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Jahn-Teller effect in the luminescence spectra of ZnS:V$^+$ and ZnSe:V$^+$

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The infrared emission spectra of ZnS:V$^+$ and ZnSe:V$^+$ are reported examining temperature dependence. The unusually rich spectra are theoretically explained by assuming a vibronic coupling due to ϵ modes. A diagonalization of the Hamiltonian matrix is performed using wave functions constructed in the Born-Oppenheimer limit. The Jahn-Teller energy is the only adjustable parameter. When this parameter is about 80 cm^{-1} for ZnS:V$^+$ and 65 cm^{-1} for ZnSe:V$^+$ good agreement between theory and experiment is found and the main features of the spectra for both systems are explained. The frequencies of the coupling modes are taken close to the TA*(L)* modes. [S0163-1829(96)04040-4]

I. INTRODUCTION AND EXPERIMENT

Normally vanadium enters the lattice of II-VI semiconductors in the substitutional position on a cation site. Then, V^{2+}(d^3) is the ionization state with neutral effective charge, but the amphoteric character of $3d$ impurities implies the expectation of possible conversions to the ionized donor state V^{3+}(d^2) or the ionized acceptor V$^+$(d^4). Indeed, both states have been detected in ZnS,[1] ZnSe,[2] ZnTe,[3] and very recently in CdTe as well.[4] The simultaneous presence of up to three different oxidation states becomes comprehensible by the close neighborhood of the respective ionization energies inside the solid (unlike the larger differences for free ions).[5] Furthermore, the optical excitations involved in recording photoluminescence spectra enable transitions among the three oxidation states V^{3+}, V^{2+}, and V$^+$.

The particular case of V$^+$ presents an interesting spectrum not completely explained so far.[6] Additional measurements for the thermal dependence of the low-temperature luminescence for V$^+$ in ZnS and ZnSe have also been performed.[7] Here we report the most recent spectra and offer an interpretation introducing a vibronic Hamiltonian that couples ϵ vibrational modes to the $^5T_2$ ground electronic multiplet.

A scheme of the energy-level splitting for the V$^+$ ground atomic multiplet as due to the tetrahedral crystalline field and spin-orbit interactions is shown in Fig. 1. We use both Bethe's and greek-letter notations for the irreducible representations of point group T_d to label the states and wave functions. Capital (lowercase) greek letters like Γ_i (γ_i) are used for the electronic levels of the upper (lower) multiplet. The electric-dipole (ED) operator transforms as the irreducible representation T_2 or Γ_5 of T_d. Allowed ED transitions (EDT's) are shown as downward arrows on the right-hand side of Fig. 1.

Crystal-field theory plus second-order spin-orbit interaction splits the $^5T_2$ multiplet into six electronic levels which in order of increasing energy are γ_1, γ_4', γ_5', γ_3, γ_4, and γ_5. They couple to ϵ vibrational modes producing a set of vibronic levels. EDT's are possible through admixture of excited atomic multiplets so that their intensities are relatively weak.

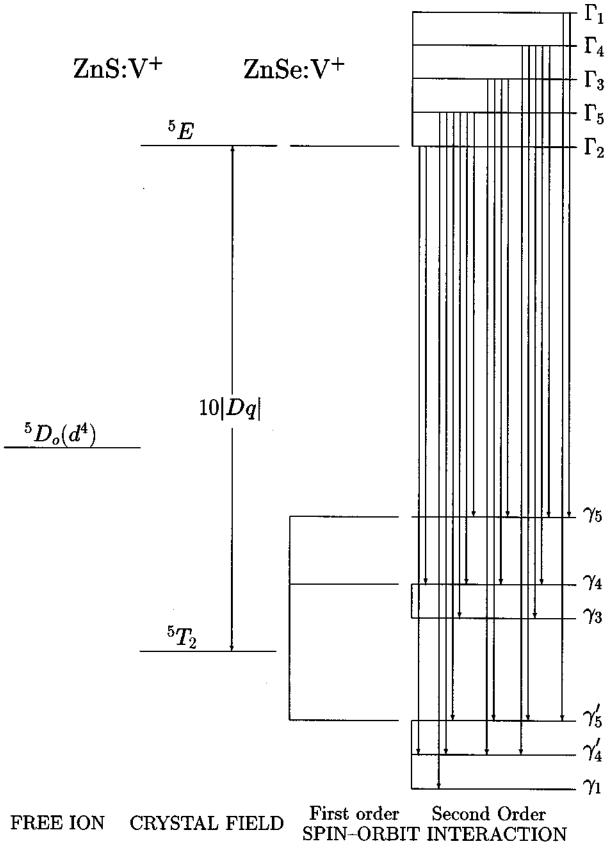

FIG. 1. Energy-level scheme of V$^+$ under crystal-field and spin-orbit interactions at site of T_d symmetry. $10|Dq|$ is the crystal-field splitting. Greek letters designate the irreducible representations of the electronic levels. Downward arrows illustrate the possible electric-dipole transitions.

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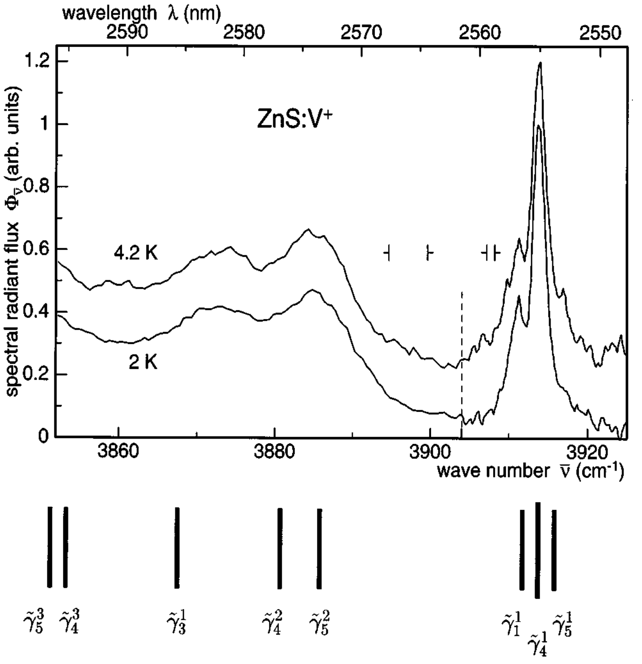

FIG. 2. No-phonon region in the ZnS:V$^+$ emission, recorded at two different temperatures (crystal A228/1 annealed in Zn vapor, V content 100 ppm approximately, traces of Cu present). The resolution is lowered for $\overline{\nu}\leqslant 3904$ from 1–5 cm^{-1}. Excitation at 11 325 cm^{-1}. The position of the calculated vibronic levels are represented below using the same energy axis.

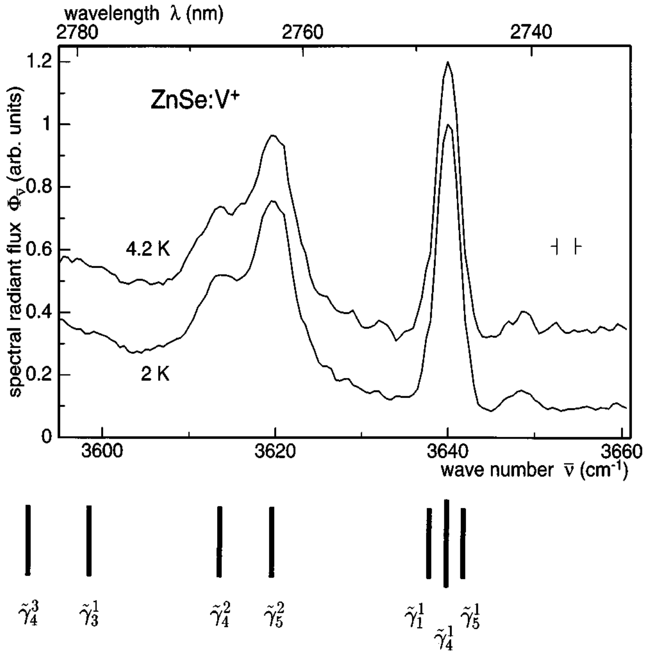

FIG. 3. No-phonon region in the ZnSe:V$^+$ emission, recorded at two different temperatures (crystal 5021 with nominal V concentration of 300 ppm). Excitation at 21 839 cm^{-1}, resolution 2.1 cm^{-1}. The positions of the calculated vibronic levels are given underneath.

The symmetry of the possible coupling modes has already been characterized.[8] The frequencies of these coupling modes [TA(L)] have been already reported.[9–14] In the analysis below, $\hbar\omega$ is not an entirely free parameter since we perform restricted variations of ± 10 cm^{-1} around the values informed in the literature. The general method is adapted from the one successfully used for Fe^{2+} in II-VI compounds.[15] This allows us to briefly present the theoretical model in Sec. III, kindly asking the interested readers to look into previous references for details.

There are several reasons to conduct the present work. First, to elucidate the role of the Jahn-Teller effect for V$^+$ ions in II-VI materials. Second, to identify the coupling modes as points in the Brillouin zone with their corresponding frequencies. Third, to report the coupling energy (the so-called Jahn-Teller energy E_{JT}). Fourth, to attempt a qualitative search of a temperature dependence of the spectra.

The crystals used were the same samples employed in previous studies,[1,2,6] viz. ZnS of largely cubic structure (zinc-blende) grown at $T\approx 750$ °C in an iodine-transport process and cubic ZnSe, melt grown in a high-pressure Bridgman furnace. In both cases, the dopant V was introduced during growth. The optical setup was described earlier.[2,15]

A survey of the V$^+$ emission in ZnS:V under Ti-sapphire laser excitation shows a broad band in the 3500–3900 cm^{-1} range, peaking near 3800 cm^{-1} (not shown here). The region with no-phonon lines (NPL's) of this system is presented in Fig. 2, showing a strong NPL at approximately 3914 cm^{-1}, that is resolved into a triplet at narrow slit width with lines at 391.7, 3914, and 3911 cm^{-1}. Lowering the temperature from 4.2 to $\approx$2 K does not influence the position or relative magnitude of the two lower-energy components while the strength of the 3917 cm^{-1} line is slightly diminished. The somewhat broader features at 3885 and 3873 cm^{-1} also do not change on this temperature drop.

As previously stated for ZnSe:V$^+$,[6] the corresponding structures (Fig. 3) are less resolved than with ZnS:V$^+$. Instead of the dominant triplet, there is just a broader line near 3640 cm^{-1} which displays inflection points on both its slopes suggesting the underlying triplet structure. In addition, even broader structures are located at 3620 and 3614 cm^{-1}. The small peak at approximately 3648 cm^{-1} is not considered in the discussion below. Regarding the less pronounced structure of the ZnSe:V$^+$ spectra, again, a redistribution of intensities on pumping the He coolant is not observed here.

II. THEORY AND CALCULATIONS

Phonons of symmetry ϵ are assumed to couple to the electronic levels of the V$^+$ ion. To account for luminescent transitions, we need to study the coupling to the electronic components of the lower multiplet like $\epsilon\otimes\gamma_i$.[16]

The vibrational component of the Hamiltonian for modes θ and ϵ of energy $\hbar\omega$ is given by

$$H_v=\hbar\,\omega(a_\theta^\dagger a_\theta+a_\epsilon^\dagger a_\epsilon+1),\qquad(1)$$

where the usual annihilation and creation operators a_α and $a_\alpha^\dagger$ are used ($\alpha=\theta,\epsilon$).

The coupling Hamiltonian can now be written as

$$H_{\mathrm{JT}}=\sqrt{\hbar\,\omega E_{\mathrm{JT}}}[(a_\theta^\dagger+a_\theta)D_\theta+(a_{z\epsilon}^\dagger+a_\epsilon)D_\epsilon],\qquad(2)$$

where E_{JT} is the Jahn-Teller energy, the only adjustable parameter in the present calculations.

The crystalline parameter $10|Dq|$ is taken as 3842 cm^{-1} for ZnS:V$^+$, and 3569 cm^{-1} for ZnSe:V$^+$. The spin-orbit parameter λ is introduced with the free-ion value, 34 cm^{-1}.[17] Modes [TA(L)] that possess ϵ symmetry will be used here. In the case of ZnS variations of $\hbar\omega$ between 65 and 85 cm^{-1} were performed, while in the case of ZnSe the variation range was between 45 and 65 cm^{-1}.[9–14] The vibronic states will be denoted by a *tilde* over the symbol of the corresponding irreducible representation ($\tilde{\gamma}_i$). The different levels possessing the same symmetry formed after considering all the occupation numbers ($N=0,1,2,\ldots$) coming from the $(\epsilon)^N$ vibrational component are distinguished by a superscript n ($\tilde{\gamma}_i^n$) following the order of increasing energy within each irreducible representation i, as is shown in Figs. 2 and 3.

Emissions originate from the levels of the excited multiplet ^5E. Still without vibrational coupling, the splitting among these levels is just a few cm^{-1}. After considering vibronic coupling for the upper multiplet of V^+ in ZnS and ZnSe, it is found that levels $\tilde{\Gamma}_2^1, \tilde{\Gamma}_1^5, \tilde{\Gamma}_3^1, \tilde{\Gamma}_4^1$, and $\tilde{\Gamma}_1^1$ tend to form one degenerate level, which explains the absence of temperature dependence.

The selection rule for a no-phonon transition is that the initial and final vibronic states have the same vibrational occupation number. This usually means that the transition leads from an excited state to a lower state with important zero-phonon components in both the initial and final states. In most cases, transitions involving one-phonon to one-phonon components are ignored. However, in the present case such transitions can contribute in an important way due to the strong Jahn-Teller effect that affects the excited multiplet.

We will concentrate on the energies of the emitted lines, which can be done with the diagonalization of the Hamiltonian corresponding to the lower multiplet only. The same technique described here cannot be used for the excited multiplet where a strong coupling appears to be present.[18] A more powerful technique valid in the strong coupling limit for the $\epsilon\times E$ case should be used.[19] Nevertheless, this discussion allows us to assume that the vibronic levels of the upper multiplet are concentrated within about 1 cm^{-1} or less. Fine calculations for the upper multiplet and magnetic-dipole transitions are left out from this presentation.

III. DISCUSSION

Spectra and theoretical results for ZnS:V^+ are reported in Fig. 2. For $E_{\mathrm{JT}}\approx 80$ cm^{-1} a fairly good agreement is obtained. The positions of the calculated levels resolve even the fine-structure details. The only discrepancy is that the experiment gives a line centered at about 41 cm^{-1} above the central line of the triplet, while theoretical calculations render the only possible level to explain such a line at 47 cm^{-1}.

The only way to explain so many lines without an important temperature dependence is that the upper multiplet is practically degenerate. However, this also means that the states in the upper multiplet present a strong admixture of more than zero-phonon contributions, allowing essentially all transitions, thus explaining the rich spectrum of V^+ in ZnS. Virtually every vibronic level can be a final state for transitions originating in the highly degenerate excited multiplet.

The triplet structure for the threshold emission of ZnS:V^+ deserves a special discussion. The three possible end states are denoted as $\tilde{\gamma}_5^1$, $\tilde{\gamma}_4^1$, and $\tilde{\gamma}_1^1$ in order of increasing energy as shown in the lower part of Fig. 2. However, if we stick to the idea that $\tilde{\Gamma}_2^1$ is an isolated low-energy level of the upper multiplet, then a single line without fine structure would be observed. Moreover, any other transition in this energy range (originating from $\tilde{\Gamma}_5^1$, for instance) would be temperature dependent. Only if all the levels in the upper multiplet are almost degenerate the triplet would be observable without a significant temperature dependence. The order of the vibronic levels is not the same as that corresponding to the electronic levels shown in Fig. 1, because of the crossing of levels of different symmetry due to the magnitude of the JT coupling. The proposal of levels shown in Fig. 2 corresponds to $E_{\mathrm{JT}}=80$ cm^{-1} and $\hbar\omega=75$ cm^{-1}.

Similar calculations and analyses can be performed for the case of ZnSe:V^+ reported in Fig. 3. Good agreement with experiment is found for $E_{\mathrm{JT}}=65$ cm^{-1} and $\hbar\omega=55$ cm^{-1}. ZnSe:V^+ presents a larger density of states towards low energies than ZnS:V^+ due to the lower frequencies in the lattice dynamics brought about by the heavier anion (Se). This fact also means larger admixture of vibronic states and more phonon-assisted transitions in the low-energy portion of the spectrum. As a consequence of this fact the emitted lines for ZnSe:V^+ will look broader and relatively weaker than those of ZnS:V^+. The triplet clearly visible for ZnS:V^+ is hidden for the case of ZnSe:V^+ where only inflection points can be seen.

The doublet that appears to the low-energy side of the threshold triplet in both spectra needs further discussion. In ZnS:V^+ levels $\tilde{\gamma}_4^2$ and $\tilde{\gamma}_5^2$ are barely separated by about 3 cm^{-1} in the theoretical scheme, not allowing for experimental resolution. Both together explain the high-energy component of the doublet. The same type of calculations for ZnSe:V^+ yields a separation of about 6 cm^{-1} between $\tilde{\gamma}_4^2$ and $\tilde{\gamma}_5^2$ and the second one appears as a pronounced shoulder towards lower energies in very good agreement with the experiment. On the other hand, the level $\tilde{\gamma}_3^1$ presents itself separated from this doublet.

No-phonon transitions contrast better with the background for ZnS:V^+ as compared with ZnSe:V^+. An extrapolation can lead to the hypothesis that in the emission spectrum of ZnTe:V^+ and CdTe:V^+ the difficulty in singling out NPL's will increase accordingly.

The Hamiltonian matrix was diagonalized successively increasing the vibrational occupation number. Stability was tested for the five low-energy vibronic levels and variations of less than 1% are obtained when passing from $N=9$ to 10. Anyhow, all results reported here correspond to $N=14$, which ensures stability.

IV. CONCLUSIONS

Vanadium as a substitutional impurity in ZnS and ZnSe presents a set of emission lines attributed to the ionization state V^+. The spectra present a richer structure than expected from plain crystal-field theory. We interpret the presence of extra lines and the small energy differences among the emissions as manifestation of a dynamic Jahn-Teller effect.

The coupling of ϵ vibrational modes of frequencies 75 cm^{-1} for ZnS, and 55 cm^{-1} for ZnSe lead to a good general trend of agreement with the observed spectra. Such modes correspond to those of TA(L) symmetry in the Brillouin zone. The strength of the coupling can be measured in terms of E_{JT}, which for values of 80 and 65 cm^{-1} yield level schemes appropriate for the interpretation of the spectra of ZnS:V^+ and ZnSe:V^+, respectively.

Contrary to what could be expected, the experiments show no significant temperature dependence of the spectra. This is an indication that the levels of the upper multiplet are not separated by several cm^{-1} as predicted by crystal-field theory. The nearly temperature-independent experimental spectra indicate that the population in the excited levels is saturated already at about 2 K.

In particular, the threshold line splits into a triplet which would violate several selection rules unless the excited levels give rise to all possible transitions without an appreciable temperature dependence. This is an indication for a strong Jahn-Teller coupling in the upper multiplet. The already weak NPL's of V^+ in ZnS and ZnSe are threatened by the uprising background, due to many additional transitions that tend to lower the energy differences as the frequency of the coupling mode diminishes.

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