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Effective atomic numbers and electron densities of $CuGaSe_2$ semiconductor in the energy range 6–511 keV

A. Çelik, U. Çevik,* E. Bacaksiz and N. Çelik

Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

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The effective atomic numbers and electron densities of the $CuGaSe_2$ semiconductor were calculated at 29 different energies from 6.9 to 511.0 keV by using the measured mass attenuation coefficients. Also, the mass attenuation coefficients for Cu, Ga, and Se elements were obtained at this energy range. The samples were irradiated using Cd-109, Co-57, Ba-133, and Na-22 radioactive sources. The x-ray energies were obtained using secondary targets. The gamma and x-rays were counted by an Ultra-LEGe detector with a resolution of 0.55 at 122.0 keV. The mass attenuation coefficients were compared with theoretical ones obtained using the XCOM program.

INTRODUCTION

A revolution in gamma and x-ray imaging with suitable detectors was started in many important applications such as medicine, on-line process control, and security during the last decades. At present, the most attractive solution is offered by compound semiconductors with a relatively wide band gap (>1.2 eV) which may operate at room temperature.[1] In such applications a very important characteristic of the semiconductor is given by its radiation attenuation. This implies that the atomic number (Z) of at least one of the constituents must be larger than 30.[2] $CuGaSe_2$ is especially attractive for thin film solar cell application because of its high optical absorption coefficient. High conversion efficiency of 19.5% was reported both on a laboratory scale and on large areas.[3] $CuGaSe_2$ chalcopyrite semiconductors enable the production of absorber materials having a wide range of band gaps varying between 1.0 and 1.68 eV.[4] Due to its suitable properties (band gap and atomic number of its constitutes) $CuGaSe_2$ may be a useful material for radiation detectors. Thus, the measuring of some parameters such as mass attenuation coefficients, effective atomic numbers, and electron densities would be useful to interpret the interaction of radiation with $CuGaSe_2$ semiconductor.

The scattering and absorption of gamma and x-rays are related to the density and atomic number of an element. In composite materials, it is related to density and effective atomic number. A single number, therefore, cannot represent the atomic number uniquely across the entire energy range, as the partial interaction cross-sections have different elemental number dependence. This number, for composite materials, is called effective atomic number and varies with energy. Many attempts have been made to determine effective atomic number and electron densities in some composite materials.[5–7]

*Correspondence to: U. Çevik, Department of Physics, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey. E-mail: ugurc@ktu.edu.tr

A convenient way of comparing the radiation characteristics of semiconductor materials such as $CuGaSe_2$, is to consider either the mass attenuation coefficient or the effective atomic number. In this article, the effective atomic number Z_{eff} and the electron number densities N_{el} have been calculated for $CuGaSe_2$ semiconductor using previously measured mass attenuation coefficient data in the photon energy regions of 6–511 keV.

THEORY

The effective atomic number and electron density for photon absorption can be obtained by using mass attenuation coefficients of the chemical compounds. The mass attenuation coefficient $(\mu/\rho)_c$ for any chemical compound is given by

$$(\mu/\rho)_c = \sum_i w_i(\mu/\rho)_i \quad (1)$$

where ρ is the mass density of the sample, w_i and $(\mu/\rho)_i$ are the weight fraction and mass attenuation coefficient of the i*th* constituent element, respectively.[8]

Theoretical values for the mass attenuation coefficients were calculated by XCOM program which was developed by Berger and Hubbell[9] (1999) for calculating mass attenuation coefficients or photon interaction cross-section for any element, compound or mixture at energies of 1 keV–100 GeV.

Values of mass attenuation coefficients were then used to determine the total molecular cross-section $\sigma_{t,m}$ by the following relation[10]:

$$\sigma_{t,m} = \left(\frac{\mu}{\rho}\right)_c \frac{M}{N_A} \quad (2)$$

where M is the molecular weight, N_A is the Avogadro's number.

The total atomic cross-section $\sigma_{t,a}$ can be easily determined from the following equation[10]:

$$\sigma_{t,a} = \frac{1}{N_A}\sum_i f_i A_i \left(\frac{\mu}{\rho}\right)_i = \frac{\sigma_{t,m}}{\sum_i n_i} \quad (3)$$

where f_i is the fractional abundance of element i with respect to number of atoms; n_i and A_i are the number of formula units and the atomic weight, respectively, of the constituent element i.

The total electronic cross-section $\sigma_{t,el}$ for the individual element is expressed by the following formula[10]:

$$\sigma_{t,el} = \frac{1}{N_A}\sum_i \frac{f_i A_i}{Z_i}\left(\frac{\mu}{\rho}\right)_i = \frac{\sigma_{t,a}}{Z_{eff}} \quad (4)$$

The total atomic and electronic cross-sections are related to the effective atomic number (Z_{eff}) through the following relation:

$$Z_{eff} = \frac{\sigma_{t,a}}{\sigma_{t,el}} \quad (5)$$

The effective electron number or electron density, N_{el} (number of electrons per unit mass) can be derived from Singh *et al.*[6]:

$$N_{el} = \frac{(\mu/\rho)_c}{\sigma_{t,el}} = \frac{N_A}{M} Z_{eff} \sum_i n_i \quad (6)$$

EXPERIMENTAL

The starting materials of $CuGaSe_2$ were synthesized from a stoichiometric mixture of its constituent elements. Copper, gallium, and selenium of 5 N purity were taken in a sealed quartz ampoule evacuated to a pressure of 10^{-3} Torr. The mixture was heated in a vertical furnace initially to a temperature of 200 °C and kept for 24 h to ensure better homogeneity and to avoid the risk of explosion due to the exothermic reaction of gallium and selenium. Then the temperature was slowly increased to 1100 °C and was maintained for 48 h. Finally, the ampoule was quenched to room temperature. The ingot obtained was pulverized and pressed into pellets with radius of 13 mm under a pressure of 3 ton cm^{-2} for measurements. High purity certified Cu, Ga, and Se elemental materials were also used to perform the mass attenuation coefficient measurement. The element Ga is in the ingot form, while the purchased Cu and Se elements are in the form of powder. The purity of the samples was better than 99.999%. The high purity level of the samples is one of the most important aspects since it reduces the uncertainty of the measured results due to the impurities. The powder samples were sieved with 400 mesh while the ingot sample was cut into small pieces and then the samples were pressed into pellets of radius 13 mm under a pressure of 3 ton cm^{-2}.

The mass attenuation coefficients were determined by performing transmission experiment in narrow beam geometry. The measurements in the energy range of 6.9 and 67.2 keV were performed by x-ray fluorescence using

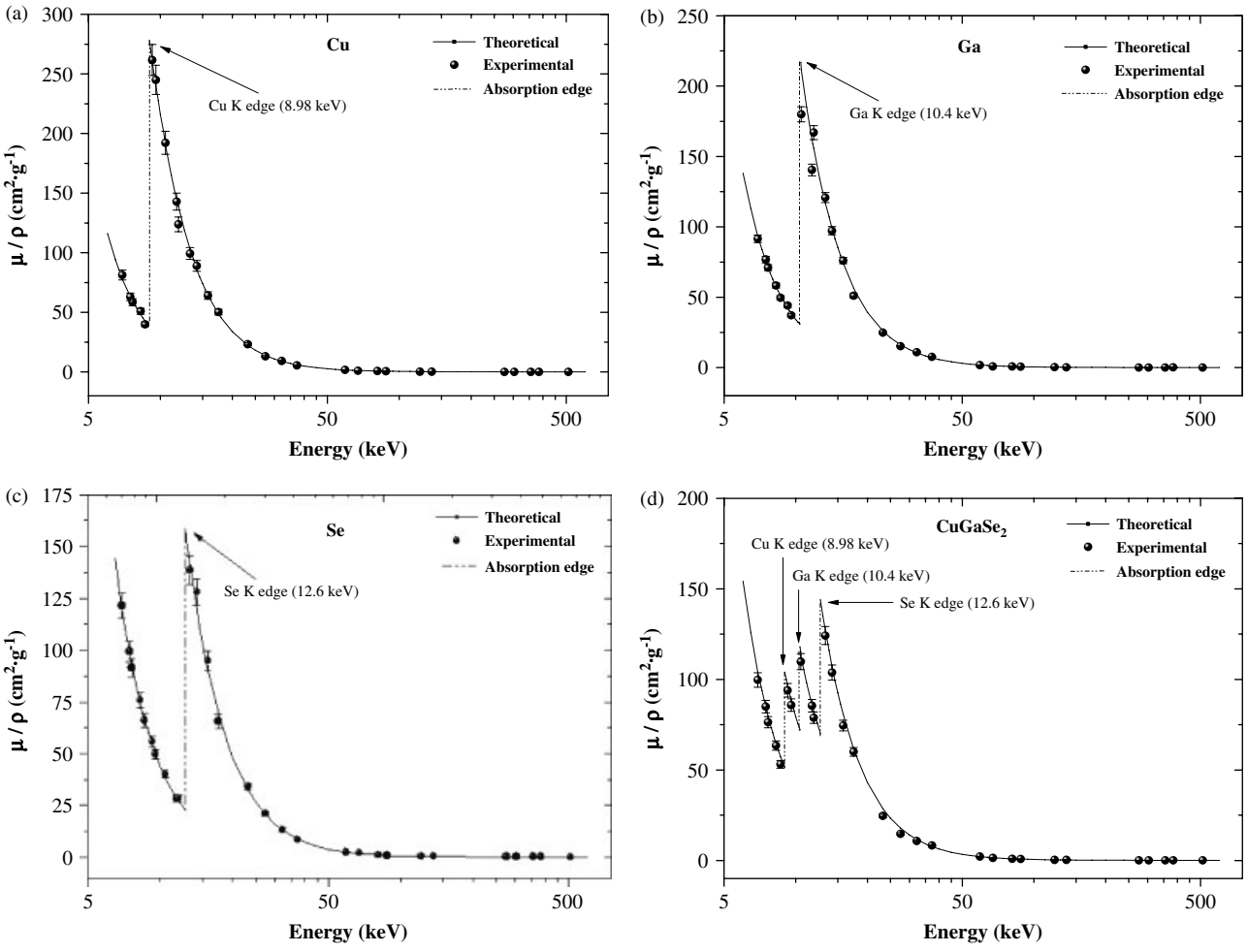

Figure 1. Mass attenuation coefficients at different energies for (a) Cu, (b) Ga, (c) Se, and (d) $CuGaSe_2$.

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a secondary target system. The gamma rays emitted from Am-241 and Co-57 annular radioactive sources were used to excite secondary targets such as Co, Ni, Zn, Ga, As, Br, Sr, Mo, Cd, Te, Ba, Nd, and W. The samples were irradiated by photons emitted from Cd-109, Co-57, Ba-133, and Na-22 radioactive sources in the energy range of 81 and 511 keV. The experimental setup can be found in detail in Cevik and Baltas.[11] The only difference in our experimental setup was the detector type used (Ultra-LEGe detector with FWHM 0.55 at 122.0 keV, active area 30 mm^2, thickness 5 mm and Be window thickness 0.4 μm).

RESULT AND DISCUSSION

The experimental and theoretical mass attenuation coefficients (μ/ρ) of Cu, Ga, Se, and $CuGaSe_2$ at different energies are listed in Table 1. It is also shown in Fig. 1(a–d) that the mass attenuation coefficients changes with the photon energy for Cu, Ga, Se, and $CuGaSe_2$, respectively. At low photon energies where the photoelectric process and its associated strong Z dependence predominate, an accurate knowledge of the purity of elemental materials and the composition of mixtures are required for obtaining correct experimental and calculated data. As shown in Table 1, a good agreement was observed at low energies between theoretical and experimental data compared with higher energies. Compton scattering is the predominant process for high energies such as studied range of 100–511 keV. Since the atomic numbers of Cu ($Z = 29$), Ga ($Z = 31$), Se ($Z = 34$), and $CuGaSe_2$ ($Z_{eff} \approx 32$) are approximately near each other, the mass attenuation coefficients of these materials at these energies are approximately same as shown in Table 1. Percent discrepancy *vs* energy was plotted in Fig. 2. While the percent discrepancy increases at absorption edges at the low-energy region, it increases with increasing energy at high energies. This can be attributed that the photoelectric effect is mainly responsible from absorption, but when energy increases, the Compton effect begins dominant. At higher energies, the contributions from scattering processes become commensurate with those from the photoelectric absorption.

The theoretical mass attenuation coefficient of $CuGaSe_2$ were calculated using the mixture rule (Eqn (1)) which is standard practice to assuming that the contribution of each element to the attenuation is additive. This assumption yields the well-known mixture rule which gives the attenuation coefficient of any substance as the sum of the appropriately

Table 1. Theoretical and experimental values of mass attenuation coefficients μ/ρ ($cm^2.g^{-1}$) for Cu, Ga, Se and $CuGaSe_2$ semiconductors

Energy (keV)	Cu		Ga		Se		$CuGaSe_2$	
	$\mu/\rho_{Theo.}$	$\mu/\rho_{Exp.}$	$\mu/\rho_{Theo.}$	$\mu/\rho_{Exp.}$	$\mu/\rho_{Theo.}$	$\mu/\rho_{Exp.}$	$\mu/\rho_{Theo.}$	$\mu/\rho_{Exp.}$
6.9	77.8	81.3 ± 4.1	93.2	91.6 ± 2.7	120	121 ± 5	104	100 ± 4
7.5	63.1	62.9 ± 3.1	75.7	76.8 ± 2.3	97.3	99.3 ± 4.0	84.7	85.0 ± 3.4
7.6	59.6	58.6 ± 2.9	71.4	71.0 ± 2.1	91.9	91.4 ± 3.7	80.0	76.4 ± 3.1
8.3	48.1	50.9 ± 2.5	57.7	58.4 ± 1.8	74.3	75.8 ± 3.0	64.6	63.5 ± 2.5
8.6	**42.7**	**40.0 ± 2.0**	51.2	49.7 ± 1.5	65.9	66.0 ± 2.6	**57.3**	**53.1 ± 2.1**
9.3	**260**	**262 ± 13**	42.3	44.1 ± 1.3	54.6	55.8 ± 2.2	**96.4**	**94.0 ± 3.8**
9.6	240	245 ± 12	**38.6**	**37.2 ± 1.1**	49.7	49.7 ± 2.0	**88.6**	**85.8 ± 3.4**
10.5	190	192 ± 10	**212**	**180 ± 5**	38.2	40.1 ± 1.6	**113**	**110 ± 4**
11.7	144	143 ± 7	162	140 ± 4	28.6	28.4 ± 1.1	85.8	85.5 ± 3.4
11.9	139	124 ± 6	156	167 ± 5	**27.4**	**28.4 ± 1.1**	**82.4**	**78.9 ± 3.2**
13.3	103	99.3 ± 5.0	117	121 ± 4	**140**	**138 ± 5**	**127**	**124 ± 5**
14.2	86.0	89.0 ± 4.5	98.6	97.3 ± 2.9	119	128 ± 5	107	104 ± 4
15.8	64.3	64.0 ± 3.2	74.4	76.1 ± 2.3	90.2	94.7 ± 3.8	80.8	74.5 ± 3.0
17.5	48.7	50.2 ± 2.5	56.5	51.1 ± 1.5	68.9	65.6 ± 2.6	61.5	60.0 ± 2.4
23.2	22.4	23.3 ± 1.2	26.1	24.9 ± 0.7	32.3	34.2 ± 1.4	28.6	27.4 ± 1.0
27.5	13.9	13.1 ± 0.7	16.3	15.3 ± 0.5	20.3	21.1 ± 0.8	17.9	16.8 ± 0.6
32.2	8.9	9.3 ± 0.5	10.5	10.9 ± 0.3	13.1	13.3 ± 0.5	11.6	10.8 ± 0.4
37.3	5.9	5.5 ± 0.3	7.0	7.7 ± 0.2	8.7	8.4 ± 0.3	7.7	8.3 ± 0.3
59.3	1.6	1.64 ± 0.08	1.93	1.74 ± 0.05	2.42	2.31 ± 0.10	2.13	2.18 ± 0.10
67.2	1.2	0.97 ± 0.05	1.38	0.90 ± 0.03	1.72	1.97 ± 0.08	1.52	1.39 ± 0.06
81.0	0.7	0.72 ± 0.04	0.85	0.84 ± 0.03	1.06	1.02 ± 0.04	0.94	0.90 ± 0.04
88.0	0.61	0.61 ± 0.03	0.70	0.66 ± 0.02	0.85	0.81 ± 0.03	0.77	0.76 ± 0.03
122.1	0.31	0.30 ± 0.02	0.34	0.34 ± 0.01	0.40	0.35 ± 0.01	0.37	0.37 ± 0.02
136.5	0.26	0.22 ± 0.01	0.28	0.27 ± 0.01	0.32	0.35 ± 0.01	0.29	0.29 ± 0.01
276.4	0.12	0.11 ± 0.01	0.12	0.07 ± 0.01	0.12	0.12 ± 0.01	0.12	0.12 ± 0.01
302.8	0.11	0.12 ± 0.01	0.11	0.12 ± 0.01	0.11	0.12 ± 0.01	0.11	0.11 ± 0.01
356.0	0.10	0.08 ± 0.01	0.10	0.11 ± 0.01	0.10	0.10 ± 0.01	0.10	0.09 ± 0.01
383.8	0.10	0.10 ± 0.01	0.10	0.11 ± 0.01	0.09	0.09 ± 0.01	0.09	0.10 ± 0.01
511.0	0.08	0.09 ± 0.01	0.08	0.07 ± 0.01	0.08	0.07 ± 0.01	0.08	0.07 ± 0.01

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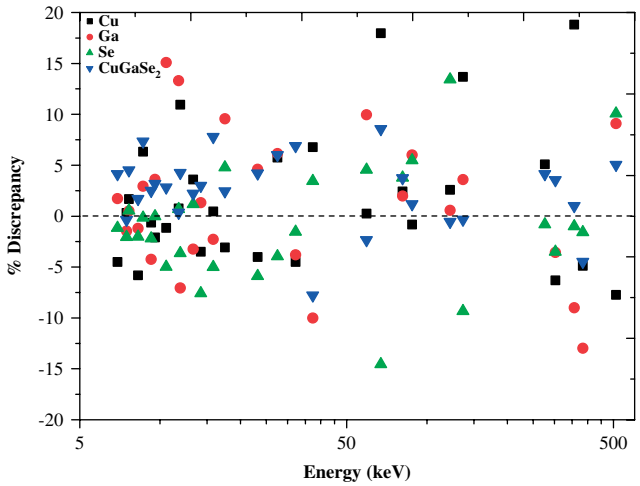

Figure 2. Percent discrepancy between experimental and theoretical mass attenuation coefficients.

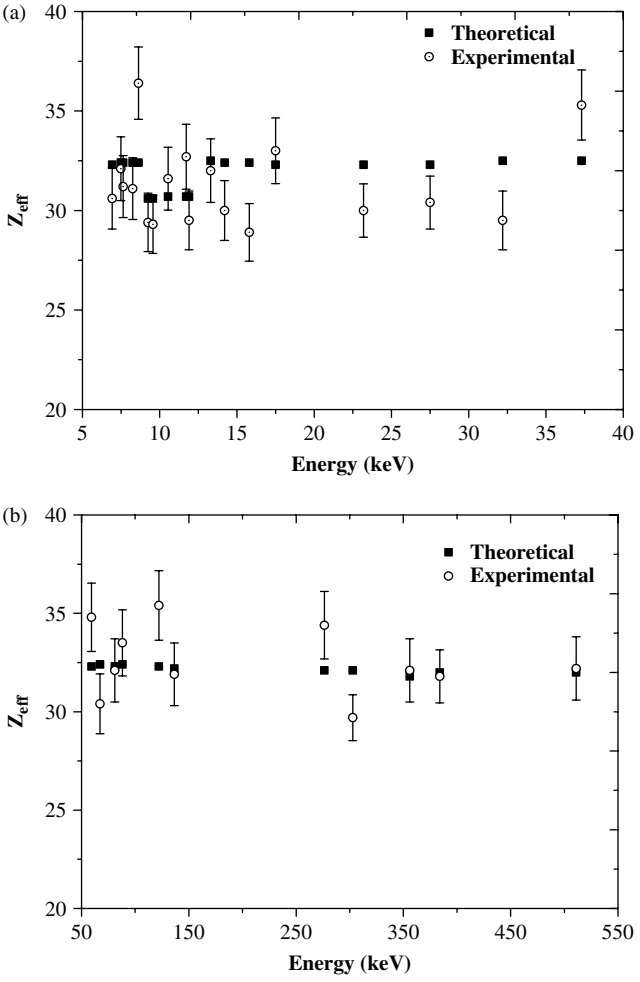

Figure 3. Effective atomic numbers for $CuGaSe_2$ at energy ranges of (a) 5–40 keV, and (b) 50–550 keV.

weighted contributions from the individual atoms. As shown in Fig. 1(d), some discontinuities were observed at mass attenuation coefficients of $CuGaSe_2$ due to absorption edges of individual atoms (Cu, Ga, and Se).

By using the experimental data of μ/ρ, the effective atomic numbers (Z_{eff}) and the electron number densities

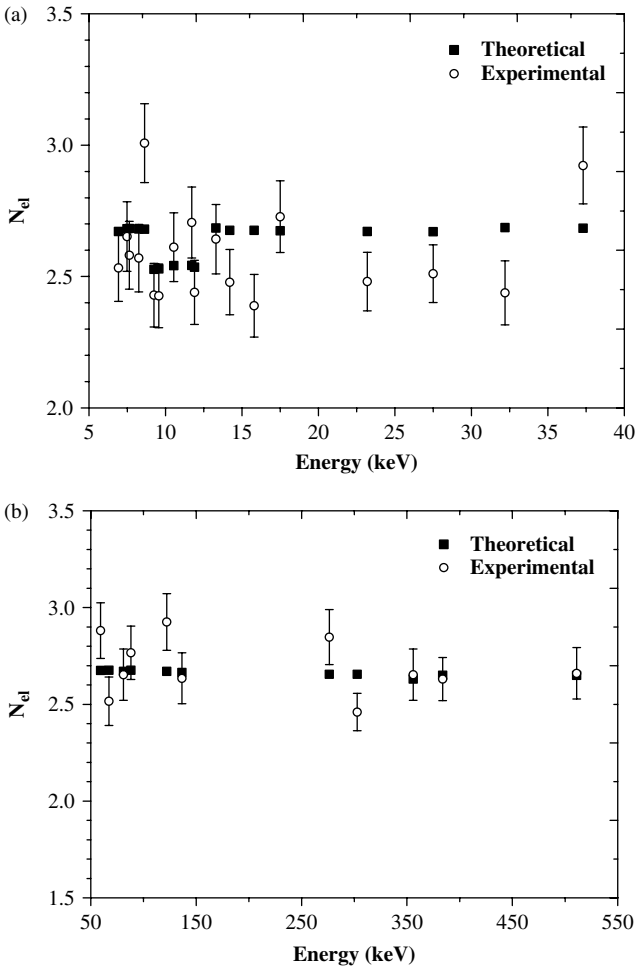

Figure 4. Electron number densities of $CuGaSe_2$ at energy range of (a) 5–40 keV, and (b) 50–550 keV.

(N_{el}) were determined from Eqns (5) and (6), respectively. Obtained results are given in Table 2 along with theoretical values calculated from $(\mu/\rho)_{theo}$ in Table 1. Typical plots of Z_{eff} and N_{el} as a function of photon energy are shown in Figs 3(a, b) and 4(a, b), respectively. As shown in Fig. 3(a), the effective atomic numbers of $CuGaSe_2$ semiconductor material decrease with increasing energy near the K absorption edges of each element. The same behavior is observed for N_{el} in Fig. 4(a). The average effective atomic numbers of $CuGaSe_2$ are approximately 32 in the range of 6–511 keV (Table 2). In contrast, the effective atomic number decreased to 30 at 9–12 keV energy range because of Cu, Ga, and Se K absorption edges. The Z_{eff} value of a material varies within a range with lowest and highest atomic numbers of its constituent elements as limits. The Z_{eff} value for $CuGaSe_2$ remains almost constant at the studied energy region. This is because of the proximity of the atomic numbers of the elements involved. In other words, Z_{eff} value lies between 29 (Cu) and 34 (Se), which is about 32. At higher energies, especially above absorption edges of Cu, Ga, and Se elements, there are no differences between effective atomic numbers up to 511 keV. It can be attributed that while the Compton effect is dominant at these energies, the photoelectric effect is negligible.

The overall error in the present measurements is estimated to be 3–5%. This error is due to the evaluation of

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Table 2. Theoretical and experimental values of effective atomic numbers (Z_{eff}) and electron densities ($N_{el} \times 10^{23}$) for $CuGaSe_2$ semiconductor

Energy (keV)	Z_{eff} (Theo.)	Z_{eff} (Exp.)	N_{el} (Theo.)	N_{el} (Exp.)
6.9	32.3	30.6 ± 1.2	2.67	2.53 ± 0.10
7.5	32.4	32.1 ± 1.3	2.68	2.65 ± 0.11
7.6	32.4	31.2 ± 1.2	2.68	2.58 ± 0.10
8.3	32.4	31.1 ± 1.2	2.68	2.57 ± 0.10
8.6	32.4	30.6 ± 1.2	2.68	2.53 ± 0.10
9.3	**30.6**	**29.4 ± 1.2**	**2.53**	**2.43 ± 0.10**
9.6	**30.6**	**29.3 ± 1.2**	**2.53**	**2.43 ± 0.10**
10.5	**30.7**	**31.6 ± 1.3**	**2.54**	**2.61 ± 0.10**
11.7	**30.7**	**32.7 ± 1.3**	**2.54**	**2.71 ± 0.11**
11.9	30.7	29.5 ± 1.2	2.54	2.44 ± 0.10
13.3	32.5	32.0 ± 1.3	2.68	2.64 ± 0.11
14.2	32.4	30.0 ± 1.2	2.68	2.48 ± 0.10
15.8	32.4	28.9 ± 1.2	2.68	2.39 ± 0.10
17.5	32.3	33.0 ± 1.3	2.67	2.73 ± 0.11
23.2	32.3	30.0 ± 1.1	2.67	2.48 ± 0.09
27.5	32.3	30.4 ± 1.1	2.67	2.51 ± 0.09
32.2	32.5	29.5 ± 1.2	2.69	2.44 ± 0.10
37.3	32.5	35.3 ± 1.4	2.68	2.92 ± 0.12
59.3	32.3	34.8 ± 1.4	2.67	2.88 ± 0.12
67.2	32.4	30.4 ± 1.2	2.68	2.52 ± 0.10
81.0	32.3	32.1 ± 1.3	2.67	2.65 ± 0.11
88.0	32.4	33.5 ± 1.3	2.68	2.77 ± 0.11
122.1	32.3	35.4 ± 1.4	2.67	2.93 ± 0.12
136.5	32.2	31.9 ± 1.3	2.66	2.63 ± 0.11
276.4	32.1	34.4 ± 1.4	2.65	2.85 ± 0.11
302.8	32.1	29.7 ± 1.4	2.66	2.46 ± 0.12
356.0	31.8	32.1 ± 1.3	2.63	2.65 ± 0.11
383.8	32.0	31.8 ± 1.6	2.65	2.63 ± 0.13
511.0	32.0	32.2 ± 1.3	2.65	2.66 ± 0.11

peak areas, thickness measurements, and counting statistics. The error originating from the counting statistics was about 0.5–2%. The rest of the uncertainty stems from the evaluation of peak areas and thickness measurements.

CONCLUSIONS

In this work, the effective atomic numbers and the electron densities of $CuGaSe_2$ semiconductor were calculated by measuring the mass attenuation coefficients of Cu, Ga, Se pure elements at the energy range of 6–511 keV. The results were compared with the theoretical ones and a good agreement was observed between them. The variation of Z_{eff} value with energy for this material can be attributed to the relative domination of the partial process such as photoelectric effect, coherent scattering, and incoherent scattering. The present data are expected to serve for the purpose of understanding the radiation interaction mechanism with $CuGaSe_2$ for potential usage as radiation detector material.

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