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Magnetoresistance and Thermoelectric Power of Semiconductors at Pressures up to 30 GPa

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Abstract. The results are observed of magnetoresistance and thermoelectric power measurements of crystalline, amorphous and defect semiconductors in pressure range 0 – 30 GPa. It is shown, that by using of the above techniques and also exploring the model of Peierls distortion of lattice it's possible to investigate the details of electron structure of materials undergoing pressure-induced phase transformations. The examples presented for chalcogens Te, Se and mercury chalcogenides HgX (X – Te, Se, S, O)

Introduction.

The development of magnetoresistance (MR) and thermoelectric power (*S*) measurements at the pressure P interval 0 - 30 GPa using sintered diamond apparatuses [1-3] made it possible to test the changes in the electron structures of materials, undergoing pressure-induced phase transitions [4-6]. The aim of this work was to give a brief review of some recent *S(P)* and MR(*P*) results for a wide row of materials and also to outlook possible way for systematically investigations based on these techniques of pressure-induced semiconductor – metal phase transitions [1-3].

Theoretical model and experimental technique.

The model taking into account p-bonds and Peierls distortion of lattice was used in [7, 8] to explain the crystal and electron structure, properties of high pressure phases and metallization under pressure of a number of materials. The basic idea of the model is that *p*-electrons in the partially filled p-bands in V, VI, VII elements and some II-VI - V-VI compounds play a dominant role for the cohesion [7]. The problem of space lattice can be decoupled into three independent linear chains, which are partially filled with electrons and consequently metallic (Fig.1). A one-dimensional metal lowers its electronic energy by Peierls distortion of the lattice leading to an energy gap at the Fermi level [7, 8]. Peierls structures have a lower density than undistorted lattices, and at certain P repulsing of the ions makes the distortion energetically disadvantageous [7]. It is interesting to note, that starting from this simple model the correct electron structure of Te was calculated in [8]. In the present paper the attempt was made to extend the above model to a wide row of materials and test experimentally the validity of this approach.

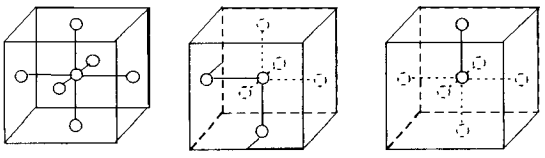

Fig1. Forming of various type of lattices from simple cubic (NaCl) structure. a) Simple cubic (NaCl) phase, central atom has six equivalent bonds; b) Trigonal chains of Te,Se: two short (solid lines) and four long (dashed lines) bonds correspond to tree-fold enlarging of cell. c) Molecular Jodine: one short and five long bonds correspond to six-fold enlarging of cubic cell [7].

The experimental set up used was described in [9]. A sample is placed between two opposite plungers of Bridgman anvils type made of tungsten carbide and superhard materials (synthetic diamond or boron nitride) capable of pressure generation up to 30 GPa [1-3,9]. The plunger displacement X, pressure P (stress F), temperature T, and the electrical voltage U of the sample were recorded using automated set up [9], and then transferred to a computer. The pressure transmitting medium was a lithographic stone [1-3,9]. A miniature version of the high pressure apparatus vas developed for galvano-magnetic measurements [1-3].

Discussion

For trigonal Te and amorphous Se samples the gradual decrease of the resistivity and of S under pressure, and at the same time the exponential rise of MR were observed (Fig.2). For Se the initial MR was negative and above 6 GPa it reversed to positive [3]. One can see, that at P ≥ 20 GPa the value of MR for Se becomes larger than for the narrow gap semiconductor Te at low P (Fig.2).

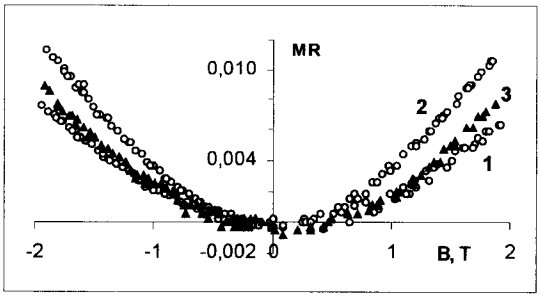

Fig.2. Magnetoresistance of Se (1,2) and Te (3) at 293 K and high pressures P, GPa: 20 (1), 23 (2), 1 (3).

The behaviour of *S(P)* and *MR(P)* dependencies for Te, Se differ from that of the HgX (X=Te, Se, S, O) compounds, which represent the structural and electric analogy of Te, Se [1]. The p-model mentioned can explain the origin of semiconductor gap in Te, Se and HgX via Peierls distortion of cubic (NaCl) structures by enlarging of unit cell 3 and 6 times, respectively, causing the corresponding splitting of electron p-band (Fig.3).

It also predicts the metallization of distorted phases under pressure in accordance with experiment. However, the model does not permit to predict the details of electron structure of materials.

The thermoelectric measurements at high pressures revealed the difference between high pressure "metal" phases of various materials, which had similar electrical properties [1-4,10-13,15-17] (Table 1). S depends on the sign of charge carriers and partial conductivity of bands. The intrinsic conductivity S is proportional to the value of the semiconductor gap E_g:

$$S\frac{|e|}{k} \approx -\frac{c-1}{c+1}\cdot\frac{E_g}{2kT}, \qquad (1)$$

where e - charge of electron, k - Boltzmann constant, $c=\sigma_n/\sigma_p$ - ratio of the conductivities of the electrons and holes [5].

For the materials under consideration the variation of *S(P)* indeed is similar to the known dependencies of energy gap on P [4, 6]. For the typical metal phases of Ge, Si, I_2, CdTe, HgTe, HgSe the values of S are positive and less than 10-20 μV/K(Table 1). But for the "poor" metal phases of ZnX, CdX, which conserve sufficient optical gap in electron spectrum [4,6] the values of S are negative and large (~100 μV/K) [20]. It turns out, that even for high pressure metal phase with the similar value of S the behaviour of MR is rather different [1,3,10,11,15,17], due to various

mechanism of charge scattering. For examples, Te, Se, HgTe, HgSe, I_2 have approximately similar decreasing dependencies of *S(P)*, while the sign of MR is negative for HgX and I_2 and there is a large positive MR in Se, Te at high pressures [3] (Fig.2). Magnetoresistance MR is connected with

Table 1.: Approximate Values of ThermoEMF of high pressure "metal" phases of some semiconductors at high pressures up to 30 GPa.

Substance	S, μV/K	P, GPa	ref.	Substance	S, μV/K	P, GPa	ref.
Te	+10	>4	[18]	ZnSe	-100	>15	[20]
Se	+25, +8	>15-25	[3]	ZnS	-100	>15	[20]
I_2	+5 +25	>20 > 20	[19] [3]	CdSe	-200	>3	[20]
HgTe	+10	>10	[19]	CdS	-400 -(500)	>3	[20]
HgSe	+10	>20	[19]	EuO	-50	>15	[15]
HgS	-50	>25	[19]	EuTe	-50	>15	[15]
HgO	-(50-80)	>15	[19]	EuSe	-30	>20	[15]
Si	+5	>10	[20]	EuS	-70	>20	[15]
Ge	+5	>9	[20]	SmTe	+20	>10	[16]
GaP	+2	>22	[20]	SmSe	+15	>5	[16]
Bi_2Te_3	+10	>15	[21]	SmS	+(20-10)	>1	[16]
In_2Te_3	+10	>10	[13]	Ga_2Te_3	+20	>5	[13]
CdTe	-50	>3	[20]	CdTe	+20	>10	[20]

the turning of electron path by Lorentz force and usually is an increasing function of the magnetic induction *B:*

$$\frac{\Delta\rho}{\rho} = const \cdot (\mu \cdot B)^2, \qquad (2)$$

Where: μ=eτ/m is charge carries mobility, τ - impulse relaxation time, m- effective mass of charge carries (electrons, holes) [5]. In free electron approximation for one-dimencional lattice

$$m = \frac{m_0}{1 + 4E_a / E_g}, \quad E_a = \frac{\hbar^2}{2m_0}\left(\frac{\pi}{a}\right)^2 \text{ and at } E_g \to 0, \quad m \approx E_g \qquad (3)$$

where a - lattice parameter, m_0 - free electron effective mass.

For direct gap semiconductors InSb, HgTe (at Γ-point of Brillouin zone) and Te, Se (at H-point) $m \sim E_g$ relation under pressure was provided by electrical and optical measurements [5]. The effective mass is also inversely proportional to the band width ΔE:

$$m^{-1} = \frac{a^2}{6h^2}\Delta E \qquad (4)$$

In narrow band materials (d-band, impurity bands, ionic crystal) *m* is large, and therefore the mobility is low [5].

Thus, positive MR characterises the mobility $\mu(P)$ of the light carriers, and hence give the information about the type of gap E_g. In the case of direct gap semiconductors (Se,Te) the

exponential rising of MR under pressure (Fig. 2) is related with the decreasing of E_g. and m. In particular cases the negative MR is observed (amorphous Se, cinnabar phases of HgX [1], molecular Iodine [17]) where positive MR is negligible due to Eq.4. Behaviour of MR under pressure show the change of scattering mechanism of the light carriers during the electron structure transformations [1-3]. From data of MR one may conclude that presumably high pressure cinnabar phases HgX are indirect gap semiconductors in contrary to analogous Te and Se.

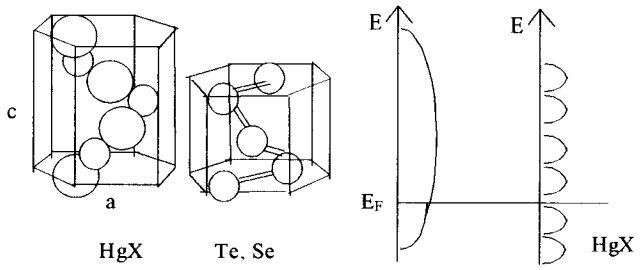

Fig.3. The Peierls distortion as origin of semiconductor gap in cinnabar high pressure phases of HgX (see text). Crystal cell is six-fold enlarged in comparision with simple cubic one (two-fold enlarged in comparision with Te, Se)

Conclusions

Peierls distortion model for various semiconductors with unfilled p-bands can predict the origin of semiconductor gap, type of crystal structure, and ultimate metallization under pressure applied, but can't detail the peculiarities of electron structure. Thermoelectric power characterize the sign and concentration of charge carriers of high pressure phases, and hence, allow to determine whether pressure-induced metal state is due to electron bands overlapping or it's due to impurities (defects). The magnetoresistance data allow to check the type of semiconductor gap (direct or indirect) and also show the dominating mechanism of charge carriers scattering. So, combine of these methods made it possible the thorough analysis of electron structure of materials at superhigh pressures.

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