

Jahn-Teller effect and the luminescence spectra of V^{2+} in ZnS and ZnSe

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A dynamical Jahn-Teller effect has been proposed to interpret the fine structure of the luminescence spectra of V^{2+} impurities in ZnS and ZnSe. The ground 4F term of the impurity is split by the crystal field into three multiplets. The spin-orbit and the spin-spin interactions are taken into account as well as a linear Jahn-Teller coupling with a trigonal phonon mode, both on the ground 4T_1 multiplet and on the excited 4T_2 multiplet. The Lanczos-recursion procedure with a proper choice of the initial state is followed to calculate the vibronic states. A comparison with experimental energies and intensities indicates that a dynamical Jahn-Teller effect plays an important role to explain the fine structure of the luminescence spectra of ZnSe: V^{2+} and ZnS: V^{2+} . In the latter, the temperature effects present in the spectra are also accounted for by the resulting energy-level scheme.

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I. INTRODUCTION

The optical properties of vanadium impurities in II-VI compounds have been investigated for a long time¹⁻⁸ and the presence of three different charge states V^{3+} , V^{2+} , and V^+ has been reported. The V^{2+} impurity presents well resolved and interesting spectra in ZnS and ZnSe; for the first, temperature effects in the emission spectra have been established.

The 4F ground term of V^{2+} (d^3) is split by a crystal field in 4T_1 ground multiplet and 4T_2 and 4A_2 excited states. The spin-orbit interaction splits the 4T_1 and 4T_2 multiplets in four sublevels following the scheme of Fig. 1. Electric-dipole emissions are possible due to small admixtures with upper atomic levels within the impurity. Coupling to vibrational modes modifies the previous simple description, giving rise to more complicated spectra as we discuss in the next paragraphs, according to the experimental spectra mentioned above.

In ZnS the emission band due to V^{2+} transitions is centered at 4800 cm^{-1} . In the spectrum at 2 K two zero-phonon lines (ZPL's) are evident at 5061 and 5033 cm^{-1} . At 4 K the spectrum of the same sample shows two additional features. On one hand, previously mentioned lines show activity toward higher energies (reflecting a slight population of a close excited level). On the other hand, the onset of different lines is clearly seen at energies 5036 , 5042 , 5062 , and 5069 cm^{-1} , suggesting the beginning of a significant population for levels slightly over ($\approx 10\text{ cm}^{-1}$) the lowest possible level at the excited multiplet. The doublet (5033 , and 5061 cm^{-1}) is repeated about 125 cm^{-1} far away, so suggesting electron-phonon assisted lines mediated by an abundant TA mode of such energy.

The line structure in the emission spectrum of ZnSe: V^{2+} is different from previous ones. The luminescence band assigned to it is centered at 4350 cm^{-1} , showing no significant variations with temperature. Five notorious ZPL's are present

at 4755 , 4751 , 4743 , 4737 , and 4723 cm^{-1} . A lower intensity line of different shape is reported at 4718 . A first satellite is found at about 70 cm^{-1} over the threshold line, indicating phonon-assisted transitions due to TA phonons of approximately that energy.

V^{2+} substitutes for the cation in zinc-blende compounds. However, the point charge model⁷ and results of EPR measurements on V^{2+} in ZnS (Ref. 18) indicate that the local symmetry at the V^{2+} site is trigonal in this compound. For the case of V^{2+} in ZnSe the trigonal distortion is smaller,⁷ but there is no certainty of which can be the dominant local symmetry. Our approach below is to consider the established trigonal distortion for ZnS systems, and also for ZnSe (even if it could be an admixture of trigonal and tetragonal distortions), letting results decide.

The model Hamiltonian and the calculation procedure are illustrated in Sec. II. Section III contains the results. Comments and conclusions are exposed in Sec. IV.

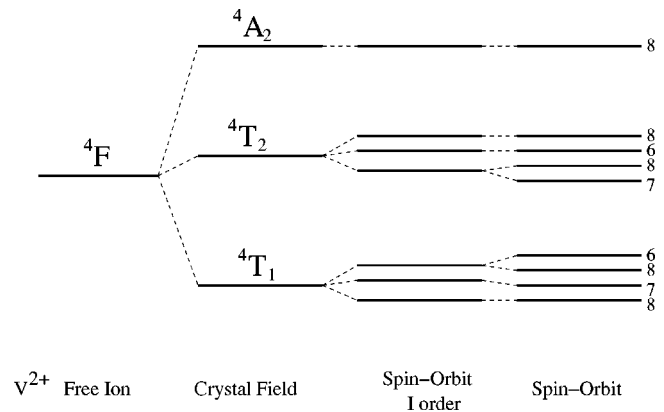


FIG. 1. Level scheme of the 4F ground term after crystal field and spin-orbit interaction. Numbers on the far right refer to labels i of irreducible representations Γ_i of the double point group T_d . Capital (lowercase) Greek letters Γ_i (γ_i) will be used to identify levels associated with 4T_2 (4T_1) multiplet.

II. MODEL HAMILTONIAN AND CALCULATION PROCEDURE

The electronic configuration d^3 of the free V^{2+} ion gives rise to a ground 4F term (28 times degenerate including spin). The nearest excited term is a 4P multiplet more than 11000 cm^{-1} over the ground level,¹ which allows us to restrict ourselves to the 4F ground multiplet. When V^{2+} substitutes for a Zn ion in zinc-blende compounds, the 4F term is split by the tetrahedral crystalline field⁹ into four excited states 4A_2 , 12 excited states 4T_2 , and 12 ground states 4T_1 . We will look at Jahn-Teller (JT) coupling involving states of 4T_2 and 4T_1 multiplets, which lead to infrared emissions near 5000 cm^{-1} , as reported in experimental spectra.⁷

The total Hamiltonian for the V^{2+} ion impurity in the 4T_1 and 4T_2 states can be written in the form

$$H = H_e + H_{so} + H_{ss} + H_L + H_{e-L}, \quad (1)$$

where $H_e + H_{so} + H_{ss}$ is the electron Hamiltonian including the spin-orbit interaction $\lambda \mathbf{S} \cdot \mathbf{L}$ and the spin-spin interaction $-\rho[(\mathbf{L} \cdot \mathbf{S})^2 + \frac{1}{2}(\mathbf{L} \cdot \mathbf{S})]$ whose explicit form can be obtained by standard methods. H_L and H_{e-L} are the lattice Hamiltonian and the electron-lattice interaction, respectively. The ${}^4T_{1,2}$ states can be coupled to many lattice modes of different energy and symmetry; however, as usual in the literature, we adopt a cluster model¹⁰ and we consider a linear interaction with a trigonal mode, based on the local distortion reported for the case of ZnS: V^{2+} . In terms of usual creation and annihilation operators for components x, y, z of the τ_2 mode, H_L and H_{e-L} takes the forms

$$H_L = \hbar \omega \left(a_x^\dagger a_x + a_y^\dagger a_y + a_z^\dagger a_z + \frac{3}{2} \right) \quad (2)$$

$$H_{e-L} = \sqrt{\hbar \omega E_{JT}} \sum_i (a_i^\dagger + a_i) D_i, \quad i = x, y, z. \quad (3)$$

Here (E_{JT}) is the Jahn-Teller energy. D_i have the form

$$D_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad D_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix},$$

$$D_z = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The Huang-Rhys factor S is given by $S = E_{JT}/\hbar \omega$. The basis functions of the vibronic model are the direct product of the electron-spin functions $|F, S_j\rangle (i = 1, \dots, 7; S_j = 3/2, \dots, -3/2)$ and of the vibrational functions $|lmn\rangle$, where l, m , and n are the occupation numbers for the partners of the phonon mode τ_2 and, in principle, occupation numbers run from zero to infinity. It is clear that a vibronic Hamiltonian does not split Kramer's degeneracy.

The small temperature activation in the spectra of ZnS: V^{2+} and no activation at all for ZnSe: V^{2+} are indication of a large quenching of the spin-orbit splitting in the

excited level (4T_2). This tells of an intermediate coupling for this level ($S \sim 2$), and eventually of one a bit smaller for the lower energy 4T_1 term. In any case, diagonalizations based on Born-Oppenheimer bases may require to reach large occupation numbers to achieve stable results. In this range of coupling the Lanczos-recursion method,^{11,12} 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.^{13,14}

We choose as initial state of the recursion the dipole-carrying state¹³ appropriate for the transitions starting on the levels of the 4T_2 multiplet. 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 initial one, all the states generated by the recursion procedure are dipole free, and the peak intensity (within a constant of proportionality) is simply given by the projection modulus squared of the eigenvalues on the initial state.

We will concentrate more on the energy of the resulting vibronic levels than on the intensities. In the experiments, intensities can fluctuate due to local values of temperature induced by the absorbed radiation that excites upper levels. Then, for simplicity, we will approximate intensities of the emitted lines by considering zero-phonon components of the vibronic states only, neglecting the small contributions coming from the components which are diagonal with a higher occupation number of the same mode.

III. RESULTS

A. Parameters

The starting value for crystal field parameter $10|Dq|$ for both of these compounds can be set at about 5000 cm^{-1} , which is roughly the separation between 4T_1 and 4T_2 multiplets; this parameter is to be refined later on for each particular host crystal once main lines have been recognized and adjusted. In any case, the energy of the A_2 level is of the order of 10000 cm^{-1} , so it is not active in the energy window searched by the experiments under consideration.

The spin-orbit coupling constant λ has been assigned the value 55 cm^{-1} , corresponding to the free-ion value.¹⁵ In spite of the almost negligible role of the spin-spin interaction in these systems we have considered it with the value $\rho = 0.18\text{ cm}^{-1}$.

Energies of the coupling phonons must be related to the lattice dynamics of ZnS and ZnSe,¹⁶ respectively. This is also realized by the already mentioned displacements of the phonon assisted replicas in each system (125 cm^{-1} for ZnS and 70 cm^{-1} for ZnSe). For the present analysis we will not vary phonon energies taking directly the values that satisfactory explained the optical spectra of Fe^{2+} in these very same host crystals.¹⁷ Then we considered coupling to representative phonons of 100 cm^{-1} for ZnS and of 70 cm^{-1} for ZnSe.

Then the only free parameter left for adjustments is the Jahn-Teller energy (E_{JT}) representing the coupling. We designate as E_{JT1} the coupling energy to the lower multiplet of symmetry 4T_1 , while E_{JT2} is the coupling energy to the

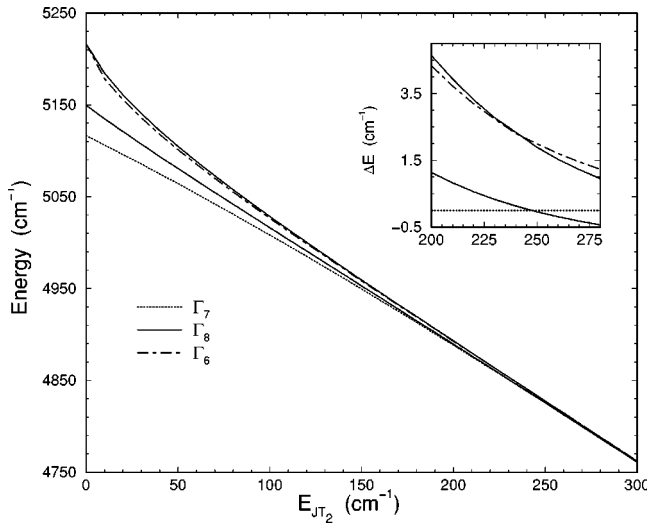


FIG. 2. Four lowest vibronic energy levels associated with the upper multiplet 4T_2 of ZnS, as functions of the Jahn-Teller energy. Energy of the coupling phonon is 100 cm^{-1} . The inset shows the energy differences among these levels (using level Γ_7 as a reference) in the region of interest.

upper multiplet of symmetry 4T_2 . We varied these parameters in the range $0\text{--}300\text{ cm}^{-1}$ as reported below.

B. ZnS:V²⁺

Figure 2 represents the energies of the four lowest vibronic levels associated with the 4T_2 excited multiplet, while Fig. 3 represents the energies of the six lowest vibronic levels associated to the 4T_1 ground multiplet. In each case the independent variable is the corresponding E_{JT} parameter. The thermal activity of the emission spectra of ZnS:V²⁺, visible when going from 2 to 4 K, tells us that the excited

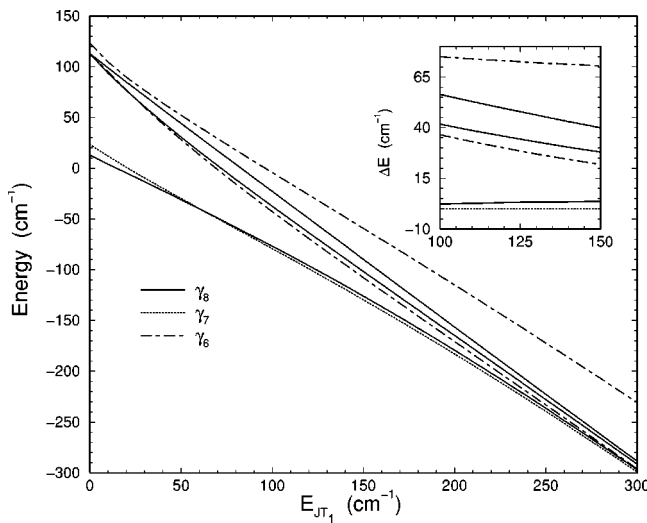


FIG. 3. Six lowest vibronic energy levels associated with the lower multiplet 4T_1 of ZnS, as functions of the Jahn-Teller energy. Energy of the coupling phonon is 100 cm^{-1} . The inset shows the energy differences among these levels (using level γ_7 as a reference) in the region of interest.

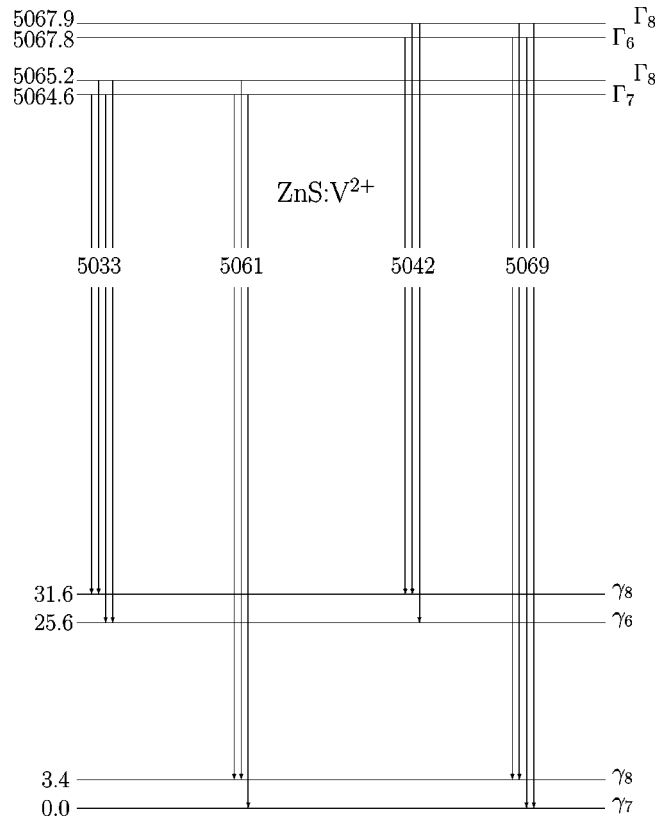


FIG. 4. Diagram representing a possible set of levels that can explain experimental spectra (within an error of a few cm^{-1}). Calculated energies of the levels are on the left-hand side, while labels indicating the symmetry of the levels are on the right. Downward arrows indicate allowed electric dipole transitions. Numbers on the arrows remind one of the approximate value of the observed transition (transitions shift a bit with temperature which can also be explained from this picture). For this diagram $E_{JT2}=220\text{ cm}^{-1}$ and $E_{JT1}=135\text{ cm}^{-1}$; values of the other parameters are given in the text.

multiplet must be split by a few cm^{-1} . This is so when E_{JT2} is over 200 cm^{-1} , as it follows from the inset of Fig. 2. On the other hand, according to Fig. 3, the four lowest vibronic energy levels of the ground multiplet are paired, γ_7 and γ_8 forming the lowest pair and γ_6 and γ_8 forming the upper pair. The average separation between these two pairs is 28 cm^{-1} when $E_{JT1}\approx 135\text{ cm}^{-1}$ according to the inset of the same figure. We then take this value for the JT energy corresponding to the coupling to the ground multiplet. If we now go back to the separation of the levels in the upper multiplet, intending to produce thermal activity at 4 K, we find that for $E_{JT2}=220\text{ cm}^{-1}$ a good agreement is found. We summarize this fit of the emission spectra for ZnS:V²⁺ in Fig. 4 where we also identify individual transitions. Calculated relative intensities weighted by corresponding Boltzmann factors also give good agreement with the observed lines. Thus, for instance, transitions to fifth and sixth levels (of symmetry γ_8 and γ_6 respectively) in Fig. 3 are weaker by a factor of 100 or more as compared to transitions reported in Fig. 4. Finally, the refined crystal-field parameter used for this system was 5089 cm^{-1} .

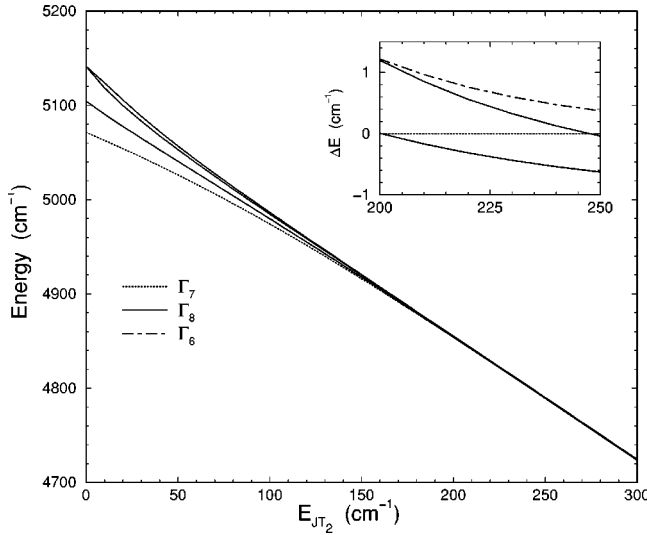


FIG. 5. Four lowest vibronic energy levels associated with the upper multiplet 4T_2 of ZnSe, as functions of the Jahn-Teller energy. Energy of the coupling phonon is 70 cm^{-1} . The inset shows the energy differences among these levels (using level Γ_7 as a reference) in the region of interest.

C. ZnSe:V $^{2+}$

This case is a bit more complicated than previous one for several reasons. First, the actual symmetry at the impurity site has not been clearly established, as previously discussed. Second, no thermal activity was noticed in the experiment for ZnSe, which does not allow a work similar to previous one to identify E_{JT2} in this case. At the most we can assume that all relevant low levels of the excited multiplet are spread in a range not larger than 2 cm^{-1} . Third, phonon energies are necessarily lower than in the previous case due to the larger masses involved, which means more admixture of vibrational components, allowing for contribution of one-phonon, two-phonon, etc. components to the intensities. Fourth, spectra were not entirely reproducible for all samples as reported in the experimental paper;⁷ in particular, the weak line at 4729 cm^{-1} was not present in all samples. In any case our procedure was similar to previous one as depicted below.

Let us begin by assuming trigonal local modes as in previous case. In Fig. 5 we plot the energies of the four lowest vibronic levels associated to the 4T_2 excited multiplet, while Fig. 6 represents the energies of the six lowest vibronic levels associated with the 4T_1 ground multiplet of ZnSe:V $^{2+}$. The independent variable is again E_{JT} for each multiplet. From the inset of Fig. 5 it is clear that for E_{JT2} over 220 cm^{-1} , levels Γ_6 , Γ_7 , Γ_8 , and Γ_8' are spread within 1 cm^{-1} , thus explaining the lack of difference between spectra at 2 and at 4 K. We can set $E_{JT2}=220\text{ cm}^{-1}$, although we will not have the possibility of a refined adjustment as in the case of ZnS:V $^{2+}$. An immediate consequence of this assumption is that separations between spectral lines will be due to the splitting of the lower multiplet, since there is no noticeable energy difference among the vibronic levels in the excited multiplet. This also explains the rounding off effect and the slight broadening of the lines in the emission spectra.

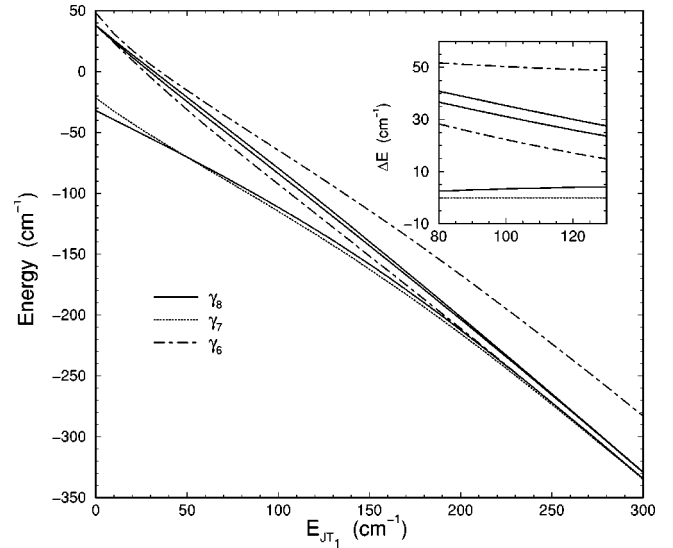


FIG. 6. Six lowest vibronic energy levels associated with the lower multiplet 4T_1 of ZnSe, as functions of the Jahn-Teller energy. The energy of the coupling phonon is 70 cm^{-1} . The inset shows the energy differences among these levels (using level γ_7 as a reference) in the region of interest.

Let us now turn our attention to Fig. 6, where we report the energy of the vibronic levels associated with the lower multiplet as a function of the coupling energy. It is not possible to find a value of this parameter that can give precisely the energies of the five most intense reported lines. However, the range for the spreading of these lines, about 33 cm^{-1} , is found somewhere for $E_{JT1} \approx 110\text{ cm}^{-1}$, as shown in the inset of Fig. 6. Thus we find the following relative positions for the five lowest vibronic levels (all referring to the lowest level): $0, 3.7, 19.6, 28.4,$ and 32.6 cm^{-1} , giving the following sequence of transitions energies from the upper 4T_2 multiplet: $4755, 4751, 4735, 4727,$ and 4722 cm^{-1} . They can be compared with the experimental transition energies at $4755, 4751, 4743, 4737,$ and 4723 cm^{-1} . Although no exact match is found for each line, the agreement for a fork of five lines is remarkable since only the Jahn-Teller energy has been varied. These are also the five most intense lines in our calculations, which is an additional agreement with experiment. However, the weak line in the spectrum at 4718 cm^{-1} (at a difference of 37 cm^{-1}) finds no partner in our calculations. The threshold line at 4755 cm^{-1} is obtained with a $10|Dq|$ value of 4836 cm^{-1} .

IV. CONCLUSIONS

The main aspects shown by the experimental luminescence spectra of V $^{2+}$ ions in ZnSe and ZnS and temperature effects are well understood in the framework of a simple vibronic model considering a coupling to trigonal modes with energies in the range of acoustical phonons. Moreover, here we took the same vibrational energies previously used to explain the vibronic coupling of Fe $^{2+}$ (also an incomplete 3d-shell ion) in the same host crystals.¹⁷

In both systems the coupling to the excited multiplet 4T_2 is larger than the coupling to the lower multiplet 4T_1 , which

is a result that can be expected if higher energies mean more extended orbitals. Such a moderately high JT coupling for orbital 4T_2 produces energy spacings of a few cm^{-1} in ZnS, which can be thermally populated when going from 2 to 4 K. However, for the case of ZnSe with a lower vibrational frequencies, the quenching is larger and no noticeable thermal variation can be expected for the same temperature interval.

Reasons for the slight discrepancy between calculated and experimental values for the six reported lines in the case of ZnSe: V^{2+} can be due to two reasons. On the one hand, the trigonal distortion is less justified here than in the case of ZnS: V^{2+} , as established by experiments already commented upon above. On the other hand, the lower frequency of this host crystal produces a greater admixture in the vibronic functions which calls for more extended computer calculations to cope with slight deviations. Work along both these lines is presently in progress, and will also include similar systems like ZnTe: V^{2+} , and CdTe: V^{2+} .

In the case of ZnS: V^{2+} , the Huang-Rhys factors S_1 and S_2 (for lower and upper multiplets respectively) are 1.0 and 2.2 respectively. In the case of ZnSe: V^{2+} these factors are 1.6 and 3.1, respectively. This tells of a moderate dynamic Jahn-Teller effect not leading to permanent distortions but able to introduce drastic changes to optical spectra calculated in the adiabatic limit. For the case of ZnSe: V^{2+} , the mixture

of zero and nonzero phonon states is becoming important; this affects mostly the intensities of the lines, giving rise to more contributions than included in our zero-phonon intensity calculations reported above.

Previous comments concerning the moderate high coupling found here also discourage the use the diagonalization method based on Born-Oppenheimer vibronic functions. On the other hand, the Lanczos recursion method used here, including up to 20 overtones in the coupling modes, proves to lead to stable values that are in good agreement with the emission spectra of ZnS: V^{2+} considered here. The adjustment in the case of ZnSe: V^{2+} , using the same procedure is quite reasonable. Actually this method has become an efficient and simple tool to calculate energies and relative peak intensities of optical transitions, by exploiting the concept of the dipole-carrying state.

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