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Enormous excitonic effects in bulk, mono- and bi- layers of cuprous halides using many-body perturbation technique

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ABSTRACT

Cuprous halides (CuX with X = Cl, Br, I), intensely studied about four decades ago by experimentalists for excitons, are again drawing attention of researchers recently. Potential of cuprous halide systems for device applications has not yet been fully explored. We go beyond the one-particle picture to capture the two-particle physics (electron-hole interaction to form excitons). We have deployed the full tool kit of many-body perturbation technique, GW approximation + Bethe Salpeter equation, to unfurl the rich excitonic physics of the bulk as well as layers of CuX. The negative spin-orbit contribution at the valence band top in CuCl, compared to CuBr and CuI, is in good agreement with experiments. We note that CuX have exceptionally strong excitons, defying the linear fit (between the excitonic binding energy and band gap) encompassing many semiconductors. The mono- and bi- layers of cuprous halides are predicted to be rich in excitons, with exceptionally large binding energies and the resonance energies in UV/visible region. Hence this work projects CuX layers as good candidates for optoelectronic applications. With advancement of technology, we look forward to experimental realization of CuX layers and harnessing of their rich excitonic potential.

1. Introduction

Wide band gap (WBG) semiconductors have strong luminescence in the visible region of the spectrum in response to the generation of a high concentration of excess charge carriers making them an inevitable candidate for optical applications. The majority of the white lighting systems are based on the InGaN based optical emitters [1–3], while semiconductors such as ZnO, ZnS, ZnSe, are used in flat panel displays and in lasing application [4,5]. The problem with the III–nitride materials is lattice-mismatching with substrates such as sapphire or SiC: a major factor leading to the generation of misfit dislocations affecting performance of the light emitting devices produced. Also continuous production of In based emitters will cause shortage of indium resources, currently at a critical stage [6]. These and some other issues certainly necessitate the search for new materials with better features which can replace the current materials. I–VII cuprous halides (CuX, X = Cl, Br, and I) have recently drawn attention in this context. Recent experiments on thin films of CuBr deposited by physical vapour deposition technique on a variety of substrates observed blue free-excitonic emission from the CuBr thin films [7]. Experiments on CuCl deposited on Si substrate illustrated that it is a promising novel material system for future WBG devices compatible with current electronic technology [8–10]. Only recently Koch [11] presented detailed UV/Vis emission spectra of these materials, showing that CuBr nicely extends the possible range of blue hues in the known emitter wavelength range. Good structural and lattice matching with GaAs and Si substrates, ease of deposition of CuBr via the vacuum evaporation method and efficient room-temperature free-excitonic emission can open the possibility of fabricating an alternative blue emitter based on CuBr technology.

Earlier experimental studies, mainly on the bulk and thin films of cuprous halides established that the physics of these systems is strongly affected by the presence of excitons [12–17]. However no theoretical studies for the same followed. Cuprous halides with ample experimental data at the bulk and thin-film level, and hitherto unexplored theoretically, make an ideal candidate for exploring not only at the bulk level but also in low dimensions for excitonic properties. Since density functional theory (DFT) level calculations fail to do justice to the excited states in general, we have employed the current state-of-the-art many-body perturbation technique for exploring excitons (a neutral excitation formed of interacting electron-hole pair) in the bulk as well as layers of CuX. Our results project CuX as possessing highly promising excitonic properties for optoelectronic applications.

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2. Computational details

The DFT calculations have been carried out using the VASP code [18,19] with generalised gradient approximation (GGA) for the exchange and correlation potential. We have employed the GW approximation [20] at different levels of sophistication to obtain the band gap. Bethe-Salpeter equation (BSE) [21] was then solved to obtain the exciton spectrum.

Bulk: We have studied the B3 phase (space group $F\bar{4}3\,m$) of CuX (X = Cl, Br, I) compounds which is their stable phase at ambient pressure. The unit cell consists of one Cu atom at (0, 0, 0) and one X atom at (1/4, 1/4, 1/4). The optimised lattice parameter, calculated using conjugate gradient algorithm with a force tolerance of 0.001 eV/Å, is 5.427, 5.723 and 6.085 Å for CuCl, CuBr and CuI, respectively. These values are in good agreement with the corresponding experimental values of 5.424, 5.695 and 6.054 Å [22], respectively.

Layers: To study the effect of lowering the dimensions on the excitons, we studied monolayer (ML) and bilayer (BL) of CuCl and CuBr. The monolayer represents an ideal 2-dimensional system theoretically. For free standing monolayers as well as bilayers, super cell geometry with a vacuum size of 25 Å was employed to ensure that these behave as isolated systems. We have studied the (111) crystallographic planes for the layers since experimentally it has been found to be the preferred direction for cuprous halide thin films [14,23]. The top view of CuX (111) plane and the side view of the super cell for (111) bilayer are shown in Fig. 1. As depicted, we note that for the layers stacked along ⟨111⟩ crystallographic orientation, each monolayer is a twin layer consisting of Cu atoms in a plane slightly shifted from the plane containing the X atoms. The Cu layers were kept fixed and the X layers allowed to relax using conjugate gradient algorithm with a force tolerance of 0.001 eV/Å while the in-plane cell vector was fixed at the bulk optimised value. Crystal structures and unit cells were visualized and drawn by using the VESTA package [24].

Electronic minimization was performed using a tolerance of 10^{-8} eV with a Gaussian smearing of the Fermi surface by 0.02 eV. The kinetic energy cutoff was set at 350 eV for self-consistency, and at 200 eV for response function. Excitonic properties were calculated by solving the Bethe Salpeter equation (BSE) in the $q \to 0$ limit. 200 unoccupied bands were included in the calculation. In order to obtain reliable binding energies it is of vital importance to fully converge the optical spectra. Also the excitonic binding energies are sensitive to the number of k points. So we did calculation for the convergence of BSE peaks w.r.t the number of k points in the BZ for the bulk CuX and found that 15 × 15 × 15 Gamma-centred **k** mesh is required for the converged results. At the same time due to the computational limitations for the layers which are supercell systems, we did the layer calculation with a fine mesh of 12 × 12 × 1 only. Spin-orbit (SO) interaction has been included in all our calculations.

3. Results and discussion

3.1. Band gap

The band gaps, E_g, calculated using local/semi-local approximations to the XC potential within DFT are well known to be underestimated. Our DFT band gaps are no exception, being only 0.472 eV, 0.455 eV and 0.980 eV for CuCl, CuBr, and CuI, respectively, close to previous calculations [28], but much too small compared to the experimental values of ~3 eV each [27,25,26]. Hence we next used GWA, one of the most successful approximations currently for calculating remarkably accurate band structures and band gaps for many materials. We started with GWA at the most common level: the single shot GW (usually called G_0W_0), i.e. the non-self-consistent evaluation of the quasi-particle self-energy, on top of some computationally less demanding scheme, GGA in our case. The band gaps thus obtained for various CuX systems, listed in Table 1, are consistent with earlier G_0W_0 results [29,30]: improved with respect to GGA gaps but still much smaller than the experimental gaps. Advancing to fully self-consistent GW (QPGW) calculations gives values in excellent agreement with the experimental band gaps for the bulk CuX (Table 1), signifying the renormalization of electronic energy bands due to many-body effects.

3.2. Spin-Orbit (SO) interaction and the excitons

The experimental investigations of the optical properties in the absorption edge region in bulk cuprous halides are concerned mainly with excitons, there being two excitons, namely $Z_{1,2}$ and Z_3 [14]. They arise from the coupling of the lowest conduction-band (CB) state Γ_6 electron to both the uppermost Γ_7 and Γ_8 valence-band (VB) holes [14,13]. The Γ_7 and Γ_8 states are formed from the SO splitting of the Γ_{15} state at the top of the VB which is a triply-degenerate state in the absence of SO interaction (Fig. 2). The spatial extent of the Γ_{15} d-levels is large, and their energies are close to those of the p-levels of the halogen. Therefore halogen-p and Cu-d levels strongly hybridize and,

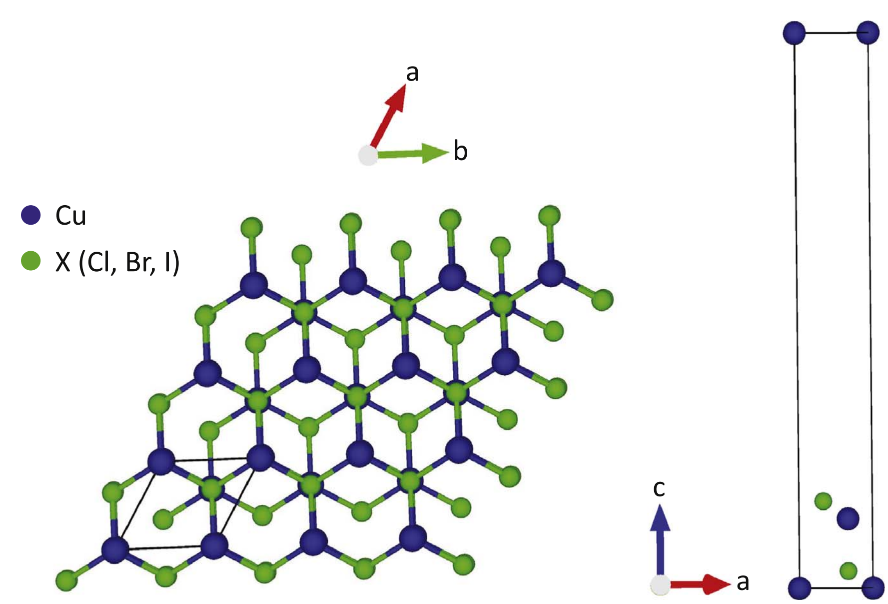

Fig. 1. (Left) Top view of the CuX (111) plane, with a unit cell marked. (Right) Side view (not to scale) of the unit cell for (111) bilayer.