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Theoretical method for calculating the electrical properties of rare earth chalcogenide compounds

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Abstract : A simple theoretical model is developed for determining the electrical transport properties of the rare earth chalcogenide compounds. This method requires only two parameters, namely, lattice constant and activation energy to calculate the electrical properties such as carrier concentration, carrier effective mass, carrier mobility, dielectric constant and electrical resistivity at different pressures. It also provides information on the type of conductivity. The results are in fair agreement with the experimental results.

Keywords : Electrical resistivity, lattice constant, chalcogenide compounds

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1. Introduction

A simple theoretical model is developed for determining the electrical properties of the rare earth chalcogenide compounds under pressure. The model correlates the lattice parameter with the electrical properties. This method requires only two parameters, namely, lattice constant and activation energy. It calculates the important electrical properties involved in transport mechanism such as carrier concentration, carrier mobility, carrier effective mass, electrical resistivity and dielectric constant. The validity of this method is tested by calculating these parameters for samarium and ytterbium monochalcogenides and compared with the available experimental results.

2. Theoretical methodology

Before going into detail, some important aspects involved in these compounds are discussed. The atoms of all rare earth elements except Eu, Sm and Yb exist in trivalent state. The divalent Eu, Sm and Yb are particularly ideal as most of them are semiconducting [1] and ionic [2]. The notable property of the rare earth chalcogenides is that they are found to be in a semiconducting state when the rare earth ion is divalent and metallic when it is trivalent [3]. It is reported from the magnetic susceptibility studies that for the compounds containing dipositive metal ions, the third valence electrons are highly localized in $4f$ levels. This would result in a full $4f$ shell for the ytterbium ions, half full for the europium ions and nearly half full for the samarium ions [4]. The highly localized f electrons do not contribute to the electrical conductivity [5]. Experimental results show that the compounds of Sm, Yb and Eu have no conduction electrons in ground state. The most likely process which gives carriers for conduction is thermal activation of electrons from the $4f$ shell to the conduction band. Such a mechanism would give n-type conductivity [5]. Here, the question of which type of scattering is dominant arises. The answer is in favour of acoustic scattering. In the case of acoustic scattering, electrical conductivity 'σ' can be calculated by using the formula [6–9]

$$\sigma = neu = 1/\rho, \tag{1}$$

where n is the carrier concentration, e is the electronic charge, u is the carrier mobility and ρ is the electrical resistivity.

The carrier concentration [10] can be calculated from the carrier effective mass m^* and activation energy ΔE by using the expression

$$n = \frac{2(2\pi m^* kT)^{3/2}}{h^3} \exp\left[-\frac{\Delta E}{2kT}\right], \tag{2}$$

where k is the Boltzmann's constant, h Planck's constant and T is the temperature.

Now, the unknown effective mass m^* can be deduced [11] from the lattice parameter a and activation energy ΔE by the formula

$$\frac{m_0}{m^*} = 1 + \frac{2\hbar^2}{m_0 a^2 \Delta E}, \tag{3}$$

where m_0 is the electron rest mass and the ΔE is the activation energy which can be calculated by

$$\Delta E = \alpha p_0. \tag{4}$$

Here, α is the rate of closing of the energy gap with pressure and p_0 is the transition pressure.

The monochalcogenides of samarium and ytterbium are ionic semiconductors [12]. In ionic lattices, thermal motion and diffusion always give rise to vacant sites abandoned by one of the lattice ions or excess ions diffusing between the lattice cells. In this case, the ion is surrounded by electrostatic Coulomb field, which is weaker than that in a vacuum by a factor ε representing the dielectric constant of the lattice [10]. An electron moving in this field is deflected from its initial path more strongly, the closer it approaches the ion, the longer it remains in the field which slows down its motion. So, the electron mobility (u) is given by

$$u = \frac{3\varepsilon^2}{16\pi^2 m^* \left[\ln(1+x) - x/(1+x)\right]} \left[\frac{h}{e}\right]^3 . \tag{5}$$

The value of x is calculated by using the formula

$$x = \left[\frac{h}{e}\right]^2 \left[\frac{e}{m^*}\right] \left[\frac{3N}{8\pi}\right]^{1/3} , \tag{6}$$

where N represents the impurity concentration which is given by

$$N = \frac{n^2}{2\left[\frac{2\pi m^* kT}{h^2}\right]^{3/4} \exp\left[-\frac{\Delta E}{2kT}\right]} , \tag{7}$$

The dielectric constant ε [10] is calculated using the expression

$$\varepsilon^2 = \frac{13.53}{\Delta E} \cdot \frac{m^*}{m_0} . \tag{8}$$

Thus, the electrical properties at various pressures have been calculated using the lattice parameter and activation energy at that pressure. The activation energy at different pressures ΔE_p is obtained as follows.

$$\Delta E_p = (\Delta E - \alpha p) \tag{9}$$

where ΔE represents the activation energy at ambient temperature and pressure and 'p' is the pressure at which the activation energy is to be calculated. The validity of this theoretical model is tested by calculating these electrical properties of SmX and YbX with X = S, Se, Te under pressure and compared with available experimental values.

3. Conclusions

A simple theoretical model is developed for determining the electrical properties under pressure. This method requires only two parameters namely the lattice constant and activation energy (Table 1) to calculate the electrical properties such as carrier concentration, carrier mobility, carrier effective mass, dielectric constant and electrical resistivity under pressure (Table 2). The variation of theoretical electrical resistivity with pressure for SmX and YbX (X = S, Se and Te) is compared with the reported experimental result [13,14] as shown in Figures 1 and 2. They are found to be in fair agreement with each other. The sign of the carrier mobility is of negative sign which implies that the samples are having n-type conductivity which agrees with the reported experimental result [1,14,15]. The limitation of this method is that it can be applied only to semiconductors and not to metals because of the dependence of the activation energy on the energy gap. So the present study has been done only in the domain of semiconductor region. SmS becomes metallic at 6.5 kbar whereas SmSe and SmTe become metallic at about 30 kbar and 50 kbar

Table 1. The values of lattice constant (a) and activation energy (ΔE) used for the present study at different pressures (P) [3,13,14].

Compound	P in kbar	a in Å	ΔE in ev	Compound	P in kbar	a in Å	ΔE in ev
SmS	0	5.970	0.080	YbS	0.0	5.680	0.400
	2	5.930	0.060		5.0	5.122	0.385
	4	5.900	0.030		10.0	4.932	0.370
	–	–	–		15.0	4.553	0.360
SmSe	0	6.200	0.440	YbSe	0.0	5.930	0.400
	5	6.173	0.366		4.5	5.912	0.390
	10	6.144	0.292		9.1	5.905	0.370
	15	6.120	0 220		13.6	5.900	0.360
	20	6.108	0.140		–	–	–
SmTe	0	6.594	0.360	YbTe	0.0	6.360	0.460
	5	6.570	0.350		5.0	6.274	0.405
	10	6.539	0.334		10.0	6.189	0.350
	15	6.505	0.321		15.0	6.147	0.300
	20	6.482	0 122		–	–	–
	25	6.413	0.0625		–	–	–

Table 2. The calculated values of carrier concentration (n), carrier effective mass (m^*), dielectric constant (ε) and carrier mobility (u) at different pressures (P).

Compound	P in kbar	n	m^* $\times 10^{-31}$ kg	ε^2	u in $m^2V^{-1}Sec^{-1}$
SmS	0	3.276×10^{23}	1.437	26.680	-1.291×10^{-3}
	2	3.277×10^{23}	1.109	27.440	-2.667×10^{-3}
	4	2.251×10^{23}	0.585	28.950	$-6\ 315 \times 10^{-3}$
SmSe	0	1.805×10^{21}	4.794	16.180	-2.403×10^{-4}
	5	6.598×10^{21}	4.355	17.670	-1.187×10^{-4}
	10	2.000×10^{22}	3.825	19.460	-4.660×10^{-3}
	15	7.127×10^{22}	3.199	21.600	-2.000×10^{-3}
	20	2.100×10^{23}	2.327	24.680	-2.053×10^{-2}
SmTe	0	$8\ 097 \times 10^{21}$	4.618	19.050	-1.018×10^{-4}
	5	9.580×10^{21}	4.537	19.250	-9.140×10^{-5}
	10	1.253×10^{22}	4.409	19.610	-1.392×10^{-4}
	15	1.552×10^{22}	4.295	19.870	-1.966×10^{-4}
	20	2.918×10^{23}	2.294	27.930	-2.210×10^{-4}
	25	4.036×10^{23}	1.316	31.270	-4.281×10^{-4}

Table 2. *(Cont'd.)*

Compound	P in kbar	n	m^* $\times 10^{-31}$ kg	ε^2	u in $\mathrm{m^2 V^{-1} Sec^{-1}}$
YbS	0	2.100×10^{21}	4.178	15.514	-6.436×10^{-5}
	5	2.361×10^{21}	3.633	14.015	-5.814×10^{-5}
	10	2.878×10^{21}	3.384	13.585	-6.171×10^{-5}
	15	2.938×10^{21}	2.996	12.362	-8.785×10^{-5}
YbSe	0.0	2.321×10^{21}	4.400	16.339	-6.320×10^{-5}
	4.5	2.749×10^{21}	4.303	16.388	-1.207×10^{-4}
	9.1	3.949×10^{21}	4.178	16.773	-8.459×10^{-5}
	13.6	4.724×10^{21}	4.112	16.968	-8.774×10^{-5}
YbTe	0	8.336×10^{20}	5.010	16.176	-5.775×10^{-5}
	5	2.284×10^{21}	4.659	17.088	-6.396×10^{-5}
	10	6.113×10^{21}	4.265	18.100	-8.971×10^{-5}
	15	1.468×10^{22}	3.888	19.247	-1.117×10^{-4}

respectively [13] Regarding the transition pressure of Yb monochalcogenides, there is contradiction between the electrical resistivity study and pressure-volume data. According

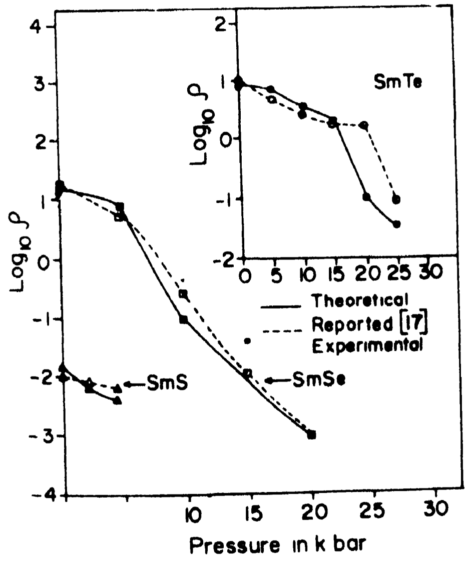

Figure 1. Theoretical (——) and reported [17] experimental (- - -) resistivity variation as a function of pressure for SmX (X = S, Se, Te).

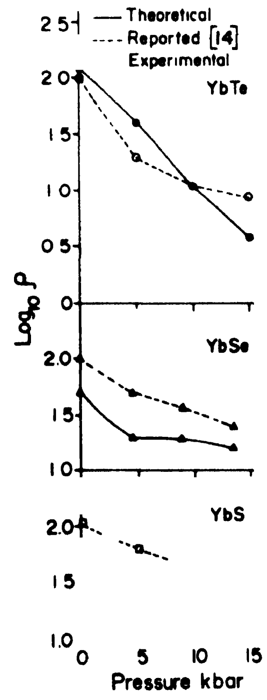

Figure 2. Theoretical (——) and reported [14] experimental (- - -) resistivity variation as a function of pressure for YbX (X = S, Se, Te).

to the electrical resistivity study upto 15 kbar, the valence transition as well as semiconductor to metal transition, is expected near 40 kbar [14]. The optical absorption study [16] supports the pressure volume data [13] which predicts that the energy gap must vanish at about 175 kbar. According to this theoretical electrical resistivity calculation, the valence transition seems to be at about 40 kbar, which supports strongly the experimental electrical resistivity data. Thus, this simple two parameter model gives a reasonably good description of electrical properties as a function of pressure.

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