High pressure luminescence of ZnTe:Cr$^{2+}$ crystals

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Abstract. Results of the high pressure low-temperature luminescence measurements of ZnTe:Cr$^{2+}$ crystals in a diamond-anvil cell are reported. The luminescence spectra associated with the $^5E \rightarrow ^5T_2$ transitions are split into three bands which exhibit quite different pressure coefficients from about 8 to 12 cm$^{-1}$. The different values of the pressure coefficients are well explained by the Jahn–Teller effect and pressure-dependent spin–orbit interaction with second-order correction, associated with pressure-dependent admixture of the Te ligand wavefunction to the d-type wavefunction of the Cr$^{2+}$ ion.

Contents

1. Introduction 2
2. Experimental 2
3. Experimental results 3
4. Discussion of the results 4
   4.1. $^5E \leftrightarrow ^5T_2$ emission and absorption 4
   4.2. Effect of hydrostatic pressure 8
5. Conclusions 9
Acknowledgment 10
References 10

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1. Introduction

Cr$^{2+}$ ion is a well-known optically active center in II–VI chalcogenides, which exhibits tunable mid-infrared laser action at room temperature in those compounds [1]. The broadband luminescence spectrum of such materials is a result of a crystal field splitting and a strong electron–phonon coupling. The Cr$^{2+}$ ion activated II–VI compounds were investigated optically as well as by electron paramagnetic resonance (EPR). They exhibit broad absorption and emission bands peaking near 5000 cm$^{-1}$, associated with optical transitions between the lowest $^5T_2 \leftrightarrow ^5E$ crystal field electronic terms [2]–[5]. The low-temperature EPR spectra show a nearly isotropic $g$-factor characteristic for the orbital singlet well separated from other terms [2]. All these observations were interpreted in terms of the crystal field theory extended to account the influence of various ligands (S, Se and Te) and including the Jahn–Teller (JT) instability of the $^5T_2$ and $^5E$ terms [3, 4]. Generally, all observations can be quantitatively described by the use of the effective parameters in the assumed interaction spin hamiltonian. Some parameters obtained from the fit to experimental spectra are not critically dependent on the shape of spectroscopic lines or their position. Thus some doubts remained as to whether the interpretation is in accord with observations. The present study was initiated by observation of the pronounced dependence of $^5E \rightarrow ^5T_2$ emission in ZnTe : Cr$^{2+}$ on hydrostatic pressure. Therefore, in this work, we partly reinterpret the previous observation in order to obtain an explanation, which includes the pressure dependence of the luminescence structure.

2. Experimental

High-pressure measurements were performed using a Diacell Products MCDAC-1 diamond-anvil cell. Argon was applied as a pressure-transmitting medium. The diamond-anvil cell was mounted onto an Oxford 1204 cryostat equipped with a temperature controller for low-temperature measurements. The R$_1$ ruby luminescence line was used as a reference pressure sensor. The polished single-crystalline samples about 30 µm thick were loaded into the cell along with a small piece of ruby. The emission spectra were excited by the 514.5 and 488 nm argon-ion laser lines and measured with the use of a DIGIKROM 240 monochromator equipped with a Judson J13TE2 thermoelectrically cooled PbS detector and a SR530 model Stanford Research lock-in amplifier. The spectra were corrected for the quantum efficiency of the system. To measure the luminescence, the argon-ion laser line was focused either on the measured ZnTe:Cr sample or on the ruby. The pressure calibration with the use of ruby luminescence was performed at low temperature. However, the pressure was changed at room temperature in order to minimize non-hydrostatic effects that are known to exist in diamond-anvil cells, especially at higher pressures. The hydrostatic conditions could be partially monitored by recording the half-width of the ruby emission. In our measurements, we observed an increase in the half-width of ruby luminescence with pressure growth. However, the half-width of the R$_1$ ruby luminescence did not exceed 5 cm$^{-1}$ at high pressures (2.5 cm$^{-1}$ at ambient pressure; 1 meV = 8.065 cm$^{-1}$). This means that the non-hydrostatic effects were rather weak.
Figure 1. The luminescence spectra of the ZnTe:Cr$^{2+}$ crystal as a function of hydrostatic pressure at $T = 10$ K, excited by the 514 nm argon-ion laser line. Letters at the top of the graph denote the luminescence peaks.

Figure 2. Pressure dependencies of the spectral position of the Cr$^{2+}$ luminescence maxima in the ZnTe:Cr crystal at $T = 10$ K. The pressure coefficients $k_i$ of the peaks of the luminescence bands are given in the graph.

3. Experimental results

Figure 1 shows the $^5E \rightarrow ^5T_2$ emission band of ZnTe:Cr$^{2+}$ as a function of hydrostatic pressure. As compared with a similar emission for ZnSe:Cr$^{2+}$ [5] the fine structure consisting of three peaks (marked on the graph) is clearly resolved.

In figure 2, the pressure dependence of the maxima for the corresponding lines is drawn. The shift of the lines on average as a whole is due to the increase in the strength of the

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cubic crystal field $\Delta = 10Dq$. The energy separation between the lines is increased too. At this moment, we mention that further we shall interpret this splitting as the combined action of the JT instability in the excited $^5E$ term and the spin–orbit (SO) splitting in the ground term $^5T_2$. As compared with ZnSe:Cr$^{2+}$ the average shift is 20–25% larger. This is related to the lower value of the bulk modulus $B_0 = 510$ kbar for ZnTe as compared with the value of $B_0 = 624$ kbar for ZnSe crystals [6, 7].

4. Discussion of the results

4.1. $^5E \leftrightarrow ^5T_2$ emission and absorption

The ligands surrounding Cr$^{2+}$ ions in II–VI compounds are tetragonally distorted along one of the cubic axes. Since none of the axes is statistically preferred, we consider in detail the distortion along the $z$-axis only. The description of tetragonal distortion caused by JT coupling differs from that given by the classical tetragonal crystal field. Both descriptions are used to interpret the optical spectra. However, there is only a limited compatibility between the parameters derived within the framework of both descriptions. This point will be discussed by making the parallel considerations.

The ground $^5T_2$ term is strongly coupled to $e$-type JT distortion (the T-e problem). The matrix of distortion energy along only $z$-axis is given as [8]:

$$E(T) = V_T \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix} Q_{3z^2-r^2}. \quad (1)$$

In the point-charge approximation of ligands, the value of $V_T$ is equal to:

$$V_T = Z \frac{8\sqrt{2}}{7} \left[ \frac{\langle r^2 \rangle}{R_0^4} + \frac{20\langle r^4 \rangle}{27 R_0^6} \right]. \quad (2)$$

where $Z$ is a ligand charge. To explain consistently the previous absorption/emission and EPR studies with these high pressure emission studies, we draw one-electron levels and many-electron terms with account for the JT instability and SO coupling. Figure 3 shows occupation of one-electron levels appropriate for the $^5T_2$ term.

In figure 3, the JT splitting assuming a positive sign of the corresponding JT coupling constants $V_T$ is shown. The slope of $t_2$ d levels is proportional to the coefficients entering the matrix (1) and the scaling due to $V_T$ is omitted. The e levels change according to the matrix for $^5E$ term as given below. The occupation on the left side of figure 3 originates in the energy gain of $E_{JT} = V_T^2 / k$, where $k$ is the elastic force constant. The occupation on the right side gives energy gain $E_{JT}/4$ and does not correspond to real physical situation. The splitting of the $^5T_2$ term corresponding to occupation in figure 3 is shown in figure 5 and it is caused by the compression along the $z$-axis. If one assumes a negative $V_T$, then it is necessary only to change the direction of the axis of distortion $Q_{3z^2-r^2}$. The tetragonal crystal field splitting of $^5T_2$ is given as [9]

$$E(^5E) = Bs - 4Ft, \quad (3)$$

$$E(^5B_2) = -2Bs + Ft, \quad (4)$$
where \( s = 2(r^2)/7 \), \( t = 8(r^4)/21 \), \( B \) and \( F \) are numerical coefficients. These energies can be partly derived from the JT coupling matrix. Looking at the formula for \( V_T \) one can recognize that the first term in brackets, when multiplied by \( Q_{3z^2-r^2} \), can be associated with \( B_s \), while the second one—with \( F_t \). The analogy is not full because \( F_t \) enters expressions (4) and (5) with opposite sign and different coefficients. The point is that we consider the JT coupling linear in displacements \( Q_{3z^2-r^2} \). There is also a term quadratic in the displacement, which produces in the lowest order the contribution proportional to \( \langle r^4 \rangle \), which gives additional contribution to \( F_t \). Equivalently this quadratic term can be considered as a correction to the elastic energy term. The expression of types (4) and (5) are usually derived by Stevens method of equivalent operators [8] and is totally based on the proper account of defect symmetry.

In the case of the \( ^5E \) term there is also a coupling to tetragonal distortion (the E-e problem). The coupling energy matrix is the following:

\[
E(E) = V_E \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} Q_{3z^2-r^2}. \tag{5}
\]

The JT coupling constant for this term is equal to

\[
V_E = Z \frac{8}{7} \left[ \frac{\langle r^2 \rangle}{R_0^2} - \frac{5}{9} \frac{\langle r^4 \rangle}{R_0^4} \right]. \tag{6}
\]

The \( \sigma_z \) Pauli matrix is the coupling energy matrix and apart from the sign differs from that in the custom description of E-e problem [10], which does not coincidence with the convention of the classical tetragonal distortion of the crystal field. The first term in brackets in the expression for \( V_T \) and \( V_E \) is the same while the second enters with the opposite sign. From this follows that \( |V_E| < |V_T| \). One electron occupation for the \( ^5E \) term is shown in figure 4 and the corresponding terms are shown in figure 5. When \( ^5T_2 \rightarrow ^5E \) transitions take place the \( ^5E \) term splitting is governed by \( V_E \) but they take place at distortion coordinate \( Q_{3z^2-r^2} = -V_T/k \). Therefore the resulting splitting of \( ^5E \) term (it is not at its equilibrium distortion) is proportional to \( V_E V_T \). Using the expression for the JT energy in the ground \( (E_{JT} = V_T^2/k) \) and in the excited term \( (E_{JT} = V_E^2/k) \) one can make replacements \( V_E V_T = \left( E_{JT} / E_{JT} \right) 2k = \sqrt{E_{JT} / E_{JT}} E_{JT} E_E 2k \).
Figure 4. The occupation of one-electron d orbitals appropriate for the excited $^5E$ term. The JT splitting (without inclusion of the elastic energy) under tetragonal distortion $Q_{3z^2-r^2}$ is shown. Provided $V_T > 0$, the energy minimum corresponds to elongation along the $z$-axis.

Figure 5. The configuration diagram of absorption/emission transitions between the $^5T_2 \leftrightarrow ^5E$ terms. The JT splitting (with inclusion of the elastic energy) under tetragonal distortion $Q_{3z^2-r^2}$ is shown. The energy minima in the ground and excited terms correspond to contraction or expansion along the $z$-axis. The end states of emission are split due to combined action of JT and SO coupling (not shown here).

The separation between terms $^5A_1$ and $^5B_1$ is equal to $4E_{JT}(a v)$. The tetragonal crystal field splitting of the $^5E$ term is given as [9]

$$E(^5A_1) = 2Bs + 64Ft,$$  \hfill (7)

$$E(^5B_1) = -2Bs + Ft.$$  \hfill (8)

Again, the $Bs$ term can be associated with the first term in brackets in expression (6) for $V_E$ while the second term is associated with $Ft$. The tetragonal crystal field expression also contains the contribution from the quadratic JT coupling (this coupling is responsible for the warping
of the ‘Mexican Hat’ surface in the E-e problem). After the absorption process the electron configuration changes from \(t_{2g}^2e_{g}^2\) to \(t_{2g}^1e\) and the new equilibrium is searched for. The \(3E\) term has two equilibrium distortions (see figure 5) but since the previous equilibrium corresponds to the compression, the smallest elastic energy change will correspond to equilibrium coordinate \(Q_{3g^2-t^2} = -V_E/k\). The separation between the \(3E\) and \(3B_2\) terms at the equilibrium coordinate \(Q_{3g^2-t^2} = -V_E/k\) is equal to \(3E_{IT}(av)\). After the emission, a process of relaxation of ligands occurs to coordinate \(Q_{3g^2-t^2} = -V_T/k\). The principal difference between the treatment of tetragonal distortion in terms of the classical crystal field theory and the JT distortion is the following. The classical crystal field model assumes that equilibrium distortion in all terms is the same as in the ground one (this is the basic assumption of the Tanabe–Sugano diagrams) [10]. In other words, the distortion does not depend on electron sharing among the \(t_{2g}\) electron orbitals. Since the absorption spectra are rather broad (also due to the thermal motion) it is possible only to determine the rough value of \(B_\gamma\). The JT description of distortion takes into account the dependence of equilibrium distortion on the particular electron configuration. However, the formulae for \(V_T\) and \(V_E\) based on the point charge model are not precise enough for numerical estimation. The JT description correctly distinguishes the absorption/emission of electrons among \(t_{2g}\) orbitals and associates it with the adjacent lattice relaxation. However, it is possible to conclude that \(V_T\) and \(V_E\) have the same sign and that \(|V_E| < |V_T|\). The energies of many electron terms and assumed transitions in \(Cr^{2+}\) ion are shown. Now, we will explain the possible physical situation of the particular experiments. This will remove some seeming controversies between various observations.

In the equilibrium configuration of the \(5T_2\) term the JT coupling is so strong that the SO coupling within this term is quenched [8]. The exponent in the Ham quenching factor \(\gamma = \exp(-3E_{JT}/2\hbar\omega)\) can be even around \(-10\), so that off-diagonal matrix elements of SO coupling are negligible. Here, \(\hbar\omega\) is the value of effective energy of the tetragonal vibrational mode. For this reason, the \(g\)-factor for the orbitally nondegenerate term is nearly isotropic across ZnS, ZnSe, ZnTe and CdTe crystals. The \(3B_2 \rightarrow 3E\) absorption is a broad band without structure. It is centered on \(3E_{JT} \approx 1000\) cm\(^{-1}\) across II–VI compounds [4]. Similarly the higher energy absorption \(3B_2 \rightarrow 5B_1\) and \(3B_2 \rightarrow 5A_1\) is a single broad band centered on \(\Delta\). The absorption to excited term is determined by the ligand distortion of the initial term. Since the amplitude of ligand distortion in the excited term \(5E\) is different, i.e. \(V_T \neq V_E\), the ligands change their position so as to adjust to the equilibrium position for the new electronic configuration \(e^1t_{2g}^3\) in the \(3E\) term. We note that due to the \(e^1t_{2g}^3 \rightarrow e^1t_{2g}^3\) electronic configuration change both the tetragonal distortion and also the breathing type distortion change. Then the emission transitions proceed from the lowest level determined by ligand deformation corresponding to the excited term. Now the splitting of \(3T_2\) is governed by \(V_T\) but at the equilibrium coordinate \(Q_{3g^2-t^2} = -V_E/k\). Since the amplitude of \(V_E\) is much smaller than \(V_T\) and the equilibrium distortion for the lowest and excited terms are far apart, the action of factor \(\gamma\) in the nonequilibrium \(5T_2\) term is ineffective. As a result, the emission line characterizes the combined action of JT distortion with the \(3E_{JT}(av)\) energy and the SO interaction. The splitting of the \(5T_2\) term under the mentioned condition is shown in figure 5 at zero pressure. From this follows that \(5T_2 \leftrightarrow 3E\) absorption/emission transitions carry totally different information because the details of the initial and final states are not the same. Immediately after the emission the \(5T_2\) level relaxes (by means of ligands displacement) to its new equilibrium position.
4.2. Effect of hydrostatic pressure

In principle, the hydrostatic pressure is equivalent to the displacement of ligands in the breathing mode fashion towards the central Cr$^{2+}$ ion. At ambient conditions, the breathing mode coupling constant (analogue of JT coupling constants) is $V_A = 0$. This is a condition of the equilibrium interatomic distance $R_0$. Application of pressure makes $V_A \neq 0$ and produces resistance against applied pressure. Since the cubic field $\Delta \propto 1/R^5$, the application of pressure increases $\Delta$, i.e. the average energy distance between the $5E-5T_2$ terms increases. As concerns the tetragonal distortion, the breathing and tetragonal mode transform according to different irreducible representations and there is no interference between them. However, the tetragonal mode coupling constants $V_E$ or $V_T$ are estimated at pure cubic crystal field distance $R_0$ which is changed by applied pressure. As a result, the tetragonal coupling mode constants $V_E$ or $V_T$, described by equations (2) and (6), increase in the point ion model approximation proportionally $1/R^4 - 1/R^6$. Thus, similarly to $\Delta$, the hydrostatic pressure effectively increases the tetragonal distortion. Since the JT distortion energy is proportional to $V^2$, it means that the average change of $E_{JT} \propto 1/R^{10}$ (provided that the force constant $k$ changes negligibly).

According to the point ion approximation, the cubic crystal field parameter $\Delta$ and the tetragonal field parameter $D = 3E_{JT}$ change with the pressure as

$$\Delta = \Delta_0 \left( \frac{R_0}{R} \right)^5,$$

$$D = 3E_{JT} = D_0 \left( \frac{R_0}{R} \right)^{10},$$

where $(R_0/R)$ changes with pressure $P$ according to Murnaghan’s equation of state [11] as

$$\left( \frac{R_0}{R} \right) = \left( \frac{PB_0'}{B_0} + 1 \right)^{1/B_0'},$$

where $B_0$ is the bulk modulus and $B_0'$ is its pressure derivative. Solving the secular equation for the JT interaction and SO interaction in the $|L, M, S, M_S\rangle$ basis, we use an approximation where the diagonal matrix elements for $5T_2$ and $5E$ states change with pressure as $\Delta_0(R_0/R)^5 + E_{JT}(R_0/R)^{10}$ and $\Delta_0(R_0/R)^5 - 2E_{JT}(R_0/R)^{10}$, respectively. We note that these relations are only approximately valid because we consider only linear JT coupling. Additionally to the pressure dependence of the diagonal matrix elements we included into calculation the following approximate dependence on pressure of SO $\lambda = \lambda_0(R_0/R)^4$ (here $\lambda$ corresponds to $\lambda_1$ in the notation of [2]. This approximation can be very roughly justified by the covalency effects which remarkably change $\lambda$ of Cr$^{2+}$. This change is due to the admixture of ligands electronic functions to the d function, so the effective function of d electrons is not limited to the volume occupied by the Cr$^{2+}$ ion. The interaction matrix elements of 3d electrons with ligands can change as $(R_0/R)^{7/2}$ [12]. This mainly contributes to the variation of $\lambda$ with the pressure. If the effective SO coupling constant is averaged over such an extended function then there are contributions from the atomic SO constants of the ligands. From atomic calculations it is known that the single electron SO coupling constant of Te is more than 10 times larger than that for the Cr$^{2+}$ ion [13]. Also the SO coupling constant of Te is much larger than those of S and Se [13]. Therefore, the modification of amplitude of SO interaction is not surprising and explains the much stronger pressure effect on Cr$^{2+}$ ions in ZnTe in comparison with previously studied Cr$^{2+}$-doped ZnSe [5].
and ZnS [14]. We also included in the second order of perturbation theory of the SO coupling between the $^5T_2$–$^5E$ terms, which gives a contribution proportional to $\lambda^2/\Delta$. Vallin suggests [2] that the SO constant between these terms is negative (in his notation $\lambda_2$). However, this does not cause problems in the calculation because the corresponding correction is proportional to $\lambda^2$. The results of such calculations are shown in figure 6.

Qualitatively, the pressure dependence of calculated emission shows the main feature observed in the experiment, shown in figure 1. The splitting into three bands having different pressure coefficients is well reproduced. However, the calculated pressure coefficients differ slightly from those observed in the experiment. In view of our discussion, we cannot firmly say that the used parameters $\lambda$ and $E_{JT}(av)$ (extracted from those determined in literature $E_{JT}(T)$ and $E_{JT}(E)$, are the most suitable. Perhaps one needs to use more parameters but, as we already mentioned, the methods of their determination are not very sensitive to the features of the experimental spectra.

5. Conclusions

The effect of pressure on luminescence spectra of Cr$^{2+}$ in ZnTe exhibits a strong difference in comparison with previously studied ZnSe:Cr$^{2+}$ and ZnS:Cr$^{2+}$. Observed pressure coefficients of luminescence peaks associated with $^5E \rightarrow ^5T_2$ transitions are different for Cr$^{2+}$ ions in ZnTe, which has not been observed for ZnSe and ZnS. This effect can be explained by the pressure-dependent modification of the SO interaction constant associated with pressure-dependent admixture of the Te ligand wavefunction to the wavefunction of the central Cr$^{2+}$ ion. The much smaller SO constants for Se and S ligands do not produce such an effect. This phenomenon is another manifestation of the nephelauxetic effect [15, 16], commonly observed in the pressure dependence of the luminescence of transition-metal and rare-earth ions.
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