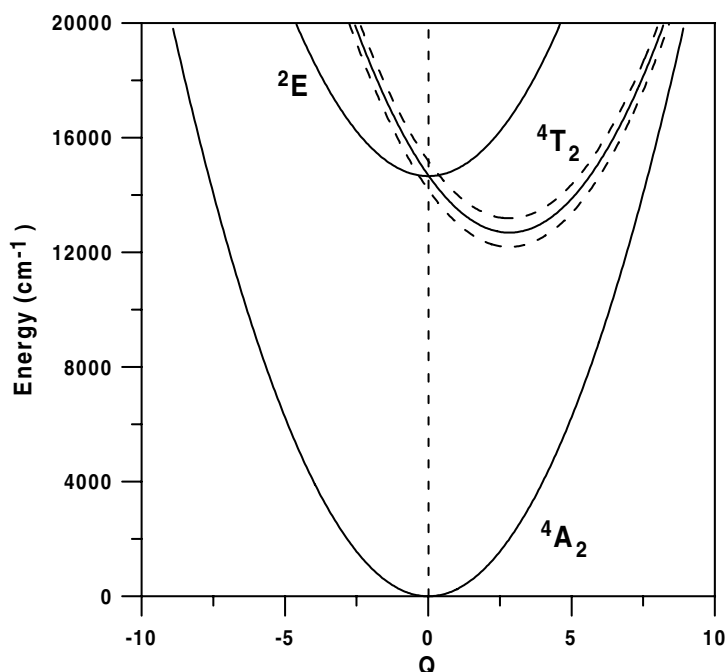
Figure 1. Configurational coordinate diagram representing the distribution of the Cr^{3+} site in glasses. The area between broken curves represents the site distribution of the crystal field splitting.

function $F(\xi)$ is taken to describe this distribution of energy levels [17–20]:

$$F(\xi) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\xi - \xi_P)^2}{2\sigma^2}\right) \tag{7}$$

where ξ_P is the centre of the distribution and $(2\sqrt{2\ln 2})\sigma$ the width at half maximum. ξ_P is the crystal field value of Cr^{3+} sites with a maximum probability and σ is the disorder width. On the basis of a point charge model, the crystal field in octahedral symmetry can be written $\xi = C/R^5$, where C is a constant and R is the distance of the transition-metal ion from six nearest-neighbour ligand ions. Therefore, the disorder width σ would reflect the distribution of the distance R at different sites. Figure 1 shows the single configurational coordinate diagram for the Cr^{3+} ion where a site variation in the crystal field parameter is taken into account. It is supposed that the vibrational energy ($S\hbar\omega$) and the energy of the ^2E sharp level (E_0) for the Cr^{3+} sites are constant. Assuming a strong electron–phonon coupling, a Gaussian band with peak energy $\xi + S\hbar\omega$ and full width at half maximum $(2\sqrt{2\ln 2})\Delta$ is taken for the optical spectra ($\sigma < \Delta$):

$$G_2(E, \xi) = \frac{1}{\sqrt{2\pi}\Delta} \exp\left(-\frac{(E - (\xi + S\hbar\omega))^2}{2\Delta^2}\right). \tag{8}$$

The Cr^{3+} absorption line-shape function, including the disorder effect, would be calculated as the integral $G_2(E) = \int F(\xi)G_2(E, \xi)\,d\xi$. The result of the integration [15] is a Gaussian function, centred at $\xi_P + S\hbar\omega$, with a width $(\Delta^2 + \sigma^2)^{\frac{1}{2}}$, which would represent the background spectrum.

In order to calculate the 'Lamb shift', we shall assume that mixing between the $^4T_2$ electronic levels and level ^2E changes with ξ, that is, the spread of electronic energy levels
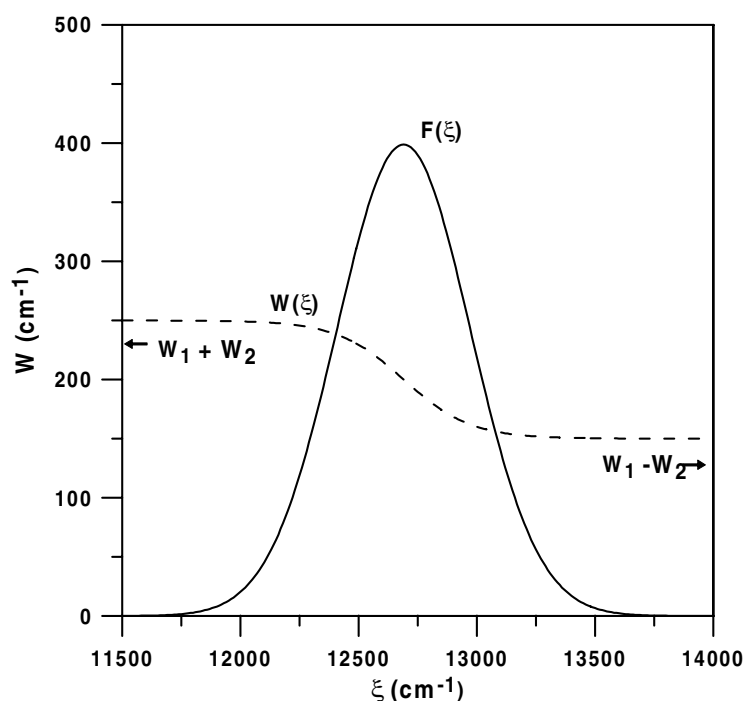
Figure 2. Variation of coupling W between the electronic levels ^2E and $^4T_2$ within the crystal field Gaussian distribution, $F(\xi)$. The curves are calculated with $\xi_P = 12\,690\,cm^{-1}$ and $\sigma = 283\,cm^{-1}$ for $F(\xi)$ and $W_1 = 200\,cm^{-1}$, $W_2 = 50\,cm^{-1}$, $W_3 = \xi_P = 12\,690\,cm^{-1}$ and $W_4 = \sigma = 283\,cm^{-1}$ for $W(\xi)$.

of the quartet ($^4T_2$) gives different spin–orbit couplings W. The site variation of the one-electron spin–orbit coupling observed in [12] and the fact [4] that not all the electronic states of $^4T_2$ and ^2E are connected by the spin–orbit interaction may support this interpretation. We shall suppose that the admixture of the $^4T_2$ electronic wavefunction into the ^2E electronic wavefunction depends on the doublet–quartet energy separation and write the interaction W as

$$W(\xi) = W_1 + W_2 \tanh\left[\frac{W_3 - \xi}{W_4}\right]. \tag{9}$$

The situation is sketched in figure 2, where we can observe how this mixing changes within the site distribution. The lower-energy ions with a lower energy separation from E_0 have a higher W, while the higher-energy ions have a low coupling. Parameters W_1 and W_2 represent the maximum and minimum values of coupling W respectively. At low energies ($\xi \ll \xi_P$) the value of W tends to $W_1 + W_2$, whereas at higher energies ($\xi \gg \xi_P$) it tends to $W_1 - W_2$. Parameters W_1 and W_2 are chosen to give values of the spin–orbit coupling corresponding to these materials. W_3 is the value of ξ in which the coupling W takes half the value of its total variation, that is, W_1 (see figure 2). W_4 is related to the slope of the curve; as W_4 increases the slope is lower. It is obvious that if we want to express a variation of W within the distribution, parameters W_3 and W_4 must be related to the maximum and width of the site distribution, ξ_P and σ, respectively.

With account taken of this site variation of W, the Lamb shift would now be calculated by the integral

$$\Delta E = \int W^2(\xi) F(\xi) G_1(E, \xi) \, d\xi = \int W^2(\xi) F(\xi) \, d\xi \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{G_2(E, \xi)}{E_0 - E} \, dE \qquad (10)$$

where the definition of the Hilbert transform has been included. The function $G_2(E)$ is normalized to π $\left(\int G_2(E) \, dE = \pi \right)$, while $F(\xi)$ is already normalized to unity. This expression has been worked out and the following double integral is obtained:

$$\Delta E = \int_{-\infty}^{+\infty} \frac{W^2(\xi)}{\Delta \sigma \sqrt{\pi}} \exp \left(-\frac{(\xi - \xi_P)^2}{2\sigma^2} \right) \exp \left(-\frac{(E_0 - (\xi + S\hbar\omega))^2}{2\Delta^2} \right)$$

$$\times d\xi \int_0^{\frac{E0 - (\xi + S\hbar\omega)}{\sqrt{2}\Delta}} \exp(t^2) \, dt. \qquad (11)$$

The spectral width $\gamma = W^2 G_2(E_0)$ which appears in the ε function (equation (3)) would now be calculated by the integral $\gamma = \int W^2(\xi) F(\xi) G_2(E, \xi) \, d\xi$. Replacing the corresponding functions, we obtain the expression for γ:

$$\gamma = \frac{1}{2\Delta\sigma} \int_{-\infty}^{+\infty} W^2(\xi) \exp \left(-\frac{(\xi - \xi_P)^2}{2\sigma^2} \right) \exp \left(-\frac{(E_0 - (\xi + S\hbar\omega))^2}{2\Delta^2} \right) \, d\xi. \qquad (12)$$

The value E_0 which appears in the last equations represents the energy of the discrete state ^{2}E. If the integrals are calculated at any value of E_0, we obtain the functional energy dependence of ΔE and γ.

The parameters of the Cr^{3+} absorption spectrum used in the calculations correspond to the glass $74P_2O_5$–$26Al_2O_3$ and they have been taken from [3]. We assume the background spectrum to be a Gaussian function with peak $E_{abs} = 14\,690$ cm^{-1} and width $(\Delta^2 + \sigma^2)^{\frac{1}{2}} = 743$ cm^{-1}, which give a value for $q = -0.03$ at $E_0 = 14\,662$ cm^{-1} in agreement with the value obtained by Lempicki *et al* [3]. From works related to the disorder of Cr^{3+}-doped glasses [17–19], a ratio $\Delta/\sigma = 2.5$ has been chosen ($\sigma = 283$ cm^{-1}). This value for the width σ would approximately imply metal–ligand distance variations given by $dR/R = 0.004$. The value for the relaxation energy $S\hbar\omega$ is taken to be 2000 cm^{-1} [17, 19]; so, ξ_P is fixed to $12\,690$ cm^{-1}.

Firstly, let us suppose that the coupling W factor is constant. Calculations from equation (11) give an energy dependence of ΔE shift which is plotted in figure 3. In this case, the value of ΔE at E_0 is always negative. As an example, for $W = 200$ cm^{-1}, which is a typical value for these materials [18], a value of -2.1 cm^{-1} for ΔE at E_0 is obtained. Figure 4(a) shows the ratio $R(E)$ obtained in this case ($W = $ const), which has been calculated by fixing the $G_1(E)$ and $G_2(E)$ functions at E_0 and taking G_1 and G_2 functions to be dependent on energy. A value of $\Gamma = 60$ cm^{-1} has been chosen in order to obtain the experimental values of $\Gamma + \gamma = 130$ cm^{-1} and $\rho^2 = 0.21$ at E_0 [3]. It can be observed that though there are differences between the profiles far away from the dip, they are quite similar near to it. This agreement is due to the slow variation of the background spectrum close to the resonance effect in this material. The line at $14\,793$ cm^{-1} represents the position where the dip should be placed according to the experimental results (see table 1). Therefore, the assumption of energy dependence in ε, q and ρ^2 in the ratio $R(E)$ ($G_1(E)$ and $G_2(E)$ not being fixed at E_0) does not explain the shift of the curve.

Let us now consider the site distribution model we have presented above, by assuming the dependence $W(\xi)$. As we have mentioned, the values of parameters W_3 and W_4 are crucial because they describe the change of coupling within the distribution. Taking the symmetric values of the distribution, that is $W_3 = \xi_P$ and $W_4 = \sigma$ and choosing adequate values for
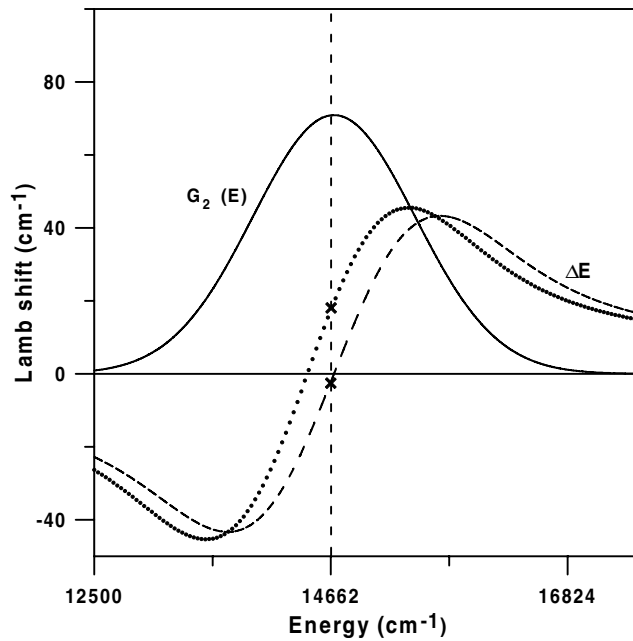
Figure 3. Solid curve: background absorption spectrum described by a single Gaussian. Dashed curve: ΔE obtained by equation (11) with $W = 200$ cm^{-1}. Dotted curve: ΔE obtained from equation (11) by taking into account the dependence of $W(\xi)$ equation (9)) with $W_1 = 160$ cm^{-1}, $W_2 = 150$ cm^{-1}, $W_3 = \xi_P = 12\,690$ cm^{-1} and $W_4 = 100$ cm^{-1}. The crosses correspond to the values of ΔE at $E_0 = 14\,662$ cm^{-1}.

W_1 and W_2, positive values for ΔE are obtained. In particular, the values $W_1 = 200$ cm^{-1}, $W_2 = 50$ cm^{-1}, $W_3 = \xi_P = 12\,690$ cm^{-1} and $W_4 = \sigma = 283$ cm^{-1} yield $\Delta E = +4.3$ cm^{-1} at E_0. Higher values are achieved if W varies more abruptly both in its value and in its shape. Varying W from 310 to 10 cm^{-1} ($W_1 = 160$ cm^{-1} and $W_2 = 150$ cm^{-1}) and increasing its slope ($W_4 = 100$ cm^{-1}) the value of the shift at E_0 increases up to $+18$ cm^{-1} with $W_3 = \xi_P = 12\,690$ cm^{-1}. Although the value of W_3 would be varied the obtained result was not improved. The energy variation of the shift (equation (11)) obtained by taking these parameters is also plotted in figure 3, where it can be seen how the shift calculated at E_0 changes from a negative value (with $W = $ const) to a positive one. The $R(E)$ obtained by taking the G_1 and G_2 functions to be variable, and introducing the functional energy dependence of ΔE and γ (equations (11) and (12)), is shown in figure 4(b). The value of γ at E_0 is 71 cm^{-1}, so Γ is also taken to be 60 cm^{-1} and parameter ρ^2 is fixed to 0.21 at E_0. One can see the displacement to higher energies of the curve calculated with our model if compared with that obtained with W constant.

Although the site distribution model gives the expected behaviour, that is, positive values for ΔE, these are low if compared with the experimental result (130 cm^{-1}). A better agreement is achieved if the vibrational relaxation energy $S\hbar\omega$ is not considered the same for all sites, particularly, supposing that the vibrational frequency is a function of the splitting parameter ξ, which would imply that the density levels vary with energy. Assuming a linear dependence of $S\hbar\omega(\xi)$ on ξ as in [21] and replacing $S\hbar\omega$ in equations (11) and (12) by the linear function $S\hbar\omega = (S\hbar\omega)_0 + K(\xi_P - \xi)$, we obtain higher values but they are still low. Using the previous parameters $W_1 = 160$ cm^{-1}, $W_2 = 150$ cm^{-1}, $W_3 = \xi_P = 12\,690$ cm^{-1} and $W_4 = 100$ cm^{-1}
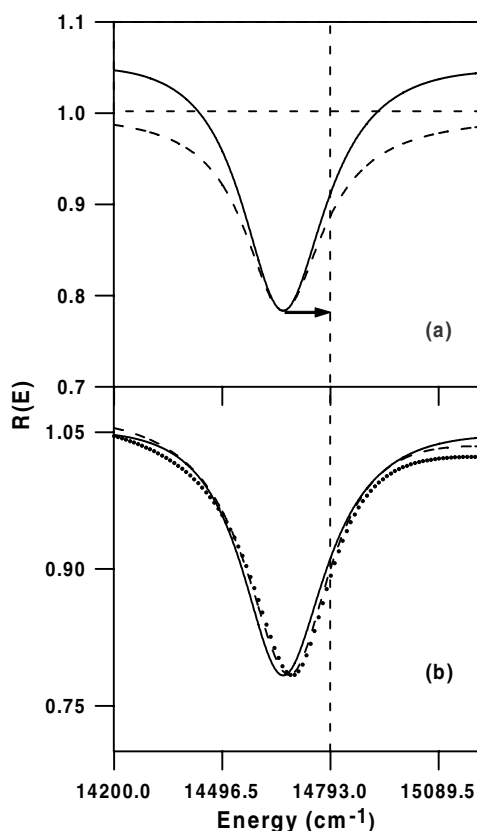
Figure 4. (a) The $R(E)$ profile obtained by taking W to be constant, with G_1 and G_2 energy-dependent functions (solid curve) and with G_1 and G_2 fixed at E_0 (dashed curve). (b) $R(E)$ obtained by taking into account the dependence of $W(\xi)$ (dashed curve) and assuming both dependences $W(\xi)$ and $S\hbar\omega(\xi)$ (dotted curve). The solid curve represents $R(E)$ with W constant. In all cases G_1 and G_2 functions are energy dependent. The vertical dashed line represents the energy position where the dip should be placed according to the experimental result.

with $(S\hbar\omega)_0 = 2000\,\mathrm{cm}^{-1}$ and $K = -1$, $\Delta E = +30\,\mathrm{cm}^{-1}$ at E_0 is obtained and the calculated ratio $R(E)$ in this case can be seen also in figure 4(b). It must be mentioned that if only the dependence of $S\hbar\omega$ on ξ were considered in the model, negative values for ΔE would be obtained.

The disagreements in the calculated ΔE values may be attributed to the following factors: (i) the experimental values of ΔE are not precise enough due to the procedure by which they have been obtained; (ii) a double Gaussian function was used as the experimental background while the background we have considered is a Gaussian function, so the background parameters may be imprecise; (iii) the discrete state E_0 may be inhomogeneously broadened and it could depend on the Cr^{3+} site. Experiments on Cr^{3+} in silicate glass [22] suggest that ions with the lowest excited state ^2E, are in sites whose symmetries are quite similar to each other. On the other hand, although previous studies of Cr^{3+}-doped materials have shown that the energy of the state ^2E usually decreases when the octahedral crystal field increases, this crystal field dependence is weak compared with that of state $^4T_2$ [23, 24]; (iv) the use of different dependences of $S\hbar\omega$ upon crystal field [25, 26] could improve the results, though it would

imply more parameters in the model; (v) the assumption of groups of distinct sites for ions with different spectroscopic parameters could give a better agreement. This would also involve more parameters in the model.

3. Conclusions

(a) The Lamb shift ΔE observed in the absorption spectra of Cr^{3+}-doped glass systems has been explained by taking into account the site effect of the Cr^{3+} ions in the glass. In agreement with experimental results, positive values for ΔE are obtained by assuming a model where a site dependence of coupling between the discrete level ^2E and level $^4T_2$ is considered.

(b) The expression relating the resonance-line shape parameter q and ΔE, which can be inferred from the Fano theory adapted by Sturge *et al* [4], $\Delta E = q[W^2 G_2(E_0)]$, would need to be changed at least in glasses. In order to analyse the validity of this theory, we should allow for the approximations considered (e.g. the adiabatic approximation, the linear interaction and the harmonicity).

Acknowledgments

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