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Exciton-phonon coupling in a CsPbBr₃ single Nanocrystal

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We have performed micro-photoluminescence measurements on a single CsPbBr₃ nanocrystal (NC) with size comparable to the Bohr diameter (7 nm). When the NC has an orthorhombic crystal symmetry, we observe an exciton fine structure composed of three peaks linearly polarized. We took advantage of the polarization properties of micro-photoluminescence to monitor *in situ* both the energy and linewidth of individual peaks when increasing temperature. We reveal that two regimes exist, at low and high temperature, which are dominated by acoustic or longitudinal optical phonons (Fröhlich term) couplings, respectively. The acoustic contribution does not change when the energy of the excitonic transition varies in the range 2.46 and 2.62 eV, *i.e.* with NC sizes corresponding to this range. We find that line broadening is mainly ruled by the Fröhlich term, which is consistent with the polar nature of CsPbBr₃.

Keywords: perovskite nanocrystals, CsPbBr₃, acoustic and optical phonons, exciton-phonon couplings, exciton fine structure, quantum dots.

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Since the first synthesis¹ of all-inorganic halide perovskite nanocrystals (NCs), these nanomaterials have attracted great attention due to their outstanding optical properties. Their emission wavelength can be tuned from ultraviolet to infra-red by substitution of halogen atoms or by using confinement effects (i.e. by changing the NC size). These NCs show a very high efficiency of emission ranging from 50 % to 90 % even at room temperature and without surface shelling thanks to a defect tolerant band structure.^{2,3} This represents a great difference with II-VI colloidal NCs for which such high efficiencies were obtained in core/shell hetero-structures. Recently, taking advantage of all these properties, different studies have explored applications of perovskite NCs in low-threshold lasers,⁴⁻⁶ LED emitters,⁷ photodetectors⁸ and single-photon sources.⁹⁻¹¹

In this letter, we address the exciton-phonon interaction in a single CsPbBr₃ NC. This interaction is responsible for the broadening of the excitonic spectral line. This is of a great importance for optoelectronic properties and performances of this material, and leads to a better knowledge and understanding of which mechanisms are active as far as the electron-phonons interactions are concerned.

Perovskite NCs are grown at 110 °C by using previously described methods.¹ Low temperature micro-photoluminescence (μ -PL) experiments were performed on highly diluted phases spin-coated on a glass with a spectral resolution of 50 μ eV. We used a CW Ar laser emitting at 475 nm with an average excitation power of 2.5 μ W and a confocal-like microscope with NA = 0.6 to excite and measure the μ -PL.¹² A large majority of single NC spectra exhibit a structure composed of a set of three lorentzian-shaped peaks, a triplet, as shown in Fig. 1(a, b). Fig. 1(c) shows a typical triplet trace of a single NC: the signal is stable on hundreds of seconds and spectral jumps are observed that may shift the three lines only by an amount equal to their linewidths. These observed temporal fluctuations are correlated on the three lines which proves that the response of a single NC is measured. The narrow linewidths observed are smaller than the typical linewidth of excitonic peaks (1 meV) observed in bulk CsPbX₃ (X = Cl, Br)¹³ or hybrid perovskites CH₃NH₃PbI₃ (5 meV)¹⁴, and smaller or comparable with already published single NC data of CsPb(Br/Cl)₃,⁹ CsPbBr₃¹⁵ and CsPbI₃.¹⁶ Several authors have associated these triplets to the emission of a band-edge exciton in NCs having an orthorhombic symmetry.¹⁵ Indeed, band-edge excitons are constituted of a hole with a total angular momentum $J^h = \frac{1}{2}$ and a z projection $J_z^h = \pm \frac{1}{2}$ and an electron with a total angular momentum $J^e = \frac{1}{2}$, and projection $J_z^e = \pm \frac{1}{2}$. In an orthorhombic crystal the four-fold degenerate exciton is

split into four levels with a dark state at the lowest energy and three bright states linearly polarized, with orthogonal polarizations (see the inset scheme, Fig. 1(a)). Polarization measurements were performed and confirmed this attribution. We added a motorized half-wave plate followed by an analyser (its direction is parallel to the grating grooves in order to obtain the largest response) before the spectrometer entrance. By rotating the half-wave plate we obtain polar diagrams as shown in Fig. 1(b). Two peaks present linear and crossed polarizations, in agreement with the scheme of the inset in Fig. 1(a). They are accompanied by a third peak of much lower amplitude with a not clearly defined polarization and corresponding to the emission from a state linearly polarized along the direction of PL collection.

To address the exciton-phonon coupling in single CsPbBr₃ NCs, we took advantage of the peak-polarization properties to monitor *in situ* the temperature dependence of the homogeneous emission linewidth of nine lines with emission energies between 2.46 eV and 2.62 eV at 5 K. The full width at half maximum (FWHM) of these lines has been obtained thanks to a Lorentzian fit of the more intense line among the fine structure components or by fitting the selectively detected linearly polarized lines obtained after a careful analysis of the corresponding emission polar diagrams. To ensure that the line of the same given single object was unambiguously followed in temperature, we verified also that the temperature dependence of the energy of each line shows the same slope as the one in the bulk (see Figure 2).¹⁷ We underline that all these peaks concern NCs for which we observed a blue-shifted energy with respect to the bulk ($E_g = 2.33$ eV at 5 K), of the emission lines. From the blue-shift of PL maxima and using the expression of the confinement energy in a cube shaped NC, $\Delta_{Ec} = \frac{3\pi^2\hbar^2}{2\mu d^2}$, we are able for a reduced mass $\mu = 0.07$,¹ to estimate NC lengths, d , concerned by our study ($5 \text{ nm} \leq d \leq 8 \text{ nm}$) which are comparable to the Bohr diameter $2a_B = 7 \text{ nm}$.¹

Fig. 3 shows an example of the temperature dependence of the linewidth, $\gamma(T)$, for an emission line linearly polarized and selectively detected in the triplet shown in figure 3(a). The temperature evolution of the line (black dots in Figure 3(b)) shows an energy blue-shift of the μ -PL maximum and a broadening of the line, while keeping a Lorentzian profile (lines in Fig. 3(b)). Following Itoh and Furumiya for CuCl,¹⁸ we assume the same typical expression for the homogeneous linewidth of excitons in the bulk single crystal and in NCs. $\gamma(T)$ is therefore modeled as:

$$\gamma(T) = \gamma_0 + A_{ac}T + B_{LO}n_{LO}(T) \quad (1)$$

where γ_0 is a residual homogeneous linewidth including spectral diffusion supposed to be temperature independent. The second and third terms are homogeneous broadening terms resulting from acoustic and LO phonons (Fröhlich) scattering with charge-phonons coupling constants A_{ac} and B_{LO} , respectively.¹⁸⁻²¹ A_{ac} includes the deformation potential and piezoelectric couplings. $n_{LO}(T) = (\exp(\frac{E_{LO}}{k_b T}) - 1)^{-1}$ is the Bose-Einstein distribution function for the LO phonons and E_{LO} is an average representative energy for the weakly dispersive LO phonon branch.^{22,23} Eq. (1) was used to fit the $\gamma(T)$ data as shown in Fig. 3(c). For the FWHM extrapolated at zero temperature, we find $\gamma_0 = 400 \pm 80 \mu\text{eV}$. We performed our measurements under conditions of non-resonant excitation, and the homogeneous linewidth might then be modified by charge distribution, or by defects, in the NC environment. Under resonant excitation very narrow linewidths ($\approx 1 \mu\text{eV}$) were observed in $\mu\text{-PL}$, for example in InGaAs/GaAs quantum dots.²⁴ Under non-resonant excitation and using a high-resolution spectroscopy method called correlation Fourier spectroscopy L. Coolen *et al.* have found a linewidth of $6.5 \mu\text{eV}$ in CdSe/ZnS NCs at 10 K.²⁵

In our experiments, exciton-LO phonons coupling reveals more important as compared to the coupling with acoustic phonons. This is due to the strong Fröhlich interaction in such a polar system as CsPbBr₃. Nevertheless, the acoustic phonons scattering linear part is clearly measurable. The average values obtained for A_{ac} is $8 \pm 3 \mu\text{eV/K}$ and for B_{LO} $42 \pm 15 \text{ meV}$, using 16 meV or 130 cm^{-1} for E_{LO} ($T_{phonon LO} = E_{LO}/k_B = 185 \text{ K}$) (see TABLE I).

Line	γ_0 (meV)	A_{ac} ($\mu\text{eV/K}$)	B_{LO} (meV)	E_{Line} (eV)
1	0.35	5	48	2.620
2	0.55	6	38	2.479
3	0.32	12	54	2.465
4	0.40	12	58	2.524
5	0.32	10	26	2.473
6	0.37	5	27	2.464
7	0.48	5	49	2.575
8	0.42	7	60	2.481
9	0.33	10	21	2.482

TABLE I. Fit parameters obtained for nine spectral lines (each of them is a single component of the exciton fine structure) studied with increasing temperature, for $T_{phonon LO} = E_{LO}/k_B = 185 \text{ K}$ ($E_{LO} = 16 \text{ meV}$). The last column gives the emission energy at 5 K.

This average E_{LO} value is indeed found in bulk lead-bromine perovskites (see below).^{20,26–28} In our measurements we have advantaged the emissions at the highest energies, and so emphasized the characteristics of the smallest single objects, with a size close to the exciton Bohr diameter. In this regime, Itoh *et al.*¹⁸, for CuCl microcrystals, and Schoenlein *et al.*²⁹, for CdSe NCs, have found values of A_{ac} close to 20 and 10 $\mu\text{eV/K}$, respectively. Very recently Shinde *et al.*³⁰ have measured values of ≈ 15 $\mu\text{eV/K}$ on CsPbBr₃ NC ensembles with sizes around the bulk Bohr diameter (7 nm). Even with this low number of examples, our mean value for A_{ac} seems typical to the cases of NCs with a size close to its bulk exciton Bohr size. No clear dependence of A_{ac} on the emission energy, and so on the NC, size has been evidenced here. A_{ac} is expected to be inversely proportional to the square of the NC size if the deformation potential contribution is dominant.^{18,31,32} Inversely for a NC size of the order of a_B , as for the case probed here, Takagahara has shown that A_{ac} is on the other hand almost size independent if the piezoelectric coupling to acoustic phonons is dominant.^{31,32} Hence the rather weak energy dependence (i.e. size dependence) of our A_{ac} values seems to evidence the main contribution of the piezoelectric coupling of excitons to phonons in a polar semiconductor as CsPbBr₃.

The LO phonon energy E_{LO} of 16 meV is somewhat lower than those typically obtained for a large range of bulk inorganic semiconductors other than lead-halide perovskites.^{20,21} On the other hand, it is close to the one obtained as an extracted linewidth parameter for some bulk hybrid-lead-halide perovskites including a Pb-I lattice (≈ 11.5 meV) or a Pb-Br lattice (≈ 15.5 meV) as in the present case for CsPbBr₃.^{20,28} A combined experimental and numerical study for orthorhombic phases assigns these energies to LO phonon modes related to internal vibrations of the Pb-halide network.³³ In CsPbBr₃, energies of phonons responsible for local polar fluctuations close to 125 cm^{-1} at room temperature²⁶ and 135 cm^{-1} at 80 K²⁷ have been also reported. Moreover, the Fröhlich constant B_{LO} we obtained through our data analysis is not so far from values measured in the bulk hybrid lead halide perovskites already mentioned, formamidinium (FA)/methylammonium (MA)-PbI₃ (40 ± 5 meV) or FA/MA-PbBr₃ (61 ± 7 meV)²⁰ and CdSe/ZnS core shell NCs (22 ± 7 meV).³⁴

In conclusion, we have characterized exciton-phonon coupling above 5 K and extracted the acoustic and Fröhlich (LO) exciton-phonon coupling constants. We conclude that there is no dependence of the acoustic contribution on the energy of the excitonic transition between 2.46 and 2.62 eV. This points out that the piezoelectric term has the dominant role, in agreement with theoretical predictions stating that no NC-size dependence should be expected for NC sizes of the order of the Bohr diameter. By extrapolating our single NC measurements until room

temperature, we obtain that the PL linewidth of CsPbBr₃ NCs would be in the order of 10 meV. This value sets a lower limit to the spectral width of the gain curve that can be achieved in lasers based on CsPbBr₃ NCs. Further investigation is required to explain the residual broadening contribution at 5 K which is measured around 400 μ eV. This value leads to an estimation of the exciton coherence time of a few picoseconds at \sim 5 K. As the lifetime measurements in literature^{9,15} reveal an effective lifetime of the order of 100 ps for the lowest exciton bright state, coherence is therefore not limited by the lifetime but by phonons scattering and spectral diffusion. Further studies are needed to determine precisely (i) the nature of the lifetime, radiative or not, (ii) the role played by the dark exciton on the bright excitons decay time when these four fine structure exciton states can be thermally mixed and govern the luminescence dynamics.

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Figure Captions

FIG. 1. μ -PL of individual orthorhombic CsPbBr₃ NCs obtained at 5 K. (a) Spectrum of a typical triplet Inset: scheme of the exciton fine structure for an orthorhombic NC. Experimental data were fitted with three single Lorentzian peaks numbered 1, 2 and 3. (b) Polarization diagram of the shown triplet in (a). Polarization diagrams numbered 1, 2 and 3 correspond to each of the three peaks present in the μ -PL spectrum. In diagram number 1 the intensity enhancement at low starting and increasing angles is due to an experimental instability of the excitation conditions of the observed NC after the first three steps in the run (data not corrected). (c) Typical trace of a single orthorhombic NC: the solid and dashed lines indicate the time positions of the two cross sections represented in the inset.

FIG. 2. Temperature dependence of the energy of nine NC excitonic transitions observed in μ -PL. To each symbol is associated a given component of the fine structure. We find an average value of the Varshni coefficient $\alpha_{\text{aver.}} \approx 0.27$ meV/K, which compares well with the bulk value.

FIG. 3. (a) μ -PL spectrum at 5 K of the triplet that contains the line followed in temperature in part (b) without (upper spectrum) and with (lower spectrum) an analyser oriented along the middle-peak polarization axis (lower spectrum), (b) Evolution of the selected line with temperature. Experimental data (black dots) were fitted with a Lorentzian profile. (c) Evolution of the linewidth with temperature. Experimental data were fitted with Eq. (1).

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