Optical Jahn-Teller effect: contribution of phonons

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Abstract

A theory of absorption and resonance Raman scattering of impurity centers in crystals with $E \times e$ - type Jahn-Teller effect in the excited state is presented. The vibronic interaction with non-totally symmetric local modes and phonons is considered. It is shown that a number of specific quantum effects are apparent in the spectra; the vibronic interaction with phonons essentially determines the structure of the spectra.

Key words: absorption spectrum, resonance Raman scattering, Jahn-Teller effect, non-adiabaticity, phonons

1. Introduction

The goal of this communication is to study the manifestations of the non-adiabaticity of the dynamical Jahn-Teller (JT) effect [1-12] in the absorption and resonance Raman scattering (RRS) spectra of impurity centres in solids. An essential feature of the JT effect in this case is the participation of the $\sim N$ Avogadro phonons of the bulk [3, 8-11, 13-15]. However, the existing theories, including the recently developed multi-configurational time-dependent Hartree approximation [12, 16-24], allow one to consider the dynamical JT effect in the systems with finite (usually of the order of 10) contributing vibrations.

The dynamical JT effect with many frequencies has been also considered in earlier works [25, 26]. The author of Ref. [25] has considered only the states with the lowest energy by using the variational procedure. In Ref. [26] an approach, allowing one to consider the effect of large number $N$ of modes within the frames of an efficient single JTE active mode, was proposed. O’Brien implies the fact that in harmonic approximation it is always possible to reduce the multimode problem to the case of vibronic interaction with single degenerated mode by adding an additional effective quadratic interaction of vibrations. She proposed a set of equations for the parameters of the effective quadratic interaction. However, it remains unclear how these equations can be solved.

Recently we proposed a method [27] allowing one to calculate the effective quadratic interaction supposing that contribution of single local mode to JT effect is stronger than that of phonons. Below we apply this method to the calculation of absorption spectrum and Raman excitation profiles (REPs) of JT systems. We are considering the trigonal centers in the crystals excited in resonance with the electronic transition from a non-degenerate to a two-fold degenerate electronic state of the $E$-representation interacting with the vibrations of $e$-representation (JT effect in this state is called the $E \otimes e$-problem). Our calculations are fully quantum mechanical, which is different from the calculations of REPs of JT systems in semi-classical approximation [28], performed earlier in [29-32].

2. Basic equations

In this communication we study absorption and RRS using the time-domain approach based on consideration of the Fourier transforms of the absorption and RRS amplitudes. In case of
the dipole-allowed electronic transition the Fourier transform of the absorption spectrum is determined by the equation [32]

$$F_i(t) = e^{-\gamma \sigma} \langle i | \mu_{\sigma} e^{i (H + V)} \mu_{\sigma} e^{-i \gamma \sigma} | i \rangle$$

analogously, the Fourier transform of the RRS amplitude (called as Raman Fourier amplitude) can be presented in the form [33]

$$A_{q\phi, lj}(t) = \Theta(t) e^{-\gamma \sigma} \langle \int | \mu_{\sigma} e^{i (H + V)} \mu_{\sigma} e^{-i \gamma \sigma} | i \rangle$$

Here $H$ is the vibrational Hamiltonian in the ground electronic state, $H + V$ is the vibronic Hamiltonian of the excited state, $\gamma$ is the decay constant of the excited state, $\Theta(t)$ is the Heaviside step function. The amplitude of the RRS $A_{q\phi, lj}(\omega)$ is given by the Fourier transform of $A_{q\phi, lj}(t)$; the REP equals $|a_{q\phi, lj}(\omega)|^2$. Equations for the Fourier amplitudes of RRS for thermal equilibrium, see in Ref. [33].

We consider absorption and Raman scattering by trigonal centers excited in resonance with the transition from $A_i$ (ground) to $E$ (excited) electronic states, representations. In harmonic approximation the vibrational Hamiltonian in the ground state reads

$$H = \sum_{\alpha, j \neq 0} \omega_j a_{\alpha j}^* a_{\alpha j}$$

(up to the unimportant here zero-point energy) with $\alpha = x, y$, $a_{\alpha j}$ and $a_{\alpha j}^*$ being the annihilation and creation operators; $\omega_j$ is the frequency of the normal mode $j$, index $\alpha$ stands for the rows of the symmetry representations. The electron(s) of the $E$-state interacts, besides totally-symmetric modes, with doubly-degenerate modes of $e$-representation (the corresponding vibronic problem is called $E \otimes e$ -problem). If one takes two components of the excited state as $|-\rangle_e = (|x\rangle - i |y\rangle)/\sqrt{2}$ and $|+\rangle_e = (|x\rangle + i |y\rangle)/\sqrt{2}$, where $|x\rangle$ and $|y\rangle$ transform as components of the polar vector, respectively, then the linear (usually main) vibronic interaction with $e$ vibrations gets the form [1-10]

$$V = \kappa \sum_{\alpha} \sigma_z Q_{\alpha}$$

where $Q_{\alpha}$ are the configurational coordinates of $e$-representation, $\sigma_z$ and $\sigma_z$ are the Pauli matrices, $\kappa$ is the constant of vibronic coupling. In polar coordinates $V = k Q (\sigma_x \cos \varphi + \sigma_y \sin \varphi)$. The adiabatic potential (AP) curves of the ground and the excited state in the space of the configurational coordinates $Q_x$ and $Q_y$ is shown in Fig.1. The adiabatic potential of the $E \otimes e$ problem (the upper potential) has a shape of the Mexican hat.

Fig.1. The scheme of the potentials and electronic transitions in the configurational coordinate space. The upper potential corresponds to the Jahn-Teller effect, $E \otimes e$-problem.
It is commonly accepted that in the case of a strong vibronic interaction, for describing optical spectra the semi-classical approximation can be used (see, e.g. [28]). In this approximation one neglects the commutator $[V, H]$. Then in the Condon approximation

$$\langle \alpha | \mu_\beta | g \rangle = M \delta_{\alpha \beta}, \ M = \text{const} \ 	ext{we get (up to the factor} \ M^2)$$

$$F(t) = \langle 0 | e^{iHt} | 0 \rangle = 1 - \tau \omega(\tau/2)$$

$$A_{xy} = (2i/\tau)A_{xx} = \Theta(t)(i/2)\left(\tau + (2 - \tau^2)w(\tau/2)\right)$$

where $\tau = t/\sqrt{2D}$, $D = \kappa^2 \langle 0 | Q^2 | 0 \rangle$, $w(x) = e^{-x^2} \int_0^x e^{y^2} dy$ is the Dawson function. The resulting spectra are given in Fig. 2.

![Fig. 2. Spectrum of absorption, first-order REP and second-order REPs for optical $E \times e$ problem in semi-classical approximation.](image)

In the semi-classical approximation it is not important whether the contributing to $V$ coordinates are normal coordinates or not. However in quantum theory it is of primary importance. Here we are considering the case when the coordinate $Q$ of the given (any) row of the $e$-representation is the linear combination of a number of normal coordinates $x_j$ (the subscript $\alpha$ is omitted for simplicity), but the main contribution to $Q$ is given by one normal coordinate $q_0$ describing the local mode. In this case $Q$ can be presented in the form

$$Q = \left(1 + \lambda^2\right)^{-1/2} \left(x_0 + \lambda \sum_{j} e_j x_j\right)$$

(3)

where $x_j$ ($j \geq 1$) are normal coordinates of phonons, $e_{ij}$ are the normalized polarization vectors; $\sum_j e_j^2 = 1$, $\lambda$ is a small dimensionless parameter. In Ref. [27] it was shown that in case of small $\lambda$ the vibronic interaction with non-totally symmetric phonons (it is given by the $\propto \lambda$ term in the brackets of Eq. (3)) can be replaced by the following quadratic interaction of the main mode with phonons:

$$H' = \lambda \sum_{\alpha \neq \gamma, j} \nu_j (a_{\alpha 0}^* + a_{\beta 0}) (a_{j0} + a_{j0}^*)$$

(4)

where

$$\nu_j = e_j \left(\omega_0^2 - \omega_j^2\right)/2\sqrt{\omega_0 \omega_j}$$

If to neglect the mode-phonon interaction $H'$ then the problem under consideration reduces to the JT problem in case of the single $e$-mode $x_0$. In this approximation vibronic interaction
with the local mode and phonons of e-representation $V$ is replaced by the vibronic interaction with the local mode of e-representation

$$V_0 = \kappa \sum \sigma \alpha x_{ao}$$

and the vibrational Hamiltonian $H$ is replaced by the Hamiltonian $H + H'$. This allows one to use, as the zero'th approximation the known numerical solutions of the latter problem and to take into account the interaction $H'$ approximately by considering it as small perturbation.

Using the eigenstates $|n, m\rangle$ of the two-dimensional harmonic oscillator as the basis one can present the stationary of the JT $E \times e$ problem as follows [2, 34-38]

$$|\nu \rangle = \sum C_{2n,j} |2n, j - 1/2\rangle + C_{2n+1,j} |2n + 1, j + 1/2\rangle$$

where the integer $n$ determines the energy $\omega_n$, of the two-dimensional oscillator, the sign-alternative $m$ determines the projection of the rotational momentum on z-axis ($|m| \leq n$), $\nu$ and $j$, determine the radial and the angular JT motion, respectively. At that the quantum number $j = m - 1/2 = 1/2, 3/2, \ldots$ is the projection of the full (electronic $s = 1/2$ and vibrational) rotational momentum on the $z (C_3)$-axis. The amplitudes $C_{j,\nu}$ and the energies $E_{\nu}$ are the solutions of the given in Refs [2, 35-38] matrix equation with a three-diagonal matrix. The states $|\nu \rangle$ and $|\nu ' \rangle$ denote the components of the two-fold degenerate states (Kramers degeneracy) and give the same contribution to the spectra.

Here we are considering the case of zero temperature. In this case only the vibrational state with $n = m = 0$ in the initial electronic state is populated and only the vibronic levels with $j = \pm 1/2$ of the excited state give contributions to RRS. We use in Eq. (1), as the basis the solutions of the single e-mode $E \times e$ problem and apply the Dyson equation [39]. We get

$$e^{i(t)]} = e^{i(t + H' + V_0)} = \hat{T} \exp \int_0^t i dt H'(\tau) e^{i(t + V_0)}$$

where $H'(\tau) = e^{i(t + V_0)} H' e^{-i(t + V_0)}$. We find for \( T = 0 \)

$$A_j(t) = \Theta(t) \sum \gamma C_{j,\gamma} C_{0,\nu} e^{iE_{\nu}} \langle \nu | \langle 0 | \hat{T} \exp \int_0^t i dt H'(\tau) | 0 \rangle \rangle$$

Applying then the cumulant expansion and taking into account first two cumulants we get (in full analogy with the calculation of $F(t)$ in Ref. [27])

$$A_j(t) = \Theta(t) \sum \gamma C_{j,\gamma} C_{0,\nu} \exp \left[ iE_{\nu} t + g_{\nu}(t) \right] .$$

$$g_{\nu}(t) = \lambda^2 \sum \gamma \sum \delta \left[ \frac{i t}{E_{\nu} - E_{\nu'} - \omega_j} + \frac{e^{(E_{\nu} - E_{\nu'} - \omega_j)} - 1}{(E_{\nu} - E_{\nu'} - \omega_j)} \right]$$

$$S_{\nu\nu'} = 2 \sum \sum \delta \left[ \sqrt{2n + 1} C_{2n,\nu'} + \sqrt{2n + 2} C_{2n+1,\nu'} \right]$$

$u_j$ is given above. Note that $e^{g_{\nu}(t)}$ are the same factors which describe the contribution of phonons in the Fourier transform of absorption [27]. At large time $t$ these factors damp due to the decay of vibronic states $\nu$ caused by creation of phonons.
3. Numerical

Below we present some results of the numerical calculations of absorption spectra and REPs for the $E \times e$ problem in the excited state, using the Debye-Van Hove model of phonons. In this model DOS of phonons equals $\rho(\omega) = (16/\pi)\omega^2 \sqrt{1 - \omega^2}$ and the interaction function $V_2^{\nu}(\omega) = \sum_j v_2^{\nu} \delta(\omega - \omega_j)$ has the form $V_2^{\nu}(\omega) = \rho(\omega)\omega (\omega_0^2 - \omega^2)/2\pi \omega_0$. The sums over $j$ in Eq. (8) were replaced by the integrals over $\omega$; the sums over $v$ and $n$ were calculated taking into account few hundreds of the levels $\nu$ and $n$. The results of the calculations of REPs of first and second order RRS for two different values of the vibronic interactions $D$ with the main mode and two different values of the vibronic interaction with phonons $\lambda^2$ are given in Figs 3 and 4. We also performed calculations for very strong vibronic interaction with the main mode $D = 1000$ and weak interaction with phonons (see Fig. 5).

![Fig. 3. Absorption spectrum and the first- and the second-order REPs of trigonal centers with $E \times e$ -type Jahn-Teller effect in the excited state. $D = 10$ is dimensionless energy of vibronic interaction with the main $e$ -mode; $\lambda$ is dimensionless vibronic interaction with non-totally symmetric phonons.](image)

![Fig. 4. The same as in Fig.3 but for $D = 20$.](image)

The absorption spectra and the REPs presented in Figs. 2-5 are given in arbitrary units, however, with correct relative intensities of the first- and the second-order RRS. The latter have a comparable intensity which is characteristic of RRS [41, 42]. The central parts of the spectra in Figs. 3-5 correspond to the excitation in the region of the conical intersection of AP in the excited state. The remarkable intensity of these parts in the spectra presented in these figures display the contribution of the non-adiabatic transitions between the sheets of AP. Somewhat smaller intensity of the high-energy part of the second-order REP as compared to absorption is due to larger size of the wave function of the finite (two-quantum) state as
compared to the initial (zero-point) state. This makes the second-order RRS more probable when excitation occurs to the lower, broader part of the conical intersection of the $E \times e$ AP (see Fig. 1) than to the higher part of it.

![Fig. 5. The same as in Fig. 3, but for $D = 1000$ and $\lambda^2 < 0.01$. The presented spectra differ essentially from the given on Fig. 2 spectra calculated in semiclassical approximation.](image)

Rather evident manifestation of the non-adiabaticity is displayed in the first-order REPs. We have in mind here the enhancement of the high-energy parts of them in Figs. 3, 4 as compared to absorption. Indeed, the first-order RRS is accompanied by a real vibronic transition in the conical intersection of the $E \times e$ AP. The coordinates of the upper part of the conical intersection are, on the average, smaller than that of the lower part of it. This results in higher probability of the vibronic transitions in the upper part of the conical intersection than in the lower part of it and in the enhancement of the higher energy part of the first-order REPs. Note that this effect works only for the moderate vibronic interaction $D$. However if $D$ is very large, then the difference in the shape of the lower and upper parts of the conical intersection in the resonance region is small, due to what the intensities of the lower and higher energy parts of the first-order REP become comparable (see Fig. 5).

In the semi-classical approximation the virtual non-adiabatic transitions are not taken into account. This explains why the intensities of the central part of the absorption spectrum and of the second-order REP in Fig. 2 is small and it tends to zero if $E \to 0$. An essentially different situation, however, exists for the first-order RRS. This scattering is accompanied by the real transition between the sheets of the AP. The probability of this transition increases with $E \to 0$, compensating the decreasing of the density of states and causing the finite intensity of the semi-classical first-order REP at $E = 0$. However, in the quantum theory this intensity strongly diminishes (see Figs. 3-5). The reason of this diminishing is in the quantum interference. Here we take into account that according to the quantum theory the first-order RRS has two scattering channels [33]: a) the channel describing the resonances for incident light and b) the channel describing the resonances for scattered light. These two channels interfere destructively. It is this destructive interference which causes the decrease of the intensity of the first-order REP in the central part of the spectrum. Interference effects exist also for the second-order RRS. Here the two channels mentioned interfere constructively and they both interfere destructively with the scattering channel, having resonance for the intermediate frequency. This combined interference is responsible for the appearance of the two deepest minima in the second-order REP in Fig. 5.

Note also one more essential difference of the spectra in the quantum and the semi-classical theory: the series of the well-distinguished peaks in the envelopes of the high-energy parts of the spectra in Figs. 3-5 are absent in the spectra given in Fig. 2, obtained in semi-classical approximation. These peaks correspond to the excitation in resonance with the high-energy quantum levels of the upper part of the conical intersection, known as the Slonczewski resonances [42].
The presented results show also the importance of the interaction with phonons: already relatively moderate increase of the corresponding interaction parameter $\lambda^2$ in Figs. 3 and 4 causes a remarkable diminishing of the vibronic structure. The Fig. 5 demonstrates that the quantum theory of absorption and RRS does not coincide with the semi-classical theory even for rather strong vibronic interaction. However, as it follows from our calculations the remarkable interaction with phonons leads in case of large $D$ to an essential diminishing of the difference of the spectra in the quantum and semi-classical.

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