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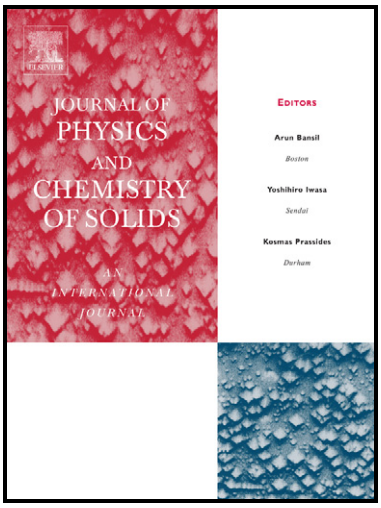

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Optical Properties of $\alpha-Se$ Revealed by ab initio Calculations

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Gboyega A. Adebayo[a,†1] and Bede C. Anusionwu[b]

†The Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, I-34100 Trieste, Italy

[a]Department of Physics, University of Agriculture, (UNAAB) PMB 2240 Abeokuta, Nigeria

[b]Department of Physics, Federal University of Technology, Owerri, Nigeria

Abstract

Detailed optical functions and optical properties of a $\alpha-monoclinic$ phase of Selenium ($\alpha-Se$) are presented over a wide range of angular frequencies ω by first-principles calculations. An optical band gap of $2.05eV$ and a mobility gap of $2.17eV \pm 0.05$ are observed in the present calculations. The imaginary part of the dielectric function has been obtained from the frequency dependent dielectric matrix and the use of the Kramers-Kronig (KK) relation allows us to determine the real part of the dielectric function. Optical functions and optical properties revealed the occurrence of a long range order in Se. For the first time, infrared and absorption spectra of monoclinic$-Se$ were studied using the Kramers-Kronig (KK) relation by ab initio method. And lastly, detailed studies of other dielectric related optical constants such as reflectivity, transmission, reflection and absorption coefficients were also presented.

keywords: Density Functional Theory, Electronic Structure, Infrared Spectra, Amorphous Semiconductors, First Principles Theory, ab initio simulation, Elemental Semiconductors.

[1]Parmanent address: Department of Physics, UNAAB. Email: gadebayo@ictp.it

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1 Introduction

Selenium is a semiconductor possessing unusual properties which are not found in other single elemental semiconductors; aside from this fact, Se is also used in photovoltaic devices such as photoreceptors and photoconductors where the unusual behavior is an advantage in reducing the band gap of Se. Up till now, information on the optical properties of different phases of this element is still very scanty. Several studies on Se concern only the structures or quench behavior of this element[1] − [5], so detailed optical functions calculations are very useful ways of interpreting the anomaly in Se. Monoclinic Se and other phases of Selenium are important because of their vast applications in electronic and optoelectronic devices. Especially, amorphous Se is an excellent photoconductor used in active matrix flat-panel imagers, digital x-ray imaging and many more devices[6] − [13]. A proper understanding of the optical constants of Se is therefore of great importance in the design of modern-day optoelectronics based technologies.

That Se exhibits many photo-induced phenomena is well known[14] − [17] and although, there seems to be some attention focused on the experimental and theoretical studies of the optical constants of Se[18], [19] there seems to be a need for more insight based on quantum mechanical calculations. This is because many of the observed effects in Se have been, practically, studied either over a small range of the optical spectrum or the majority of available calculations are based on vibrational density of state (DOS). This calls for a more accurate method to determine the optical properties of Se. First principle or ab initio calculations using the Density Functional Theory (DFT) approach coupled with the use of the pseudopotential provide the exact approach for obtaining accurate information on electronic band structures and optical properties over the entire electromagnetic spectrum.

In this article, we present the optical properties of monoclinic $\alpha{-}Se$ from the frequency-dependent dielectric function over a wide photon-energy range. The present calculations explores the frequency dependent dielectric matrix to determine the imaginary part of the dielectric function from which the Kramers-Kronig

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relation has been applied to obtain the real part. This allows us to obtain better optical properties of Se over the fundamental lattice vibration DOS approach. To our knowledge, no frequency-dependent dielectric matrix based ab initio calculation exists on monoclinic $\alpha{-}Se$.

The present work is organized in the following sections: Section 2 gives the important theoretical account of the computational procedure used in our work, while Section 3 states the main results and discussion. Finally, in Section 4, concluding remarks are provided.

2 Computational Technique

The absorption coefficient α and the complex refractive index $\tilde{n}$ are among the most important optical constants of a material. The extinction coefficient, $k(\omega)$ which is the imaginary part of $\tilde{n}$ and α are related through the equation

$$\alpha(\omega) = \frac{\omega\epsilon^{(2)}(\omega)}{ck(\omega)} \tag{1}$$

where "c" is the speed of light. We obtained the reflectivity from the equation

$$R(\omega) = \frac{(n(\omega)-1)^2 + k(\omega)^2}{n(\omega)+1)^2 + k(\omega)^2} \tag{2}$$

while the optical conductivity is given as

$$\sigma(\omega) = \frac{\omega\epsilon^{(2)}(\omega)}{4\pi} \tag{3}$$

From a knowledge of the refractive index, it is easy to determine the transmission and the reflection coefficients by employing

$$T_{coef} = \frac{4n_1(\omega)n_2(\omega)}{(n_1(\omega)+n_2(\omega))^2} \tag{4}$$

and

$$R_{coef} = \left[\frac{n_1(\omega)-n_2(\omega)}{n_1(\omega)+n_2(\omega)}\right] \tag{5}$$

Here, the subscripts are the indices of refractive in air and Se.

Using plane wave basis sets, electron-ion interactions are described by the PAW pseudopotentials in the frame work of the Vienna Ab initio Simulation Package[20][21].

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After optimizing the system, a $16 \times 16 \times 16$ mesh with a Monkhorst Pack was used to implement a DFT method. In the determination of the partial occupancies of the wave functions, we employed the tetragonal method by setting the width of the smearing to $0.1eV$. A quasi-Newton algorithm[21] was employed to achieve instantaneous ground state ionic relaxation. In the present calculations, an appreciable number of empty states in the conduction band are required to estimate the dielectric function and optical properties, for this reason, a two-step DFT calculation is implemented, we have used 50 bands from which convergence with size of the system used has been observed.

Band transitions calculations were performed by determining the joint density of state (JDOS) based on the calculations of DOS functions

$$DOS = (N(E_i) - N(E_{i-1}))/\Delta E \tag{6}$$

Here ΔE is the energy difference between two grid points, where

$$N(E_i) = \int_{-\infty}^{E_i} n(E)dE \tag{7}$$

In terms of photon energy, JDOS is then written as

$$JDOS(\hbar\omega) = \frac{4}{V^2} \sum_{v,c} \delta(E_c - Ev - \hbar\omega) \tag{8}$$

V is the volume of a sample, E_v and E_c are energies of the valence and conduction bands respectively. Therefore,

$$JDOS(\hbar\omega) = \int_{-\infty}^{\infty} N_v(E)N_c(E + \hbar\omega)dE \tag{9}$$

The spectra-dependence of the imaginary part of the dielectric function was obtained through a summation over empty states

$$\epsilon^{(2)}_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}} \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \omega)$$
$$\times < u_{c\mathbf{k}+\epsilon_\alpha q}|u_{v\mathbf{k}} >< u_{c\mathbf{k}+\epsilon_\beta q}|u_{v\mathbf{k}} >^* \tag{10}$$

The function $u_{c\mathbf{k}}$ refers to the periodic part of the wave functions at the k-point $\mathbf{k}$. Using the KK relation, we determined the real part $\epsilon^{(1)}(\omega)$ of $\epsilon(\omega)$ thus[20]

$$\epsilon^{(1)}_{\alpha\omega}(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\epsilon^{(2)}_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \tag{11}$$

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Here, ω' is an integration variable, while P is the principal value of integration which is needed to avoid singularity at $\omega = \omega'$ and η is a complex shift.

3 Results and Discussion

The absorption coefficient is an important aspect in the technology of optical waveguide engineering as it gives an insight into absorbed photons by a material. In Fig.1 we show our calculated absorption coefficient $\alpha(\omega)$ for $\alpha{-}Se$. In the infrared region, there is an occurence of a weak "symmetric peak" centred at around $0.25eV$ and another peak situated at $16eV$ with minima depressions on both sides; furthermore, a split third peak is noticed at around $21.25eV$ with a single minimum depression to the right. Lastly, there are several oscillational small peaks between $26eV$ and $50eV$.

A major deduction from Fig.1 is that $\alpha{-}Se$ has an optical band gap of $2.05eV$, and a mobility gap of $2.17eV \pm 0.05$ which corresponds to the observed value in amorphous Selenium[22], [23] at ambient condition. The small peaks region could be a region of multiple reflection where the absorption coefficient is very small. Generally, optical properties of semiconductors are exhibited at a photon energy below 4eV and from band theory the density of states (DOS) diagram is a key to understanding the optical properties of an amorphous semiconductor like Selenium. Consequently, density of states and absorption coefficient curves can be used to explain band and mobility gaps in Selenium. A quick glance at Fig.1 and Fig.4 show clearly that the only observed peak satisfying the condition mentioned above has an energy gap that approximately equals $2.05eV$. This value is relatively close to measured values of $2.53eV$ and $2.3eV$ by Knights and Davis[24], and Caywood and Taynai[25] respectively. Also, a perusal of these figures shows localized states in the energy band. A major difference between crystalline and amorphous states is the existence of localized states called mobility gap in the band gaps. Mobility gap in semiconductors can be attributed to the existence of a high degree of short range spatial order in atomic structures. In the present calculations, the mobility gap of $(2.17 \pm 0.05)eV$ is observed in the absorption coefficient and in the joint density of

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states.

Fig.2 shows the imaginary part of the dielectric function due to $\alpha{-}Se$. The curve shows typical features of amorphous materials. We see clearly the four-region divisions which we believe correspond to transmittance values according to which $\alpha{-}Se$ could be transparent, weak absorptive, strong absorptive and reflective. The oscillatory tail could be attributed to region of multiple reflections. The Kramers-Kronig relation of eqn.11 was derived under general conditions and is therefore valid for semiconductors as well as for normal crystals, while refractive indices are derived from dielectric functions, any large change in the imaginary part of the dielectric function and refractive index are very often indications of some differences in the bonding and thus the structure of a material. Therefore, in contrast to crystalline structures, the abrupt change in Fig.2 can be attributed to the amorphous nature of Selenium.

In Fig.3, we present the transmission and reflection coefficients $(Fig.3a)$ alongside the reflectivity $(Fig.3b)$ in $\alpha{-}Se$.

In the low frequencies region, there are few noticeable peaks $(Fig.3b)$ around $16eV$, $21eV$ and $36eV$. The region of high reflectivity corresponds to points in the lowest transmission and highest reflection coefficients. These graphs depict a long range order in Selenium at high frequencies as can also be seen in Fig.4 where a plot of JDOS is presented. The unusual behaviour of Selenium as photoreceptor and photoconductor which tends to reduce the band gap in Selenium can be explained in terms of decreasing optical band gap energy which may be induced as a result of multiple optical reflections like the one observed in the tail of Fig.2 while formation of stable glasses of Se in chalcogenide are made possible by excellent infrared transparency, and a high refractive index among others which are inferred from Figures 1 and 3a. Fig.4 portrays the existence of several localized states in Selenium, the electron-hole interaction effect in the energy distribution of those states can not be underestimated at a large $\hbar\omega$. This is most noticeable between $\hbar\omega \approx 33eV$ and $42.5eV$ where there are overlaps of electron traps and hole traps. There are deep

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shallow traps both in the valence and conduction bands of Fig.4, worthy of mention are the electron traps at $\approx 23eV$ which extend into a well ≈ 0.4 in arbitrary units. A mobility gap of $2.17ev\ \pm 0.05$ is observed between $-2eV$ and $2.5eV$. There are several other mobility gaps, some of which have overlapping electron-hole state interactions. One can infer from these overlaps therefore, superpositions of molecular orbital states and bearing in mind that linear combinations of these orbitals will result in both anitbonding and bonding states.

Although, the DFT method employed in the present calculations is highly accurate since it relies on quantum ab initio calculations, however, only calculated energies up to $15eV$ of the electromagnetic spectrum can be considered accurate. The above statement is borne out by the fact that Selenium is a semiconductor and at high energies, due to artifacts in calculations, bands may not be calculated correctly while at energies exceeding $15eV$ a calculated refractive index may become smaller than unity.

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4 Conclusion

We have obtained the optical functions and optical properties of Se by applying quantum mechanical-based ab initio calculations which give essential features of the calculated quantities over an extended photon-energy range. An optical band gap of $2.05eV$ has been obtained in the present work, while the mobility gap from the density of state calculation shows a value of $2.17eV \pm 0.05$. Four regions corresponding to transmittance values in the extinction coefficient of $\alpha{-}Se$, a transparent region, weak and strong absorption regions and a reflective region. Other optical constants which are related to the dielectric functions such as absorption coefficient, transmission and reflection coefficients as well as the refractive index of $\alpha{-}Se$ were also presented.

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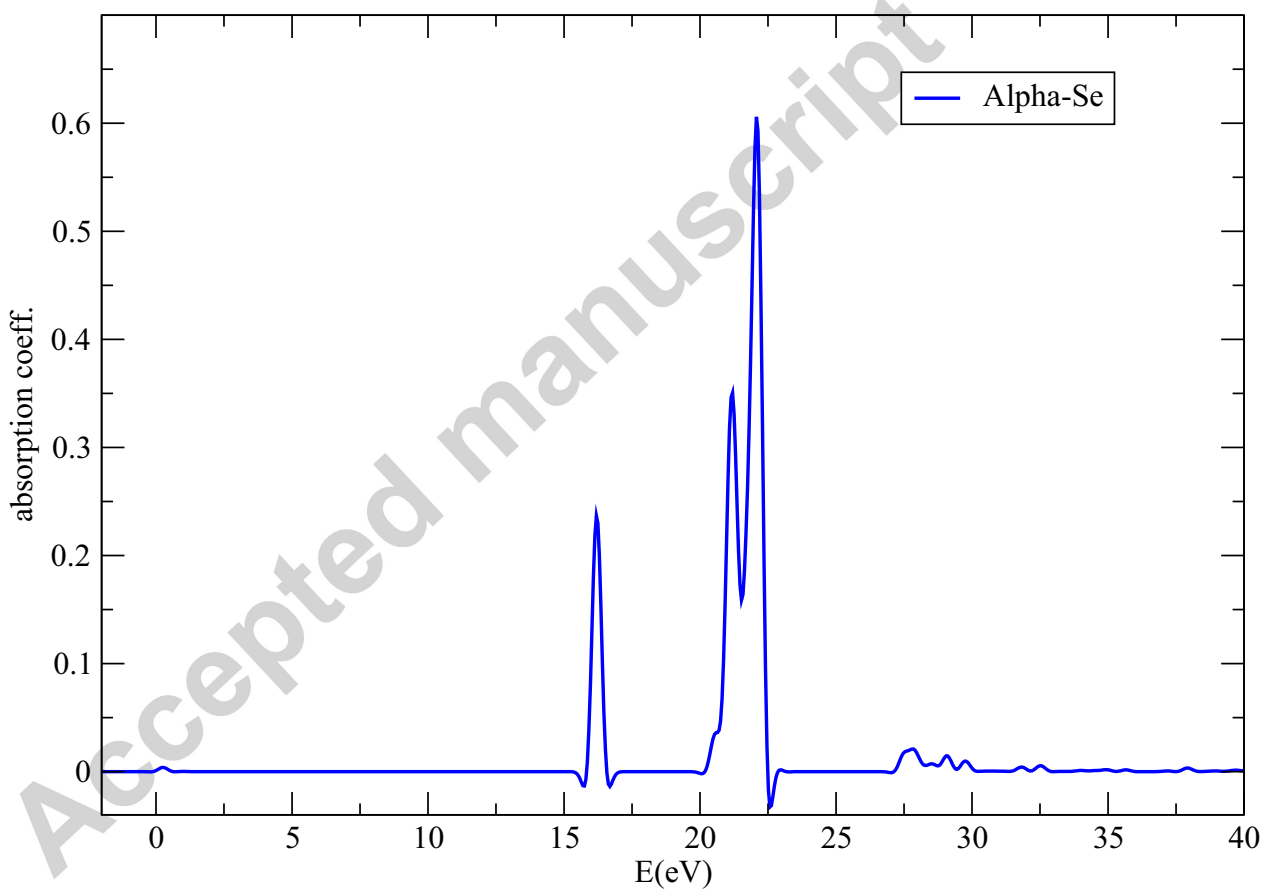

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Figure 1: Absorption coefficient in Alpha Selenium at high pressure

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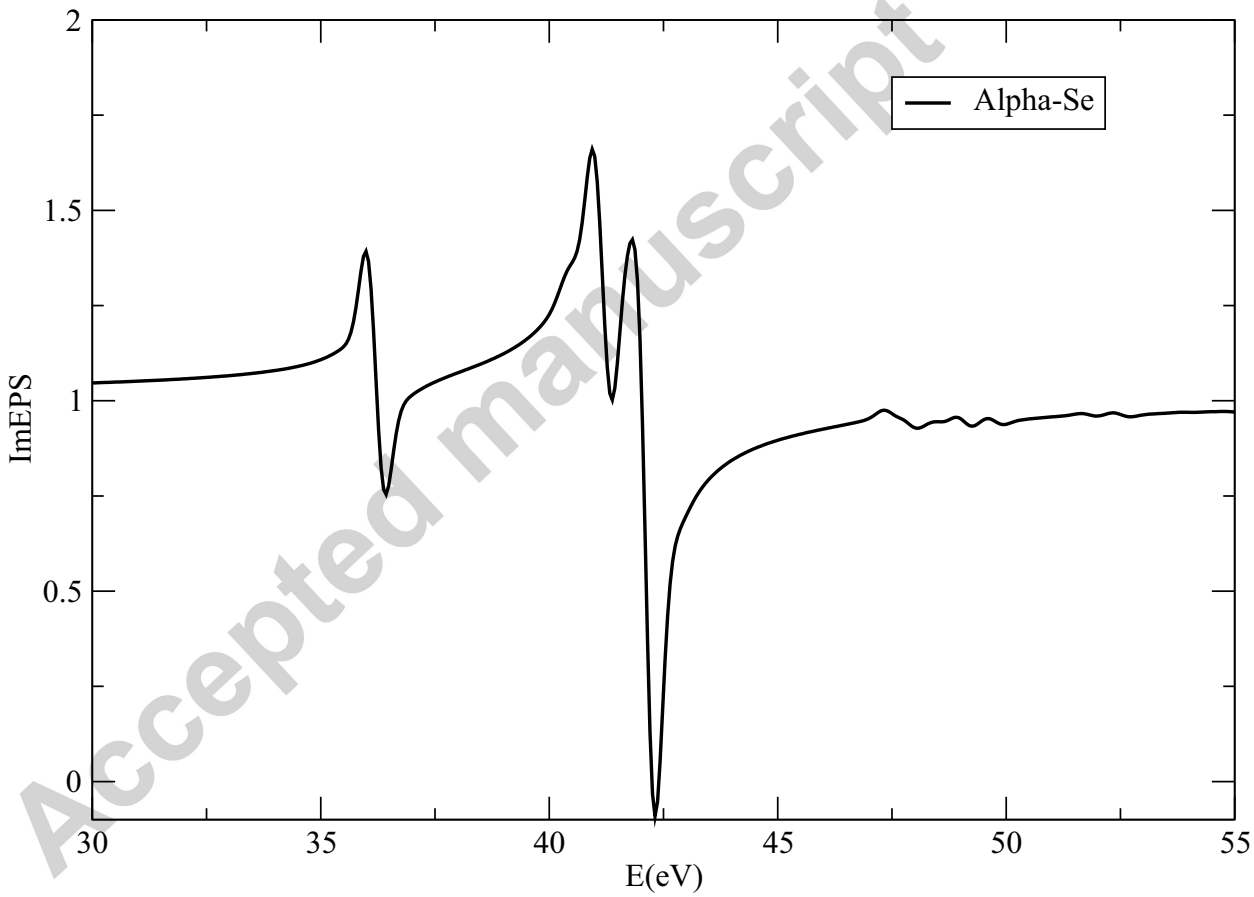

Figure 2: Imaginary part of the dielectric function due to $\alpha - Se$

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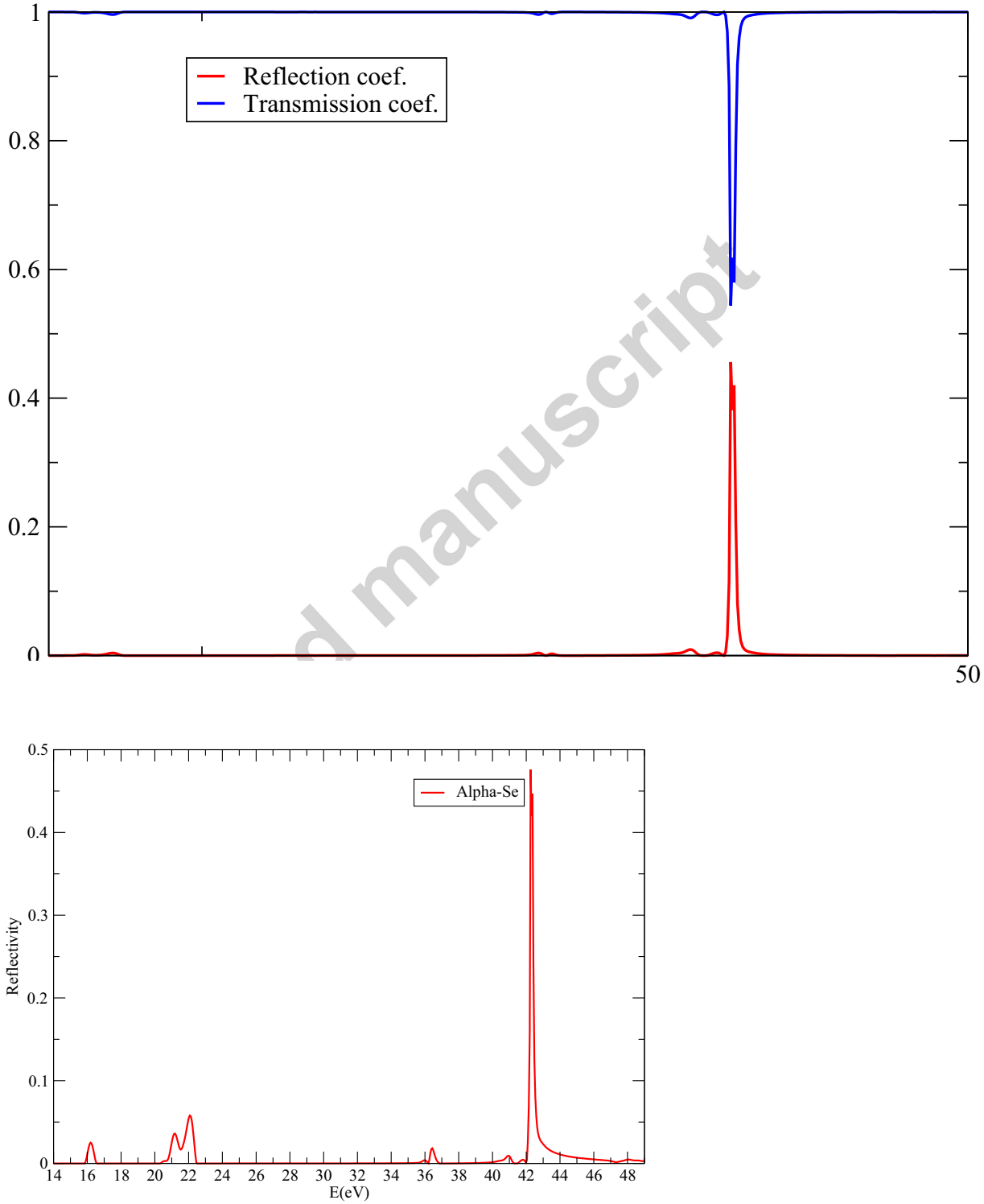

Figure 3: Optical coefficients and Reflectivity of Selenium at high pressure

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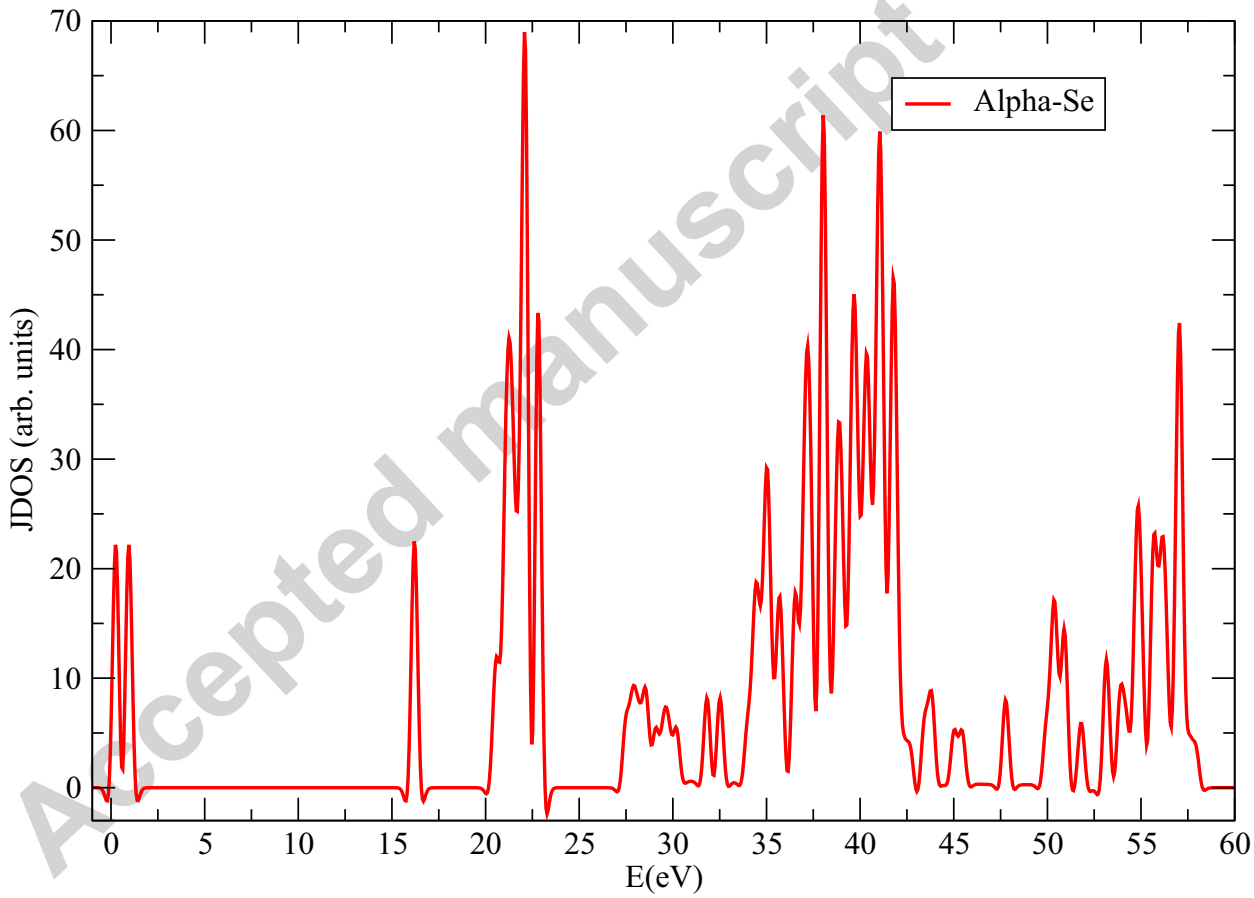

Figure 4: The joint density of state due to $\alpha-Se$

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