Supplemental Material to "An individual Cr atom in a semiconductor quantum dot: optical addressability and spin-strain coupling"

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In this supplemental material, we first describe the influence of strain on the fine structure of a Cr atom embedded in a II-VI zinc-blende semiconductor. We then present the complete electron-hole-Cr spin effective Hamiltonian used to model a low symmetry singly Cr-doped II-VI quantum dot. We finally present additional data on Cr-doped quantum dots: the temperature dependence of the PL of X-Cr and some statistics on the energy splitting of X-Cr and X^2-Cr.

CR ENERGY LEVELS IN A II-VI SEMICONDUCTOR

Cr atoms are incorporated into II-VI semiconductors as Cr^{2+} ions on cation sites forming a deep impurity level. The ground state of a free Cr^{2+} is ^{5}D with the orbital quantum number L=2 and a spin S=2 yielding a 25-fold degeneracy. In the crystal field of T_d symmetry of the tetrahedral cation site in zinc-blende crystal, the degeneracy is partially lifted (see Fig. 1): the ^{5}D term splits into 15-fold degenerate orbital triplet $^5T_2$ and 10-fold degenerate orbital doublet ^{5}E. The Jahn-Teller distortion reduces the symmetry to D_{2d} and leads to a splitting of the $^5T_2$ ground state into a 5-fold degenerate $^5B_2$ orbital singlet and a ^{5}E orbital doublet .

The ground state orbital singlet $^5B_2$ is further split by the spin-orbit interaction. In a strain free crystal, it was found that the ground state splitting can be described by the spin effective Hamiltonian [1]:

$$\mathcal{H}_{Cr,CF} = D_0 S_z^2 + \frac{1}{180} F[35S_z^2 - 30S(S+1)S_z^2 + 25S_z^2] + \frac{1}{6} a[S_1^4 + S_2^4 + S_3^4] \quad (1)$$

with the Cr spin S=2 and $|D_0| \gg |a|, |F|$. In the model presented here, we use $a = 0$ and $F = 0$. The x, y, z principal axes were found to coincide with the cubic axes (1,2,3) giving rise to three identical sites, each given by (1) but with the z axis of each along a different cubic axis (1,2,3). A value of $D_0 \approx +30\mu eV$ was estimated from Electron Paramagnetic Resonance (EPR) measurements in highly diluted bulk (Cd,Cr)Te [1].

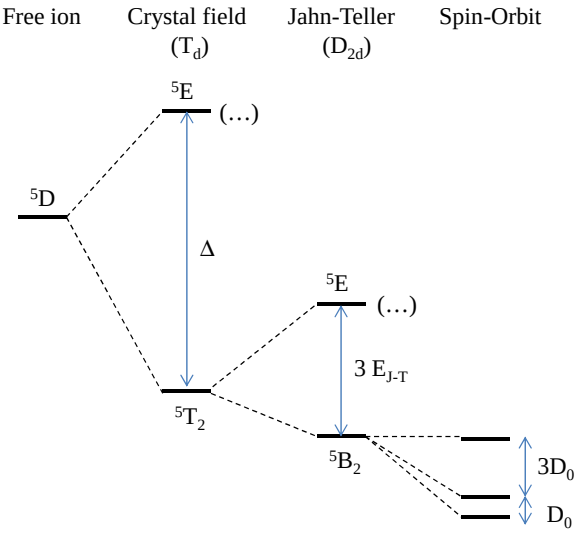

FIG. 1: Scheme of the energy level splitting of Cr^{2+} at a cation site in II-VI compounds having zinc blende structure (T_d) with a crystal field parameter Δ, a Jahn-Teller energy E_{J-T} and a spin-orbit level spacing D_0.

Static biaxial compressive strain in the (001) plane, as observed in self-assembled quantum dots, reduces the symmetry to D_{2d} and destabilize the Cr 3d orbitals d_{xz} and d_{yz} having an electron density pointing along the [001]

axis (z axis). The Cr ground state is then a 5-fold degenerated orbital singlet formed from the d_{xy} orbital. It corresponds to the Jahn-Teller ground state with a tetragonal distortion along the [001] axis [2].

An applied stress will also influence the Cr spin fine structure splitting through the modification of the crystal field and the spin-orbit interaction [1]. For an arbitrary strain tensor, the general form of the Cr ground state spin effective Hamiltonian is

$$\mathcal{H}_{Cr,\varepsilon} = c_1 e_A S_\theta + c_2 e_\theta S_\theta + c_3 e_\epsilon S_\epsilon + c_4 e_\zeta S_\zeta + c_5 (e_\xi S_\xi + e_\eta S_\eta) \tag{2}$$

with S_i defined as:

$$\begin{aligned} S_\theta &= S_z^2 - \frac{1}{2}[S_x^2 + S_y^2] \\ S_\epsilon &= \frac{1}{2}\sqrt{3}[S_x^2 - S_y^2] \\ S_\xi &= S_y S_z + S_z S_y \\ S_\eta &= S_x S_z + S_z S_x \\ S_\zeta &= S_x S_y + S_y S_x \end{aligned} \tag{3}$$

and e_i defined similarly as:

$$\begin{aligned} e_\theta &= \varepsilon_{zz} - \frac{1}{2}[\varepsilon_{xx} + \varepsilon_{yy}] \\ e_\epsilon &= \frac{1}{2}\sqrt{3}[\varepsilon_{xx} - \varepsilon_{yy}] \\ e_\xi &= \varepsilon_{yz} + \varepsilon_{zy} \\ e_\eta &= \varepsilon_{xz} + \varepsilon_{zx} \\ e_\zeta &= \varepsilon_{xy} + \varepsilon_{yx} \\ e_A &= \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \end{aligned} \tag{4}$$

For flat self-assembled quantum dots with dominant large biaxial strain we have a strain tensor:

$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_\parallel & 0 & 0 \\ 0 & \varepsilon_\parallel & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix} \tag{5}$$

with

$$\varepsilon_{zz} = -2\frac{C_{11}}{C_{12}}\varepsilon_\parallel \tag{6}$$

where $C_{11} \approx 5.4\ 10^{10} Pa$ and $C_{12} \approx 3.7\ 10^{10} Pa$ are the elastic constants of CdTe [3]. For this strain configuration, the Cr fine structure is controlled by the spin-lattice coupling coefficients c_1 (symmetric coefficient) and c_2 (tetragonal coefficients). Strain-coupling coefficients estimated from EPR measurements in bulk Cr doped CdTe are listed in table I.

TABLE I: Values for spin to strain coupling coefficients of Cr in bulk CdTe (in meV) extracted from ref.[1].

c_1	c_2	c_3	c_4	c_5
-0.25±2	+4.9 ±2	-1.25±0.5	+4.9±2	+3.7±1.25

For a pure CdTe layer lattice matched on ZnTe, we have $\varepsilon_\parallel = (a_{ZnTe} - a_{CdTe})/a_{CdTe} \approx -5.8\%$ with $a_{CdTe} = 6.48\mathring{A}$ and $a_{ZnTe} = 6.10\mathring{A}$. The strain controlled part of the spin Hamiltonian $\mathcal{H}_{Cr,\varepsilon}$ becomes:

$$\mathcal{H}_{Cr,\varepsilon_\parallel} = \frac{3}{2}\varepsilon_\parallel[2c_1(1-\frac{C_{12}}{C_{11}}) - c_2(1+2\frac{C_{12}}{C_{11}})]S_z^2 = D_0 S_z^2 \tag{7}$$

where we can estimate $D_0 \approx 1\pm0.6$ meV from the values of the spin-strain coupling coefficients in CdTe (table I). However one should note the quantum dots could be partially relaxed and may contain a significant amount of Zn. We were not able to find spin to strain coupling coefficients for Cr in ZnTe and (Cd,Zn)Te alloy in literature. A value of $D_0 \approx +280\mu$eV, much larger than for CdTe, was however estimated in strain-free Cr-doped bulk ZnTe [1]. Larger spin-strain coupling coefficients could then expected for Cr in ZnTe and (Cd,Zn)Te alloys.

Finally, an anisotropy of the strain in the quantum dot plane (001) with principal axis along [010] or [100] axes ($\varepsilon_{xx} \neq \varepsilon_{yy}$ and ε_{xy}=ε_{yx}=0) would affect the Cr fine structure through the tetragonal coefficient c_3. This coupling can be described by an additional term in the spin-strain Hamiltonian

$$\mathcal{H}_{Cr,\varepsilon\perp} = \frac{3}{4}c_3(\varepsilon_{xx}-\varepsilon_{yy})(S_x^2 - S_y^2) = E(S_x^2 - S_y^2) \tag{8}$$

This anisotropy term E couples Cr spin states separated by two units and in particular S_z=+1 to S_z=-1 which are initially degenerated. It could be exploited to induce a large strain mediated coherent coupling between a mechanical oscillator and the Cr spin [4].

OPTICAL TRANSITIONS IN A CR-DOPED QUANTUM DOT

The complete electron-hole-Cr Hamiltonian in self-assembled quantum dot ($\mathcal{H}_{X-Cr}$) can be separated into six parts:

$$\mathcal{H}_{X-Cr} = \mathcal{H}_{Cr,\varepsilon} + \mathcal{H}_{c-Cr} + \mathcal{H}_{mag} + \mathcal{H}_{e-h} + \mathcal{H}_{band} + \mathcal{H}_{scat} \tag{9}$$

$\mathcal{H}_{Cr,\varepsilon}$ describes the fine structure of the Cr atom and its dependence on local strain as presented in the previous section.

$\mathcal{H}_{c-Cr}$ describes the coupling of the electron and hole with the Cr spin. It reads

$$\mathcal{H}_{c-Cr} = I_{eCr}\overrightarrow{S}.\overrightarrow{\sigma} + I_{hCr}\overrightarrow{S}.\overrightarrow{J} \tag{10}$$

with I_{eCr} and I_{hCr} the exchange integrals of the electron ($\overrightarrow{\sigma}$) and hole ($\overrightarrow{J}$) spins with the Cr spin ($\overrightarrow{S}$).

An external magnetic field couples via the standard Zeeman terms to both the Cr spin and carriers spins and a diamagnetic shift of the electron-hole pair can also be included resulting in

$$\mathcal{H}_{mag} = g_{Cr}\mu_B\overrightarrow{B}.\overrightarrow{S} + g_e\mu_B\overrightarrow{B}.\overrightarrow{\sigma} + g_h\mu_B\overrightarrow{B}.\overrightarrow{J} + \gamma B^2 \tag{11}$$

The electron-hole exchange interaction, $\mathcal{H}_{e-h}$, contains the short range and the long range parts. The short range contribution is a contact interaction which induces a splitting δ_0^{sr} of the bright and dark excitons and, in the reduced symmetry of a zinc-blend crystal (T_d), a coupling δ_2^{sr} of the two dark excitons. The long range part also contributes to the bright-dark splitting by an energy δ_0^{lr}. In quantum dots with C_{2v} symmetry (ellipsoidal flat lenses for instance [5]) the long range part also induce a coupling δ_1 between the bright excitons. Realistic self-assembled quantum dots have symmetries which can deviate quite substantially from the idealized shapes of circular or ellipsoidal lenses. For a C_s symmetry (truncated ellipsoidal lens), additional terms coupling the dark and the bright excitons have to be included in the electron-hole exchange Hamiltonian. Following Ref. [5], the general form of the electron-hole exchange Hamiltonian in the heavy-hole exciton basis $|+1\rangle$, $|-1\rangle$, $|+2\rangle$, $|-2\rangle$ for a low symmetry quantum dot (C_s) is

$$\mathcal{H}_{e-h} = \frac{1}{2}\begin{pmatrix} -\delta_0 & e^{i\pi/2}\delta_1 & e^{i\pi/4}\delta_{11} & -e^{i\pi/4}\delta_{12} \\ e^{i\pi/2}\delta_1 & -\delta_0 & e^{-i\pi/4}\delta_{12} & -e^{-i\pi/4}\delta_{11} \\ e^{-i\pi/4}\delta_{11} & e^{i\pi/4}\delta_{12} & \delta_0 & \delta_2 \\ -e^{-i\pi/4}\delta_{12} & -e^{i\pi/4}\delta_{11} & \delta_2 & \delta_0 \end{pmatrix} \tag{12}$$

TABLE II: Values of the parameters used in the model of Cr-doped CdTe/ZnTe quantum dot presented in figure 3 of the main text. The value of the parameters not listed in the table is 0. The chosen values are typical for CdTe/ZnTe quantum dots and can be compared with parameters extracted from Mn-doped quantum dots [7, 8].

I_{eCr}	I_{hCr}	δ_0	δ_1	δ_{12}	δ_{11}	$\frac{\delta_{xz}}{\Delta_{lh}}$	$\frac{\delta_{xx,yy}}{\Delta_{lh}}$	D_0	g_{Cr}	g_e	g_h	γ	η	T_{eff}
μeV	μeV	meV	μeV	μeV	μeV			meV				$\mu eV/T^2$	μeV	K
-70	-280	-1	250	150	50	0.05	0.05	2.5	2	-0.7	0.4	1.5	25	25

The terms δ_{11} and δ_{12}, not present in symmetry C_{2v}, give an in-plane dipole moment to the dark excitons [6]. The term δ_{12} which couples $|\pm 1\rangle$ and $|\mp 2\rangle$ excitons respectively is responsible for the dark-bright anti-crossing observed on the low energy side of the emission of Cr-doped quantum dots.

The band Hamiltonian, $\mathcal{H}_{band} = E_g + \mathcal{H}_{vbm}$, stands for the energy of the electrons (i.e. the band gap energy E_g), and the heavy-holes (hh) and light-holes (lh) energies ($\mathcal{H}_{vbm}$) [7, 8]. To describe the influence of a reduced symmetry of the quantum dot on the valence band, we considered here the four lowest energy hole states $|J, J_z\rangle$ with angular momentum $J = 3/2$. A general form of Hamiltonian describing the influence of shape or strain anisotropy on the valence band structure can be written in the basis $(|\frac{3}{2}, +\frac{3}{2}\rangle, |\frac{3}{2}, +\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle)$ as:

$$\mathcal{H}_{vbm} = \begin{pmatrix} 0 & -Q & R & 0 \\ -Q^* & \Delta_{lh} & 0 & R \\ R^* & 0 & \Delta_{lh} & Q \\ 0 & R^* & Q^* & 0 \end{pmatrix} \tag{13}$$

with

$$Q = \delta_{xz} - i\delta_{yz}; R = \delta_{xx,yy} - i\delta_{xy} \tag{14}$$

Here, R describes the heavy-hole / light-hole mixing induced by an anisotropy in the quantum dot plane xy and Q takes into account an asymmetry in the plane containing the quantum dot growth axis z. The reduction of symmetry can come from the shape of the quantum dot (Luttinger Hamiltonian) or the strain distribution (Bir and Pikus Hamiltonian). Δ_{lh} is the splitting between lh and hh which is controlled in quantum dots both by the in-plane biaxial strain and the confinement.

Considering only an in-plane anisotropy (Q=0), it follows from (13) that the valence band mixing couples the heavy-holes $J_z = \pm 3/2$ and the light-holes $J_z = \mp 1/2$ respectively. For such mixing, the isotropic part of the short range exchange interaction, which can be written in the form $2/3\delta_0^{sr}(\overrightarrow{\sigma}.\overrightarrow{J})$, couples the two bright excitons. This mixing is also responsible for a weak z-polarized dipole matrix element of the dark excitons coming from the light-hole part of the hole wave function.

A deformation in a vertical plane (Q term) couples the heavy-holes $J_z = \pm 3/2$ and the light-holes $J_z = \pm 1/2$ respectively. In this case, the short range electron-hole exchange interaction couples $|+1\rangle$ and $|+2\rangle$ exciton on one side and $|-1\rangle$ and $|-2\rangle$ exciton on the other side.

For a general description and as it was observed in Mn-doped quantum dots [8–10], we can also take into account the perturbation of the wave function of the exciton in the initial state of the optical transition by the hole-Cr exchange interaction. This perturbation depends on the value of the exchange energy between the Cr spin S_z and the hole spin J_z and can be represented, using second order perturbation theory, by an effective spin Hamiltonian [8–10]

$$\mathcal{H}_{scat} = -\eta S_z^2 \tag{15}$$

with $\eta > 0$.

Using the Hamiltonian of the excited state $\mathcal{H}_{X-Cr}$ and the Hamiltonian of the ground state

$$\mathcal{H}_{Cr} = \mathcal{H}_{Cr,\varepsilon} + g_{Cr}\mu_B \overrightarrow{B}.\overrightarrow{S} \tag{16}$$

we can compute the spectrum of a quantum dot containing a Cr atom. The occupation of the X-Cr levels is described by an effective spin temperature T_{eff} and the optical transitions probabilities are obtained calculating the matrix

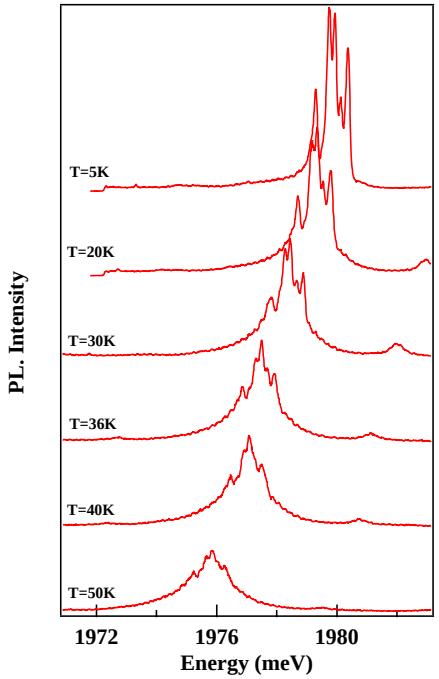

FIG. 2: Temperature dependence of the photoluminescence of X-Cr in a Cr-doped QD (QD4 in the main text).

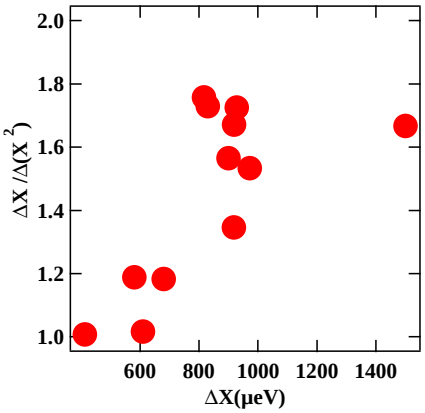

FIG. 3: Ratio of the overall splitting (i.e energy difference between the two extreme bright exciton lines) of X^2-Cr and X-Cr as a function of the splitting of X-Cr for 12 different Cr-doped QDs.

elements $|\langle S_z|X, S_z\rangle|^2$ where X and S_z stands for the 8 possible exciton states and the Cr spin respectively. The resulting photoluminescence spectra calculated with the parameters listed in table II are presented in figure 3 of the main text.

COMPLEMENTARY DATA ON PHOTOLUMINESCENCE OF CR-DOPED QUANTUM DOTS

The temperature dependence of the X-Cr emission in QD4 at zero magnetic field is presented in figure 2. With the increase of the temperature, we observe a significant line broadening induced by the interaction with acoustic phonons. In the investigated temperature range where we still obtain a significant PL intensity and resolved PL lines (below T=50K), no contribution of the $S_z=\pm 2$ Cr spins states are observed in the emission of the exciton.

Figure 3 presents some statistics on the values of the overall energy splitting of X-Cr (ΔX) and X^2-Cr (ΔX^2) obtain on 12 Cr-doped quantum dots. For most of the investigated dots, ΔX remains below 1 meV and ΔX^2 is also smaller than ΔX suggesting an interaction between the Cr spin and the biexciton.

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