Study of Charge Transfer and Structure Factor Calculation of Europium Selenide (EuSe)

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The presence of charge transfer in EuSe is analyzed by experimental and theoretical X-ray diffraction data. The direction and amount of charge transfer are inferred by plotting and comparing the structure factor of the components. Thus a charge transfer of 0.22 electrons is obtained in EuSe from europium (Eu) to selenium (Se).

Key words: EuSe; Charge Transfer; Valence Fluctuation; XRD.
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1. Introduction

Rare earth compounds have increasingly been studied in the last decades and much valuable information on magnetism, crystal fields and related phenomena of these materials has been obtained. The growing interest in rare earth compounds is activated by the unique physical properties associated with the localized character of the 4f levels of rare earth ions [1, 2]. The rare earth monochalcogenides are structurally simplest materials, and numerous experimental works have been done on the destabilization behaviour of the f-shell of these compounds. Till now, the theoretical description of these transitions remains a challenging problem. This paper deals with the presence of charge transfer in EuSe based on structure factor calculation. All III-V compounds with zinc blende structure involve a charge transfer between the nearest neighbours. Similarly, II-VI semiconductors like zinc selenide (ZnSe) involve charge transfer [3]. Though different techniques are available to determine the charge transfer, according to Cochran [4] only X-ray diffraction (XRD) and piezo

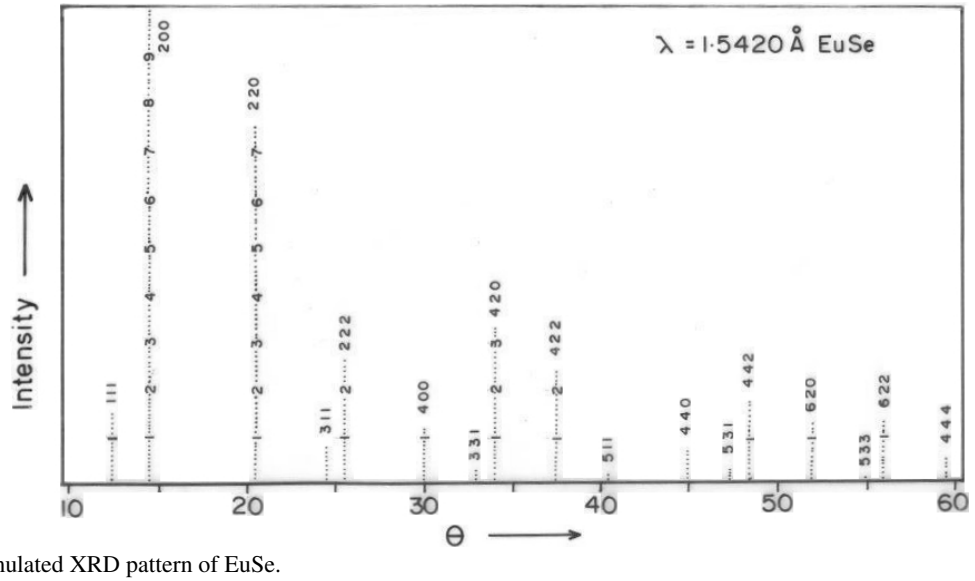

Fig. 1. Simulated XRD pattern of EuSe.

Table 1. Experimental and theoretical XRD data of plane indices (*hkl*), interplanar spacing (*d*), relative intensity (I/I_0) and structure factors (F_{hkl}) of EuSe.

Sl.	Experimental [5]			Theoretical			
No.	*hkl*	*d*	I/I_0	*hkl*	*d*	I/I_0	F_{hkl}
1	111	3.560	30	111	3.5709	15.3	87.5
2	200	3.087	100	200	3.0925	100.0	302.0
3	220	2.184	100	220	2.1867	74.9	273.0
4	311	1.851	30	311	1.8648	7.9	76.0
5	222	1.783	50	222	1.7855	26.3	252.3
6	400	1.545	30	400	1.5462	12.1	236.1
7	–	–	–	331	1.4189	3.2	67.5
8	420	1.381	100	420	1.3830	32.9	222.9
9	422	1.261	70	422	1.2625	24.2	211.7
10	–	–	–	511	1.1903	1.9	62.2
11	–	–	–	333	1.1903	0.6	62.2
12	440	1.093	30	440	1.0934	8.0	193.7
13	–	–	–	531	1.0455	2.8	58.7
14	442	1.030	70	442	1.0308	14.1	186.1
15	600	1.030	70	600	1.0308	3.5	186.1
16	620	0.977	50	620	0.9779	13.3	179.3
17	–	–	–	533	0.9432	1.4	56.3
18	622	0.933	50	622	0.9324	13.2	173.1
19	–	–	–	444	0.8927	4.6	167.4

electric studies could give precisely the sign and magnitude of charge transfer. Therefore, the presence of charge transfer in EuSe has been studied both theoretically and experimentally by using X-ray diffraction technique, and the results are presented in this paper.

2. X-Ray Diffraction

X-Ray diffraction data have shown that EuSe crystallizes in NaCl type structure with space group $Fm\bar{3}m$ [5]. The theoretical X-ray powder diffraction (XRD) pattern has been simulated by using the Lazy-Pulverx programme and is shown in Figure 1. The theoretical XRD data have been compared with the experimental ones in Table 1, which gives the indices of planes (*hkl*), interplanar spacing (*d*), relative intensity (I/I_0) and the deduced structure factors (F_{hkl}) of EuSe. It has been observed that the experimental and theoretical XRD data are in good agreement.

3. Theory

Saravanan et al. [6–9] have done X-ray diffraction studies on the III-V semiconductors such as GaAs, InSb, GaP and InP over the entire reciprocal space [10]. The model proposed by Saravanan et al. has been used for confirming the presence of charge transfer in these semiconductor compounds [6–9]. The same model has been followed in the present work and the X-ray diffraction data [5] have been used.

In the present method the elemental components of structure factors are plotted versus $\sin\theta/\lambda$. Then the form factors at $\sin\theta/\lambda = 0$ will be equal to the atomic number (Z) of the element. Any deviation from the value of Z can be attributed to the charge transfer [3]. The splitting of the total structure factors into individual components is accomplished by exploiting the structure factor expressions of $h+k+l = 4n$ and $4n+2$ type reflection. That is

$$F_1^0 = 4(f_{\mathrm{Eu}} + f_{\mathrm{Se}}) \quad \text{for} \quad h+k+l = 4n,$$
$$F_2^0 = 4(f_{\mathrm{Eu}} - f_{\mathrm{Se}}) \quad \text{for} \quad h+k+l = 4n+2.$$

By suitable mathematical manipulations, the individual components of the structure factor of Eu and Se are

$$f_{\mathrm{Eu}} = (F_1^0 + F_2^0)/8$$

and

$$f_{\mathrm{Se}} = (F_1^0 - F_2^0))/8.$$

But, the F_1^0 and F_2^0 values are at different $\sin\theta/\lambda$ values. So, one cannot add or subtract these quantities to get the component structure factor [11]. Hence, the atomic form factors f_{Eu} and f_{Se} have been found from scattering factor curves. The experimental and theoretical atomic form factors of EuSe for $\sin\theta/\lambda$ (after applying scaling correction) are presented in Table 2 and plotted in Figure 2.

4. Results and Discussion

EuSe crystallizes with face-centered cubic structure lattice parameter of 6.185 Å and the space group of $Fm\bar{3}m$. It has four Eu atoms and four Se atoms per unit cell. The experimental atomic form factors have been calculated from the XRD data. The theoretical simulated XRD pattern obtained by the Lazy-Pulverx programme is shown in Figure 1. Both the theoretical and experimental XRD data are found to be in good agreement, as shown in Table 1. Table 1 also gives the structure factors F_{hkl} of EuSe. The experimental and theoretical atomic form factors for different $\sin\theta/\lambda$, after applying the scaling correction, are reported in Table 2 and plotted in Figure 2. The values of individual form factors f^0 at $\sin\theta/\lambda$ are given in Table 3. When charge is transferring from Eu to Se in EuSe, f_{Eu}^0 should decrease and f_{Se}^0 should increase. It is well known that the atomic number of Eu is 63 and of Se it is 34. Therefore, the atomic form factors f_{z0} of the neutral atom of

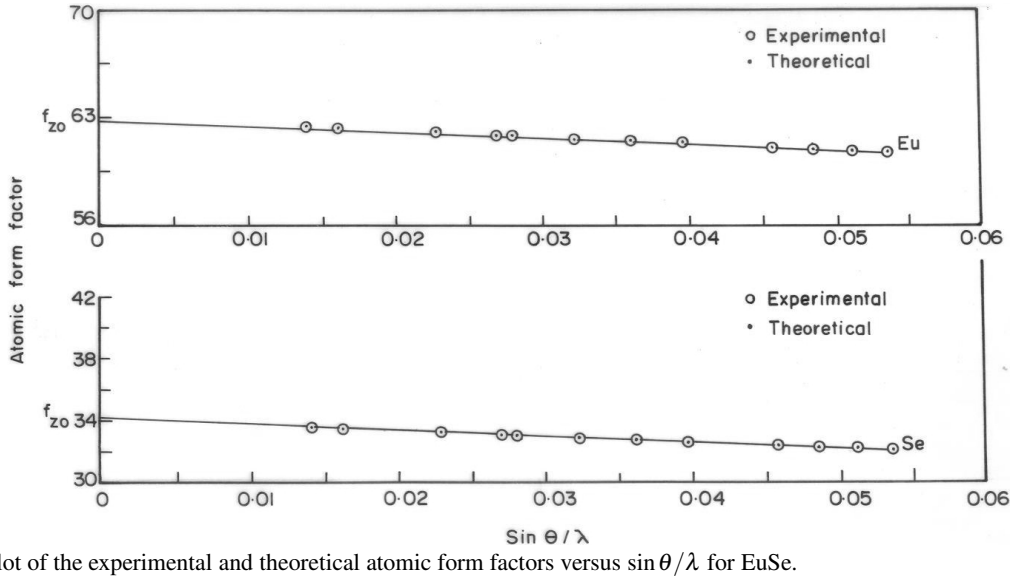

Fig. 2. Plot of the experimental and theoretical atomic form factors versus $\sin\theta/\lambda$ for EuSe.

Table 2. Atomic form factors of EuSe.

Sl. No.	Experimental $\sin\theta/\lambda$	f_{Eu}	f_{Se}	Theoretical $\sin\theta/\lambda$	f_{Eu}	f_{Se}
1	0.01405	62.34307	33.52920	0.01400	62.31022	33.52920
2	0.01620	62.20073	33.47080	0.01617	62.23358	33.49270
3	0.02289	61.91606	33.21533	0.02287	61.92701	33.20800
4	0.02701	61.69708	33.12044	0.02681	61.69708	33.11314
5	0.02804	61.69708	33.06204	0.02800	61.72993	33.06204
6	0.03236	61.45620	32.90876	0.03234	61.44526	32.91606
7	0.03621	61.31387	32.81387	0.03615	61.30292	32.82117
8	0.03965	61.17153	32.62409	0.03960	61.11679	32.63139
9	0.04575	60.84307	32.43431	0.04573	60.83212	32.44161
10	0.04854	60.70073	32.33942	0.04850	60.68978	32.37591
11	0.05117	60.61314	32.28830	0.05113	60.61310	32.28102
12	0.05359	60.47080	32.19343	0.05362	60.47080	32.18613

Eu and Se are indicated by f_{z0} in Figure 2. It makes clear that f^0_{Eu} is smaller than the atomic number of Eu by 0.22. Consequently, f^0_{Se} is larger than the atomic number of Se by more or less the same amount. This indicates the transfer of 0.22 electrons from Eu to Se which confirms the presence of charge transfer. Thus, the presence of an intermediate valence fluctuation in EuSe agrees with experimental reports [12 – 15].

Table 3. Values of elemental form factor components at $\sin\theta/\lambda = 0$.

Element	Experimental f^0	Theoretical f^0
Eu	62.78	62.78
Se	34.24	34.24

5. Conclusions

The simulated theoretical XRD pattern agrees with the experimental XRD data. The structure factor of EuSe and the atomic form factors are calculated. The presence of charge transfer of 0.22 electrons from Eu to Se is confirmed in EuSe which agrees with the intermediate valence fluctuation observed experimentally [12 – 15].

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