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Excitonic effects in bulk CuBr using Time Dependent DFT

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Abstract: With a view towards studying the effect of lowering the dimensionality on excitons, we have first investigated the excitonic effects in bulk CuBr, which is a direct band-gap semiconductor with zinc blende structure. We have employed time-dependent density functional theory for this investigation. Both, the random phase approximation and the bootstrap approximation, for the exchange-correlation kernel are used. Our results show a strong signature of excitons in bulk CuBr and we expect this to be further enhanced on lowering the dimension, a work planned in near future.

Keywords: CuBr; Excitons; Time Dependent Density Functional Theory; Bootstrap kernel.

I. Introduction and calculational details:

Optical properties of semiconductors, their alloys and heterostructures are dominated by excitons whose behaviour provides a great deal of information about electronic structure, in general, and optical conductivity, in particular [1]. Copper halide semiconductors (CuCl, CuBr, CuI) crystallize under normal conditions in the zincblende (B3) phase (space group $F\bar{4}3m$) [2]. Both CuCl and CuBr are mixed ionic electronic semi conducting materials. CuBr has the advantage of superior electronic conductivity, better ambient and thermal stability. It has a large direct band gap (E_g), 2.91 eV [3], with large excitonic binding energies (108 meV) [4].

Here we report the signature of excitons in bulk CuBr using Time Dependent Density Functional Theory (TDDFT) [5]. Such a study has not been reported on CuBr earlier. TDDFT extends Density Functional Theory (DFT) into the time domain and is a formally exact method for studying optical spectra. In practice, however, accuracy of TDDFT results depends on the approximation for the exchange-correlation (XC) kernel. We have used Bootstrap approximation in the present work [6]. This kernel is known to give optical spectra in excellent agreement with experiments [6], and is computationally less expensive than solving the Bethe Salpeter equation, which is an exact technique for studying excitons. We also report the optical properties of CuBr using the usual random phase approximation (RPA) [7], which does not account for excitonic physics. We see a clear signature of excitons in bulk CuBr by comparing our TDDFT results with those of RPA.

We have studied the stable B3 phase of the bulk CuBr. The unit cell consists of one Cu atom at (0, 0, 0) and one Br atom at (1/4, 1/4, 1/4). All calculations are performed using the full potential linearized augmented

plane wave method as implemented in the Electrons in k-space (Elk) code [9]. This method is highly accurate but relatively computationally expensive compared to the pseudo-potential method. Hence structural optimisation was performed using the projector augmented wave method as implemented in the Vienna Ab-initio Simulation Package (VASP) [10]. The generalized gradient approximation (GGA) was employed for the exchange and correlation potential [11]. All the calculations are converged in terms of the cut-off energy for plane wave basis set and the size of the k-point mesh for the Brillouin zone integrations. For self-consistent convergence 408 k points and for density of states (DOS) calculations 1140 k points in the irreducible wedge of the Brillouin zone (IBZ) were used. Optical calculations are performed with 8000 k points in the IBZ.

II. Results and discussion:

Our calculated equilibrium value of the lattice constant $a = 5.723 \text{ \AA}$ agrees well with the reported value of $5.732 \text{ \AA}$ [12]. The partial DOS for Cu s, p, d states and Br-p states, along with total DOS of CuBr is shown in Fig.1. It shows that the main valence band (VB) is primarily composed of the Cu-d states, with a small contribution from the Br-p states, while the lower VB is mainly composed of Br-p states and some Cu-d states. Both the VBs are fairly narrow with band width of $\sim 2.5 \text{ eV}$ each. The conduction band (CB), sprawling over a wide range of energies, has main contribution from Br-3d and Br-3p states. Our calculated energy gap 0.464 eV is lower, as expected for DFT calculations, than the experiment [3].

The calculations for dielectric function, $\epsilon_2(\omega)$ are performed by scissor shifting the ground state Kohn-Sham (KS) energy eigenvalues to make the KS gap equal to the experimental value. Presence of excitons shows up as the shifting down of the spectral weight and enhancement of the peak as compared to the RPA results [6]. Our results are consistent with this finding. From Fig.2 it's clear that our TDDFT peak is enhanced and shifted slightly to lower energy compared to RPA results. The inset in Fig.2 shows the comparison of our RPA results with previously reported RPA result [8]. Though both the results are matching in the lower energy side, much discrepancy for higher energies suggests that previous work has not included enough range of the CB energies for calculating the optical transitions.

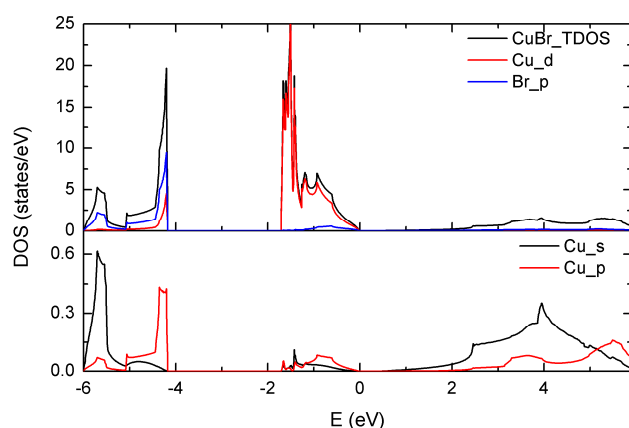
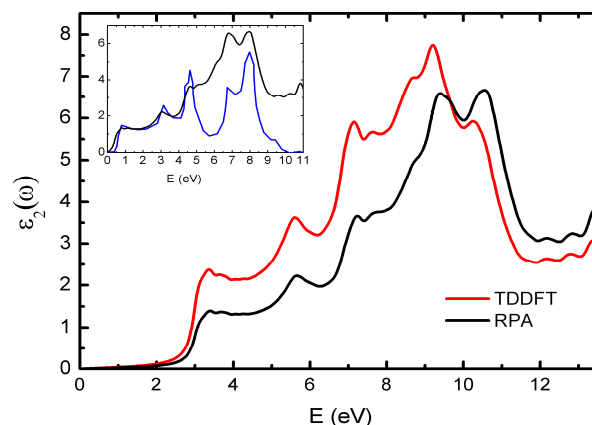


Figure.1. Total and partial DOS of CuBr. Energy zero is taken at the top of the valence band. Br-s states are deep lying at around -17 eV , hence not shown. Note that the y-scale in the lower panel is only up to $0.7 \text{ states per eV}$.



In summary, we find that the bootstrap kernel within the TDDFT calculations in bulk CuBr shows a strong signature of excitons which is an effective tool for studying electromagnetic interactions in systems. This is the starting step for our study to see the excitonic physics that emerges when the dimension of the system is lowered i.e. for monolayers and interfaces.

Figure.2. Imaginary part of dielectric function vs. photon energy. The inset shows our RPA result (Black curve) vs. previous calculation (Blue curve) from Ref. [8]. The results are scissor's shifted only in the main plot.

References:

1. Bajaj K K., Use of excitons in materials characterization of semiconductor system, Mater.Sci. Eng., 2001, R 34, 59-120.
2. Blacha A., Christensen N.E. and Cardona M., Electronic structure of the high-pressure modifications of CuCl, CuBr, CuI, Phys. Rev. B, 1986, 33, 2413-2421.
3. Ves S., Glotzel D., Cardona M. and Overhof H., Pressure dependence of the optical properties and the band structure of the copper and silver halides, Phys. Rev. B, 1981, 24, 3073.

4. Lucas F O., Cowley A., Daniels S. and McNally P.J., CuBr blue light emitting electroluminescent thin film devices, Phys. Status Solidi C 8, 2011, 9, 2919-2922.
5. Runge E. and Gross E.K.U., Density-Functional Theory for Time-Dependent Systems, Phys. Rev. Lett, 1984, 52, 997.
6. Sharma S., Dewhurst J.K., Sanna A. and E. K. U. Gross, Bootstrap Approximation for the Exchange-Correlation Kernel of Time-Dependent Density-Functional Theory, Phys. Rev. Lett, 2011, 107, 186401
7. Stephen L.Abler., Quantum Theory of the Dielectric Constant in Real Solids, Phys. Rev., 1962, 126, 413.
8. Amrani B., Benmessabih T., Tahiria M., Chibouba I., Hiadsia S. and Hamdache E, First principles study of structural, elastic, electronic and optical properties of CuCl, CuBr and CuI compounds under hydrostatic pressure, Physica B, 2006, 381, 179-186.
9. Elk open source code:<http://elk.sourceforge.net/>
10. Kresse G. and J. Hafner J., Ab initio molecular dynamics for liquid metals. Phys. Rev. B, 1993, 47,558.
11. Perdew J.P., Chevary J.A., Vosko S.H, Jackson K.A., Pederson M.R., Singh D.J. and Fiolhais C., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B, 1992, 46, 6671.
12. El Haj Hassan F., Zaoui A. and Sekkal W., Structural properties of copper halides, Mater. Sci Eng, 2001, B87, 40-47.
