New shape of inhomogeneously broadened resonance lines in semi-infinite media: Sm^{2+} luminescence in CaF_2/Si(111) thin films

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The inhomogeneous broadening of resonance lines by the elastic fields of dilatation centers in a semi-infinite medium is analyzed in the case in which the elastic defects and the probes are distributed in a narrow surface layer (in a thin film). The new shape of the resonance line is derived theoretically. The theory provides an interpretation of experiments on the luminescence of Sm^{2+} in CaF_2/Si(111) thin films.

At low temperatures, the inhomogenous broadening of resonance lines (both optical lines and the lines of magnetic resonances) is caused primarily by an interaction of local centers with electric or elastic field of defects.[1,2] The rapid growth in the number of experiments on 2D or quasi-2D systems by optical methods has raised the problem of the shape of the resonance lines in these bounded media. There are two features which distinguish quasi-2D semiconductor and insulator structures in a qualitative way from ordinary 3D entities. In the first place, image forces cause a qualitative change in the elastic and electric fields of the defects. As we will show below, the elastic field of the defects acquires some new components in this case. Second, the spatial distribution of defects is different in a bounded medium. We show below that these two circumstances lead to a new shape of the inhomogeneous strain-related broadening of resonance lines, even in the simplest case, in which dilatation centers consitute the source of the stress. The theory derived here agrees with experimental data in terms of the shape of the low-temperature photoluminescence line of Sm^{2+} centers in CaF_2/Si(111) thin films.

We consider the pertinent case in which the elastic properties of the film or the 2D layer are approximately the same as those of the substrate. We assume that there is a linear relationship between the shift of the optical frequency of the probe, $\Delta\omega$, and the components of the strain. If $\Delta\omega$ is determined primarily by a completely symmetric strain [this is the case in CaF_2:Sm^{2+}/Si(111) films], we have

$$\Delta\omega = a\,\mathrm{div}\,\mathbf{u}, \qquad (1)$$

where a is the strain-energy constant, and $\mathbf{u}$ is the strain (a vector). The particular dependence of div$\mathbf{u}$ on the coordinates of the defects and the probes, along with the distribution functions of the defects and the probes, determines the shape of the resonance line. A new $\Delta\omega(\mathbf{r})$ dependence in a semi-infinite medium leads to a new line-shape (different from that in bulk crystals). A dilatation center is described by a potential field. The corresponding force is equal to the gradient of a δ-function. Using the boundary conditions at $z=0$, which correspond to the absence of a stress at the solid-vacuum interface, i.e., $\sigma_{xz}=\sigma_{yz}=\sigma_{zz}=0$, we find

$$\mathrm{div}\, u = \frac{\tilde{\alpha}}{4\pi(1-\sigma)r^3}\left[1-\frac{3(z+z_0)^2}{r^2}\right]. \tag{2}$$

Here $r^2=x^2+y^2+z^2+(x+z_0)^2$; x, y, z are the coordinates of the elastic defect; z_0 is the coordinate of the probe; σ is the Poisson ratio; and the constant $\tilde{\alpha}$ determines the strength of the dilatation center. We assume that the distributions of both the dilatation centers and the probes are uniform in the surface layer (in the film) of thickness L, while there are no dilation centers or probes in the rest of the crystal (in the substrate). The shape of the resonance line, inhomogeneously broadened by the dilatation centers, can then be written as follows on the basis of statistical theory:

$$J(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t}\frac{1}{L}\int dz_0 e^{-\frac{N}{SL}\int\int\int[1-\exp(-i\Delta\omega t)]dxdydz}, \tag{3}$$

where N is the number of dilatation centers, and S is the surface area of the crystal or the thin film. For the quasi-2D case of interest here, with $NL^2/S \ll 1$, we find a new type of resonance line from (4):

$$J(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t} e^{-n_S|\alpha_0 t|^{2/3}-in_S|\beta_0 t|^{2/3}\operatorname{sign} t}, \tag{4}$$

$$\alpha_0=\tilde{\alpha}_1\left[\frac{2\pi}{3}\int_0^{\infty} dx\left(\frac{1-\cos x}{x^{5/3}}\right)\right]^{3/2};\quad \beta_0=\tilde{\alpha}_1\left[\frac{2\pi}{3}\int_0^{\infty} dx\frac{\sin x}{x^{5/3}}\right]^{3/2}, \tag{5}$$

where $n_S=N/S$, and $\alpha_1=a\tilde{\alpha}/4\pi(1-\sigma)$. It can be seen from (7) and (8) that in this limit the lineshape is independent of the film thickness; the Fourier transform of the symmetric part of the line falls off as $\exp(-|t|^{2/3})$, i.e., more slowly than in the case of Lorentzian curve [in the latter case the decay would be $\propto\exp(-|t|)$]. This result means that the symmetric part of the new lineshape has wings which are greater than in the case of a Lorentzian curve (Fig. 1). In addition, $J(\omega)$ is strongly asymmetric (Fig. 1); the asymmetry is so pronounced that the shift of the peak of the resonance line is roughly 2.5 times the half-width at half-maximum of the symmetric part of the line. The width of the asymmetric lineshape found here and the shift of its peak are proportional to $n_S^{3/2}$. Note that the lineshape found here cannot be described correctly by the moment method [see (4)]. In a real situation, dilatation centers of at least two types may exist: centers with strengths $\tilde{\alpha}$ of opposite sign. This situation may be realized physically if a semi-infinite crystal contains centers associated with vacancies and interstitial atoms. As a result, we need to make the replacements $n_S\alpha_0^{2/3}\to n_{S,1}\alpha_{0,1}^{2/3}+n_{S,2}\alpha_{0,2}^{2/3}$ and $n_S\beta_0^{2/3}\to n_{S,1}\beta_{0,1}^{2/3}+n_S\beta_{0,2}^{2/3}$ in (4). In this case, their contributions to the asymmetric part of $J(\omega)$ may of course cancel out. Experimental-

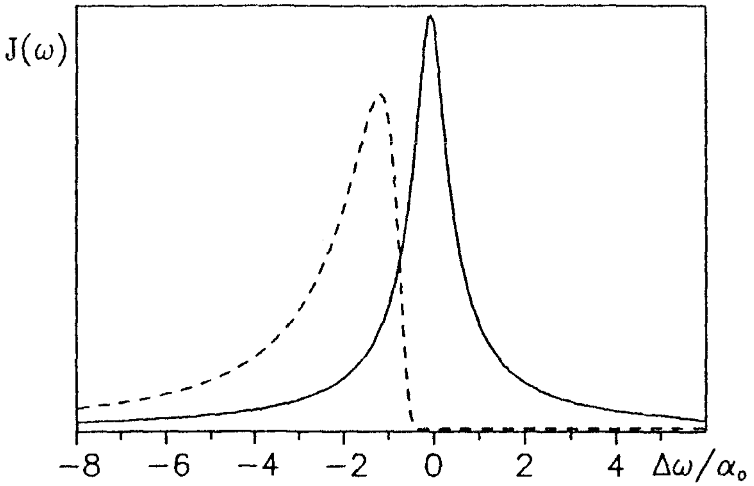

FIG. 1. Shape of the inhomogeneously broadened resonance line for the case of a broadening by dilatation centers in a narrow surface layer ($NL^2/S \ll 1$). Solid line—The asymmetries due to the dilatation centers of different signs cancel out ($\beta_0 = 0$); dashed line—broadening by dilatation centers of one sign ($\beta_0 = 2.29\alpha_0$).

ly, the lineshape might then correspond to the symmetric part of $J(\omega)$ in (4).

In the opposite limit, $NL^2/S \gg 1$, the lineshape is again symmetric, according to (3), and it can be written as a series expansion in moments. While the first moment turns out to be zero, if the parameter NL^2/S is sufficiently large, the symmetric part of the lineshape approaches $\sim \alpha^{-5/6} L^{-1} \lambda(5/6, \alpha L^3)$, where $\alpha = 8(\hbar\omega)^2 \pi^{-2} a^{-2} n_S^{-1}$, and $\gamma(n,m)$ is the incomplete gamma function. The width of the symmetric part of the line, $\omega_{1/2}$, is greater than the asymmetry effects, and we have $\omega_{1/2} \sim a n_S^{1/2} L^{-3/2}$.

Let us analyze the experimental results on the shape of the Sm^{2+} photoluminescence line in CaF_2 thin films on Si(111) substrates. The elastic constants of CaF_2 and Si are very nearly the same. On technical grounds we can assume that both the dilatation centers and the probes (Sm^{2+}) are distributed in a surface layer of the crystal which has the elastic properties of CaF_2 and that the thickness of this layer is equal to the thickness of the film, L. The type of probe which we are considering here is extremely promising for studies of inhomogeneous broadening caused by elastic fields near a surface, with $\mathrm{div}\mathbf{u} \neq 0$.

Divalent samarium ions in a CaF_2 crystal replace Ca^{2+} ions. When they are optically excited at liquid-helium temperature, one observes a narrow nonphonon emission line ($\lambda_0 = 708.5$ nm in unstressed fluorite crystals) and a broad vibron wing. The initial state for this radiative transition has the symmetry[4] Γ_1^-, while the final state has the symmetry Γ_4^+, and its energy changes only slightly upon the application of a load. The change in the energy of the $\Gamma_1^- \to \Gamma_4^+$ optical transition due to the elastic deformation is then described by expression (1). Studying the lineshape of the SM^{2+} photoluminescence in CaF_2 films is thus the most direct way to study the effect of the

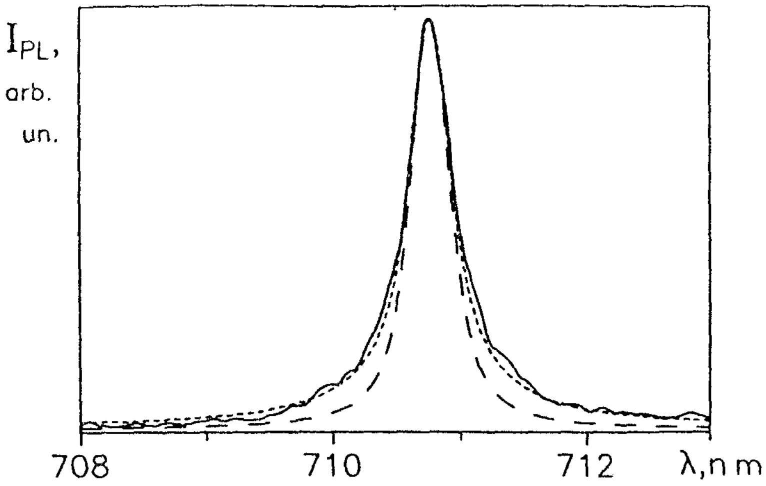

FIG. 2. Solid line—Shape of the Sm^{2+} photoluminescence line in a CaF_2/Si(111) thin film with a thickness $L = 7$ nm; dotted line—approximation of this line by the theory derived in this letter; dashed line—Lorentzian curve with the same width at half-maximum.

elastic fields of dilatation centers. An experiment carried out as in Ref. 5 has shown that for relatively thin films, with $L = 8$ nm, and for fairly narrow lines, with a width ~0.27 nm (in which case we can expect the condition $NL^2/S \ll 1$ to hold), one observes an essentially symmetric line, with wings stronger than those on a Lorentzian curve (Fig. 2). A fit of theoretical expression (4) to the experimental lineshape, under the condition that the asymmetric effect cancels out, reveals a good agreement between theory and experiment. Working from the observed linewidth, and using the corresponding values of the strain energy[6] and the elastic constants, we find $\tilde{a}n^{3/2} = 2.5 \times 10^{-3}$ cm$^{3/2}$ from (4). If the dilatation center gives rise to a displacement $\delta x \simeq 0.1$ Å, the concentration of dilatation centers is $n = 4.4 \times 10^{15}$ cm^{-3}. This value looks reasonable, and it leads to the satisfaction of the condition $NL^2/S = nL^3 \ll 1$ with $L = 8$ nm. As the film thickness is increased, the width of the photoluminescence line also increases. According to the theory derived above, this increase signifies an increase in N and leads us to expect a symmetric line, with wings which are weaker than those on a Lorentzian curve. This is precisely the behavior of the lineshape which is observed experimentally.

A corresponding analysis of the inhomogeneous broadening for the case of charged point defects and elastic fields of dislocations near a crystal–vacuum interface also leads to lineshapes which are different from those for a bulk sample.

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