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A vibronic model for the absorption spectra of Cr^{2+} ions in $CdSe_xS_{1-x}$

Sophia Klokishner[1], Oleg Reu[1], Sergei Ostrovsky[1], Andrew Palii[1] and Elias Towe[2]

[1] Institute of Applied Physics, Academy of Sciences of Moldova, Academy Street 5, MD-2028, Kishinev, Moldova
[2] Electronics Engineering Department, Carnegie-Mellon University, Pittsburgh, PA 15213, USA

E-mail: klokishner@yahoo.com

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Abstract

In the present paper we report a vibronic model for the absorption bands of the Cr^{2+} ion in CdSe and $CdSe_{0.6}S_{0.4}$ crystals. For the most probable impurity clusters, $CrSe_4$, $CrSe_3S$, $CrSeS_3$ and $CrSe_2S_2$, the crystal field splittings and the vibronic coupling parameters are estimated with the aid of the exchange charge model of the crystal field accounting for the exchange and covalence effects. On this basis the transitions responsible for the formation of the optical bands arising from the $CrSe_4$, $CrSe_3S$, $CrSeS_3$ and $CrSe_2S_2$ species are determined and the profiles of the absorption bands corresponding to these species are calculated. The total spectrum of the $CdSe_{0.6}S_{0.4}$:Cr^{2+} crystal is obtained by summation over partial spectra arising from all mentioned species. The profiles of the absorption bands in CdSe:Cr^{2+} and $CdSe_{0.6}S_{0.4}$:Cr^{2+} calculated on the basis of the numerical solution of the dynamical vibronic problems prove to be in quite good agreement with the experimental data.

In memory of Professor Yurii Perlin (17 September 1917–10 March 1990)—to highlight his exceptional achievements and kudos.

1. Introduction

Room-temperature mid-IR (2–5 μm) sources of radiation combining variable spatial coherence with continuous ultrabroad or multiwavelength spectra are of vital importance for many areas of research and technical applications. Since the pioneering research works of Deloach *et al* [1] and Page *et al* [2] on detailed investigation of the spectral properties of metal-doped zinc chalcogenides, laser operation on the $^5E \rightarrow {}^5T_2$ transition in the Cr^{2+} ion in chalcogenide host materials [3, 4] like ZnSe, CdSe, ZnS and CdMnTe has been demonstrated. Recently an optical study of $CdSe_xS_{1-x}$ crystals doped with Cr^{2+} has been performed [5]. Due to the larger thermal

conductivity of CdS compared to CdSe the CdSeS alloy may be considered as an improvement over the CdSe system. Alloying with CdS gives the possibility of shifting the position of the $^5E \rightarrow {}^5T_2$ band in the Cr^{2+} ion towards higher energies and increasing the band gap of the host material, which might decrease the chance of excited state absorption. Thus, recent experimental findings clearly indicate wide prospects for the application of II–VI crystals doped with transition metal ions. At the same time investigations of new materials for IR quantum electronics will be successful if these investigations are supported by theoretical modelling of the spectroscopic and relaxation characteristics of the systems under consideration. The cornerstone in the theoretical consideration of the optical spectra of doped crystals and the lifetimes of excited impurity states is the vibronic coupling of the metal ions with the lattice vibrations. It is this interaction that closely relates to the possibility of tunable lasing on broad phonon assisted bands and the main features of the active media. Although the first fundamental works on the vibronic Jahn–Teller (JT) interactions and optical spectra of the impurity ions in II–VI crystals were performed in the early 1970s the problem of the lifetimes and band shapes for the vibronically assisted transitions is far from being solved and applied for actual lasing materials. In the initial model proposed in [6] the experimental data on Cr-doped II–VI compounds were interpreted in terms of a strong static JT coupling with the vibrational modes of e-symmetry in the ground $^5T_2$ state. The model suggested in [7] for ZnSe:Cr^{2+} was also based on the assumption that only the e-mode participates in the intra-ion absorption and luminescence transitions. In this paper the quadratic vibronic interaction in the excited ^5E state was taken into account. A dynamic JT model was developed in [8]. Further study of II–VI crystals doped with Cr^{2+} ions and other transition metal ions [9, 10] led to essential progress and also demonstrated that the data obtained using different experimental methods could be explained from a common point of view under the assumption of the dynamic JT effect. At the same time the main outcome of the recent papers [10, 11] concerned the structure of the zero-phonon lines of V^{2+} and Cr^{2+} ions in II–VI compounds at low temperatures. In [11] it was found that e-modes only lead to intensities that do not agree well with those of the zero-phonon doublet observed both in emission and absorption in the cases of ZnS and ZnSe, while t_2 modes give a good explanation of transition energies and transition strengths in the same cases. Due to the lack of information regarding the vibronic coupling constants the models developed earlier for transition metal ion (TMI)-doped II–VI compounds were based on the consideration of the interaction of the impurity centre with the only kinds of JT modes (e or t_2), with the subsequent determination of the vibronic coupling constant from the fit to experimental data. Quantum-mechanical calculations of the shapes of the optical bands with allowance for the JT effect in both the initial and final states have not been performed.

A theoretical study of the vibronic JT interaction in a series of II–VI crystals doped with Cr^{2+} ion was reported for the first time in our recent papers [12, 13]. For the tetrahedrally coordinated Cr^{2+} ion (high-spin d^4 configuration) the vibronic coupling parameters were evaluated in the framework of the exchange charge model of the crystal field accounting for the exchange and covalence effects [14–16], and on the basis of these calculations the JT problem was formulated. An examination of the optical absorption bands in CdSe:Cr^{2+} and mixed $CdSe_xS_{1-x}$:Cr^{2+} ($x > 0$) crystals has never been performed. In the present communication we report a model of the absorption bands of the Cr^{2+} ion in CdSe and $CdSe_{0.6}S_{0.4}$. Within the framework of this model for the $CdSe_{0.6}S_{0.4}$:Cr^{2+} system the most probable distributions of selenium and sulfur atoms in the nearest surroundings of Cr^{2+} will be determined. First, for these ligand surroundings of Cr^{2+} the crystal field splittings and the vibronic coupling parameters will be microscopically calculated. Then, the subsequent evaluation of the profiles of the optical absorption bands in CdSe:Cr^{2+} and mixed $CdSe_{0.6}S_{0.4}$:Cr^{2+} crystals will be performed.

2. Possible arrangements of selenium and sulfur atoms in the nearest surroundings of cadmium

The observed shift of the $^5E \rightarrow {}^5T_2$ band position in the $CdSe_{0.6}S_{0.4}$ crystal can be attributed to the formation of impurity complexes with different contents of sulfur and selenium atoms in the nearest surroundings of the Cr^{2+} ion. As the first step we examine a pure $CdSe_{0.6}S_{0.4}$ crystal and calculate the number of complexes in which the Cd^{2+} ions are surrounded by: (i) four selenium atoms; (ii) three selenium atoms and one sulfur atom; (iii) two selenium atoms and two sulfur atoms; (iv) three sulfur atoms and one selenium atom; (v) four sulfur atoms. The probability of existence of a certain tetrahedral surrounding is given by the expression

$$P_i = C_m^n P_{\mathrm{Se}}^n P_{\mathrm{S}}^m, \tag{1}$$

where P_{Se} and P_{S} are the fractional concentrations of Se and S atoms, respectively, i.e. the probabilities that the given neighbour of the Cd^{2+} ion is a selenium or a sulfur atom, $C_m^n = n!/(m!(n-m)!)$ is the binomial coefficient that describes the number of possible combinations for m objects to be placed in n sites ($m \leqslant n$), n and m are the numbers of Se and S atoms in the considered neighbourhood configuration, respectively. Then, for the fractional concentrations $P_{\mathrm{Se}} = 0.6$ and $P_{\mathrm{S}} = 0.4$, one can easily calculate the probabilities of existence of all mentioned distributions:

$$\begin{aligned} P_1 = C_0^4 P_{\mathrm{Se}}^4 = 0.1296; \qquad P_2 = C_1^4 P_{\mathrm{Se}}^3 P_{\mathrm{S}} = 0.3456; \qquad P_3 = C_3^4 P_{\mathrm{Se}} P_{\mathrm{S}}^3 = 0.1536; \\ P_4 = C_2^4 P_{\mathrm{Se}}^2 P_{\mathrm{S}}^2 = 0.3456 \qquad P_5 = C_4^4 P_{\mathrm{S}}^4 = 0.0256. \end{aligned} \tag{2}$$

From equation (2) it follows that the second and fourth configurations are the most probable ones; at the same time the first and third configurations are less frequent, but also give an appreciable contribution. Finally, the fifth configuration has a negligible probability and will be neglected in all subsequent calculations. We assume that the Cr^{2+} ions are distributed randomly in the $CdSe_{0.6}S_{0.4}$ lattice and substitute the Cd^{2+} ones in different mixed surroundings of sulfur and selenium with equal probability. Under such an assumption the number of impurity clusters $CrSe_4$, $CrSe_3S$, $CrSe_2S_2$ and CrS_3Se prove to be proportional to P_1, P_2, P_3 and P_4, respectively. The total absorption spectra of the $CdSe_{0.6}S_{0.4}$:Cr^{2+} system will be calculated as a sum of spectra arising from $CrSe_4$, $CrSe_2S_2$, $CrSe_3S$ and CrS_3Se species. Each particular contribution in this sum will be multiplied by the corresponding statistical weight given by equation (2).

3. The Hamiltonian of the system

The total Hamiltonian for the impurity ion in a crystal can be represented as

$$H = H_{\mathrm{e}}(\boldsymbol{r}, \boldsymbol{R}_0) + H_{\upsilon}(q) + H_{\mathrm{e}\upsilon}(\boldsymbol{r}, q), \tag{3}$$

where $\boldsymbol{r}$ and q are the sets of the electronic and vibrational coordinates, respectively. $H_{\mathrm{e}}(\boldsymbol{r}, \boldsymbol{R}_0)$ is the electronic Hamiltonian determining the wavefunctions and the eigenvalues of the impurity ion in a fixed nuclear configuration $q = 0$. This configuration corresponds to the positions of the ions $\boldsymbol{R} = \boldsymbol{R}_0$ in the host lattice and does not take into account the lattice relaxation arising from the embedding of the ion in the ground state. $H_{\upsilon}(q)$ is the Hamiltonian of the free lattice vibrations:

$$H_{\upsilon} = \sum_{\tilde{\mu}\tilde{\Gamma}\tilde{\gamma}} \frac{\hbar\omega_{\tilde{\mu}\tilde{\Gamma}}}{2} \left(q_{\tilde{\mu}\tilde{\Gamma}\tilde{\gamma}}^2 - \frac{\partial^2}{\partial q_{\tilde{\mu}\tilde{\Gamma}\tilde{\gamma}}^2} \right), \tag{4}$$

where $q_{\tilde{\mu}\tilde{\Gamma}\tilde{\gamma}}$ are the symmetry adapted vibrational coordinates corresponding to the irreducible representations (irreps) $\tilde{\Gamma}$ (including multiple representations) and $\omega_{\tilde{\mu}\tilde{\Gamma}}$ is the frequency of the

vibration $\bar{\mu}\bar{\Gamma}$ (symbol $\bar{\mu}$ enumerates the repeating vibrational representations). Denoting the displacements of the ions of the impurity complex from their positions $\boldsymbol{R}_p^0$ (at $q = 0$) by $\Delta\boldsymbol{R}_p = \boldsymbol{R}_p - \boldsymbol{R}_p^0$ ($\boldsymbol{p}$ is the index of the position) these vibration coordinates can be written as:

$$q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}} = \frac{1}{l_{\bar{\Gamma}}} \sum_{\boldsymbol{p}} \boldsymbol{U}_{\boldsymbol{p}}^{\bar{\mu}\bar{\Gamma}\bar{\gamma}} \Delta\boldsymbol{R}_{\boldsymbol{p}}, \tag{5}$$

where $\boldsymbol{U}_{\boldsymbol{p}\alpha}^{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ ($\alpha = x, y, z$) are the elements of the unitary matrix for the transformation of the Cartesian displacements $\Delta\boldsymbol{R}_{\boldsymbol{p}}$ into the dimensionless coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$, $l_{\bar{\mu}\bar{\Gamma}} = (\hbar\omega_{\bar{\mu}\bar{\Gamma}}/f_{\bar{\mu}\bar{\Gamma}})^{1/2}$ and $f_{\bar{\mu}\bar{\Gamma}}$ is the force constant corresponding to this vibration. Finally, the last part of the Hamiltonian (3) is the vibronic interaction for the impurity ion (related also to the positions $\boldsymbol{R} = \boldsymbol{R}_0$). The operator $H_{e\upsilon}$ consists of the parts corresponding to the vibrational irreps of the impurity cluster of the defined symmetry:

$$H_{e\upsilon} = \sum_{\bar{\mu}\bar{\Gamma}\bar{\gamma}} \upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r}) q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}. \tag{6}$$

The operator $\upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r})$ with the dimension of energy can be expressed as:

$$\upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r}) = \sum_{\boldsymbol{p},i} \frac{\partial W(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{p}})}{\partial q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}}\bigg|_{q_{\mu\bar{\Gamma}\bar{\gamma}}=0} = l_{\bar{\mu}\bar{\Gamma}} \sum_{\boldsymbol{p},i} \frac{\partial W(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{p}})}{\partial \boldsymbol{R}_{\boldsymbol{p}}}\bigg|_{\boldsymbol{R}_{\boldsymbol{p}}=\boldsymbol{R}_{\boldsymbol{p}}^0} \times \boldsymbol{U}_{\boldsymbol{p}}^{\bar{\mu}\bar{\Gamma}\bar{\gamma}} = \sum_i \upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r}_i), \tag{7}$$

where $W(\boldsymbol{r}_i - \boldsymbol{R}_{\boldsymbol{p}})$ is the potential energy of the interaction between the ith electron of the ion and the $\boldsymbol{p}$th atom of the host crystal in the position $\boldsymbol{R}_{\boldsymbol{p}}^0$.

The next step of our consideration is the derivation of the symmetry adapted vibrational coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ and operators $\upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r})$ of electron-vibrational interaction for the impurity complexes $CrSe_4$, $CrSe_3S$, $CrSe_2S_2$ and CrS_3Se. We assume that the replacement of selenium atoms by sulfur ones does not displace the position of the Cr^{2+} ion in the mentioned complexes and leads only to the change of the symmetry of the immediate environment due to the different radii of Se and S atoms. It is supposed that in the complexes $CrSe_4$ and $CrSe_2S_2$ the symmetry of the ligand field is T_d and C_{2v} (figures 1(a) and (b)), respectively, while in the complexes $CrSe_3S$ and CrS_3Se the Cr ions acquire a trigonal symmetry surrounding (C_{3v}) (figures 1(c) and (d)). In the case of a tetrahedral complex $CrSe_4$ we are dealing with the full symmetric A_1 tetragonal E and two trigonal vibrations, $T_2{}^{(1)}$ and $T_2{}^{(2)}$. For this complex the symmetry adopted coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ and the operators $\upsilon_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r})$ obtained in the exchange charge model of the crystal field [12–16] are given in [13]. For the complex $CrSe_3S$ of C_{3v} symmetry the active vibrations are two full symmetric vibrations $A_1^{(1)}$, $A_1^{(2)}$ and two doubly degenerate vibrations $E^{(1)}$ and $E^{(2)}$. The corresponding symmetrized displacements $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ are given in the appendix. In the case when the local Cr^{2+} surroundings consist of three S and one Se atom the symmetry adopted coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ are also expressed by relations (A.1) with the single difference that now the mass m corresponds to the sulfur atom while the selenium atom possesses the mass M. The low-symmetry complex C_{2v} only possesses one-dimensional vibrations: three full symmetric vibrations $A_1^{(1)}$, $A_1^{(2)}$, $A_1^{(3)}$ and three nonsymmetric vibrations A_2, B_1 and B_2. The vibrational coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ for this complex are also given in the appendix.

4. Absorption band of the $CrSe_4$ complex

The ground ^5D term of a free Cr^{2+} ion (high-spin electronic configuration d^4) is split by the tetrahedral crystal field in a $CrSe_4$ species into the orbital triplet $^5T_2(t_2{}^2e^2)$ and orbital doublet

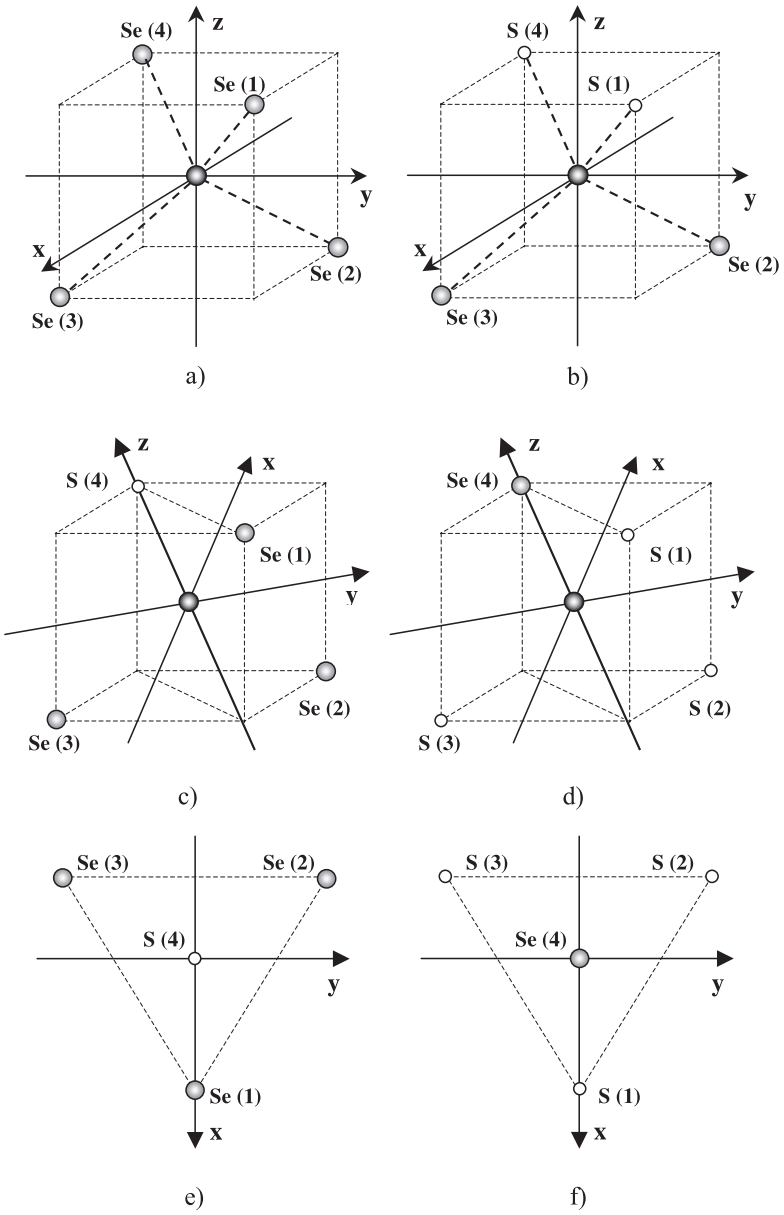

Figure 1. Ligand arrangements in the $CrSe_{4-y}S_y$ ($y = 0$–3) clusters with the indication of corresponding frames of reference: (a) $CrSe_4$; (b) $CrSe_2S_2$; (c) $CrSe_3S$; (d) $CrSeS_3$; top view of $CrSe_3S$ (e) and $CrSeS_3$ (f) species.

$^5E(t_2^3e)$, the former being the ground term (figure 2(a)). In the strong crystal field basis the determinant wavefunctions $|t_2{}^n(S_1\Gamma_1)e^m(S_2\Gamma_2)S\Gamma\gamma M_S\rangle$ for these two terms $S\Gamma$ of Cr^{2+} ion are given by:

$$|t_2{}^3(^4A_2)e(^2E)^5Eu, M_S = 2\rangle = |\xi\eta\varsigma\upsilon|, \qquad |t_2{}^2(^3T_1)e^2(^3A_2)^5T_2\zeta, M_S = 2\rangle = |\xi\eta u\upsilon|, \tag{8}$$

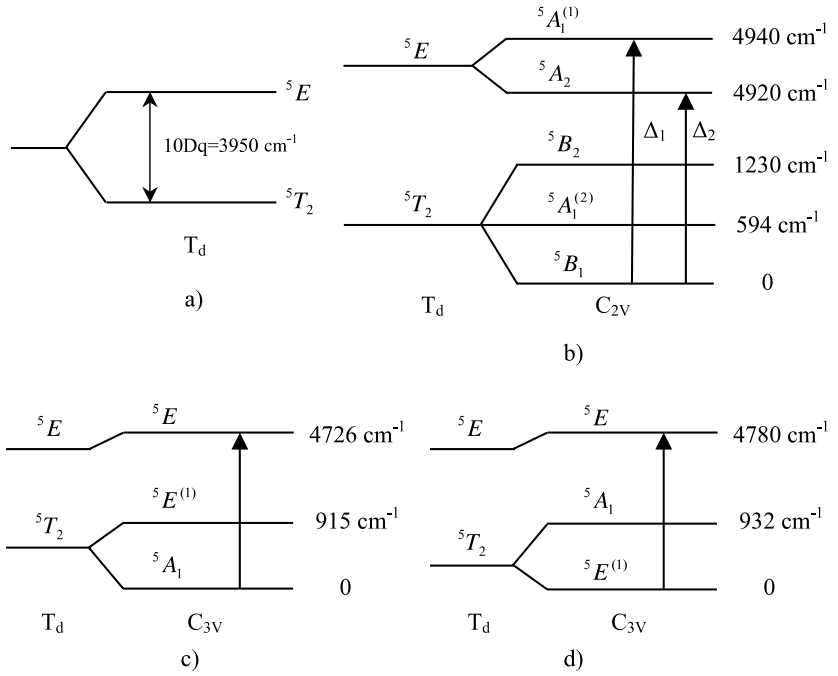

Figure 2. Crystal field splittings for the impurity $CrSe_{4-y}S_y$ ($y = 0$–3) clusters: (a) $CrSe_4$; (b) $CrSe_2S_2$; (c) $CrSe_3S$; (d) $CrSeS_3$.

where the symbol γ enumerates the basis functions of the irrep Γ(E and T_2), M_S is the spin projection and the conventional notation $|\ldots|$ is used for the Slater determinants. The standard cubic basis sets for the one-electron d-functions $T_2(\xi, \eta, \varsigma)$ ($\xi \propto yz, \eta \propto xz, \zeta \propto xy$) and $E(u, \upsilon)$ ($u \propto 3z^2 - r^2, \upsilon \propto \sqrt{3}(x^2 - y^2)$) are used. In equation (8) the only wavefunction for each degenerate term is given; the basis is related to the C_2 axis of the tetrahedron.

First, we present the Hamiltonian (3) of the system in the form [12, 13]

$$H = H_0 + H', \tag{9}$$

where

$$H_0 = H_e(\boldsymbol{r}, \boldsymbol{R}_0) + v_{A_1}(\boldsymbol{r})q_0 + \frac{\hbar\omega_{A_1}}{2}q_0^2 + \frac{\hbar\omega_{A_1}}{2}\left(Q^2 - \frac{\partial^2}{\partial Q^2}\right) + \sum_{\mu_1\bar{\Gamma}\bar{\gamma}} \frac{\hbar\omega_{\mu_1\bar{\Gamma}}}{2}\left(q_{\mu_1\bar{\Gamma}\bar{\gamma}}^2 - \frac{\partial^2}{\partial q_{\mu_1\bar{\Gamma}\bar{\gamma}}^2}\right) \tag{10}$$

$$H' = \upsilon_{A_1}(\boldsymbol{r})Q + \sum_{\mu_1\bar{\Gamma}\bar{\gamma}} v_{\mu_1\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r})q_{\mu_1\bar{\Gamma}\bar{\gamma}} \tag{11}$$

$Q = q_{A_1} - q_0$ is the full symmetric coordinate counted off from the new equilibrium position

$$q_0 = -V_{T_2}/\hbar\omega_{A_1}, \qquad \langle {}^5T_2(t_2^2e^2)\big|v_{A_1}(\boldsymbol{r})\big|{}^5T_2(t_2^2e^2)\rangle = V_{T_2} \quad \text{and}$$
$$\upsilon_{A_1}(\boldsymbol{r}) = \boldsymbol{v}_{A_1}(\boldsymbol{r}) + \hbar\omega_{A_1}q_0 \tag{12}$$

is the redefined vibronic operator for full symmetric A_1 vibrations adapted to the new positions of the ions, the index μ_1 stands for tetragonal E and trigonal $T_2{}^{(1)}$, $T_2{}^{(2)}$ vibrational modes of the tetrahedral complex.

One can easily prove that

$$\langle {}^5\mathrm{T}_2 \big| \upsilon_{\mathrm{A}_1}(\boldsymbol{r}) \big| {}^5\mathrm{T}_2 \rangle \equiv \upsilon_{\mathrm{A}_1}(\mathrm{T}_2) = 0, \qquad \langle {}^5\mathrm{E} | \upsilon_{\mathrm{A}_1}(\boldsymbol{r}) | {}^5\mathrm{E} \rangle \equiv \upsilon_{\mathrm{A}_1}(\mathrm{E}) = \upsilon_t - \upsilon_\mathrm{e}, \tag{13}$$

where υ_t and υ_e are the single electron matrix elements. The vibronic Hamiltonian for the ${}^5\mathrm{T}_2 \otimes (\mathrm{e} + 2\mathrm{t}_2)$ JT problem is the following:

$$\begin{aligned} H_{\mathrm{e}\upsilon}(\mathrm{T}_2) = {} & \upsilon_\mathrm{E}(\mathrm{T}_2)(\boldsymbol{O}_{\mathrm{E}u} q_{\mathrm{E}u} + \boldsymbol{O}_{\mathrm{E}\upsilon} q_{\mathrm{E}\upsilon}) + \upsilon^{(1)}_{\mathrm{T}_2}(\mathrm{T}_2)(\boldsymbol{O}_{\mathrm{T}_2\xi} q^{(1)}_{\mathrm{T}_2\xi} + \boldsymbol{O}_{\mathrm{T}_2\eta} q^{(1)}_{\mathrm{T}_2\eta} + \boldsymbol{O}_{\mathrm{T}_2\varsigma} q^{(1)}_{\mathrm{T}_2\varsigma}) \\ & + \upsilon^{(2)}_{\mathrm{T}_2}(\mathrm{T}_2)(\boldsymbol{O}_{\mathrm{T}_2\xi} q^{(2)}_{\mathrm{T}_2\xi} + \boldsymbol{O}_{\mathrm{T}_2\eta} q^{(2)}_{\mathrm{T}_2\eta} + \boldsymbol{O}_{\mathrm{T}_2\varsigma} q^{(2)}_{\mathrm{T}_2\varsigma}). \end{aligned} \tag{14}$$

For the ${}^5\mathrm{E} \otimes (\mathrm{a}_1 + \mathrm{e})$ problem one finds

$$H_{\mathrm{e}\upsilon}(\mathrm{E}) = \upsilon_\mathrm{E}(\mathrm{E})(\boldsymbol{O}'_{\mathrm{E}u} q_{\mathrm{E}u} + \boldsymbol{O}'_{E\upsilon} q_{E\upsilon}) + \upsilon_{\mathrm{A}_1}(\mathrm{E}) \boldsymbol{O}_{\mathrm{A}_1} Q. \tag{15}$$

All matrices in equations (14) and (15) are defined through the Clebsch–Gordan coefficients: $\langle \Gamma\gamma | \boldsymbol{O}_{\bar\Gamma\bar\gamma} | \Gamma\gamma' \rangle = \langle \Gamma\gamma | \Gamma\gamma' \bar\Gamma\bar\gamma \rangle$ for the T_d point symmetry group. In equations (14) and (15) the values $\upsilon^{\mu}_{\bar\Gamma}(\Gamma) = [\Gamma]^{-1/2} \langle \Gamma \parallel \nu_{\mu\bar\Gamma} \parallel \Gamma \rangle$ ($[\Gamma]$ is the dimension of the irrep Γ) are the vibronic coupling constants for the vibrations $\mathrm{T}_2^{(1)}$, $\mathrm{T}_2^{(2)}$ and E, $\langle \Gamma \parallel \upsilon_{\mu\bar\Gamma} \parallel \Gamma \rangle$ is the reduced matrix element of the operator $\upsilon_{\mu\bar\Gamma\bar\gamma}(\boldsymbol{r})$, while $\upsilon_{\mathrm{A}_1}(\mathrm{E}) = \langle E \parallel \nu_{\mathrm{A}_1} \parallel E \rangle / \sqrt{2} - \langle \mathrm{T}_2 \parallel \nu_{\mathrm{A}_1} \parallel \mathrm{T}_2 \rangle / \sqrt{3}$. The ground ${}^5\mathrm{T}_2(\mathrm{t}_2{}^2\mathrm{e}^2)$ and excited ${}^5\mathrm{E}(\mathrm{t}_2^3\mathrm{e})$ terms of the Cr^{2+} ion are orbitally degenerate, resulting in $\mathrm{T}_2 \otimes (\mathrm{a}_1 + \mathrm{e} + 2\mathrm{t}_2)$ and $\mathrm{E} \otimes (\mathrm{a}_1 + \mathrm{e})$ JT vibronic problems. In the exchange charge model of the crystal field [14–16] the expressions for the vibronic coupling constants are as follows:

$$\begin{aligned} \upsilon_{\mathrm{A}_1}(\mathrm{E}) &= -\frac{2e^2 l_{\mathrm{A}_1}}{27R^6}(25Z\langle r^4\rangle + 18R^4 G(S_4(R) - RS'_4(R))), \\ \upsilon_\mathrm{E}(\mathrm{E}) &= -\frac{8e^2 l_\mathrm{E}}{63R^6}(5Z\langle r^4\rangle - 9Z\langle r^2\rangle R^2 - 18R^4 G S_2(R) + 18R^4 G S_4(R)), \\ \upsilon_\mathrm{E}(\mathrm{T}_2) &= \frac{4\sqrt{2}e^2 l_\mathrm{E}}{189R^6}(20Z\langle r^4\rangle + 27Z\langle r^2\rangle R^2 + 54R^4 G S_2(R) + 72R^4 G S_4(R)), \\ \upsilon^{(1)}_{\mathrm{T}_2}(\mathrm{T}_2) &= \frac{2\sqrt{2}e^2 l^{(1)}_{\mathrm{T}_2}}{189R^6}((100\langle r^4\rangle + 81\langle r^2\rangle R^2)Z - 18GR^4(-3S_2(R) - 4S_4(R) \\ &\quad + 3RS'_2(R) + 4RS'_4(R))) \\ \upsilon^{(2)}_{\mathrm{T}_2}(\mathrm{T}_2) &= \frac{4e^2 l^{(2)}_{\mathrm{T}_2}}{189R^6}((27R^2\langle r^2\rangle - 50\langle r^4\rangle)Z + 18GR^4(3S_2(R) - 10S_4(R))) \end{aligned} \tag{16}$$

where $l_{\bar\Gamma} = (\hbar\omega_{\bar\Gamma}/f_{\bar\Gamma})^{1/2}$, $\omega_{\mu\bar\Gamma}$ is the frequency of the vibration $\bar\Gamma$ and $f_{\bar\Gamma}$ is the force constant, R is the distance between the Cr^{2+} ion and the ligands, $S_2(R)$, $S_4(R)$ are the overlap integrals [12, 13]:

$$\begin{aligned} & S_l(R) = S_s^2(R) + S_\sigma^2(R) + \gamma_l S_\pi^2(R), \qquad \gamma_2 = 1, \qquad \gamma_4 = -4/3, \\ & S_s(R) = \langle 3d, m = 0 | n''s \rangle, \qquad S_\sigma(R) = \langle 3d, m = 0 | n''p, m = 0 \rangle, \\ & S_\pi(R) = \langle 3d, m = \pm 1 | n''p, m = \pm 1 \rangle, \end{aligned}$$

$|3dm\rangle$ and $|n''s\rangle$, $|n''pm\rangle$ are the Cr^{2+} and the ligands wavefunctions, respectively, $S'_l(R) = \frac{\mathrm{d}S_l(R)}{\mathrm{d}R}$. In all subsequent calculations we employ the simplest version of the exchange charge model with the only phenomenological dimensionless parameter G that has been determined with the aid of the relation

$$Dq = -\frac{2(5Ze^2\langle r^4\rangle + 18R^4 G S_4(R))}{135R^5} \tag{17}$$

and shown to be equal in CdSe:Cr^{2+} and CdS:Cr^{2+} crystals (see table 1). The overlap integrals $S_2(R)$, $S_4(R)$ have been computed using the radial atomic 'double zeta' 3d wavefunctions of

Table 1. Parameters of the exchange charge model for CdSe and CdS crystals doped with Cr^{2+} ions (a_0 is the Bohr radius).

Crystal	Dq (cm^{-1})	G	R (Å)	$S_2(R)$	$S_4(R)$	$S_2'(R)$ (a_0^{-1})	$S_4'(R)$ (a_0^{-1})	$\hbar\omega$ (cm^{-1})	Z
CdS	−465	2.71	2.52	0.0163	0.0102	−0.0212	−0.0102	80	2
CdSe	−395	2.71	2.62	0.0149	0.0091	−0.0180	−0.008	60	2

Table 2. Vibronic coupling constants (in cm^{-1}) for the $CrSe_4$ complex.

$\upsilon_E(T_2)$			$\upsilon^{(1)}_{T_2}(T_2)$			$\upsilon^{(2)}_{T_2}(T_2)$			$\upsilon_{A_1}(E)$			$\upsilon_E(E)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total
66	49	115	106	154	260	27	−20	7	−24	−74	−98	73	15	88

chromium, 4s, 4p functions of selenium and 3s, 3p functions of sulfur given in [17]. It should be mentioned that for species $CrSe_{4-y}S_y$ ($y = 1$–3) with mixed ligand surroundings the energy levels and vibronic coupling constants are determined through overlap integrals $S_l(R_i)$ and their derivatives $S_l'(R_i) = \frac{dS_l(R_i)}{dR_i}$, where $R_i = R$, R_0, R and R_0 are the distances between the Cr^{2+} ion and Se and S atoms, respectively The evaluated overlap integrals and their derivatives as well as the parameters used for calculations of the vibronic coupling constants are collected in table 1. The calculated vibronic coupling constants for all active modes of the $CrSe_4$ complex are given in table 2. Each vibronic constant is presented as a sum of contributions arising from the electrostatic field of point ligand charges and from the exchange charge field, the last can be considered as a measure of the effect of covalence. It is seen that the main contribution to the vibronic coupling constants $\upsilon_E(T_2)$, $\upsilon^{(2)}_{T_2}(T_2)$, $\upsilon_E(E)$ in most cases comes from the field of point charges. Meanwhile, the exchange charge field yields a dominant contribution to the vibronic parameters $\upsilon^{(1)}_{T_2}(T_2)$ and $\upsilon_{A_1}(E)$. The data listed in table 2 also show that for the ^5E term the interaction with the E and A_1 modes is approximately of the same strength. The JT interaction with the $T_2^{(1)}$ vibrations proves to be dominant within the $^5T_2$ term. The interaction of this term with the E-mode is more than two times weaker than that with the $T_2^{(1)}$ vibrations. At the same time the interaction with the second vibration of T_2 symmetry is negligible for this term. The results obtained from the calculation of the vibronic coupling constants have been used for the description of the observed absorption band arising on the transition $^5T_2 \rightarrow {}^5E$ of the $CrSe_4$ cluster. Taking into account the predominant role of the interaction of the ground $^5T_2$ term with the trigonal $T_2^{(1)}$ vibrations at the first step in the evaluation of the shape of the absorption $^5T_2 \rightarrow {}^5E$ band we will consider three-mode JT problems $(e + a_1) \otimes E$ for the ^5E state and $t_2 \otimes T_2$ for the $^5T_2$ state. It should also be noted that for the Cr^{2+} ion the spin–orbital interaction (the constant of this interaction $\lambda = 57\ cm^{-1}$ [6]) is much weaker than the interaction with the $T_2^{(1)}$ vibrations of the $CrSe_4$ complex. At the same time the effects of spin–orbital interaction, such as the splitting of the zero-phonon lines, are observed at very low temperatures. Taking into account both these factors in the calculation of the shape of the $^5T_2 \rightarrow {}^5E$ band at room temperature the effect of spin–orbital interaction was not considered.

The ground $^5T_2$ term is well isolated from the excited ones so that the hybrid vibronic states corresponding to the dynamical JT problem in this state can be expressed as an expansion in terms of the products of zeroth-order approximation electronic functions and the harmonic oscillator functions for the full symmetric, tetragonal and trigonal vibrations

$$\psi^{(\upsilon)}_{n_1,n_u,n_\upsilon} = \Phi_{n_1}(Q)\Phi_{n_u}(q_u)\Phi_{n_\upsilon}(q_\upsilon) \sum_{\substack{\gamma=\xi,\eta,\zeta \\ n_\xi,n_\eta,n_\zeta}} C^{(\upsilon)}_{\gamma,n_\xi,n_\eta,n_\zeta} \Phi_{n_\xi}(q_\xi)\Phi_{n_\eta}(q_\eta)\Phi_{n_\zeta}(q_\zeta)\big|\gamma\rangle, \tag{18}$$

where the symbol υ enumerates the hybrid (electron–vibrational) states, $n_1 \equiv n_{A_1}$, $|\gamma\rangle$ stands for the electronic wavefunctions ξ, η, ς of the $^5T_2$ state, $\Phi_{n_1}(Q)$, $\Phi_{n_u}(q_u)$, $\Phi_{n_\upsilon}(q_\upsilon)$, $\Phi_{n_\xi}(q_\xi)$, $\Phi_{n_\eta}(q_\eta)$, $\Phi_{n_\varsigma}(q_\varsigma)$ denote the harmonic oscillator wavefunctions corresponding to the A_1, E and $T_2^{(1)}$ vibrations, respectively; actually the coefficients $C^{(\upsilon)}_{n_\xi,n_\eta,n_\varsigma}$ form the eigenvectors of the infinite JT matrix. The energies of the vibronic levels arising from the $t_2 \otimes T_2$ problem can be presented as

$$E^{(\upsilon)}_{n_1,n_u,n_\upsilon} = \hbar\omega(n_u + n_\upsilon + 1) + \hbar\omega(n_1 + 1/2) + \varepsilon^{(\upsilon)}_{T_2}, \tag{19}$$

where the values $\varepsilon^{(\upsilon)}_{T_2}$ will be determined from the solution of the $t_2 \otimes T_2$ JT problem for the $^5T_2$-term. For the excited ^5E state the vibronic wavefunction looks as follows

$$\psi^{(\upsilon')}_{n_1',n_\xi,n_\eta,n_\varsigma} = \Phi_{n_1'}(Q - Q^0)\Phi_{n_\xi}(q_\xi)\Phi_{n_\eta}(q_\eta)\Phi_{n_\varsigma}(q_\varsigma) \sum_{\substack{\gamma'=u,\upsilon \\ n_u,n_\upsilon}} C^{(\upsilon')}_{\gamma',n_u,n_\upsilon}\Phi_{n_u}(q_u)\Phi_{n_\upsilon}(q_\upsilon)|\gamma'\rangle, \tag{20}$$

where $Q^0 = -\upsilon_{A_1}(E)/\hbar\omega$, $\gamma' = u, v$; the sense of other notations is the same as in equation (18). For the ^5E term the linear interaction with the full symmetric vibration results in the adiabatic problem, giving rise to a shift Q^0 of the equilibrium position of the Q-coordinate. The corresponding to (20) energy levels can be presented as

$$E^{(\upsilon')}_{n_1',n_\xi,n_\eta,n_\varsigma} = 10Dq - \frac{(\upsilon_{A_1}(E))^2}{2\hbar\omega} + \hbar\omega(n_1' + 1/2) + \hbar\omega(n_\xi + n_\eta + n_\varsigma + 3/2) + \varepsilon^{(\upsilon')}_E, \tag{21}$$

where energies $\varepsilon^{(\upsilon')}_E$ will be obtained from the solution of the $e \otimes E$ vibronic problem.

In numerical calculations of the eigenvalues and eigenvectors of the dynamic vibronic problems $e \otimes E$ and $t_2 \otimes T_2$ the vibronic matrices were truncated. For the $e \otimes E$ problem the number N of unperturbed vibrational states satisfied the condition $(n_u + n_\upsilon \leqslant N)$, where in the calculation $N = 100$ was taken. For the $t_2 \otimes T_2$ problem the inequality $n_\xi + n_\eta + n_\varsigma \leqslant 60$ held. The general dimension of the vibronic matrix for the E term was $10\,302 \times 10\,302$. For the T_2 term the dimension of the matrix was $119\,133 \times 119\,133$. The Lanczos recursion procedure with a proper choice of the initial state was used to calculate the vibronic functions and energies [18].

The shape $F_1(\Omega)$ of the absorption band can be presented as

$$F_1(\Omega) = \frac{1}{Z} \sum_{\substack{\upsilon,\upsilon' \\ n_\xi,n_\eta,n_\varsigma \\ n_1,n_1',n_u,n_\upsilon}} \mathrm{Exp}\left[-\frac{E^{(\upsilon)}_{n_1,n_u,n_\upsilon}}{kT}\right] \overline{\left|\left\langle \psi^{(\upsilon')}_{n_1',n_\xi,n_\eta,n_\varsigma}\left|\vec{u}\vec{d}\right|\psi^{(\upsilon)}_{n_1,n_u,n_\upsilon}\right\rangle\right|^2} \times \delta(E^{(\upsilon')}_{n_1',n_\xi,n_\eta,n_\varsigma} - E^{(\upsilon)}_{n_1,n_u,n_\upsilon} - \hbar\Omega), \tag{22}$$

where $\vec{d}$ and $\vec{u}$ are the dipole moment and polarization vectors, respectively, the symbol $\overline{|\ldots|^2}$ means the averaging over the light polarization,

$$Z = \sum_{\substack{\upsilon, \\ n_1,n_u,n_\upsilon}} \mathrm{Exp}\left[-\frac{E^{(\upsilon)}_{n_1,n_u,n_\upsilon}}{kT}\right] = \sum_\upsilon \mathrm{Exp}\left(-\frac{\varepsilon^{(\upsilon)}_{T_2}}{kT}\right) \Big/ 8\sinh^3(\beta/2)$$

is the partition function for the ground states, equation (22) contains averaging over the initial states $(n_1, n_u, n_\upsilon, \upsilon)$ and summation over the final $(n_1', n_\xi, n_\eta, n_\varsigma, \upsilon')$ ones, $\beta = \hbar\omega/kT$, hereunder the frequencies of the full symmetric, tetragonal and trigonal vibrations are taken to be equal. The averaging and summation over the states of the A_1 oscillator can be performed

in the conventional way [19] and leads to a well known spectral distribution referred to as 'Pekarian'. After some transformations equation (22) can be written as

$$F_1(\Omega) = \frac{|\langle {}^5\mathrm{E} \parallel d_{\mathrm{T}_1} \parallel {}^5\mathrm{T}_2\rangle|^2}{3Z_1} \sum_{\substack{\nu,\nu' \\ n_\xi,n_\eta,n_\zeta \\ n_u,n_\upsilon}} \mathrm{Exp}\left[-\frac{E^{(\nu)}_{n_u,n_\upsilon}}{kT}\right]\mathrm{Exp}\left[-\frac{1}{2}a\coth\left(\frac{\beta}{2}\right)\right]$$
$$\times \sum_{n=-\infty}^{\infty} I_n\left(\frac{a}{2\sinh(\beta/2)}\right)\mathrm{Exp}\left[\frac{n\beta}{2}\right]\left\{\frac{1}{12}(C^{(\nu)}_{\xi,n_\xi,n_\eta,n_\zeta})^2\left(\sqrt{3}C^{(\nu')}_{u,n_u,n_\upsilon}\right.\right.$$
$$\left. + C^{(\nu')}_{\upsilon,n_u,n_\upsilon}\right)^2 + \tfrac{1}{12}(C^{(\nu)}_{\eta,n_\xi,n_\eta,n_\zeta})^2\left(\sqrt{3}C^{(\nu')}_{u,n_u,n_\upsilon} - C^{(\nu')}_{\upsilon,n_u,n_\upsilon}\right)^2$$
$$\left. + \tfrac{1}{3}\left(C^{(\nu)}_{\zeta,n_\xi,n_\eta,n_\zeta}\right)^2 (C^{(\nu')}_{\upsilon,n_u,n_\upsilon})^2\right\}\delta(E^{(\nu')}_{n_\xi,n_\eta,n_\zeta} - E^{(\nu)}_{n_u,n_\upsilon}$$
$$+ \hbar\omega n - (\upsilon_{\mathrm{A}_1}(\mathrm{E}))^2/(2\hbar\omega) - \hbar\Omega) \tag{23}$$

$$Z_1 = \sum_{\nu}\mathrm{Exp}\left(-\frac{\varepsilon^{(\nu)}_{\mathrm{T}_2}}{kT}\right)\Big/ 4\sinh^2(\beta/2), \qquad a = \left(\frac{\upsilon_{\mathrm{A}_1}(\mathrm{E})}{\hbar\omega}\right)^2,$$

$$E^{(\nu)}_{n_1,n_u,n_\upsilon} - E^{(\nu)}_{n_u,n_\upsilon} = \hbar\omega(n_1 + 1/2), \qquad E^{(\nu')}_{n'_1,n_\xi,n_\eta,n_\zeta} - E^{(\nu')}_{n_\xi,n_\eta,n_\zeta} = \hbar\omega(n'_1 + 1/2), \tag{24}$$

where $\beta = \hbar\omega/kT$, $I_n(\frac{a}{2\sinh(\beta/2)})$ is the modified Bessel function and a is the heat release parameter (the Pekar–Huang–Rhys parameter) and $\langle {}^5\mathrm{E} \parallel d_{\mathrm{T}_1} \parallel {}^5\mathrm{T}_2\rangle$ is the reduced matrix element of the transition dipole moment. From equation (23) it is seen that the resultant optical band is represented by the convolution of two discrete distributions: one is the optical band arising from the JT interaction solely (transitions $n_u, n_\upsilon, \nu \rightarrow$ and $n_\xi, n_\eta, n_\varsigma, \nu'$) and another one is the Pekarian [19] with the heat release parameter a formed by the $n_1 \rightarrow n'_1$ transitions

$$P(10Dq + \hbar\omega n - (\upsilon_{\mathrm{A}_1}(\mathrm{E})^2/2\hbar\omega) - \hbar\Omega) = \mathrm{Exp}\left[-\frac{1}{2}a\coth\left(\frac{\beta}{2}\right)\right]\sum_{n=-\infty}^{\infty} I_n\left(\frac{a}{2\sinh(\beta/2)}\right)$$
$$\times \mathrm{Exp}\left[\frac{n\beta}{2}\right]\delta(10Dq + \hbar\omega n - (\upsilon_{\mathrm{A}_1}(\mathrm{E})^2/2\hbar\omega) - \hbar\Omega). \tag{25}$$

In order to get the envelope curve (that appears due to the dispersion of the lattice vibrations) the shape function of the individual line related to the transition between hybrid vibronic states $(n_1, n_u, n_\upsilon, \nu)$ and $(n'_1, n_\xi, n_\eta, n_\varsigma, \nu')$ is assumed to be of the Gaussian form

$$\frac{1}{\sqrt{2\pi\lambda^2}}\mathrm{Exp}\left[-\frac{(E^{(\nu')}_{n_\xi,n_\eta,n_\zeta} - E^{(\nu)}_{n_u,n_\upsilon} + \hbar\omega n - (\upsilon_{\mathrm{A}_1}(\mathrm{E})^2/2\hbar\omega) - \hbar\Omega)^2}{2\lambda^2}\right]. \tag{26}$$

To smooth the quantum discrete structure of the calculated band the second central moment of the individual lines λ should be comparable with the $\hbar\omega$ value. In further calculations for the $CrSe_4$ moiety we put $\lambda = \hbar\omega = \hbar\omega_{\mathrm{CdSe}} = 60\ \mathrm{cm}^{-1}$ (see table 1). While calculating the transition band at 300 K, $N_1 = 4600$ and $N_2 = 2800$ vibronic levels which originate from the states ${}^5\mathrm{E}$ and ${}^5\mathrm{T}_2$ and fall into the ranges $\Delta E({}^5\mathrm{E}) = 4000\ \mathrm{cm}^{-1}$ and $\Delta E({}^5\mathrm{T}_2) = 812\ \mathrm{cm}^{-1}$, respectively, were taken into account. So the full number N_{tot} of examined vibronic transitions that form the ${}^5\mathrm{T}_2 \rightarrow {}^5\mathrm{E}$ absorption band at 300 K was $N_2 = 12\,880\,000$. In the following in the sums over the Bessel functions n was taken in the limits $-30 \leqslant n \leqslant 30$. Figure 3 represents the absorption spectra $K_1(\Omega) \sim \Omega F_1(\Omega)$ ($K_1(\Omega)$ is the absorption coefficient) of the $CrSe_4$ species at 300 K. A reasonably fair agreement with the experimental data [5] was obtained for $Dq = -395\ \mathrm{cm}^{-1}$ and vibronic coupling constants $\upsilon^{(1)}_{\mathrm{T}_2}(\mathrm{T}_2) = 300\ \mathrm{cm}^{-1}$, $\upsilon_{\mathrm{E}}(\mathrm{E}) = 100\ \mathrm{cm}^{-1}$ and $\upsilon_{\mathrm{A}_1}(\mathrm{E}) = -100\ \mathrm{cm}^{-1}$. The values of the vibronic parameters obtained by fitting are close

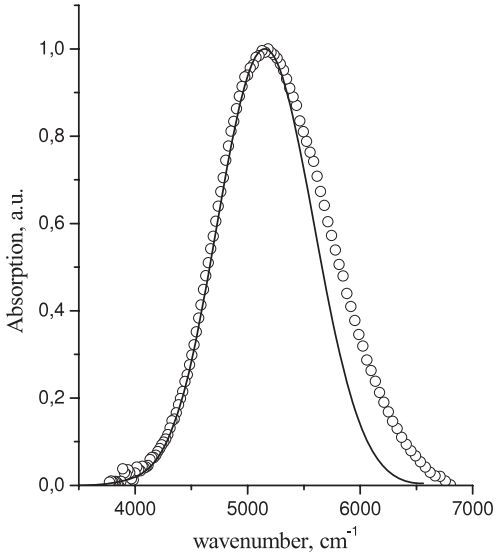

Figure 3. Absorption spectrum of the CdSe:Cr^{2+} crystal at $T = 300$ K: circles, experimental data [5]: solid line, calculated spectra in the case of $\upsilon_{\mathrm{E}}(\mathrm{E}) = 100\ \mathrm{cm}^{-1}$, $\upsilon^{(1)}_{\mathrm{T}_2}(\mathrm{T}_2) = 300\ \mathrm{cm}^{-1}$, $\upsilon_{\mathrm{A}_1}(\mathrm{E}) = -100\ \mathrm{cm}^1$, $Dq = -395\ \mathrm{cm}^{-1}$.

to those calculated in the exchange charge model (see table 2). The obtained result serves as a convincing confirmation that the model employed describes reasonably the contribution of the $CrSe_4$ species to the observed absorption spectra of $CdSe_{0.6}S_{0.4}$:Cr^{2+}.

5. Contribution from the $CrSe_3S$ and $CrSeS_3$ impurity clusters to the absorption band

5.1. $CrSe_3S$ complex

When one of the four Se atoms is replaced by a S atom the symmetry of the ligand surroundings, as was stated above, is lowered to C_{3v} from T_d. The crystal field operator written in the frame of reference related to the C_3 axis (figure 1(c)) looks as follows:

$$V_{\mathrm{CF}}(\mathrm{C_{3v}}) = \frac{2e^2\sqrt{\pi}}{405(R_0R)^5}\left\{-81\sqrt{5}R^2(A_2^- + 2\mathrm{B}_2{}^-)Y_{20}(\theta,\varphi) + \frac{2\sqrt{70}}{R_0^4}[5(A_4^+ + A_4^-) + 18(B_4^+ + B_4^-)][Y_{43}(\theta,\varphi) - Y_{4-3}(\theta,\varphi)] + [14(5A_4^+ + 18B_4^+) - 13(5A_4^- + 18B_4^-)]Y_{40}(\theta,\varphi)\right\}, \tag{27}$$

where

$$A_p^{\pm} = \langle r^p\rangle Z(R_0^{p+1} \pm R^{p+1}), \qquad B_p^{\pm} = (R_0R)^pG[R_0S_p(R) \pm RS_p(R_0)].$$

In the trigonal crystal field (27) the ground $^5T_2$ term of Cr^{2+} splits into two levels, $^5E^{(1)}$ and $^5A_1$, while the excited state ^5E state remains unsplit (figure 2(c)). The wavefunctions of

Table 3. Vibronic coupling constants (in cm^{-1}) for the $CrSe_3S$ complex.

$\nu^{(1)}_{A_1}(^5A_1)$			$\nu^{(2)}_{A_1}(^5A_1)$			$\nu^{(1)}_{A_1}(^5E)$			$\nu^{(2)}_{A_1}(^5E)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total
24	50	74	83	148	231	−16	−49	−65	−2	−6	−8
$\upsilon^{(1)}_{A_1}(^5E)$			$\upsilon^{(2)}_{A_1}(^5E)$			$\upsilon_{E^{(1)}}(^5E)$			$\upsilon_{E^{(2)}}(^5E)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total
−40	−99	−139	−85	−154	−239	55	11	66	−0.3	0.1	−0.2

these levels have the form

$$
\begin{aligned}
|^5E_x\rangle &= \frac{1}{\sqrt{2}}(-|x_1x_0x_{-1}u_1| + |x_1x_0x_{-1}u_{-1}|),\\
|^5E^{(1)}_x\rangle &= \frac{1}{\sqrt{2}}(-|x_1x_0u_{-1}u_1| + |x_0x_{-1}u_{-1}u_1|),\\
|^5A_1\rangle &= |x_1x_{-1}u_{-1}u_1|.
\end{aligned}
\tag{28}
$$

In equation (28) for each degenerate term the only wavefunction is given; the basis is related to the C_3 axis of the distorted tetrahedron. The trigonal one-electron states (complex trigonal basis) relevant to this coordinate system are expressed in terms of the d-functions $\xi = yz, \eta = xz, \zeta = xy(t_{2g}), u = 3z^2 - r^2, v = \sqrt{3}(x^2 - y^2)(e_g)$ defined in the tetragonal basis as follows:

$$
\begin{aligned}
&|x_+\rangle = -(1/\sqrt{3})(\varepsilon\xi + \varepsilon^*\eta + \zeta), \qquad |x_-\rangle = (1/\sqrt{3})(\varepsilon^*\xi + \varepsilon\eta + \zeta),\\
&|x_0\rangle = (1/\sqrt{3})(\xi + \eta + \zeta), \qquad u_+ = -(1/\sqrt{2})(u + \mathrm{i}v),\\
&u_- = (1/\sqrt{2})(u - \mathrm{i}v), \qquad \varepsilon = \exp(2\pi\mathrm{i}/3).
\end{aligned}
\tag{29}
$$

The energy gaps $E(^5E^{(1)}) - E(^5A_1) = 915\ cm^{-1}$ and $E(^5E) - E(^5A_1) = 4726\ cm^{-1}$ were calculated using the crystal field potential (27), the wavefunctions (28), (29) and the parameters given in table 1. The obtained $E(^5E^{(1)}) - E(^5A_1)$ gap value appreciably exceeds the thermal energy at room temperature and, thus, the absorption band originating from $CrSe_3S$ species can be assigned to the optical transition $^5A_1 \rightarrow {}^5E$. The $^5A_1$ term interacts with the $A_1^{(1)}$ and $A_1^{(2)}$ vibrations of the surrounding ligands, while the ^5E term in addition to these two modes interacts with the $E^{(1)}$ and $E^{(2)}$ modes. At the next step we employ the standard procedure [12, 13] of shifting the reference points of the symmetrized coordinates $q^{(1)}_{A_1}$ and $q^{(2)}_{A_1}$ in (3) to the nuclear configurations consistent with the ground $^5A_1$ state and introduce new vibrational coordinates $Q_{A_1^{(1)}} = q^{(1)}_{A_1} + \nu^{(1)}_{A_1}(^5A_1)/\hbar\omega$, $Q_{A_1^{(2)}} = q^{(2)}_{A_1} + \nu^{(2)}_{A_1}(^5A_1)/\hbar\omega(\nu^{(i)}_{A_1}(^5A_1) = \langle{}^5A_1|\nu_{A_1^{(i)}}(\boldsymbol{r})|{}^5A_1\rangle, (i = 1, 2))$ and vibrational operators $\upsilon_{A_1^{(1)}}(\boldsymbol{r}) = \nu_{A_1^{(1)}}(\boldsymbol{r}) - \nu_{A_1^{(1)}}(^5A_1)$, $\upsilon_{A_1^{(2)}}(\boldsymbol{r}) = \nu_{A_1^{(2)}}(\boldsymbol{r}) - \nu^{(2)}_{A_1}(^5A_1)$ corresponding to these modes. Such a procedure is identical to that described in section 4 for the $CrSe_4$ species (see equations (11)–(13)) and, therefore, we omit its description here. The redefinition of the operators corresponding to $A_1^{(1)}$ and $A_1^{(2)}$ leads to $\upsilon^{(i)}_{A_1}(^5A_1) = \langle{}^5A_1|\upsilon_{A_1^{(i)}}(\boldsymbol{r})|{}^5A_1\rangle = 0$ and $\upsilon^{(i)}_{A_1}(^5E) = \nu^{(i)}_{A_1}(^5E) - \nu_{A_1^{(i)}}(^5A_1)$, where $\nu^{(i)}_{A_1}(^5E) = \langle{}^5E \parallel \nu_{A_1^{(i)}}(\boldsymbol{r}) \parallel {}^5E\rangle/\sqrt{2}, (i = 1, 2)$. The evaluation of the corresponding vibronic coupling constants was performed in the exchange charge model of the crystal field [12–16]. In table 3 for each vibronic constant the contributions arising from the exchange and point charge fields are indicated. From table 3 it is seen that the interaction of the ^5E state with the $E^{(2)}$ vibration is weak in comparison with those with $A_1^{(1)}$, $A_1^{(2)}$ and $E^{(1)}$ vibrations. Therefore, this interaction will not be taken into account in further calculations.

The electron-vibrational wavefunction corresponding to the $^5A_1$ state can be represented as

$$\Psi(^5A_1, n^{(1)}_{A_1} n_{A_1^{(2)}} n_{E_x} n_{E_y}) = |^5A_1\rangle \Phi_{n_{A_1^{(1)}}}(Q_{A_1^{(1)}}) \Phi_{n_{A_1^{(2)}}}(Q_{A_1^{(2)}}) \Phi_{n_{E_x}}(q_{E_x}) \Phi_{n_{E_y}}(q_{E_y}), \tag{30}$$

where $\Phi_{n_{A_1^{(1)}}}(Q_{A_1^{(1)}})$, etc, are the wavefunctions of the harmonic oscillator. The corresponding energies appear as follows

$$E^{A_1}(n_{A_1^{(1)}}, n_{A_1^{(2)}}, n_{E_x}, n_{E_y}) = -\frac{(\upsilon^{(1)}_{A_1}(^5A_1))^2}{2\hbar\omega} - \frac{(\upsilon^{(2)}_{A_1}(^5A_1))^2}{2\hbar\omega} + \hbar\omega\left(n_{A_1^{(1)}} + \frac{1}{2}\right) + \hbar\omega(n_{A_1^{(2)}} + \tfrac{1}{2}) + \hbar\omega(n_{E_x} + \tfrac{1}{2}) + \hbar\omega(n_{Ey} + \tfrac{1}{2}). \tag{31}$$

The vibronic Hamiltonian for the $E \otimes (e + a_1^{(1)} + a_1^{(2)})$ problem in the ^5E state takes on the form

$$H_{e\upsilon}(^5E) = \upsilon^{(1)}_E(^5E)(\boldsymbol{O}_{Ex} q_{Ex} + \boldsymbol{O}_{Ey} q_{Ey}) + \upsilon^{(1)}_{A_1}(^5E)\boldsymbol{O}_{A_1} Q_{A_1^{(1)}} + \upsilon^{(2)}_{A_1}(^5E)\boldsymbol{O}_{A_1} Q_{A_1^{(2)}}, \tag{32}$$

where the elements of the matrices $\boldsymbol{O}_{\bar\Gamma\bar\gamma}$ represent the Clebsch–Gordan coefficients $\langle\Gamma\gamma|, \boldsymbol{O}_{\bar\Gamma\bar\gamma}|\Gamma\gamma'\rangle = \langle\Gamma\gamma|\Gamma\gamma'\bar\Gamma\bar\gamma\rangle$ for the C_{3v} point symmetry group [20]

$$\boldsymbol{O}_{E_x} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \boldsymbol{O}_{E_y} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$\upsilon^{(1)}_E(^5E) = \langle ^5E \parallel \nu^{(1)}_E(\boldsymbol{r}) \parallel {}^5E\rangle/\sqrt{2}$. The hybrid vibronic functions corresponding to the dynamical JT problem in the excited ^5E term are written as

$$\Psi^E_\nu(n^{(1)}_{A_1}, n^{(2)}_{A_1}) = \Phi_{n^{(1)}_{A_1}}(Q_{A_1^{(1)}} - Q^0_{A_1^{(1)}}) \Phi_{n^{(2)}_{A_1}}(Q_{A_1^{(2)}} - Q^0_{A_1^{(2)}}) \sum_{\substack{\gamma=x,y \\ n_{Ex}, n_{Ey}}} C^E_\nu(\gamma, n_{E_x}, n_{E_y}) \times \Phi_{n_{E_x}}(q_{E_x}) \Phi_{n_{E_y}}(q_{E_y})|\gamma\rangle. \tag{33}$$

Here $Q^0_{A_1^{(1)}} = -\frac{\upsilon^{(1)}_{A_1}(^5E)}{\hbar\omega} \equiv a_1^{(^5E)}$, $Q^0_{A_1^{(2)}} = -\frac{\upsilon^{(2)}_{A_2}(^5E)}{\hbar\omega} \equiv a_2^{(^5E)}$. The energies of the vibronic states $\Psi^E_\nu(n_{A_{11}}, n_{A_{12}})$ are

$$\varepsilon(n_{A_1^{(1)}}, n_{A_1^{(2)}}, \nu) = \Delta_1^{(^5E)} + \hbar\omega(n_{A_1^{(1)}} + \tfrac{1}{2}) + \hbar\omega(n_{A_1^{(2)}} + \tfrac{1}{2}) + \varepsilon^E_\nu, \tag{34}$$

where $\Delta_1^{(^5E)} = \Delta - ((\nu^{(1)}_{A_1}(^5E))^2 + (\nu^{(2)}_{A_1}(^5E))^2)/(2\hbar\omega)$, Δ is the crystal field energy gap between the states ^5E and $^5A_1$ and ε^E_ν are the eigenvalues of the $^5E \otimes e$ JT vibronic problem. For the numerical solution of this problem the vibronic matrix was truncated, the number N of the harmonic oscillator states satisfied the condition $n_x + n_y \leqslant N$, where in calculations N was taken to be equal to 60. The general dimension of the matrix was 3782×3782. The Lanczos method was applied for calculation of the hybrid vibronic states and wavefunctions. The procedure of derivation of the formula for the absorption band shape is described in detail in section 4. Therefore, we do not go into details below. Performing the transformations similar to those in section 4 we obtain the following expression for the shape of the absorption band arising from the $CdSe_3S:Cr^{2+}$ species:

$$F_2(\Omega) = \frac{1}{Z_2}\mathrm{Exp}\left[-\frac{(a_1{}^{(^5E)})^2}{2}\coth\left(\frac{\beta}{2}\right)\right]\mathrm{Exp}\left[-\frac{(a_2{}^{(^5E)})^2}{2}\coth\left(\frac{\beta}{2}\right)\right] \times \sum_{\substack{\nu, n_{A_{11}}, n_{A_{12}}, \\ n_{Ex}, n_{Ey}}} \mathrm{Exp}\left[-\frac{E^{A_1}(n_{A_{11}}, n_{A_{12}}, n_{E_x}, n_{E_y})}{kT}\right]\left\{\frac{1}{3}|C^E_\nu(E_u, n_{E_x}, n_{E_y})|^2\right.$$

$$+\frac{1}{3}|C_{\upsilon}^{E}(E_{\upsilon},n_{E_x},n_{E_y})|^2\Bigg\}\sum_{n_1=-\infty}^{\infty}\sum_{n_2=-\infty}^{\infty}I_{n_1}\left(\frac{(a_1{}^{(5E)})^2}{2Sh(\beta/2)}\right)I_{n_2}\left(\frac{(a_2{}^{(5E)})^2}{2Sh(\beta/2)}\right)$$
$$\times\,\mathrm{Exp}\left[\frac{n_1\beta}{2}\right]\mathrm{Exp}\left[\frac{n_2\beta}{2}\right]\frac{1}{\sqrt{2\pi\lambda^2}}$$
$$\times\,\mathrm{Exp}\left[-\frac{(\Delta_1+\hbar\omega(n_1+n_2)-\hbar\omega(n_{E_x}+n_{E_y}+1)+\varepsilon_{\upsilon}^{E}-\hbar\Omega)^2}{2\lambda^2}\right]$$
$$\times\,\frac{|\langle{}^5\mathrm{E}\parallel d_{\mathrm{E}}\parallel{}^5\mathrm{A}_1\rangle|^2}{2}, \tag{35}$$

where $\langle{}^5\mathrm{E}\parallel d_{\mathrm{E}}\parallel{}^5\mathrm{A}_1\rangle$ is the matrix element of the effective dipole moment, the symbol d_{E} denotes the component of the dipole moment which transforms according to the irreducible representation E of the C_{3v} point group; as in (22) the averaging over the light polarization was performed while deriving (35). Finally,

$$Z_2=\mathrm{Exp}\left(\frac{(\nu_{\mathrm{A}_1}^{(1)}({}^5\mathrm{A}_1))^2+(\nu_{\mathrm{A}_1}^{(2)}({}^5\mathrm{A}_1))^2}{2\hbar\omega kT}\right)\frac{1}{4\sinh^2(\beta/2)} \tag{36}$$

is the partition function for the ground states (31). In calculations for species $CrSe_{4-y}S_y$(y = 0–3) the vibrational frequency was approximately taken as

$$\hbar\omega=\hbar\omega_{\mathrm{CdSe}}\sqrt{\frac{m_{\mathrm{Se}}(4m_{\mathrm{Cd}}+(m_{\mathrm{Se}}(4-y)+m_{\mathrm{S}}y))}{(m_{\mathrm{Se}}+m_{\mathrm{Cd}})(m_{\mathrm{Se}}(4-y)+m_{\mathrm{S}}y)}}.$$

In the limiting cases of $y = 0$ and 4 this expression gives a reasonable result: $\hbar\omega=\hbar\omega_{\mathrm{CdSe}}=60\ \mathrm{cm}^{-1}$

$$\hbar\omega_{\mathrm{CdS}}=\hbar\omega_{\mathrm{CdSe}}\sqrt{\frac{m_{\mathrm{Se}}(m_{\mathrm{Cd}}+m_{\mathrm{S}})}{m_{\mathrm{S}}(m_{\mathrm{Cd}}+m_{\mathrm{Se}})}}\approx 80\ \mathrm{cm}^{-1}.$$

The latter coincides with the value known from literature [6] and given in table 1.

In figure 4 the calculated spectra arising from different species $CrSe_{4-y}S_y$(y = 1–3) with mixed ligand surroundings are shown. The contribution $K_2(\Omega)\sim\Omega F_2(\Omega)$ of the $CrSe_3S$ species to the absorption spectra ($K_2(\Omega)$ is the absorption coefficient) of the $CdSe_{0.6}S_{0.4}$:Cr^{2+} crystal has been calculated with the aid of parameters given in tables 1 and 3. It is seen that that this contribution is significant (figure 4). The maximum of the band arising from this species is blue shifted as compared with that belonging to the band from $CrSe_4$ species.

5.2. $CrSeS_3$ complex

The symmetry of the impurity complex $CrSeS_3$ is also C_{3v}. The trigonal crystal field splits the state ${}^5\mathrm{T}_2$ into two levels ${}^5\mathrm{E}^{(1)}$ and ${}^5\mathrm{A}_1$, with ${}^5\mathrm{E}^{(1)}$ being the ground state (figure 2(d)). The splitting of the ${}^5\mathrm{T}_2$ state can be described by the crystal field operator (27) if a substitution $R\rightleftarrows R_0$ is made. However, now the order of the levels ${}^5\mathrm{E}^{(1)}$ and ${}^5\mathrm{A}_1$ is reversed as compared to the case of the $CrSe_3S$ species (figure 2(c)). The calculated energy gap 932 cm^{-1} between the states ${}^5\mathrm{E}^{(1)}$ and ${}^5\mathrm{A}_1$ is large in comparison with the thermal energy and the absorption band is formed by the only transition ${}^5\mathrm{E}^{(1)}\rightarrow{}^5\mathrm{E}$. To determine the vibronic problems to be solved for these levels the vibronic coupling constants have been calculated (table 4) with the aid of wavefunctions (28) and corresponding vibrational operators. The redefinition of the vibronic operators $\mathrm{A}_1^{(1)}$ and $\mathrm{A}_1^{(2)}$ similar to that described in section 5.1 (see also (12)

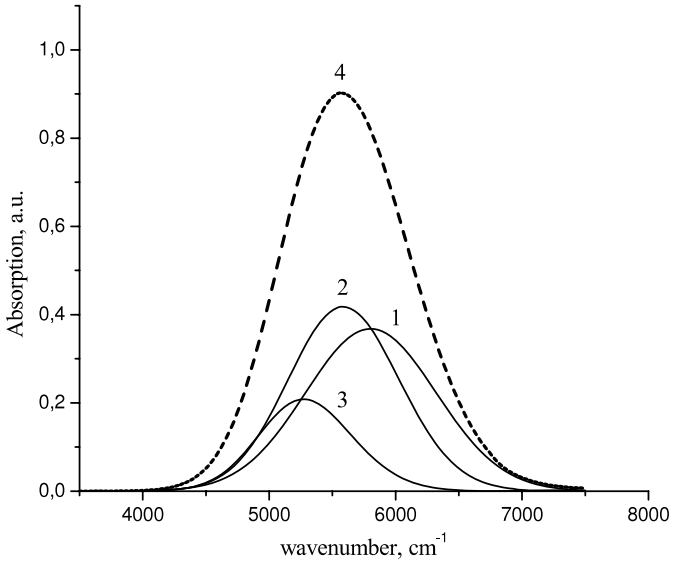

Figure 4. Calculated contributions from species with mixed ligand surroundings of the Cr^{2+} ion to the total absorption spectra at $T = 300$ K: 1, $CrSe_3S_1$: 2, $CrSe_2S_2$: 3, $CrSe_1S_3$: 4, total spectrum arising from $CrSe_{4-y}S_y$ species ($y = 1$–3).

Table 4. Vibronic coupling constants (in cm^{-1}) for the $CrSeS_3$ complex.

$\upsilon^{(1)}_{A_1}(^5E^{(1)})$			$\upsilon^{(2)}_{A_1}(^5E^{(1)})$			$\upsilon^{(1)}_{E}(^5E^{(1)})$			$\upsilon^{(2)}_{E}(^5E^{(1)})$		
pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total
14	45	59	−40	−74	−114	−9	−72	−81	19	37	56
$\upsilon^{(1)}_{A_1}(^5E)$			$\upsilon^{(2)}_{A_1}(^5E)$			$\upsilon^{(1)}_{A_1}(^5E)$			$\upsilon^{(2)}_{A_1}(^5E)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total	pc	ec	Total
−20	−59	−79	1	5	6	−34	−104	−138	41	79	120
$\upsilon^{(1)}_{E}(^5E)$			$\upsilon^{(2)}_{E}(^5E)$								
pc	ec	Total	pc	ec	Total						
61	12	73	10	2	12						

and (13)) leads to vanishing vibronic constants $\upsilon^{(i)}_{A_1}(^5E^{(1)})(i = 1, 2)$ for the ground $^5E^{(1)}$ state and $\upsilon^{(1)}_{A_1}(^5E) = -138\ cm^{-1}$, $\upsilon^{(2)}_{A_1}(^5E) = 120\ cm^{-1}$ for the excited ^5E state. For both $^5E^{(1)}$ and ^5E terms the interaction with the $E^{(1)}$ mode is stronger than that with the $E^{(2)}$ mode. Therefore, in further calculations we consider only the interaction of these terms with the $E^{(1)}$ mode. For the ground $^5E^{(1)}$ term the Hamiltonian of vibronic interaction looks as follows

$$H_{e\upsilon}(^5E^{(1)}) = \upsilon^{(1)}_{E}(^5E^{(1)})(q_{E_x}\boldsymbol{O}_{E_x} + q_{E_y}\boldsymbol{O}_{E_y}). \tag{37}$$

In fact we solve the vibronic two-mode $E \otimes e$ problem with the interaction constant $\upsilon^{(1)}_{E}(^5E^{(1)}) = -100\ cm^{-1}$ which slightly differs from the calculated one (see table 4). The eigenvalues and eigenvectors for this problem can be written as

$$
\begin{aligned}
E_{\nu}^{gr}(n_{\mathrm{A}_1^{(1)}}, n_{\mathrm{A}_1^{(2)}}) &= -\frac{(\nu_{\mathrm{A}_1}^{(1)}({}^5\mathrm{E}^{(1)}))^2}{2\hbar\omega} - \frac{(\nu_{\mathrm{A}_1}^{(2)}({}^5\mathrm{E}^{(1)}))^2}{2\hbar\omega} + \hbar\omega\left(n_{\mathrm{A}_1^{(1)}} + \frac{1}{2}\right) \\
&\quad + \hbar\omega\left(n_{\mathrm{A}_1^{(2)}} + \tfrac{1}{2}\right) + \varepsilon_{\nu}^{gr}, \\
\Psi_{\nu}^{gr}(n_{\mathrm{A}_1^{(1)}}, n_{\mathrm{A}_1^{(2)}}) &= \Phi_{n_{\mathrm{A}_1^{(1)}}}(Q_{\mathrm{A}_1^{(1)}})\Phi_{n_{\mathrm{A}_1^{(2)}}}(Q_{\mathrm{A}_1^{(2)}}) \sum_{\substack{\gamma=x,y \\ n_{E_x}, n_{E_y}}} C_{\nu}^{gr}(\gamma, n_{E_x}, n_{E_y}) \\
&\quad \times \Phi_{n_{E_x}}(q_{E_x})\Phi_{n_{E_y}}(q_{E_y})|\gamma\rangle,
\end{aligned} \tag{38}
$$

where the values ε_{ν}^{gr} will be determined from the solution of the E ⊗ e JT problem for the ${}^5\mathrm{E}^{(1)}$ term, $\nu_{\mathrm{A}_1}^{(i)}({}^5\mathrm{E}^{(1)}) = \langle {}^5\mathrm{E}^{(1)} \parallel \nu_{\mathrm{A}_1^{(i)}}(\boldsymbol{r}) \parallel {}^5\mathrm{E}^{(1)}\rangle/\sqrt{2}$, $(i = 1, 2)$. For the ${}^5\mathrm{E}$ term the vibronic $\mathrm{E}\otimes(\mathrm{e} + \mathrm{a}_1^{(1)} + \mathrm{a}_1^{(2)})$ problem is examined, the eigenvectors and eigenfunctions complying with this problem can be represented as

$$
\begin{aligned}
E_{\nu}^{ex}(n_{\mathrm{A}_1^{(1)}}, n_{\mathrm{A}_1^{(2)}}) &= \Delta - \frac{(\nu_{\mathrm{A}_1}^{(1)}({}^5\mathrm{E}))^2}{2\hbar\omega} - \frac{(\nu_{\mathrm{A}_1}^{(2)}({}^5\mathrm{E}))^2}{2\hbar\omega} + \hbar\omega\left(n_{\mathrm{A}_1^{(1)}} + \frac{1}{2}\right) \\
&\quad + \hbar\omega\left(n_{\mathrm{A}_1^{(2)}} + \tfrac{1}{2}\right) + \varepsilon_{\nu}^{ex}, \\
\Psi_{\nu}^{ex}(n_{\mathrm{A}_1^{(1)}}, n_{\mathrm{A}_1^{(2)}}) &= \Phi_{n_{\mathrm{A}_1^{(1)}}}(Q_{\mathrm{A}_1^{(1)}} - \tilde{Q}^0_{\mathrm{A}_1^{(1)}})\Phi_{n_{\mathrm{A}_1^{(2)}}}(Q_{\mathrm{A}_1^{(2)}} - \tilde{Q}^0_{\mathrm{A}_1^{(2)}}) \\
&\quad \times \sum_{\substack{\gamma=x,y \\ n_{E_x}, n_{E_y}}} C_{\nu}^{ex}(\gamma, n_{E_x}, n_{E_y})\Phi_{n_{E_x}}(q_{E_x})\Phi_{n_{E_y}}(q_{E_y})|\gamma\rangle,
\end{aligned} \tag{39}
$$

where

$$
\begin{aligned}
&\tilde{Q}^0_{\mathrm{A}_1{}^{(1)}} = -\tilde{\upsilon}_{\mathrm{A}_1}^{(1)}({}^5\mathrm{E})/(\hbar\omega) \equiv \tilde{\mathrm{a}}_1^{({}^5\mathrm{E})}, \qquad \tilde{Q}^0_{\mathrm{A}_1{}^{(2)}} = -\tilde{\upsilon}_{\mathrm{A}_1}^{(2)}({}^5\mathrm{E})/(\hbar\omega) \equiv \tilde{\mathrm{a}}_2^{({}^5\mathrm{E})}, \\
&\tilde{\upsilon}_{\mathrm{A}_1}^{(i)}({}^5\mathrm{E}) = \nu_{\mathrm{A}_1}^{(i)}({}^5\mathrm{E}) - \nu_{\mathrm{A}_1}^{(i)}({}^5\mathrm{E}^{(1)}),
\end{aligned}
$$

and ε_{ν}^{ex} is the solution of the E ⊗ e problem for the ${}^5\mathrm{E}$ term. While solving the vibronic E ⊗ e problems for the initial and final terms of the optical transition ${}^5\mathrm{E}^{(1)} \rightarrow {}^5\mathrm{E}$ the condition $n_{E_x} + n_{E_y} \leqslant N$ $(N = 60)$ was retained as in the case of $CrSe_3S$ species. The shape $F_3(\Omega)$ of the absorption band arising from the impurity cluster $CrSeS_3$ is given by the expression

$$
\begin{aligned}
F_3(\Omega) = \frac{1}{Z_4}&\mathrm{Exp}\left[-\frac{(\tilde{\mathrm{a}}_1^{({}^5\mathrm{E})})^2}{2}\coth\left(\frac{\beta}{2}\right)\right]\mathrm{Exp}\left[-\frac{(\tilde{\mathrm{a}}_2^{({}^5\mathrm{E})})^2}{2}\coth\left(\frac{\beta}{2}\right)\right]\sum_{\nu,\nu'}\mathrm{Exp}\left[-\frac{E_{\nu}^{E_{gr}}}{kT}\right] \\
&\times\Bigg\{\sum_{n_{E_x}, n_{E_y}}[(C_{\nu'}^{ex}(x, n_{E_x}, n_{E_y}))^* C_{\nu}^{gr}(x, n_{E_x}, n_{E_y}) + (C_{\nu'}^{ex}(y, n_{E_x}, n_{E_y}))^* \\
&\times C_{\nu}^{gr}(y, n_{E_x}, n_{E_y})]^2\frac{|\langle {}^5\mathrm{E} \parallel d_{\mathrm{E}} \parallel {}^5\mathrm{E}^{(1)}\rangle|^2}{4} + \sum_{n_{E_x}, n_{E_y}}[(C_{\nu'}^{ex}(x, n_{E_x}, n_{E_y}))^* \\
&\times C_{\nu}^{gr}(y, n_{E_x}, n_{E_y}) + (C_{\nu'}^{ex}(y, n_{E_x}, n_{E_y}))^* C_{\nu}^{gr}(x, n_{E_x}, n_{E_y})]^2 \\
&\times\frac{|\langle {}^5\mathrm{E} \parallel d_{\mathrm{E}} \parallel {}^5\mathrm{E}^{(1)}\rangle|^2}{4} + \sum_{n_{E_x}, n_{E_y}}[(C_{\nu'}^{ex}(x, n_{E_x}, n_{E_y}))^* C_{\nu}^{gr}(y, n_{E_x}, n_{E_y}) \\
&- (C_{\nu'}^{ex}(y, n_{E_x}, n_{E_y}))^* C_{\nu}^{gr}(x, n_{E_x}, n_{E_y})]^2\frac{|\langle {}^5\mathrm{E} \parallel d_{A_2} \parallel {}^5\mathrm{E}^{(1)}\rangle|^2}{2}\Bigg\} \\
&\times\sum_{n_1=-\infty}^{\infty}\sum_{n_2=-\infty}^{\infty} I_{n_1}\left(\frac{(\tilde{\mathrm{a}}_1^{({}^5\mathrm{E})})^2}{2Sh(\beta/2)}\right) I_{n_2}\left(\frac{(\tilde{\mathrm{a}}_2^{({}^5\mathrm{E})})^2}{2Sh(\beta/2)}\right)\mathrm{Exp}\left[\frac{n_1\beta}{2}\right]\mathrm{Exp}\left[\frac{n_2\beta}{2}\right] \\
&\times\frac{1}{\sqrt{2\pi\lambda^2}}\mathrm{Exp}\left[-\frac{(\tilde{E}_{\nu'}^{ex} - \tilde{E}_{\nu}^{gr} + \hbar\omega(n_1 + n_2) - \hbar\Omega)^2}{2\lambda^2}\right],
\end{aligned} \tag{40}
$$

where

$$\tilde{E}_{\nu}^{gr} = -\frac{(\upsilon_{A_1}^{(1)}({}^5E^{(1)}))^2}{2\hbar\omega} - \frac{(\upsilon_{A_1}^{(2)}({}^5E^{(1)}))^2}{2\hbar\omega} + \varepsilon_{\nu}^{gr},$$

$$\tilde{E}_{\nu}^{ex} = \Delta - \frac{(\upsilon_{A_1}^{(1)}({}^5E))^2}{2\hbar\omega} - \frac{(\upsilon_{A_1}^{(2)}({}^5E))^2}{2\hbar\omega} + \varepsilon_{\nu}^{ex},$$

$$Z_4 = \sum_{\nu} \mathrm{Exp}\left[-\frac{\tilde{E}_{\nu}^{gr}}{kT}\right],$$

where the notation $\langle {}^5E \parallel d_E \parallel {}^5E^{(1)}\rangle$ has the same sense as in (3) and $\langle {}^5E \parallel d_{A_2} \parallel {}^5E^{(1)}\rangle$ is the reduced matrix element of the dipole moment component that transforms according the irreducible representation A_2 of the C_{3v} point group. The partial contribution $K_3(\Omega) \sim \Omega F_3(\Omega)$ of the $CrSeS_3$ species was calculated with the aid of parameters given in tables 1 and 4 and it is depicted in figure 4 (curve 3). It is obvious that this species also give a blue shifted band relative to that originating from the $CrSe_4$ one. At the same time the intensity of this band is lower in comparison with the intensity of the band belonging to the $CrSe_3S$ cluster.

6. Absorption band of the impurity $CrSe_2S_2$ cluster

When the nearest neighbour surrounding of the Cr^{2+} ion consists of two selenium and two sulfur atoms the symmetry of the impurity complex is C_{2v} and the crystal field potential looks as follows

$$\begin{aligned} V_{CF}(C_{2v}) = {} & \frac{ie^2\sqrt{\pi}}{135(R_0R)^5}\{i\sqrt{70}(5A_4^+ + 18B_4^+)[Y_{44}(\theta,\varphi) + Y_{4-4}(\theta,\varphi)] \\ & + 4\sqrt{10}(5A_4^- + 18B_4^-)[Y_{42}(\theta,\varphi) - Y_{4-2}(\theta,\varphi)] \\ & + 14i(5A_4^+ + 18B_4^+)Y_{40}(\theta,\varphi) \\ & + 18\sqrt{30}R_0^2R^2(A_2^- + 2B_2^-)[Y_{22}(\theta,\varphi) - Y_{2-2}(\theta,\varphi)]\}, \end{aligned} \tag{41}$$

where the functions $A_p^{\pm}$ and $B_p^{\pm}$ are determined in (27). In this case the energy spectrum of the Cr^{2+} ion consists of five levels ${}^5A_1^{(1)}, {}^5A_2, {}^5B_2, {}^5B_1, {}^5A_1^{(2)}$. The states ${}^5A_1^{(1)}$ and ${}^5A_2$ originate from the cubic ${}^5E$ state, while the states ${}^5B_2, {}^5B_1, {}^5A_1^{(2)}$ arise from the splitting of the ground ${}^5T_2$ term (figure 2(b)). The wavefunctions of these states are

$$\begin{aligned} & |{}^5A_2\rangle = -|u\xi\eta\zeta|, \qquad |{}^5A_1^{(1)}\rangle = C_1|\xi\eta u\upsilon| + C_2|\upsilon\xi\eta\zeta|, \\ & |{}^5B_1\rangle = (|\xi\zeta u\upsilon| - |\eta\zeta u\upsilon|)/\sqrt{2}, \qquad |{}^5B_2\rangle = (|\xi\zeta u\upsilon| + |\eta\zeta u\upsilon|)/\sqrt{2}, \\ & |{}^5A_1^{(2)}\rangle = -C_2|\xi\eta u\upsilon| + C_1|\upsilon\xi\eta\zeta|, \end{aligned} \tag{42}$$

where the coefficients C_1 and C_2 can be obtained from the diagonalization of the crystal field potential (41). The energies of the levels ${}^5A_1^{(1)}, {}^5A_2, {}^5B_2, {}^5B_1, {}^5A_1^{(2)}$ in the crystal field have been calculated with the aid of the crystal field potential (41), wavefunctions (42) and overlap integrals given in table 1. The obtained energy gaps between the ground ${}^5B_1$ level and the excited ${}^5A_1^{(2)}$ and ${}^5B_2$ ones exceed essentially the thermal energy, and the absorption band of the $CrSe_2S_2$ cluster at room temperature arises from the optical transitions ${}^5B_1 \rightarrow {}^5A_2, {}^5B_1 \rightarrow {}^5A_1^{(1)}$ between orbitally nondegenerate states interacting with one-dimensional vibrations. While calculating the structure of the multiphonon absorption band the interaction of the terms ${}^5B_1, {}^5A_2$ and ${}^5A_1^{(1)}$ with the vibrations $A_1^{(1)}, A_1^{(2)}$ and $A_1^{(3)}$ was

Table 5. Vibronic coupling constants (in cm^{-1}) for the $CrSe_2S_2$ complex.

$\nu_{A_1}^{(1)}(^5B_1)$			$\nu_{A_1}^{(2)}(^5B_1)$			$\nu_{A_1}^{(3)}(^5B_1)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total
17	36	53	70	131	201	16	2	18
$\nu_{A_1}^{(1)}(^5A_1{}^{(1)})$			$\nu_{A_1}^{(2)}(^5A_1{}^{(1)})$			$\nu_{A_1}^{(3)}(^5A_1{}^{(1)})$		
pc	ec	Total	pc	ec	Total	pc	ec	Total
−17	−52	−69	2	−15	−13	63	18	81
$\upsilon_{A_1}^{(1)}(^5A_1{}^{(1)})$			$\upsilon_{A_1}^{(2)}(^5A_1{}^{(1)})$			$\upsilon_{A_1}^{(3)}(^5A_1{}^{(1)})$		
pc	ec	Total	pc	ec	Total	pc	ec	Total
−34	−88	−122	−68	−146	−214	47	16	63
$\nu_{A_1}^{(1)}(^5A_2)$			$\nu_{A_1}^{(2)}(^5A_2)$			$\nu_{A_1}^{(3)}(^5A_2)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total
−19	−53	−72	−15	−17	−32	−58	−8	−6 6
$\upsilon_{A_1}^{(1)}(^5A_2)$			$\upsilon_{A_1}^{(2)}(^5A_2)$			$\upsilon_{A_1}^{(3)}(^5A_2)$		
pc	ec	Total	pc	ec	Total	pc	ec	Total
−36	−89	−125	−85	−148	−233	−74	−10	−84

taken into account. The vibrational coordinates for modes $A_1^{(1)}$, $A_1^{(2)}$, $A_1^{(3)}$ and the vibrational operators corresponding to these modes were redefined:

$$\begin{aligned} &Q_{A_1^{(1)}} = q_{A_1}^{(1)} + \nu_{A_1}^{(1)}(^5B_1)/\hbar\omega, \qquad && Q_{A_1^{(2)}} = q_{A_1}^{(2)} + \nu_{A_1}^{(2)}(^5B_1)/\hbar\omega, \\ &Q_{A_1^{(3)}} = q_{A_1}^{(3)} + \nu_{A_1}^{(3)}(^5B_1)/\hbar\omega, && \upsilon_{A_1^{(1)}}(\boldsymbol{r}) = \nu_{A_1^{(1)}}(\boldsymbol{r}) - \nu_{A_1}^{(1)}(^5B_1), \\ &\upsilon_{A_1^{(2)}}(\boldsymbol{r}) = \nu_{A_1^{(2)}}(\boldsymbol{r}) - \nu_{A_1}^{(2)}(^5B_1), && \upsilon_{A_1^{(3)}}(\boldsymbol{r}) = \nu_{A_1^{(3)}}(\boldsymbol{r}) - \nu_{A_1}^{(3)}(^5B_1), \end{aligned} \tag{43}$$

here $\nu_{A_1}^{(i)}(^5B_1) = \langle {}^5B_1|\nu_{A_1{}^{(i)}}(\boldsymbol{r})|{}^5B_1\rangle$, $(i = 1\text{–}3)$. As a result the electron-vibrational energies and states complying with the ground $^5B_1$ term can be written as

$$\begin{aligned} &E^{^5B_1}(n_{A_1^{(1)}}, n_{A_1^{(2)}}, n_{A_1^{(3)}}) = \varepsilon^{^5B_1} + \hbar\omega\big(n_{A_1^{(1)}} + n_{A_1^{(2)}} + n_{A_1^{(3)}} + \tfrac{3}{2}\big), \\ &\psi^{^5B_1}(n_{A_1^{(1)}}, n_{A_1^{(2)}}, n_{A_1^{(3)}}) = \Phi_{n_{A_1^{(1)}}}(Q_{A_1^{(1)}})\Phi_{n_{A_1^{(2)}}}(Q_{A_1^{(2)}})\Phi_{n_{A_1^{(3)}}}(Q_{A_1^{(3)}})|{}^5B_1\rangle \end{aligned} \tag{44}$$

here

$$\varepsilon^{^5B_1} = -\frac{1}{2\hbar\omega}\big((\nu_{A_1}^{(1)}(^5B_1))^2 + (\nu_{A_1}^{(2)}(^5B_1))^2 + (\nu_{A_1}^{(3)}(^5B_1))^2\big).$$

For the excited states $^5A_1^{(1)}$ and $^5A_2$ participating in the optical transitions $^5B_1 \rightarrow {}^5A_1^{(1)}$, $^5B_1 \rightarrow {}^5A_2$ the strongest is the interaction with the $A_1^{(2)}$ mode, at the same time the interaction with the $A_1^{(1)}$ and $A_1^{(3)}$ vibrations is weaker, but appreciable (table 5). For this reason the interaction of the excited terms $^5A_1^{(1)}$ and $^5A_2$ with all active vibrations is taken into account. The electron-vibrational wavefunctions and corresponding energies for the excited terms $^5A_1^{(1)}$ and $^5A_2$ are:

$$\begin{aligned} &E^{(\Gamma)}(n_{A_1^{(1)}}, n_{A_1^{(2)}}, n_{A_1^{(3)}}) = \varepsilon^{(\Gamma)} + \hbar\omega\big(n_{A_1^{(1)}} + n_{A_1^{(2)}} + n_{A_1^{(3)}} + \tfrac{3}{2}\big), \\ &\psi^{(\Gamma)}(n_{A_1^{(1)}}, n_{A_1^{(2)}}, n_{A_1^{(3)}}) = \Phi_{n_{A_1^{(2)}}}(Q_{A_1^{(2)}} - Q^0_{A_1^{(2)}}(\Gamma))\Phi_{n_{A_1^{(2)}}} \\ &\qquad \times (Q_{A_1^{(2)}} - Q^0_{A_1^{(2)}}(\Gamma))\Phi_{n_{A_1^{(3)}}}(Q_{A_1^{(3)}} - Q^0_{A_1^{(3)}}(\Gamma))|\Gamma\rangle, \end{aligned} \tag{45}$$

here $\Gamma = {}^5A_1^{(1)}, {}^5A_2$,

$$Q^0_{A_1^{(i)}}(\Gamma) = -\frac{\upsilon^{(i)}_{A_1}(\Gamma)}{\hbar\omega} \equiv a_i{}^{(\Gamma)}, \qquad \upsilon^{(i)}_{A_1}(\Gamma) = \nu^{(i)}_{A_1}(\Gamma) - \nu^{(i)}_{A_1}({}^5B_1), \quad (i = 1\text{–}3),$$

$$\varepsilon^{(\Gamma)} = \Delta^{(\Gamma)} - \frac{1}{2\hbar\omega}((\nu^{(1)}_{A_1}(\Gamma))^2 + (\nu^{(2)}_{A_1}(\Gamma))^2 + (\nu^{(3)}_{A_1}(\Gamma))^2).$$

The shape of the absorption band arising from the ${}^5B_1 \rightarrow {}^5A_1^{(1)}$ and ${}^5B_1 \rightarrow {}^5A_2$ transitions is described as follows:

$$\begin{aligned} F_4(\Omega) = \sum_{\Gamma={}^5A_1{}^{(1)},{}^5A_2} \Bigg\{ & \frac{1}{3}\mathrm{Exp}\left[-\frac{(a_1{}^{(\Gamma)})^2}{2}\coth\left(\frac{\beta}{2}\right)\right]\mathrm{Exp}\left[-\frac{(a_2{}^{(\Gamma)})^2}{2}\coth\left(\frac{\beta}{2}\right)\right] \\ & \times \mathrm{Exp}\left[-\frac{(a_3{}^{(\Gamma)})^2}{2}\coth\left(\frac{\beta}{2}\right)\right] \sum_{n_1,n_2,n_3=-\infty}^{\infty} I_{n_1}\left(\frac{(a_1{}^{(\Gamma)})^2}{2Sh(\beta/2)}\right) I_{n_2}\left(\frac{(a_2{}^{(\Gamma)})^2}{2Sh(\beta/2)}\right) \\ & \times I_{n_3}\left(\frac{(a_3{}^{(\Gamma)})^2}{2Sh(\beta/2)}\right)\mathrm{Exp}\left[\frac{n_1\beta}{kT}\right]\mathrm{Exp}\left[\frac{n_2\beta}{kT}\right]\mathrm{Exp}\left[\frac{n_3\beta}{kT}\right]\frac{1}{\sqrt{2\pi\lambda^2}} \\ & \times \mathrm{Exp}\left[-\frac{(\varepsilon^{(\Gamma)} - \varepsilon^{{}^5B_1} + \hbar\omega(n_1+n_2+n_3) - \hbar\Omega)^2}{2\lambda^2}\right]\frac{|\langle\Gamma \parallel d_{\tilde{\Gamma}} \parallel {}^5B_1\rangle|^2}{2}\Bigg\}, \end{aligned} \tag{46}$$

where $\tilde{\Gamma} = B_1, B_2$ for $\Gamma = {}^5A_1^{(1)}, {}^5A_2$, respectively. The contribution $K_4(\Omega) \sim \Omega F_4(\Omega)$ of the $CrSe_2S_2$ species to the total absorption spectra was calculated with the aid of parameters given in tables 1 and 5, and it is depicted in figure 4 (curve 2). It is obvious that this species gives the highest contribution to the band arising from impurity chromium clusters with mixed ligand surroundings. The position of the maximum of the band belonging to $CrSe_2S_2$ species almost coincides with that for the total band (figure 4, curve 4) originating from all $CrSe_{4-y}S_y (y = 1\text{–}3)$ species with mixed ligand surroundings.

7. Comparison of theory and experiment. Concluding remarks

The total absorption spectrum of the $CdSe_{0.6}S_{0.4}{:}Cr^{2+}$ crystal has been calculated by summation over partial spectra arising from all species described above taking into account their statistical weights obtained in section 2. The form-function of the absorption band arising from the $CdSe_{0.6}S_{0.4}{:}Cr^{2+}$ system can be presented in the following form:

$$F(\Omega) = P_1F_1(\Omega) + P_2F_2(\Omega) + P_3F_3(\Omega) + P_4F_4(\Omega), \tag{47}$$

where the numerical values of the probabilities $P_i (i = 1\text{–}4)$ are given by equation (2). For numerical calculation of the absorption coefficient $K(\Omega) \sim \Omega F(\Omega)$ at 300 K the parameters given in tables 1–5 were used. Insofar as all optical transitions participating in the formation of the absorption band of the $CdSe_{0.6}S_{0.4}{:}Cr^{2+}$ crystal are symmetry allowed for the first approximation in calculations the values of the matrix elements $|\langle\Gamma \parallel d_{\tilde{\Gamma}} \parallel \Gamma'\rangle|^2$ were taken as equal. In figure 5 the experimental and calculated spectra are shown together. Insofar as the theoretical calculations make it possible to separate the contributions of different $CrSe_{4-y}S_y$ species $(y = 0\text{–}3)$ to the total spectrum both the contributions of species with mixed ligand surroundings and $CrSe_4$ species are presented in figure 5. Figure 5 clearly demonstrates that the main contribution to the absorption spectra comes from species $CrSe_{4-y}S_y (y = 1\text{–}3)$ with mixed ligand surroundings. Namely, these species are responsible for the observed blue shift of the absorption band in the infrared range. Quite good agreement with the experiment was found.

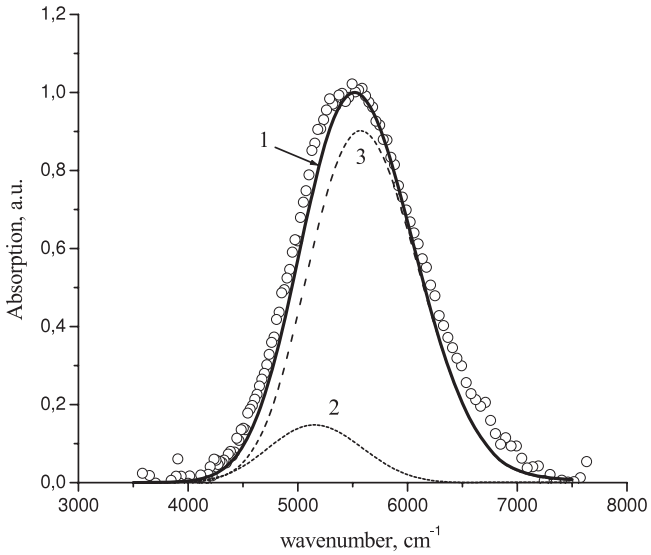

Figure 5. Absorption band of the $CdSe_{0.6}S_{0.4}:Cr^{2+}$ at $T = 300$ K, with circles showing experimental data [5]: 1, total calculated spectrum: 2, partial contribution of the $CrSe_4$ species: 3, partial contribution of species $CrSe_3S_1$, $CrSe_2S_2$, $CrSe_1S_3$ with mixed ligand surroundings.

The results obtained can be summarized as follows. Here we have presented a model of optical spectra of $CdSe_{0.6}S_{0.4}:Cr^{2+}$ crystals that takes into account the possibility of formation of impurity clusters with mixed ligand surroundings. The most probable nearest neighbour arrangements of the Cr^{2+} ion are found to include (i) four selenium atoms, (ii) three selenium and one sulfur atom or three sulfur and one selenium atom, (iii) two selenium and two sulfur atoms. For these arrangements of the Cr^{2+} ion the crystal field acting on this ion and the interaction of the d-electrons with the vibrations of the nearest ligand surroundings were considered in a realistic model of the crystal field with allowance for covalency effects. For all impurity clusters $CrSe_{4-y}S_y$ ($y = 0$–3) the crystal field splittings and the vibronic coupling parameters have been microscopically calculated. Then, on this basis the vibronic JT problems have been defined and solved numerically. The total spectrum of the $CdSe_{0.6}S_{0.4}:Cr^{2+}$ crystal calculated by summation over partial spectra arising from all mentioned species is in good agreement with the experimental one.

In order to discuss the real $CdSe_{0.6}S_{0.4}:Cr^{2+}$ system in more detail the adopted model needs to be generalized in several aspects. A new computational approach to the problem of optical spectra of the $CrSe_4$ cluster that takes into account all active vibrations interacting with Cr^{2+} ion should be developed. In calculations for the clusters $CrSe_{4-y}S_y$ ($y = 0$–3), the frequencies of the vibrations were taken in accordance with the composition of the nearest surrounding ligand. This question is also in need of special consideration. In spite of these restricting assumptions, the developed model gives a simultaneous explanation in its framework of the experimental data on both $CdSe_{0.6}S_{0.4}:Cr^{2+}$ and $CdSe:Cr^{2+}$ crystals and reflects the main features of the observed spectra.

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Appendix

(a) Symmetry adapted vibrational coordinates for the $CdSe_3S:Cr^{2+}$ complex of C_{3v} symmetry:

$$
\begin{aligned}
q^{(1)}_{A_1} &= \frac{[(2x_1 - x_2 - x_3 + \sqrt{3}y_2 - \sqrt{3}y_3)\sqrt{\frac{m}{12}} - (z_1 + z_2 + z_3)\frac{M}{3\sqrt{m}} + z_4\sqrt{M}]}{\sqrt{M + m + \frac{M^2}{3m}}}\\
q^{(2)}_{A_1} &= \frac{[-(2x_1 - x_2 - x_3 + \sqrt{3}y_2 - \sqrt{3}y_3)\frac{M}{\sqrt{12m}}(1 + \frac{M}{3m}) - (z_1 + z_2 + z_3)\frac{M}{3\sqrt{m}} + z_4\sqrt{M}]}{\sqrt{\frac{M^2}{m}(1 + \frac{M}{3m}) + \frac{M^2}{3m} + M}}\\
q^{(1)}_{E_x} &= \frac{[-\frac{M}{3\sqrt{m}}(2x_1 + \frac{x_2}{2} + \frac{x_3}{2} - \frac{\sqrt{3}}{2}y_2 + \frac{\sqrt{3}}{2}y_3) + \sqrt{M}x_4 + \sqrt{\frac{m}{6}}(2z_1 - z_2 - z_3)]}{\sqrt{\frac{2M^2}{3m} + M + m}}\\
q^{(2)}_{E_x} &= \frac{\frac{M}{3\sqrt{m}}\left(2x_1 + \frac{x_2}{2} - \frac{\sqrt{3}}{2}y_2 + x_3 + \frac{\sqrt{3}}{2}y_3\right) + \frac{M}{\sqrt{6m}}\left(1 + \frac{2M}{3m}\right)(2z_1 - z_2 - z_3) - \sqrt{M}x_4}{\sqrt{\frac{2M^2}{3m} + \frac{M^2}{m}(1 + \frac{2M}{3m})^2 + M}}\\
q^{(1)}_{E_y} &= \frac{[-\frac{M}{2\sqrt{3m}}(-x_2 + \sqrt{3}y_2 + x_3 + \sqrt{3}y_3) + \sqrt{\frac{m}{2}}(z_2 - z_3) + \sqrt{M}y_4]}{\sqrt{\frac{2M^2}{3m} + M + m}}\\
q^{(2)}_{E_y} &= \frac{[\frac{M}{2\sqrt{3m}}(-x_2 + y_2 + x_3 + \sqrt{3}y_3) + \frac{M}{\sqrt{2m}}(1 + \frac{2M}{3m})(z_2 - z_3) - \sqrt{M}y_4]}{\sqrt{\frac{2M^2}{3m} + \frac{M^2}{m}(1 + \frac{2M}{3m})^2 + M}}
\end{aligned}
\tag{A.1}
$$

where m and M are the masses of selenium and sulfur atoms, respectively. The numbering of ligands in (A.1) and further on corresponds to that given in figure 1.

(b) Symmetry adapted vibrational coordinates for the $CdSe_2S_2:Cr^{2+}$ complex of C_{2v} symmetry

$$
q^{(1)}_{A_1} = \frac{[(x_1 - x_4 + y_1 - y_4)\sqrt{\frac{M}{4}} + (x_3 - x_2 + y_2 - y_3)\sqrt{\frac{m}{4}} + (z_1 + z_4)\sqrt{\frac{M}{2}} - (z_2 + z_3)\sqrt{\frac{m}{2}}]}{\sqrt{\frac{M^2}{m} + 2M + m}}
$$

$$
q^{(2)}_{A_1} = \frac{[(x_1 - x_4 + y_1 - y_4)\sqrt{\frac{M}{4}} - (x_3 - x_2 + y_2 - y_3)\frac{M}{\sqrt{4m}}]}{\sqrt{M + \frac{M^2}{m}}}
$$

$$
q^{(3)}_{A_1} = \frac{[(x_1 - x_4 + y_1 - y_4)\sqrt{\frac{M}{4}} + (x_3 - x_2 + y_2 - y_3)\sqrt{\frac{m}{4}} - \frac{m}{\sqrt{2M}}(z_1 + z_4) + (z_2 + z_3)\sqrt{\frac{m}{2}}]}{\sqrt{M + 2m + \frac{m^2}{M}}}
$$

$$
q_{A_2} = \frac{[(x_1 - y_1 - x_4 + y_4)\sqrt{\frac{M}{4}} + (x_3 + y_3 - x_2 - y_2)\sqrt{\frac{m}{4}}]}{\sqrt{M + m}}
$$

$$q_{B_1} = \frac{[(x_1 + y_1 + x_4 + y_4)\sqrt{\frac{M}{4}} - (x_2 + y_2 + x_3 + y_3)\frac{M}{\sqrt{4m}} + (z_1 - z_4)\sqrt{\frac{M}{4}}]}{\sqrt{\frac{M^2}{m} + 2M}}$$

$$q_{B_2} = \frac{[(x_1 - y_1 + x_4 - y_4)\sqrt{\frac{M}{4}} - (x_2 - y_2 + x_3 - y_3)\frac{M}{\sqrt{4m}}]}{\sqrt{\frac{M^2}{m} + M}} \tag{A.2}$$

where, as in (A.1), m and M are the masses of the selenium and sulfur atoms, respectively.

The operators $v_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}(\boldsymbol{r})$ corresponding to the vibrational coordinates $q_{\bar{\mu}\bar{\Gamma}\bar{\gamma}}$ have been obtained with the aid of relations (7) and (A.1), (A.2).

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