Pressure-Induced Enhanced Optical Absorption in Sulvanite Compound Cu₃TaX₄ (X = S, Se, and Te): An *ab Initio* Study

Himanshu Joshi,* Amit Shankar, Nihal Limbu, Mahesh Ram, Amel Laref, Prasanta Kumar Patra, Oksana Bakhtiyarova Ismailova, Lalhriat Zuala, Suman Chatterjee, and Dibya Prakash Rai

**ABSTRACT:** *Ab initio* study on the family of ternary copper chalcogenides Cu₃TaX₄ (X = S, Se, and Te) is performed to investigate the suitability of these compounds to applications as photovoltaic absorber materials. The density functional theory based full potential linearized augmented plane wave method (FP-LAPW method) is employed for computational purposes. The electronic structure and optical properties are determined including electron–electron interaction and spin–orbit coupling (SOC), within the generalized gradient approximation plus Hubbard *U* (GGA+*U*) and GGA+*U*+SOC approximation. The large optical band gaps of Cu₃TaS₄ and Cu₃TaSe₄ considered ineffective for absorber materials, and also the hole effective mass has been modulated through applied pressure. These materials show extreme resistance to external pressure, and are found to be stable up to a pressure range of 10 GPa, investigated using phonon dispersion calculations. The observed optical properties and the absorption coefficients within the visible-light spectrum make these compounds promising materials for photovoltaic applications. The calculated energy and optical band gaps are consistent with the available literature and are compared with the experimental results where available.

1. **INTRODUCTION**

To fight issues like global warming and climate change, a viable long-term solution is the usage of renewable sources for energy generation. The development of sustainable and environmentally friendly high-performance semiconductors is of paramount importance in this regard. It will accelerate the progress of required technology for the production of renewable and green energy sources such as solar cells and photovoltaic and thermoelectric materials.¹ One such class of semiconductors is the ternary copper chalcogenides, forming the members of the family Cu₃−M−VI A₄ (M = V, Nb, Ta; and VI A = group VI A elements, generally chalcogen atoms S, Se, or Te), known as the sulvanite group of compounds. Recent theoretical and experimental works²−⁴ on sulvanite compounds report them to be indirect band gap semiconductors, exhibiting tunable photoemission properties, large optical band gaps, and excellent electro-optic properties.⁵,⁶ The nontoxic, as well as earth-abundant elemental constituents, have attracted further attention of researchers in investigating the potential application of these compounds. They have cubic symmetry, and interestingly their band gap increases in substitutional sequence V → Nb → Ta but decreases in the sequence S → Se → Te. This ability to selectively control the band gap by varying stoichiometry provides a broad range of applications⁷ and is highly potent to engineer photovoltaic materials for efficient visible-light absorption. Materials ideal for visible-light absorbers are direct band gap semiconductors such as Cu(In/Ga)Se₂ (CIGS), CdTe, and Cu₂ZnSn(S/Se)₄ (CZTSS),⁸ with an energy gap in the range of 1.5 eV and with an absorption coefficient as high as α = 10⁵ cm⁻¹.⁹ Although these materials have record efficiencies of 20.5%, 19.6%, and 12.6%, respectively,²⁰ the high toxicity of Cd and the rarity of In make these materials unsuitable for widespread application. Consequently, photovoltaic systems consisting of relatively abundant and environmentally amicable elements like Si, Al, Zn, Cu, S, P, and Se and fulfilling the above requirements have to be chosen. A potential emerging class of materials is perovskite hybrid halide compounds, with efficiency reaching up to 17%.¹¹,¹² However, the stability of these organic–inorganic hybrids is an issue, and long-term as well as high temperature stability is still questionable due to the weak chemical bonding of the organic cations.¹³

Studies on indirect band gap semiconductors like Si show that photovoltaic efficiency is determined mainly by the...
2. COMPUTATIONAL DETAILS

Developing and optimizing noble and improved materials in a laboratory is a lengthy, costly, and tedious task involving rigorous test series and expensive prototyping. *Ab initio* calculation methods are used to guide this process. Such calculations allow insights into the atomistic and electronic process, responsible for various material characteristics, thus assisting in avoiding the tedious laboratory task. In view of this ever growing significance of computational methods, these DFT based calculations serve as the backbone of this work. The DFT-based Wien2k code,

which implements the all-electron orbital-based FP-LAPW method, is employed. The ground states were determined with calculations performed within Perdew–Burke–Ernzerhof’s generalized gradient approximation (GGA).

The underestimation of the band gap magnitude with PBE is a well-known issue and is documented in almost every *ab initio* based report. This happens because band gap is expressed as the difference in eigenvalues of the conduction band minimum (CBM) and the valence band maximum (VBM). However, in exact Kohn–Sham DFT, they differ by a derivative discontinuity, \( \Delta_{XC} \) and the band gap is expressed as

\[
E_g = E_{g}^{KS} + \Delta_{XC}
\]  

where \( E_{g}^{KS} = \epsilon_{CBM} - \epsilon_{VBM} \). The derivative discontinuity in GGA and as well as in the local density approximation (LDA) is exactly zero (\( \Delta_{XC} = 0 \)) due to the unrealistic self-Coulomb repulsion accounted for by these functionals and is the reason for gap underestimation. One of many solutions to this issue is the correction of the self-Coulomb repulsion error by applying precise Hartee–Fock exchange, but it demands high computational time and resources. In such cases, the computationally cheap GGA+U method comes in handy, which includes the calculation of the onsite Coulomb self-interaction term (\( U \)) to reduce the self-Coulomb repulsion error, and is thus employed as a correction over GGA. Also, due to the presence of heavy atoms like Ta and Te in the system under investigation, the SOC interactions are considered (GGA+SOC and GGA+U+SOC) to accurately determine different electronic states in the electronic band structure. The method of incorporating \( U \) correction requires optimized \( U \) values, inspected either by first-principles calculation or by tuning the \( U \) value empirically, seeking agreement with the experimental results. However, \( U \) values optimized through first-principles
calculation have significantly low values and thus might not provide a noteworthy correction over the band gaps. Therefore, when no prior data are available, GGA+U is not a predictive approach, and in such cases, the semilocal exchange imposed by the modified Becke–Johnson (mBJ) potential is found to describe accurate band ordering with energy gaps being used. A value of \( U = 9.3 \text{ eV} \) was applied to Cu and Ta d states, which reproduced valence band features as well as band gaps comparable with experiments. The self-consistency criterion was achieved by setting energy convergence criterion to \( 10^{-5} \text{ Ry} \), and a dense \( k \)-mesh of \( 20 \times 20 \times 20 \) was considered in the first Brillouin zone. Experimental verifications on \( \text{Cu}_3\text{TaX}_4 \) \( (X = \text{S, Se, and Te}) \) have shown the absence of magnetic ordering in the materials. Therefore, constrained magnetic calculations were performed, using experimentally determined lattice constants to achieve experimental compatibility.

3. RESULTS

a. Structural Properties and Stability with High Pressure. Ternary copper chalcogenides \( \text{Cu}_3\text{TaX}_4 \) \( (X = \text{S, Se, and Te}) \) crystallize in cubic symmetry with space group \( P4\overline{3}m \) \((#215)\). The basis atom with \( \text{Cu}_i \) \((i = 1, 2, 3) \) and Ta and \( \text{X}_j \) \((j = 1, 2, 3, 4) \) is expressed in Bravais representation in the unit cell as:

\[
\begin{align*}
B_{\text{Cu}}^1 &= (1/2, 0, 0) \\
B_{\text{Cu}}^2 &= (0, 1/2, 0) \\
B_{\text{Cu}}^3 &= (0, 0, 1/2) \\
B_{\text{Ta}} &= (0, 0, 0) \\
B_{\text{X}}^1 &= (u, u, u) \\
B_{\text{X}}^2 &= (-u, -u, -u) \\
B_{\text{X}}^3 &= (-u, u, -u) \\
B_{\text{X}}^4 &= (u, -u, -u)
\end{align*}
\]

The Cu atoms occupy the edge, whereas Ta atoms lie at the corner of the cubic cell with tetrahedral coordination to the X atom \( (X = \text{S, Se, and Te}) \) and vacant cube center (Figure 1a). The structure can be considered as a 3D packing of the \( \text{M} \text{X}_4 \) tetrahedron and edge-sharing \( \text{Cu} \text{X}_4 \). Atomic distances inside the cell are highly sensitive to the internal parameter value \( (u) \) of the chalcogen atom. The distances \( \text{Ta} \text{X} \) and \( \text{Cu} \text{X}_i \) in ideal sulvanite structure with \( u = 0.25 \) are equal. Our calculated internal parameter values for S-, Se-, and Ta-based systems are, respectively, 0.2471, 0.2486, and 0.261; thus, for \( u > 0.25 \) (as in the case of \( \text{Cu}_3\text{TaTe}_4 \)), the Ta–X distance is longer than Cu–X, and for \( u < 0.25 \) (as in the case of \( \text{Cu}_3\text{TaS}_4/\text{Se}_4 \)), the Ta–X distance is shorter than Cu–X. The lattice constants were optimized within GGA, GGA+U, and GGA+SOC methods, determined by an energy vs volume fit with the third order Murnaghan’s equation of state. However, no significant differences were observed with the three methods, except that the GGA+U method overestimated the lattice constants by about 0.72%, and hence we present the results obtained by GGA (Table 1). The pressure variation of a lattice
constant with pressure was obtained by fitting the equilibrium lattice constant, bulk modulus, pressure derivative of the bulk modulus, and the equilibrium volume with Murnaghan’s equation of state. Figure 2 displays the dependence of optimized lattice constants with pressure, varied in the range of 0–10 GPa, and shows that with increasing pressure the lattice constant decreases following a linear relationship. From 0 to 10 GPa, the lattice constant changes by 8.6%, 8.75%, and 9.2%, respectively, for S, Se, and Te species, suggesting that Cu$_3$TaTe$_4$ is the most sensitive and Cu$_3$TaS$_4$ is the least sensitive to external pressure.

To check the feasibility in structure synthesis at high pressure, the formation energies ($E_f$) of the compounds were evaluated (Table 2). The results are based upon the GGA, GGA+SOC, and mBJ calculations performed at 10 GPa of pressure. All the compounds under investigation were found to be stable at least up to a pressure range of 10 GPa, verified from their phonon dispersion properties (Figure 2). However, with a slight increase in pressure above this range, Cu$_3$TaTe$_4$ showed a drastic increase in $E_f$ value from $-2.8$ eV/atom to $-0.03$ eV/atom, suggesting the decrease in feasibility of formation. Above 13 GPa pressure, similar characteristics were observed for Cu$_3$TaSe$_4$ whereas Cu$_3$TaS$_4$ was found to withstand pressure as high as 17 GPa. At pressure ranges below 10 GPa, no significant differences in the electronic and optical characteristics were observed and therefore are not discussed in detail. The formation energies were calculated as

$$E_f = \frac{1}{x+y+z} (E_{\text{Cu}_3\text{TaX}_4} - xE_{\text{CuS}} - yE_{\text{TaS}} - zE_{\text{XSe}})$$

(2)

with $X = \text{S, Se, and Te}$, where $E_{\text{Cu}_3\text{TaX}_4}$ is the total energy of the unit cell of Cu$_3$TaX$_4$, $E_{\text{XSe}}$ are the energies of the isolated atoms of Cu, Ta, and X, and $x$, $y$, and $z$ are the composite atoms of Cu, Ta, and X, respectively. Low negative $E_f$ values indicate the energy favorability of the structure and denote the ease of experimental synthesis. The obtained $E_f$ results comply with the lattice constant vs pressure plot (Figure 2b), where the response to external pressure is obtained from the slope of the linear fit for each compound (Table 2), and also with that of the percentage compressibility. The $E_f$ value is lowest for Cu$_3$TaS$_4$, and correspondingly its slope and percentage compressibility are also the lowest, illustrating a low response to external pressure and also better stability at high pressure as compared to the other two compounds.

The phonon dispersion plots illustrated in Figure 2 confirm the dynamical stability of the compounds concern-
gap value immediately fall in the viable gap window of 0.9−1.6 eV, making them appealing as absorber materials.

To account for the participation of different states in electronic transition, the partial density of states (PDOS) of the systems, plotted with various calculation schemes, at 0 and 10 GPa pressure are, respectively, shown in Figures 4 and 5. The states in the region between −3 and 0 eV represent the valence band (VB), and that between 0 and 3 eV represents the conduction band (CB). The localized d-states of Cu and Ta atoms dominate the DOS characteristics at the VB and CB, respectively. The domination led by d-states results in diminished DOS peaks with GGA+U because of the restriction imposed to the number of d-state valence electrons under this scheme, which ultimately reduces the occupation. Also, the diminished amplitude of DOS peaks with inclusion of SOC is due to the reduction in electronic state occupation. The VB edges are primarily of Cu 3d and X np (for X = S, n = 3; X = Se, n = 4; X = Te, n = 5) character with less density of Cu 3d at the top of the VB in Te-based systems. The CB edge is primarily due to Ta 5d, where Cu 3d and X np densities near the bottom of the CB decrease as one moves from S to Te.

The electronic PDOS at 10 GPa pressure shows reduced DOS amplitudes in comparison to 0 GPa, which led to the light masses of charge carriers. The CB edge has similar Ta 5d dominant character as in 0 GPa pressure, but the density contributions from Cu 3d and X np are almost negligible at the

Figure 3. (a)−(c) Band structure of Cu$_3$TaX$_4$ (X= S, Se, and Te) at 0 and (d)−(f) at 10 GPa pressure computed using various calculation schemes. The inset on the right panel of each band structure shows the total electronic density of states (TDOS) in units of states/eV. The dashed black line at 0 eV of energy indicates the Fermi level ($E_F$).
CBM. However, a completely different characteristic is observed at the VBM. The top of the VB is Cu 3d dominant in S-based material, with contributions from Ta 5d, which bypasses Xnp density. As one moves down the group from S to Te, the Ta 5d contribution increases, equaling Cu 3d in Se systems and bypassing both Cu 3d and Xnp in Te-based systems. This change in orbital character explains the narrowing of band gaps with applied pressure as the higher energy d states of Cu and Ta now fully contribute to the band edges to form the fundamental band gap. As a result of applied pressure, the VBM is shifted to the forbidden region, which designates relative ease in hole formation, ultimately leading to enhanced p-type conductivity. Cu3TaTe4 has the highest VBM at 10 GPa and also the lowest effective mass of p-type charge carriers; therefore, this material is predicted to show the best absorber property. However, the low band gap of the compound with induced pressure is still a concern, and thus the optical characteristics of the materials are further investigated. Also the reduced electron effective mass of the materials and low-lying CBM with pressure suggest the susceptibility to n-type doping, which could further tune their photovoltaic performance.

c. Optical Properties. To accurately determine the potentiality of the compounds in absorber material technology, their response to the incident photon energy should be closely investigated, particularly in the visible energy spectrum. The complex dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) determines the complete response to disturbance caused by incident radiations. The imaginary part of the dielectric function, \( \varepsilon_2(\omega) \), was determined by evaluating the matrix elements of the unoccupied and the occupied states, using Wien2k code. The real part \( \varepsilon_1(\omega) \) is derived from \( \varepsilon_2(\omega) \), employing the Kramer–Kronig equation. All other optical constants follow from the

|                | \( E_g \) (GGA) | \( E_g \) (mBJ) | \( E_g \) (GGA+SOC) | available result | \( m^* \) (CBM) | \( m^* \) (VBM) |
|----------------|----------------|----------------|---------------------|-----------------|----------------|----------------|
| Cu3TaS4 0 GPa | 1.85           | 2.52           | 2.12                | 2.04            | 1.98           | 1.72           |
| Cu3TaSe4 0 GPa| 1.63           | 2.24           | 2.19                | 2.70 (exptl)    | 2.10           | 1.78           |
| Cu3TaTe4 0 GPa| 1.16           | 1.60           | 1.39                | 2.35 (exptl)    | 1.71           | 1.79           |
| Cu3TaS4 10 GPa| 1.35           | 1.54           | 1.25                |                 | 1.74           | 1.02           |
| Cu3TaSe4 10 GPa| 1.01           | 1.20           | 0.99                |                 | 1.59           | 0.95           |
| Cu3TaTe4 10 Gpa| 0.51           | 0.7            | 0.4                 |                 | 1.54           | 0.72           |

Table 3. Calculated Energy Band Gaps (\( E_g \)) in eV and Carrier Effective Mass (\( m^* \)) along the Band Edges in Cu3TaX4 (X = S, Se, and Te) at 0 and 10 GPa Pressure

Figure 4. Partial electronic density of states (PDOS) of Cu3TaX4 (X = S, Se, and Te) computed using GGA, GGA+U, and GGA+U+SOC schemes at 0 GPa pressure. The dashed black line at 0 eV energy represents the Fermi level (\( E_F \)). (a), (d), (g) show the PDOS of Cu3TaX4 with GGA; (b), (e), (h) show the PDOS of Cu3TaX4 with GGA+U, and (c), (f), (i) shows the PDOS of Cu3TaX4 with GGA+U+SOC. The valence band edges are set to \( E_F \).

Figure 5. Partial electronic density of states (PDOS) of Cu3TaX4 (X = S, Se, and Te) computed using GGA, mBJ, and GGA+SOC schemes at 10 GPa pressure. The dashed black line at 0 eV energy represents the Fermi level (\( E_F \)). (a), (d), and (g) show PDOS of Cu3TaX4 with GGA; (b), (e), (h) show PDOS of Cu3TaX4 with mBJ; and (c), (f), (i) show PDOS of Cu3TaX4 with GGA+SOC. The valence band edges are set to \( E_F \).

Ref 4. Ref 8. Ref 38.
dielectric functions using standard equations. The intra-band transition contribution to the dielectric functions are inconspicuous, given the semiconducting nature of the compounds, and also the indirect interband transitions are neglected with comparison to direct interband transition, considering low photon momentum. The plot of the real part of the dielectric function with respect to the incident photon energy, at 0 and 10 GPa pressure, is shown in Figure 6(a),(b),

(c). The real part shows various peaks which increase from GGA+U to GGA to GGA+U+SOC at 0 GPa, indicating a strong dependence of optical behavior with spin–orbit interaction. The real dielectric function attains negative values with increasing photon energy, which indicates complete reflection of the incident electromagnetic radiation in these energy regions. The \( \varepsilon_r(\omega) \) plot at 10 GPa pressure shows similar characteristics and has no effect of SOC on the optical response. The imaginary part of the dielectric function, shown in Figure 6(d),(e),(f), shows the first critical points at around 1.8 eV for Cu₃TaS₄ and around 1.5 eV for Cu₃TaTe₄ at 0 GPa with GGA, which determines the threshold energy for direct optical transition between the valence and the conduction band. The threshold value increases with the choice of GGA to GGA+U+SOC to GGA+U. At 10 GPa pressure, the threshold value decreases to about 1.2, 1, and 0.7 eV, respectively, with GGA for Cu₃TaS₄, Cu₃TaSe₄, and Cu₃TaTe₄, which is almost independent of the choice of mBJ or SOC.

The optical conductivity plots shown in Figure 7(a)–(c) show a forbidden conduction region with energies corresponding to higher infrared and lower visible spectra, which further reconfirms the semiconducting nature of the compound. The threshold energy values for conduction are similar to the threshold energy observed in the imaginary \( \varepsilon_2(\omega) \), which at 10 GPa pressure represents direct optical transition from the highest point of the VB to the lowest CB at the \( \Gamma \)-point. Similarly, the other high peaks observed in the conductivity as well as the imaginary \( \varepsilon_2(\omega) \) at 10 GPa represent a direct optical transition from the highest point of the first VB to the second lowest CB at the \( \Gamma \)-point and so on. The optical absorptions, in Figure 7(e),(f), show high absorption coefficients in the visible energy region, which is further optimized from \( 10^4 \) cm\(^{-1} \) to \( 10^5 \) cm\(^{-1} \) in the lower limit of the visible spectrum due to induced pressure. The absorption curves show that photoconductivity begins from photon energy values other than zero, which is because of the distinct energy gap observed in the materials. The absorption edges ascend to high-energy values on choosing GGA+U+SOC and GGA+U, which is due to the widening of energy band gaps with the choice of these calculation schemes. Also, at 10 GPa, only a small shift on the absorption edge, for the calculation employing mBJ, is observed, which is consistent with the very small change in band gap observed in this pressure range. The absorption values increase with the increase of photon energy up to 4 eV and attain values as high as \( 10^6 \) cm\(^{-1} \) in the higher visible energy region for Cu₃TaTe₄, predicting potentiality for solar-cell applications.

The theoretical optical band gaps (\( E_G^{\text{opt}} \)) (Figure 8(a)–(f)) plotted using Tauc’s relation are evaluated from the intercept drawn at \( (\alpha h \nu)^{1/2} = 0 \) of the \( (\alpha h \nu)^{1/2} \) vs photon energy \( (h \nu) \) plot, and the values are listed in Table 4. Close agreement with the available experimental results is achieved for Cu₃TaS₄ and Cu₃TaSe₄, whereas for Cu₃TaTe₄ due to the lack of experimental data, comparisons are made with the available theoretical results. No literature was available to compare the

![Figure 6](image1)

![Figure 7](image2)

![Figure 8](image3)
results at 10 GPa pressure. The observed optical band gaps are the same as the direct gaps at X symmetry points in the case of 0 GPa, and at 10 GPa the gaps correspond to those at the Γ point. The direct lowest-energy optical transitions at M for 0 GPa are forbidden, while those at R are weak. Thus, with no strong absorptions predicted in these k-points, the optical gaps are considered at X for all of Cu3TaX4. However, for 10 GPa pressure, the VB at the X symmetry point has a considerable contribution from the p-states of the X chalcogen atom, and the direct transition between the VB and CB at this point is still allowed due to the d–d transition of Cu and Ta but is relatively weak. However, at the Γ-point, the dominant contribution from Ta d and Cu d to both the VB and CB edges leads to a strong overlap and thus a strong transition, due to which the optical band gap is instead at Γ for all of Cu3TaX4 at 10 GPa. The optical band gaps are wider compared to the electronic gaps in the case of Cu3TaTe4, and taking into consideration the underestimation led by GGA and the accuracy of mBJ in gap prediction, the mBJ calculated optical gap of 0.89 eV is considered for the compound. Thus, it can be seen that as a result of induced pressure the Eg opt of all three compounds fall immediately in the viable gap window of 0.9–1.6 eV, which is considered the optimum value for efficient absorber material. Also, Cu3TaTe4 which was found to be most pressure sensitive, shows maximum tuning of its absorption coefficient.

4. CONCLUSION

In summary, the modulation of optical absorption has been performed by ab initio first-principles methods on Cu3TaX4, considering the onsite Coulomb self-interaction parameter (U) and the SOC effects by applying pressure. The compounds were found to be stable at least up to a pressure range of 10 GPa, verified from their formation energies and the phonon dispersion curves. The energy band gaps calculated using GGA+U were found to be in close vicinity with the available experimental results. With applied pressure, the overall effective mass of the VB as well as the CB for all materials, suggesting these systems to act efficiently both as n-type or p-type semiconductors. The lower few effective masses of VBs, with pressure, in comparison to CBs ensure the domination of hole mobility which is a fundamental characteristic for achieving high PV efficiencies. Despite the indirect gap nature of the compounds, the optical band gaps obtained with induced pressure all lie in the optimum spectral range for PV absorber materials, and the absorption coefficient is enhanced almost up to 10 times in the case of Cu3TaSe4. Owing to the close proximity in the fundamental indirect and the optical gaps in the compounds, they should bypass the efficiency of silicon absorber materials in PV application. Also, considering the small energy difference between the VBM of the three compounds at 10 GPa pressure and also the close similarity in their lattice constants and optical gaps, their properties could further be tuned. For example, by combining the three materials and differing the S/Se/Te concentration, the optical gaps could be tuned theoretically to any value between 0.93 and 1.57 eV. Therefore, considering the promising results herein reported, the pressure systems are guaranteed to show excellent photovoltaic performance.

Table 4. Calculated optical band gaps (Eg opt) in eV and the absorption coefficient (α) with respect to 2 eV of photon energy at 0 and 10 GPa pressure

| Compound | Eg opt (GGA) | Eg opt (GGA+U) | Eg opt (GGA+U+SOC) | available result | α × 10^3 (cm)^{-1} |
|----------|-------------|----------------|-------------------|-----------------|-------------------|
| Cu3TaS4  | 1.85        | 2.55           | 2.26              | 2.60 (theo)     | 0.13              |
|          |             |                |                   | 2.70 (exp)      |                   |
| Cu3TaSe4 | 1.76        | 2.35           | 2.21              | 2.22 (theo)     | 0.15              |
|          |             |                |                   | 2.35 (exp)      |                   |
| Cu3TaTe4 | 1.5         | 1.91           | 1.68              | 1.69 (theo)     | 0.77              |

Ref 8. Ref 38. Ref 41.

AUTHOR INFORMATION

Corresponding Author

Himanshu Joshi – Condensed Matter Theory Research Lab, Kurseceng College, Darjeeling 734203, India; Department of Physics, St. Josephs College, Darjeeling 734103, India; orcid.org/0000-0001-8717-0042; Email: himanshuabijoshi09@gmail.com

Authors

Amit Shankar – Condensed Matter Theory Research Lab, Kurseceng College, Darjeeling 734203, India

Nihal Limbu – Condensed Matter Theory Research Lab, Kurseceng College, Darjeeling 734203, India; Department of Physics, North Eastern Hill University, Shillong, Meghalaya 793022, India

Mahesh Ram – Condensed Matter Theory Research Lab, Kurseceng College, Darjeeling 734203, India; Department of Physics, North Eastern Hill University, Shillong, Meghalaya 793022, India

Amel Laref – Physics Department, Faculty of Science, King Saud University, Riyadh 11451, Saudi Arabia

Prasanta Kumar Patra – Department of Physics, North Eastern Hill University, Shillong, Meghalaya 793022, India

Oksana Bakhtiyarova Ismailova – Uzbekistan-Japan Innovation Center of Youth, Tashkent 100180, Uzbekistan; Turin Polytechnic University in Tashkent, Tashkent 100095, Uzbekistan; orcid.org/0000-0001-8972-546X

Lalhriat Zuala – Physical Sciences Research Center (PSRC), Department of Physics, Pachhunga University College, Mizoram University, Aizawl, Mizoram 796001, India

Suman Chatterjee – Department of Physics, University of North Bengal, Darjeeling 734013, India

Dibya Prakash Rai – Physical Sciences Research Center (PSRC), Department of Physics, Pachhunga University

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