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Hot lines in the infrared absorption spectra of Fe^{2+} in III-V compounds

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We attempt an explanation of the main features of the high-temperature infrared absorption spectra of Fe^{2+} in III-V compounds (GaAs and GaP). We consider a linear Jahn-Teller interaction with two lattice modes of E symmetry, having energies in the range of acoustical and optical phonons, respectively. The upper vibronic states originating from all electronic states of the free ion must be considered to cope with the many possible transitions that arise at temperatures that populate several low-energy vibronic levels. We use Lanczos-recursion procedures to find energies and wave functions. A comparison with experimental energies and intensities is performed. A discussion comparing present findings with previous results based only on cold lines is also done.

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I. INTRODUCTION

Iron is a substitutional impurity in III-V crystals and therefore most of its ionic properties are similar through this family of compounds. We will deal here with two of such systems: namely, GaAs:Fe^{2+} and GaP:Fe^{2+}.

The electronic configuration $3d^6$ of the free Fe^{2+} ion gives rise to a ground ^5D multiplet (25 times degenerate including spin). When Fe^{2+} substitutes for a Ga ion in III-V compounds the ^5D term is split by the tetrahedral crystalline field into two multiplets: ground ^5E (10 times degenerate) and excited $^5T_2$ (15 times degenerate), with an energy separation Δ of about $10|Dq|$, where $|Dq|$ is the one-electron crystal-field parameter. The degeneracy of these levels can be partially removed by the spin-orbit interaction. We will indicate by γ_i the levels belonging to the lower multiplet (γ_1, γ_4, γ_3, γ_5, and γ_2, in order of increasing energy) and with Γ_i the levels belonging to the upper one (Γ_5, Γ_4, Γ_3, Γ_1, Γ_5', and Γ_4').

Low-temperature absorption spectra of substitutional Fe^{2+} in III-V and II-VI compounds connect the singlet ground state of symmetry γ_1 (spherically symmetric) to excited states of symmetry Γ_5 by means of electric-dipole transitions. Such absorptions have been used to characterize the Jahn-Teller effect for excited vibronic states. However, such analysis reveals only part of the Jahn-Teller coupling since excited levels from symmetries other than Γ_5 cannot be accounted for. When temperature is raised, excited states of symmetries γ_4, γ_3, γ_5, and γ_2 are successively populated, allowing absorptions ending in states of all possible symmetries, thus exploring the Jahn-Teller coupling in a complete way. Such spectra are very rich showing "hot lines" modulated by temperature.[1–3] Even if many phonons can interact with the electronic orbitals, the main features of the complex low-temperature experimental spectra can be accounted for by considering a linear Jahn-Teller coupling to two lattice modes of E symmetry: one acoustical and one optical (replicated through the Brillouin zone according to all possible symmetry operations).[4] This principle will now be applied to explain the main features of absorption experimental spectra as temperature is increased.

This two-phonon model interaction leads to the diagonalization of very large, although sparse, rank matrices. So the Lanczos-recursion procedure,[5,6] combined with the concept of a dipole-carrying state,[7] becomes a powerful tool to find the eigenstates of localized impurities in semiconductors.[8] In Sec. II the theoretical model and the main points of the calculation procedure are presented. Section III is devoted to a discussion of the results which are compared with the available experimental information. Section IV contains the conclusions.

II. MODEL HAMILTONIAN AND CALCULATION PROCEDURE

Excited levels of Fe^{2+} are several to many eV above the ground $3d^6$ configuration which corresponds to a ^5D multiplet ($3d^54s$ is more than 70 000 cm^{-1} apart). The crystalline field produces a very small admixture of atomic levels in the impurity, thus explaining transitions among levels of the ground multiplet (electric-dipole transitions among pure ^5D states are forbidden). However, the main components of the wave functions within the ground ionic manifold in the crystal are still ^5D. So we will restrict ourselves to the 25 states spanning this levels, which split into 15 excited $^5T_2$ states and 10 ^5E ground states. Such splitting is over 3000 $cm^{-1}$for the systems under consideration.

To evaluate the Jahn-Teller effect on the absorption spectra of these compounds we consider the functions belonging to the $^5T_2$ multiplet, denoted by $|F_iS_j\rangle$ ($i=1,2,3$; $j=1,\ldots,5$), where $|F_i\rangle$ are the many-electron wave functions transforming as bases for the irreducible representation $^5T_2$ of the point group T_d; $|S_j\rangle$ are appropriate corresponding combinations of the spin functions for $S=2$ with S_z taking five possible values: $+2$, $+1$, 0, -1, and -2. The very weak vibronic coupling of the γ_i levels is well known,[9] so we will not attempt any further investigation of them.

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The total Hamiltonian for the Fe^{2+} ion impurity in the $^5T_2$ states can be written in the form

$$H = H_e + H_{SO} + H_L + H_{e\text{-}L}. \tag{1}$$

where $H_e + H_{SO}$ is the electron Hamiltonian including the spin-orbit interaction $\lambda \mathbf{S}\cdot\mathbf{L}$, whose explicit form can be obtained with standard methods. H_L and $H_{e\text{-}L}$ are the lattice Hamiltonian and the electron-lattice interaction, respectively. The $^5T_2$ excited states can be coupled to many lattice modes of different energy and symmetry; however, as usual in the literature, we adopt a cluster model[10] and we consider a linear interaction with two modes (of E symmetry) simultaneously. In terms of the usual creation and annihilation operators for the components θ and ϵ of the acoustical mode (index A) as well as the optical mode (index O), H_L and $H_{e\text{-}L}$ take the form

$$\begin{aligned} H_L = {} & \hbar\omega_A(a^\dagger_{A\theta}a_{A\theta} + a^\dagger_{A\epsilon}a_{A\epsilon} + 1) \\ & + \hbar\omega_O(a^\dagger_{O\theta}a_{O\theta} + a^\dagger_{O\epsilon}a_{O\epsilon} + 1), \end{aligned} \tag{2}$$

$$\begin{aligned} H_{e\text{-}L} = {} & K_A[(a^\dagger_{A\theta} + a_{A\theta})D_\theta + (a^\dagger_{A\epsilon} + a_{A\epsilon})D_\epsilon] \\ & + K_O[(a^\dagger_{O\theta} + a_{O\theta})D_\theta + (a^\dagger_{O\epsilon} + a_{O\epsilon})D_\epsilon]. \end{aligned} \tag{3}$$

Here K_A and K_O are the coupling constants expressed as

$$K_A = \sqrt{E_{JTA}\hbar\omega_A}, \quad K_O = \sqrt{E_{JTO}\hbar\omega_O}, \tag{4}$$

in terms of Jahn-Teller energies (E_{JT}) and frequencies (ω) of the corresponding coupling modes. Huang-Rhys factors S are also defined as $S_A = E_{JTA}/\hbar\omega_A$ and $S_O = E_{JTO}/\hbar\omega_O$. Here D_θ and D_ϵ have the form

$$D_\theta = \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D_\epsilon = \begin{pmatrix} \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{5}$$

A basis function of the vibronic model is the direct product of an electron-spin function $|F_iS_j\rangle$ ($i = 1,2,3,\ j = 1,\ldots,5$) and a vibrational function $|lmnp\rangle$, where $l,\ m,\ n,\ p$ are the occupation numbers for the θ and ϵ components of the acoustical and optical modes, respectively. The phonon occupation numbers N_A and N_B are successively increased to ensure the stability of the found solutions (stronger coupling requiring larger values of these numbers). For these systems a middle strength of the coupling is expected, and in this range the Lanczos-recursion method,[5,6] with a proper number of overrecursions, works very well. For details of the application of this method and calculation procedures we refer to previous papers.[7,8]

We choose as initial state of the recursion the dipole-carrying state appropriate for the transitions starting on the levels of the ^5E multiplet. In effect at very low temperature (2 K) only the γ_1 level is populated, but at higher temperatures also transitions from $\gamma_4,\ \gamma_3,\ \gamma_5$, and γ_2 levels should be considered with appropriate population probabilities. Let P be the projector on the $^5T_2$ multiplet; then, the dipole-carrying state for a transition starting on a state $|\gamma_\nu\rangle$ is so constructed:

$$|u^\sigma_\nu\rangle \equiv P\mu_\sigma|\gamma_\nu\rangle \equiv \sum_{i,j} \langle F_iS_j;0|\mu_\sigma|\gamma_\nu;0\rangle |F_iS_j;0\rangle, \tag{6}$$

where μ_σ ($\sigma = x,y,z$) is the electric-dipole operator and $|0\rangle$ the ground vibrational state.

Such a state is a particular linear combination of dipole-allowed states, with coefficients proportional to the matrix elements of the dipole operator. When it is chosen as the initial one, all the states generated by the recursion procedure are dipole free; namely, the dipole matrix elements with $|\gamma_\nu\rangle$ are equal to zero. Then the absorption peak intensity (within a constant of proportionality) is simply given by the projection modulus squared of the eigenvectors on the initial state.

III. REVIEW OF SPECTRA AND RESULTS

The experimental absorption spectra[2,3,11] for $GaP:Fe^{2+}$ and $GaAs:Fe^{2+}$ available for different samples and at various temperatures exhibit several common features. At very low temperature ($\sim$2 K) a first zero-phonon line (ZPL) at $\sim$3300 cm^{-1} (GaP) and $\sim$3000 cm^{-1} (GaAs) dominates. A weaker ZPL comes next at about 50 cm^{-1} over the leading threshold absorption line (region A). Then there is a clear ZPL in the intermediate part of the whole absorption range (region B) having a shoulder toward lower energies; such a shoulder is activated by temperature due to absorptions originating from levels $\gamma_4,\ \gamma_3$, and γ_5. We leave out of consideration those possible transitions originating from the γ_2 level due to their low statistical weight: such a level is a singlet located 60 or more cm^{-1} over the threshold line. Their contribution to the absorption spectra at 20 K, corresponding to the temperature of the experiments considered here, is clearly negligible. About 500 cm^{-1} over the leading ZPL, a broad structure is evident (region C). Let us now review specific characteristics of the spectra of each compounds beginning by GaP which is done in more detail.

$GaP:Fe^{2+}$

The low-temperature Fourier transform spectrum is extended and well resolved, producing a strong ZPL line at 3342.3 cm^{-1}. The second line is at 3396 cm^{-1}, followed by a structure, centered around 3455 cm^{-1}. The ZPL for range B is clear at 3645 cm^{-1}. Then the structure for range C is very broad going from 3850 to 4100 cm^{-1}approximately. When the temperature increases, levels $\gamma_4,\ \gamma_3$, and γ_5 (γ_2 is left out for reasons explained above) progressively populate, making now possible electric-dipole transitions to vibronic levels of final symmetry $\Gamma_3,\ \Gamma_4$, and Γ'_4 that go undetected at very low temperatures. These transitions are precisely the hot lines we want to account for here under the approach described above.

The phonon energies of the two modes included in the Jahn-Teller interaction are in the range of acoustical and optical phonon modes, respectively,[12] and the Jahn-Teller ener-

TABLE I. Energies and relative peak intensities of relevant transitions of GaP:Fe^{2+} calculated with the Lanczos-recursion method. The starting state of the transition is indicated and the available experimental data (Ref. 3) are also reported for comparison. The calculations are made with the following choice of parameters: $\lambda = -100\ \mathrm{cm}^{-1}$, $\hbar\omega_A = 105\ \mathrm{cm}^{-1}$, $E_{JTA} = 180\ \mathrm{cm}^{-1}$; $\hbar\omega_O = 350\ \mathrm{cm}^{-1}$, $E_{JTO} = 50\ \mathrm{cm}^{-1}$; $N_A = N_O = 30$.

Levels	E_{calc} (cm^{-1})	I_r	E_{expt} (cm^{-1})
$\boldsymbol{\gamma}_1$	3342.3	1.00	3342.3
γ_4	3329.5	0.38	3329.5
γ_3	3318.7	0.08	3318.7
γ_5	3302.7	0.06	3302.5
$\boldsymbol{\gamma}_1$	3392.8	0.01	3395
γ_4	3378.5	0.07	3378
γ_3	3367.7	0.01	
γ_5	3351.7	0.01	
$\boldsymbol{\gamma}_1$	3455.0	0.16	3455
γ_3	3445.3	0.06	
γ_4	3442.2	0.04	
γ_3	3425.1	0.04	3416
γ_5	3410.4	0.04	3405
$\boldsymbol{\gamma}_1$	3558.9	0.02	3558
γ_4	3546.1	0.03	3545
γ_3	3535.3	0.1	
γ_5	3504.3	0.03	
$\boldsymbol{\gamma}_1$	3596.6	0.13	
γ_5	3592.2	0.03	
γ_4	3586.3	0.04	
$\boldsymbol{\gamma}_1$	3648.4	0.19	3644.8
γ_4	3635.6	0.03	3632
γ_3	3624.8	0.01	
γ_4	3619.0	0.1	3621
γ_5	3618.7	0.01	
γ_3	3608.2	0.02	
γ_5	3605.8	0.01	3605
$\boldsymbol{\gamma}_1$	3715.9	0.04	3720
γ_4	3703.1	0.02	3705.2
γ_3	3692.3	0.003	3694.3

gies have been chosen in such a way to have agreement with the energies and intensities of the experimental transitions at low temperature.[4] It is worthwhile to notice that a change of a few percent in the phonon energies and in the Jahn-Teller energies does not change the calculated spectra in a significant way. We also expect that coupling to other modes of similar energies—for instance, resonant modes of Fe^{2+}—can effectively broaden the spectral features. The best parameter values to deal with this system are $\hbar\omega_A = 105\ \mathrm{cm}^{-1}$, $\hbar\omega_O = 350\ \mathrm{cm}^{-1}$; $E_{JTA} = 180\ \mathrm{cm}^{-1}$, $E_{JTO} = 50\ \mathrm{cm}^{-1}$; the spin-orbit coupling constant has been taken equal to the free ion[13] value, i.e., $\lambda = -100\ \mathrm{cm}^{-1}$. The calculations have been carried out within the Lanczos-recursion procedure with $N_A = N_B = 30$, which is in fact more than enough to reach stability within three significant digits. To calculate the hot lines we have taken as the initial state of the Lanczos chain the corresponding dipole-carrying state constructed following Eq. (6).

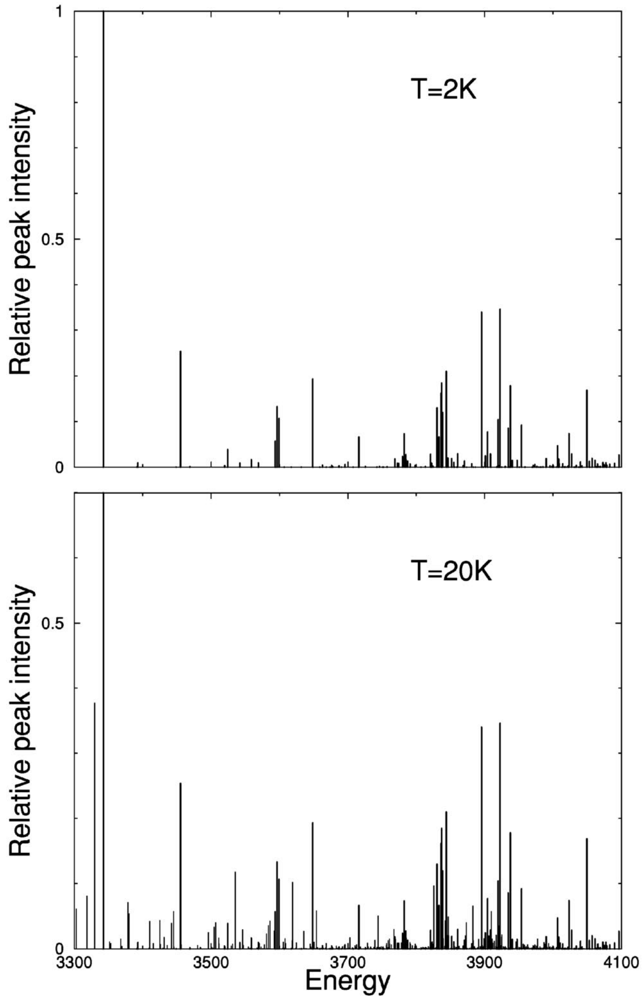

FIG. 1. Calculated spectra of GaP:Fe^{2+} for dipole transitions starting on γ_1 level (upper part, $T = 2$ K) and on γ_1, γ_4, γ_3, and γ_5 levels (lower part, $T = 20$ K). The parameters used are the same as in Table I. (Notice difference in the vertical scale between upper and lower part.)

In Table I we include calculated energies whose relative peak intensity (multiplied, when necessary, by the Boltzmann factor at $T = 20$ K) is $\geqslant 10^{-3}$; the starting level of the transition is also indicated. These results agree quite well with experimental spectra at low and high temperature, confirming the goodness of the proposed interaction model. Differently from other interpretations[3] we think that the transition at 3644.6 cm^{-1} is a transition from the $|\gamma_1\rangle$ to the $|\Gamma_5\rangle$ level and due to the interaction with the optical mode. In effect, we have verified[4] that when the acoustical mode only is considered region *B* of the spectrum is lost, and when only coupling to the optical mode is considered region *A* of the spectrum is lost.

The intense sharp transition to the spin-orbit partner level $|\Gamma_5'\rangle$ predicted by plain crystal-field theory is replaced by a huge number of medium- or low-intensity transitions spread over a few hundred cm^{-1} above 3850 cm^{-1}. They form

TABLE II. Energies and relative peak intensities of relevant transitions of GaAs:Fe^{2+} calculated with the Lanczos-recursion method. The starting levels of the transition are indicated and the available experimental data (Refs. 2 and 11) are also reported for comparison. The data labeled with * are taken from Ref. 11. The calculations are made with the following choice of parameters: $\lambda = -100$ cm^{-1}, $\hbar\omega_A = 85$ cm^{-1}, $E_{JTA} = 160$ cm^{-1}; $\hbar\omega_O = 260$ cm^{-1}, $E_{JTO} = 40$ cm^{-1}; $N_A = N_O = 30$.

Levels	E_{calc} (cm^{-1})	I_r	E_{expt} (cm^{-1})
γ_1	3001.9	1.00	3001.9
γ_4	2987.6	0.23	2987.6
γ_3	2977.0	0.04	2977.0
γ_5	2960.1	0.03	2960.1
γ_1	3046.3	0.21	$\sim 3050^*$
γ_4	3031.9	0.03	3025
γ_1	3097.7	0.14	$\sim 3090^*$
γ_4	3083.4	0.03	
γ_5	3075.8	0.01	
γ_3	3072.8	0.01	3069

region C of the experimental spectrum, similarly to what happens for Fe^{2+} in to II-VI compounds.[4] By inspection of the lower part of Fig. 1 it is evident how hot lines show up in the spectrum. For comparison, low-temperature lines are shown in the upper part of this figure.

GaAs: Fe^{2+}

For this compound Fourier transform infrared spectroscopy[2] also gives well-resolved optical absorption spectra, and hot lines are evident in the spectra at $T > 2$ K. The experimental spectra at very low temperature exhibit a strong ZPL at 3001.9 cm^{-1} followed by weak lines at approximately[11] 3050 cm^{-1} and[2,11] 3090 cm^{-1} (region A). Another ZPL is clearly seen approximately at[2] 3250 cm^{-1} (region B); then, in the energy range[2] 3400–3550 cm^{-1} a broad structure appears (region C). When the temperature increases, the transitions from the other levels of the ^5E multiplet thermally populated produce new lines and larger humps. Following the strategy adopted in the previous case, we have considered the coupling with lattice mode TA(L) ($\hbar\omega_A = 85$ cm^{-1}, $E_{JTA} = 160$ cm^{-1}) and a TO(L) mode ($\hbar\omega_O = 260$ cm^{-1}, $E_{JTO} = 40$ cm^{-1}) simultaneously. In Table II we report the main transitions calculated, with energy in region A, in comparison with the available experimental values.

Figure 2 exhibits a more complete picture of the cold lines calculated ($T = 2$ K) as well as of the hot lines ($T = 20$ K). In particular the experimental hump in the energy range 3150–3200 cm^{-1} is reproduced considering the transitions starting from the γ_4, γ_3, and γ_5 levels.

We interpret the experimental transition around 3250 cm^{-1} as due to the coupling with the optical mode and in effect the calculated energy for the transition from the γ_1 level is 3242.5 cm^{-1}. Among the hot lines, only the transition from the γ_4 level (3228.2 cm^{-1}) has a relative peak intensity not completely negligible ($I_r = 0.02$). Moreover, the calculations confirm that, as for GaP:Fe^{2+} and for Fe^{2+} in II-VI compounds,[8] the shoulder of the experimental large structure under 3500 cm^{-1} is due to the transition from the ground state to the many vibronic states with the Γ_5' component.

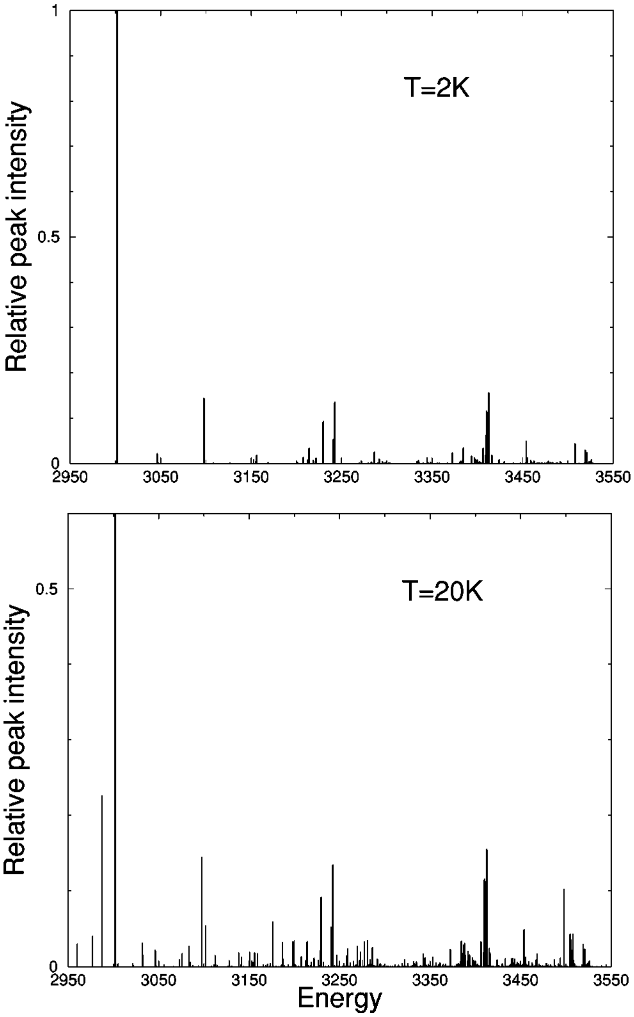

FIG. 2. Calculated spectra of GaAs:Fe^{2+} for dipole transitions starting on the γ_1 level (upper part) and on the γ_4, γ_3, and γ_5 levels (lower part). The parameters used are $\hbar\omega_A = 85$ cm^{-1}, $E_{JTA} = 160$ cm^{-1}, $\hbar\omega_O = 260$ cm^{-1}, and $E_{JTO} = 40$ cm^{-1}.

IV. CONCLUSIONS

The main aspects shown by the experimental absorption spectra of Fe^{2+} ions in GaP and GaAs, at low and high temperature, are well understood in the framework of a two-mode vibronic model with phonon energies in the range of acoustical and optical lattice modes respectively. Jahn-Teller coupling for these systems is found to be intermediate, with Huang-Rhys factors of almost 2 for the coupling to the acoustical phonon. Coupling to the acoustical phonon is mainly responsible for the activity near the absorption edge.

Coupling to the optical mode explains the isolated low-temperature ZPL in the intermediate part of the absorption spectrum and also the corresponding hot lines in that area. Hot lines turn out to be weaker than low-temperature lines as can be foreseen. However, calculations yield several lines of moderate intensity which coincide with regions of activity in the experimental spectra.

Thus, the complex high-temperature spectrum finds a general explanation for two similar compounds such as GaP:Fe^{2+} and GaAs:Fe^{2+}. The Lanczos-recursion method has been an efficient and simple tool to calculate the energies and the relative peak intensities of the optical transitions, by exploiting the concept of the dipole-carrying state.

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