The Lattice Anharmonicity-Induced Broadenings of Defect Spectral Lines.

H. C. Chow

Department of Physics, Southern Illinois University at Edwardsville
Edwardsville, IL 62026, USA

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Summary. — The effect of the anharmonicity of the host lattice to the defect optical absorption and emission is studied. Anharmonicity contributes to the defect optical linewidths via phonon lifetime effect and defect-phonon scattering mediated by a second phonon. Numerical estimates of these contributions indicate that the anharmonic broadenings may not be negligible in some insulating crystalline hosts.

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Because of their role in many optical devices, the study of the optical properties of defects and impurities in (otherwise optically inert) insulating crystalline solids is a topic of active interest. When the defects are sufficiently far apart so that the interactions amongst themselves may be neglected, the spectral lines reflect individual defect’s energy level structures, but the position of an optical line, the linewidth and its temperature dependence are all influenced by the interaction of the defect with the host lattice. In considering its role, one usually takes the lattice as being harmonic[1], although the need to elucidate the effects of the unavoidable lattice anharmonicity has long been recognized[2]. This note reports two mechanisms whereby lattice anharmonicity can broaden defect spectral lines. In what follows are given the closed expressions for the anharmonic contributions to the linewidths, qualitative explanations of these two mechanisms, and the results of numerical assessment of their importance.

The system under consideration may be described by the following Hamiltonian in the second quantized form:

\[
H = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_q \omega_q b_q^\dagger b_q + \sum_{ij} \sum_q \left( V_{ijq} b_q + V_{jiq}^* b_q^\dagger \right) a_i^\dagger a_j + \\
+ \sum_{q_1, q_2} V(q_1, q_2, q_3) (b_{q_1} + b_{-q_1}^\dagger)(b_{q_2} + b_{-q_2}^\dagger)(b_{q_3} + b_{-q_3}^\dagger) + ...,
\]
where the terms on the r.h.s. are, respectively, the Hamiltonians of the defect, the harmonic lattice of the host, defect-lattice coupling, and the anharmonic part of the lattice potential. Here \( \tilde{\varepsilon}_i \) is the defect energy level of state \( |i\rangle \), \( \omega_q \) the energy of phonon mode \( q(h=1) \), \( V_{ijq} \) the defect-lattice coupling matrix element, and \( V(q_1, q_2, q_3) \) the cubic anharmonic parameter. With the use of Kubo’s formula, one relates the optical absorption lineshape function \( F(\omega) \) at the incident frequency with the Fourier transform of the fluctuations of the dipole moment, \( \mathbf{M} = \sum_{i,j} M_{iq} a_i a_j \). If one avails oneself of the standard many-body theory [3] and, particularly, the techniques dealing with the ladder approximation [4], one finds that the lineshape function comprises a series of Lorentzian functions, each of which corresponds to an optical transition between a pair of (renormalized) defect levels. The linewidth \( \Gamma_{ab} \) of such an individual transition between states \( |a\rangle \) and \( |b\rangle \) is the sum of the level widths \( \Gamma_a \) and \( \Gamma_b \). Specifically, the level width \( \Gamma_a \) of the state \(|a\rangle \) receives contributions from three sources: \( \Gamma_a = \Gamma_a^{(1)} + \Gamma_a^{(2)} + \Gamma_a^{(3)} \), with

\[
\Gamma_a^{(1)} = \pi \sum_{i, q} |V_{aiq}|^2 \left[ (1 + n_q) \delta(\varepsilon_a - \varepsilon_i + \Omega_q) + n_q \delta(\varepsilon_a - \varepsilon_i - \omega_q) \right],
\]

\[
\Gamma_a^{(2)} = \sum_{i, q} \gamma_q |V_{aiq}|^2 \left[ \frac{n_q + 1}{(\varepsilon_a - \varepsilon_i + \omega_q)^2} + \frac{n_q}{(\varepsilon_a - \varepsilon_i - \omega_q)^2} \right],
\]

\[
\Gamma_a^{(3)} = \sum_{i, q_1, q_2} |V_{aiq}|^2 |V(-q, q_1, q_2)|^2 \frac{2(\varepsilon_a - \varepsilon_i)}{(\varepsilon_a - \varepsilon_i)^2 - \omega_q^2} \cdot \{(n_{q_1} + n_{q_2} + 1)[\delta(\varepsilon_a - \varepsilon_i - \omega_{q_1} - \omega_{q_2}) - \delta(\varepsilon_a - \varepsilon_i + \omega_{q_1} + \omega_{q_2})] + \}

+ (n_{q_1} + n_{q_2})[\delta(\varepsilon_a - \varepsilon_i + \omega_{q_1} - \omega_{q_2}) - \delta(\varepsilon_a - \varepsilon_i - \omega_{q_1} + \omega_{q_2})]\}
\]

In eqs. (2)-(4) \( \varepsilon_a \) is the renormalized defect energy level, \( n_q = [\exp[-\Omega_q/kT] - 1] \) is the phonon distribution function, \( \Omega_q \) and \( \gamma_q \) are, respectively, the renormalized energy and width of the phonon mode \( q \). For a cubic lattice the latter takes the form

\[
\gamma_q = 18\pi \sum_{q_1, q_2} |V(q, -q_1, -q_2)|^2 \left[ (n_{q_1} + n_{q_2} + 1)[\delta(\Omega_q - \omega_{q_1} - \omega_{q_2}) - \delta(\omega_q + \omega_{q_1} + \omega_{q_2})] + (n_{q_1} - n_{q_2})[\delta(\Omega_q + \omega_{q_1} - \omega_{q_2}) - \delta(\omega_q - \omega_{q_1} + \omega_{q_2})]\right].
\]

Equation (2) describes the linewidth owing to the so-called direct relaxation process [1], which arises from an absorption or emission of a phonon as the defect makes a transition. This process occurs even in a harmonic lattice. Of central importance to the present note are, however, the contributions of the lattice anharmonicity to the defect linewidths, which are contained in eqs. (3) and (4) and which may be understood as follows. The width \( \Gamma_a^{(2)} \) in eq. (3) is essentially a phonon lifetime effect. An optical transition between two defect levels may involve any number of phonons provided the number of phonons before and after the transition remains conserved. In an anharmonic crystal the phonons are endowed with finite widths (as typified by eq. (5)) and thus there is a latitude in the energy spread even in the phonon-number-conserved defect transitions. Another way of stating this result is via the aid of diagrams such as fig. 1a). There a defect level is shown to be coupled