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THE EFFECT OF LATTICE POTENTIAL CURVATURE VARIATIONS ON DEFECT LINESHAPE FUNCTION

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The variations of lattice potential curvature as a result of the occupancy of defect energy states can induce asymmetric broadenings in the spectral lines of the defect. We derive an explicit expression for the asymmetric lineshape function when the defect interacts with a comtinuum of lattice vibrational modes under such a circumstance and show that the second moment exhibits a T^4-dependence.

With the advent of tunable lassers optical spectroscopy of defects and impurities in insulating solids continues to be a field of active interest [1]. The defect is usually a localized electronic system; optical absorption or emission involving any two states manitests itself in a sharp line, the so-called zero-phonon line, whose linewidth, for low concentrations of defects at least, is due principally to the interaction with the host lattice.

The theoretical foundation for treating the defect-solid systems is the (suitably modified) Born-Oppenheimer approximation According to the latter approximation, the potential whose curvature governs the lattice vibration frequencies depends on the energy level in which the electronic state is occupied. It has been shown [2,3] that if allowance is given to the circumstance that the lattice curvature varies with the defect state, the zero-phonon line is *asymmetrically* broadened, a conclusion which is based on an examination of the Fourier transform of the lineshape function. However the analysis is performed under the simplifying assumption that the defect interacts with only one mode of lattice vibrations. This assumption would be appropriate if the phonons involved belong to a localized mode, but for a vast majority of systems the interaction embraces a continuous spectrum of lattice modes. It is the purpose of this note to attempt an improvement of that previous analysis by considering the lineshape function for a defect in interaction wiht a phonon continuum of whatever dispersion. Below are given the exact expressions of the zero-phonon lineshape function and its second moment as well as an argument for the latter's usefulness.

Consider an optical transition between two defect states $|a>$ and $|b>$. Let Ω_a and Ω_b, be their respective energy levels ($\hbar = 1$), and let $\omega_{qa}(\omega_{qb})$ be the phonon energy of phonon state $|q>$ when the defect is in state $|a>$ ($|b>$), the label branch being included in the notation. All energies are the renormalized values. Then the exact Fourier transform $\Gamma_{ab}(t)$ of the lineshape function $\Gamma_{ab}(\omega)$ is [3]

$$\Gamma_{ab}(t) = \exp\{it(\Omega_a - \Omega_b) - \sum_q \left|\frac{V_{bq}}{\omega_{qb}} - \frac{V_{aq}}{\omega_{qa}}\right|^2 [\frac{1-e^{i\omega_{qb}t}}{e^{\beta\omega_{qa}-it(\omega_{qa}-\omega_{qb})}-1} + \frac{1-e^{-i\omega_{qb}t}}{1-e^{-\beta\omega_{qa}+it(\omega_{qa}-\omega_{qb})}}]\}\prod_q \frac{1-e^{-\beta\omega_{qa}}}{1-e^{-\beta\omega_{qa}+it(\omega_{qa}-\omega_{qb})}} \quad (1)$$

where V_{aq} and V_{bq} are the defect-lattice interaction matrix element and $\beta = 1/kT$, k is the Boltzmann constant and T the temperature.

Our previous calculations of the optical lineshape [3] and of the analogous Raman spectrum [4] indicate that the exponential factors in the numerators within the square bracket of Eq.(1) lead to phonons absorption and emission process and that unless the number of phonons absorbed is compensated by the number of phonons emitted, these contribute spectrally to the sidebands accompanying the zero-phonon line. Hence for the purpose of studying the zero-phonon line, one expands Eq. (1) in powers of $\exp(\pm i\omega_{qb}t)$ etc. and collect only those terms which respect the phonon-number conservation stipulation, i.e. the terms which correspond to transitions from $|\Omega_a \ldots m\omega_{qa}\ldots>$ to $|\Omega_b \ldots m\omega_{qb}\ldots>$ (m being an integer). The result denoted by $\Gamma^{(0)}_{ab}(t)$ is

$$\Gamma^{(0)}_{ab}(t) = e^{i\omega_J t}\exp(-\sum U_q)\left(\sum_{S_1=1}^{\infty} e^{-S_1\chi_1}\sum_{r_1=0}^{S_1} L^{(2r_1)}_{S_1-r_1}(2U_1)\frac{U_1^{2r_1}}{r_1!r_1!}\right)$$
$$\left(\sum_{S_2=1}^{\infty} e^{-S_2\chi_2}\sum_{r_2=0}^{S_2} L^{(2r_2)}_{S_2-r_2}(2U_2)\frac{U_2^{2r_2}}{r_2!r_2!}\right)\cdots(1-e^{-\beta\omega_1})(1-e^{-\beta\omega_2})\cdots \quad (2)$$

where, and hereafter, the following abbreviated notations are used

$$\omega_0 \equiv \Omega_a - \Omega_b,\ \chi_q \equiv \beta\omega_q - it\Delta_q,\ \Delta_q \equiv \omega_{qb} - \omega_{qa},$$
$$\omega_q \equiv \omega_{qa},\ U_q = \left|\frac{V_{bq}}{\omega_{qa}} - \frac{V_{aq}}{\omega_{qb}}\right|,\ \chi_i \equiv \chi_{qi},\ U_i \equiv U_{qi},\ \text{etc.} \quad (3)$$

In arriving at Eq. (2) use has been made of the generating function for associated Laguerre polynomials $L^{(\alpha)}_n$ in the form

$$\exp[-zt/(1-t)]/(1-t)^{\alpha+1} = \sum_n L^{(\alpha)}_n(z)t^n$$

as well as the property of the double sum

$$\sum_{r=0}^{\infty}\sum_{n=0}^{\infty} f(r,n) = \sum_{s=0}^{\infty}\sum_{r=0}^{s} f(r, s-r),$$

which is valid for any bi-indicial function $f(r,n)$. Eq. (2) may be further simplified by utilizing the product formula of the Laquerre polynomials L_S:

$$L_s(u)L_s(v) = \frac{\Gamma(1+s)}{s!}\sum_{z=0}^{s}\frac{L^{(2r)}_{s-r}(u+v)(uv)^r}{\Gamma(1+r)r!} \quad (4)$$

leading to

$$\Gamma^{(0)}_{ab}(t) = e^{i\omega_0 t}\exp(-\sum_q U_q)\sum_{S_1\ldots S_q\ldots S_n}\left(\prod_q\frac{[Ls_q(U_q)]^2}{Z_q}\right)e^{-\sum_q S_q\chi_q} \quad (5)$$

in which N is the total number of lattice vibration modes and Z_q is the partition function for a single-mode oscillator, $Z_q = (1-e^{-\beta\omega_q})^{-1}$. The lineshape function $\Gamma^{(0)}_{ab}(\omega)$ for the zero-phonon line can now be obtained by taking the Fourier transform of Eq. (5):

$$\Gamma^0_{ab}(\omega) = \exp(-\textstyle\sum_q U_q)\sum_{S_1\ldots S_q\ldots S_n}\left(\prod_q\frac{e^{-\beta S_q\omega_q}}{Z_q}[L_s(U_q)]^2\right)$$
$$\delta(\omega-\omega_0-\textstyle\sum_q S_q\Delta_q) \quad (6)$$

The presence of a series of closely spaced Dirac's delta functions makes it quite apparent the asymmetric nature of lineshape for optical trensitions under consideration.

Even though for application to specific systems Eq. (7) can be readily evaluated numerically using the standard Brillouin zone integration techniques, one may more easily assess the significance of the phonon frequency variations on asymmetric line broadening by considering the second moment $\overline{(\Delta\omega)^2}$ of the lineshape:

$$\overline{(\Delta\omega)^2} = \int_{-\infty}^{+\infty}(\omega-\omega_0)^2\Gamma^{(0)}_{ab}(\omega)d\omega \quad (7)$$

With the use of Eq. (6), the second moment takes the form

$$\overline{(\Delta\omega)^2} = \exp(-\textstyle\sum U_q(2\nu_q+1))\{\sum_q\Delta_q^2[\nu_q(\nu_q+1)-2U_q\nu_q(\nu_q+1)(2\nu_q+1)]$$
$$+\left[\textstyle\sum_q\Delta_q[\nu_q-2U_q\nu_q(\nu_q+1)]\right]^2\} \quad (8)$$

where $\nu_q = (e^{\beta\omega_q}-1)^{-1}$ is the phonon distribution function. In the Debye approximation this second moment is seen to exhibit a T^4-dependence for temperatures higher than Debye's temperature. Thus, in addition to the asymmetric shape, the measurement of the temperature dependence of the second moment can serve to affirm or negate the influence of variation of lattice potential curvatures on optical absorption vis a vis the effect of random environment which is also a known mechanism for asymmetric spectral broadening (the so-called inhomogeneous broadening.) The latter is more sensitivite to defect concentration then to the temperature of the host lattice.

In summary, we obtain an explicit expression for the asymmetric lineshape function and we point out the T^4-dependence of the second moment as a signature for the influence of lattice curvature difference on optical transitions of defects. Lattice curvature variations also influence defect Raman lines [4] and exciton absorption lines [5]; it would be of interest to see how much of the present analysis can be carried over to these areas.

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