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# First-principles investigation of structural, electronic, optical and dynamical properties in CsAu

**Research Article**

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**Abstract:** The structural, electronic, optical and dynamical properties of CsAu compound in the CsCl(B2) phase were investigated using the density functional theory (DFT) within the generalized gradient approximation (GGA). The calculated lattice constant, static bulk modulus and first-order pressure derivative of the bulk modulus are reported and compared with previous experimental and theoretical calculations. The calculated electronic band structure for this compound is in good agreement with available theoretical and experimental studies. The present band calculation indicates that CsAu compound has an indirect gap at R→X points. Furthermore, the linear photon-energy-dependent dielectric functions have been calculated. For the first time, the electronic structure results are used, within the implementation of a linear-response technique, for calculations of phonon properties.

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**Keywords:** density functional theory • generalized gradient approximation • electronic structure • optical properties • phonons

## 1. Introduction

The electronic structure of CsAu has been more extensively studied on numerous occasions [1–12]. Solid CsAu structure is known to be an ionic semiconductor with an indirect band gap of approximately 2.5 eV with a minimum energy gap [2]. Therefore, it is indicated that CsAu contains a band gap characteristic of a semiconductor, as expected for a compound in which the bonds have a strong ionic character with gold being the negative ion [2]. The CsAu compound has the CsCl crystal structure in which each ion has eight unlike-ion neighbors. That is, the CsAu compound crystallizes in the CsCl crystal structure and has a lattice constant of 4.258 Å [13]. At 590°C, it liquefies to give a melt that shows the ionic conductivity [14]. At room temperature, the Cs and Au ions of CsAu are ordered at $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ positions, respectively.

In addition, the electronic structure and optical properties of CsAu crystal structure have been studied in some detail;

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Spicer studied the photoemission and the band structure of the semiconducting compound CsAu [2]. Liu et al. determined the electronic band structure of CsAu through a combination of the Green's function and quantum-defect methods [3]. Liu calculated the optical properties of CsAu from the electronic energy bands in the photon energy range from 0.01 to 0.40 Ry [6]. Christensen et al. carried out the self-consistent non-relativistic and relativistic LMTO band structure calculations for CsAu [9]. Koenig et al. performed the self-consistent relativistic band structure calculations for the alkali metal gold compound CsAu [10]. Rodriguez et al. studied how the nature of the Au-alkali metal bond changes when the size and electronegative of the alkali are varied, and investigated the electronic structure of the Au-alkali alloy films using core and valance level photoemission [11]. Spicer et al. investigated the semiconducting properties of the compound CsAu [13]. Wooten et al. established the measurements of receptivity and the Hall constant in the temperature range $4.2-300$ K, and measurements of the Seebeck coefficient in the temperature range $77-300$ K [15]. Heiz et al. generated the mixed metal cluster of sodium and cesium with gold in a supersonic expansion from the mixed vapor phase, and investigated experimentally and computationally their tendency towards binary cluster formation, relative thermodynamic stability and ionization potentials [16]. Carley et al. studied the formation of cesium-gold alloys by the deposition of cesium on to an Au (100) surface by both core-level (X-ray induced) and valance-level (He (II) radiation) spectroscopies [17]. Knatko et al. investigated the formation of a CsAu alloy during deposition of Cs on an Au substrate by threshold photoemission spectroscopy [18].

The aim of the present work is to investigate the structural, electronic and dynamical properties of CsAu compound by employing the density functional theory. The band structure and optical properties are obtained from the application of the plane-wave pseudopotential method, within the generalized gradient approximation. These results are used, within a linear-response approach, to calculate the phonon dispersion curves for CsAu in the B2 structure. Phonon dispersion curves as well as phonon density of states (DOS) were calculated in order to shed more light on the lattice dynamics. Atomic displacement patterns of phonon modes at the Γ-point for CsAu in the B2 phase are presented and discussed.

## 2. Computational details

The self-consistent norm-conserving pseudopotentials were generated by using the FHI98PP code with a Troullier-Martins-scheme [19] for all atoms of CsAu crystal. The Perdew-Burke-Ernzerhof GGA functional (PBE-GGA-96) [20] were used to include the exchange-correlation effects. The pseudopotential for only valence electrons was generated to investigate the effects on the physical properties of the crystal. For a Cs atom the 6s electron, and for an Au atom the 5d and 6s electrons, were investigated as the true valence. The basis set for the electronic wave functions were chosen to be plane waves. The conjugate gradient minimization method [21] was used with the ABINIT code [22] for solving Kohn-Sham equations [23]. All the calculations included one molecule cubic unit cell. With the choice of cut-off energies at 25 hartree using a $6 \times 6 \times 6$ Monk-Horst-Pack mesh grid [24], a good convergence for the bulk total energy calculation was successfully produced. In additon, the irreducible Brillouin zone was sampled with $14 \times 14 \times 14$ k-points to calculate the optical properties of CsAu.

The phonon calculations have been performed by using the code PWSCF[1]. Having obtained self-consistent solutions of Kohn-Sham equations, the lattice-dynamical properties were calculated within the framework of the self-consistent density functional perturbation theory [25, 26]. In order to obtain the full phonon spectrum we evaluated 8 dynamical matrices on a $4 \times 4 \times 4$ grid in **q** space. The dynamical matrices at arbitrary wave vectors can be evaluated by means of a Fourier deconvolution on this mesh. A $10 \times 10 \times 10$ k-points mesh was used for sampling the irreducible segment of the Brillouin zone for phonon dispersion curves and density of states.

For a material having a polar crystal structure and a spontaneous polarization, $\vec{P}_s$, the total polarization consists of two terms: $\vec{P}_{tot} = \vec{P}_s + \vec{P}_i$, where $\vec{P}_i$ is the polarization induced by incoming light and given by formula [27]

$$P^i(\omega) = \chi^{(1)}_{ij}(-\omega,\omega)E^j(\omega) + \chi^{(2)}_{ijk}E^j(\omega)E^k(\omega) + \dots . \quad (1)$$

In Eq. (1), $\chi^{(1)}_{ij}$ is the frequency-dependent linear optical susceptibility tensor and is given by

$$\begin{aligned} \chi^{(1)}_{ij}(-\omega,\omega) &= \frac{e^2}{\hbar\Omega}\sum_{nm\vec{k}} f_{nm}(\vec{k})\frac{r^i_{nm}(\vec{k})r^j_{mn}(\vec{k})}{\omega_{mn(\vec{k})-\omega}} \\ &= \frac{\varepsilon_{ij}(\omega)-\delta_{ij}}{4\pi}, \end{aligned} \quad (2)$$

where $n$, $m$ denote energy bands, $f_{mn}(\vec{k}) \equiv f_m(\vec{k}) - f_n(\vec{k})$ is the Fermi occupation factor, $\Omega$ is the volume,

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$\omega_{mn}(\vec{k}) \equiv \omega_m(\vec{k}) - \omega_n(\vec{k})$ is the frequency differences, $\hbar\omega_n(\vec{k})$ is the energy of band $n$ at wave vector $\vec{k}$, $\varepsilon_{ij}(\omega)$ is the frequency-dependent dielectric tensor, and the $r_{nm}$ are the matrix elements of the position operator. It is seen from Eq. (2) that the dielectric function can be associated with the susceptibility: $\varepsilon_{ij}(\omega) = 1 + 4\pi\chi_{ij}^{(1)}(-\omega, \omega)$. In Eq. (1) $\chi_{ijk}^{(2)}$ is the frequency-dependent second-order susceptibility tensor, however the non-linear optical response for cubic CsAu single crystal has not been investigated in this work.

It is a well-known fact that the properties of the ground-state are determined by Kohn-Sham equations. The self-energy effects must be included when the optical response calculations are made, since the unoccupied conduction bands have no physical importance and a band gap problem appears at low energy values. In order to include the self-energy effects, the scissor approximation [28] was used and chosen at 1.6 eV in the present work using the experimental energy gap 2.5 eV for CsAu by Spicer [2].

## 3. Results and discussion

The CsAu crystal has a cubic structure and belongs to the space group Pm-3m (No. 221). The investigated CsAu contains one molecule with two atoms per unit cell. The compound CsAu crystal has a lattice constant of 4.258 Å [13]. At room temperature, the Cs and Au ions of CsAu crystal are ordered at $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ positions, respectively. The lattice parameter of CsAu can also be obtained using the pseudopotential method based on the density functional theory under the GGA; that is, by minimization of the crystal total energy to crystal volume ratio, the theoretical lattice constant has been obtained as $a = 4.219$ Å. The obtained lattice constant is used in all calculations. The atomic positions obtained from first principle are $(0,0,0)$ and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ for Cs and Au, respectively.

All physical properties of a material are related to the total energy. For example, the equilibrium lattice constant of a crystal is the lattice constant that minimizes the total energy. Therefore, the physical properties of a material can be determined by the calculation of the total energy. However, optical properties are not readily understandable on the basis of the total energy alone. Fig. 1 shows the total energy as a function of the volume of CsAu under the GGA. The calculated and experimental volume values were compared, and the deviation of the calculated equilibrium volume given by the GGA calculation from the experimentally determined value was found to be 2.7%.

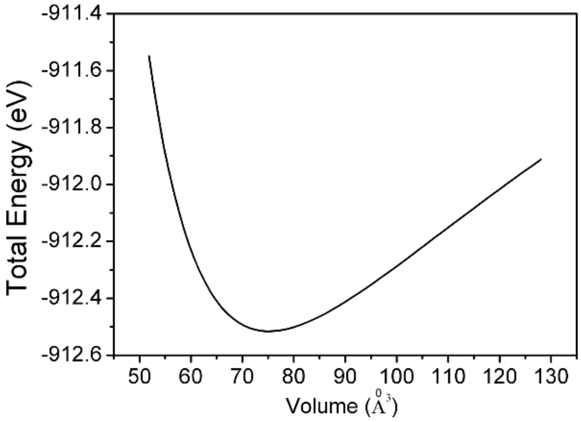

**Figure 1.** Total energy as a function of the volume for cubic CsAu.

The investigation of the electronic band structure of cubic CsAu is very useful as it helps us to understand the electronic and optical properties of the material better. At this point, what we first need is to describe our calculated electronic structure. The energy-band structure calculated using the GGA for cubic CsAu is shown in Fig. 2 where the origin of energy was arbitrarily set to be at the valance band maximum.

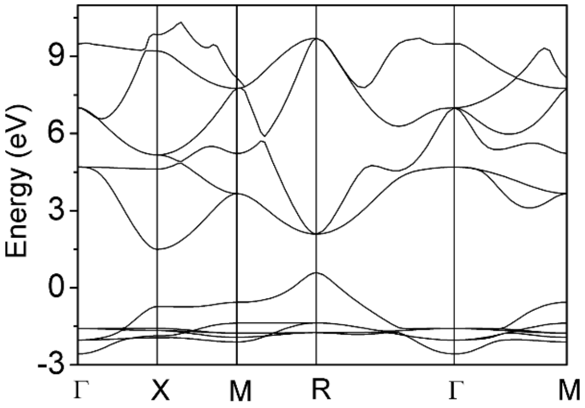

**Figure 2.** The calculated electronic band structure for cubic CsAu.

The band structure calculations have been performed in the high-symmetry directions of the first BZ. The band structure of cubic CsAu has been calculated and plotted on the surface of the BZ. The $k$ points denoting irreducible BZ are marked with letters in Fig. 2. The maximum of the valence band and minimum of the conduction band are located at the R and X high symmetry point, respectively, in the BZ

The present band structure for cubic CsAu shows an indirect band gap in the R→X high symmetry direction. The band gap calculated using the GGA is 0.91 eV. It is seen that the obtained band gap is smaller than the experimental result of 2.5 eV [3]; The underestimation of the band gap is due to the generic nature of the density functional theory.

In the present work, we also studied the linear optical properties of cubic CsAu. The optical functions calculated by neglecting all lattice vibrational effects and pertaining only to the electronic transitions are shown in Fig. 3. The optical response was calculated in the photon energy range of 0 – 30 eV using the calculated band structure. As a result of the calculations, we saw that a 0 – 20 eV photon-energy range is sufficient for most optical functions. Thus, we have derived the values of real and imaginary parts of the dielectric function as a function of the photon energy.

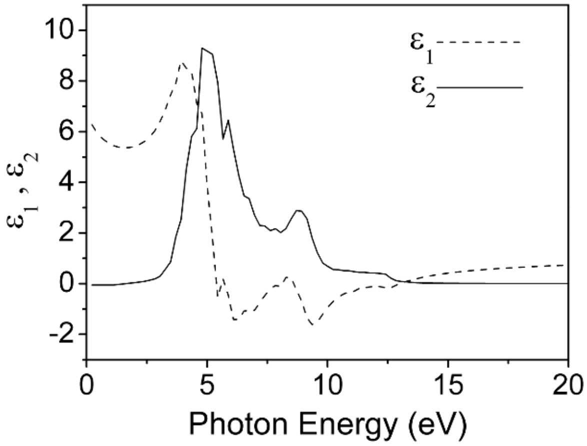

**Figure 3.** Calculated real and imaginary parts of optical dielectric function for CsAu.

The real and imaginary parts of the frequency-dependent linear dielectric function are shown in Fig. 3. The imaginary part of the dielectric constant, $\varepsilon_2$, shows several main peaks located at 3.30, 3.70, 4.33, 4.98, 5.86, 6.74, 7.39, 7.80 and 8.77 eV. These peaks correspond to the optical transitions from the valance band to the conduction band. In the light of this information, we see that CsAu exhibits two fundamental oscilator bands at 3.30 and 3.70 eV. From Fig. 3, it is seen that the 0 – 3.30 eV photon-energy range is characterized by high transparency, no absorption and a small reflectivity which explain the origin of the peak structure in the reflectivity and absorption coefficient spectra. In addition, the 3.30 – 6.00 eV photon-energy range is characterized by strong absorption and appreciable reflectivity which means that optical absorption increases more quickly in this photon-energy range. Moreover, the 6.00 – 12.00 eV photon-energy range is characterized by high reflectivity.

Fig. 3 also shows the real parts of the frequency-dependent linear dielectric functions obtained from the imaginary parts by Kramers-Kronig conversion. The static dielectric constant, $\varepsilon_0$, of CsAu is calculated as 6.30. The function $\varepsilon_1$ is equal to zero at 5.40, 5.58, 5.67, 8.08, 8.59 and 13.03 eV. The interband transition at these points consists mostly of plasmon excitations, and the scattering probability of volume loss is directly connected to the energy loss function.

## 4. Dynamical properties

CsAu crystallizes with the CsCl-type structure at ambient pressure with two atoms per unit cell. The cesium atom is positioned at $(0, 0, 0)$ and gold at $(0.5, 0.5, 0.5)$. The phonon dispersion curves and one-phonon density of states for CsAu in B2 structure are given in Fig. 4. There are a total of six phonon branches. Due to symmetry, the distinct number of branches is reduced along the principal symmetry directions Γ-X and Γ-R. The phonon dispersion curves show one important feature; the longitudinal optic (LO) and transverse optic (TO) phonon modes are split at the zone center. For this material our calculated results for the TO and LO modes at the zone center are 1.69 THz and 2.27 THz, respectively. The splitting between LO and TO phonon branches at the zone center is 0.58 THz. At the X point the calculated frequencies are 1.10 THz (TA), 1.28 THz (LA), 1.27 THz (TO) and 2.09 THz (LO). There is no clear gap between the acoustic and optic branches for the CsAu. An interesting feature is seen from the phonon dispersion curves of CsAu in the symmetry direction of Γ-R. At about $q = 2 \times \frac{\pi}{a}\,(0.33, 0.33, 0.33)$, the LA branch crosses the TA branches. Also, the LO and TO branches cross two times at about $q = 2 \times \frac{\pi}{a}\,(0.32, 0.32, 0.32)$ and $q = 2 \times \frac{\pi}{a}\,(0.22, 0.22, 0.22)$.

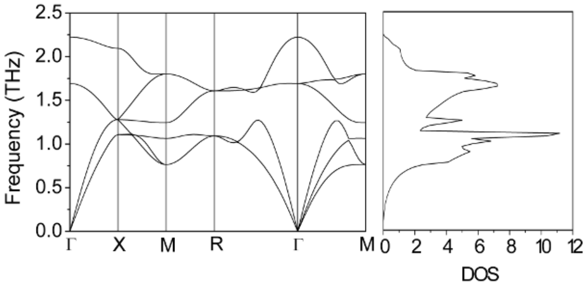

**Figure 4.** Calculated phonon dispersion curves and phonon density of states for CsAu.

The peaks were observed to be distributed mainly around five frequency ranges in the total DOS in CsAu. First, the peak located between 0.77 THz and 0.96 THz is due to the transverse acoustic (TA) phonon modes. Second, the peak between 1.04 THz and 1.15 THz is also obtained mainly from the LA and TA phonon modes. The next peak, at about 1.20 THz is significantly stronger and corresponds to the LA branch which is quite flat along the X-M and M-R directions. The sharp peak centered at 1.25 THz is due to the flatness of the TO phonon modes along the X-M and Γ-M directions. The last peak, between 1.58 THz and 1.84 THz is mainly a result of the LO phonon. Fig. 5 depicts the shapes of these zone-center optical phonon modes. In this figure, while lower modes involve opposing vibrations of Cs and Au atoms in the z-axis, the higher modes involve opposing vibrations of Cs and Au atoms in the x-axis.

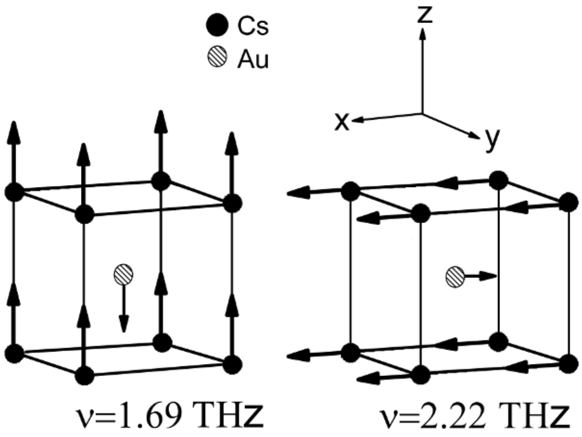

**Figure 5.** Schematic eigendisplacements of vectors representing optical zone-centre phonon modes for CsAu.

The phonon dispersion curves of CsAu in the CsCl structure could not be compared with the experimental and theoretical works, and therefore one cannot make any comment on the success of these ab initio calculations. The calculated phonon dispersion curves of CsAu compound will certainly be very useful for the interpretation of future experiments and theoretical works.

## 5. Conclusions

In this work, the structural, electronic, optical and dynamical properties of cubic CsAu crystal structure have been studied in detail using the density functional methods under the GGA. The results of implemented structural optimization under the GGA and the experiments agree with each other well. Through calculation, it is found that the fundamental gap of CsAu crystal structure is indirect in the symmetry direction of R→X in the BZ. The calculated band gap by GGA is 0.91 eV at the R→X point and is smaller than the experimental result of 2.5 eV because of the discontinuity in the pseudopotential method. The linear dielectric function has been investigated as the function of the photon energy. For the first time, the phonon dispersion curves and density of states of CsAu in B2 structure have been calculated and discussed in detail. Schematic illustration of the eigendisplacements of the phonon modes at Γ point are presented and discussed.

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