

## CONCENTRATION PHASE TRANSITION IN $\text{Ag}_2\text{Te}$ WITH AN EXCESS OF Ag

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The concentration phase transition (CPT) was observed in samples  $\text{Ag}_2\text{Te}$  with the excess of  $\text{Ag} > 0,01$  at.% at investigation of the concentration and temperature dependences of electric and thermoelectric properties. It is supposed, that the appearance of CPT is connected with the formation of the new sublattice of Ag in  $\text{Ag}_2\text{Te}$  beginning from the excess  $\sim 0,01$  at.%. It is shown that the first sublattice of  $\text{Ag}_1$  atoms creates the two-electrons donor and the second- ( $\text{Ag}_2$ ) one-electron donor. The last fact is caused by the position of the Fermi level lower or inside of the impurity state.

Electric and thermoelectric properties of  $\text{Ag}_2\text{Te}$  have been investigated with the excess of Ag up to  $\sim 0,25$  at.%. Concentration phase transition (CPT) is observed in crystals with excess of Ag 0.1-12 at.%. Transition is connected with the appearance of new sublattice Ag in  $\text{Ag}_2\text{Te}$ .

$\text{Ag}_2\text{Te}$  is classified among narrow-band semiconductors with high electron mobility, small lattice thermal conduction and having the structural phase transition in the temperature range 390-450K [1-3]. Therefore investigation of concentration and temperature dependences of kinetic parameters is important for revealing of application field in electron technology.

Investigations are carried out on a series of  $\text{Ag}_2\text{Te}$  samples: the stoichiometric composition with the excess of Te (up to 1.0 at.%) and Ag (up to 0.25 at.%). As it is known [2], the excess of Te up to 1.0 at.% does not cause a falling of the second phase, any changes in crystal structure are not observed and causes the formation of  $p\text{-Ag}_2\text{Te}$  [3]; and it is established, that the hole concentration is proportional to Te content [1]. Excess of Ag in homogeneity region leads to the formation of  $n\text{-Ag}_2\text{Te}$ .

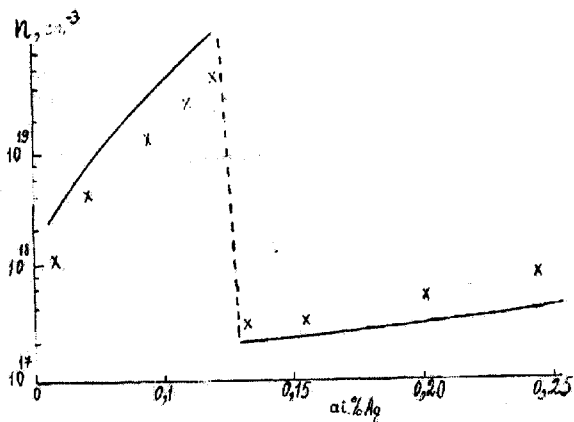


Fig.1 Electron concentration dependence on the excess of Ag. Solid line is calculated.

At investigation of kinetic effects in  $n\text{-Ag}_2\text{Te}$  it is found that the excess of Ag up to  $\sim 0,10$  at.% leads to the rise of the electron concentration ( $n$ ) up to  $n \sim 5 \cdot 10^{19} \text{cm}^{-3}$  and the excess of Ag up to  $\sim 0,12$  at.% decreases  $n$  sharply about by a factor of  $10^2$  (fig.1), i.e. CPT takes place. This fact has not been described in literature.

With this aim concentration and temperature dependences of the Hall coefficient  $R$ , electroconductivity  $\sigma$  and thermo-

electromotive force  $\alpha_0$  have been investigated for revealing of CPT mechanism in  $n\text{-Ag}_2\text{Te}$ .

Samples have been obtained by the common technology with the excess of Ag up to 0.25 at.%. Refined silver with 99.99% purity and Te of TA-1 model after two fold distillation in vacuum were used for  $\text{Ag}_2\text{Te}$  synthesis. Samples were cut out to the shape of the parallelepiped with sizes  $2 \times 3 \times 10 \text{ mm}^3$ . Obtained experimental data of temperature dependences  $R(T)$ ,  $\sigma(T)$  and  $\alpha_0(T)$  for two samples of  $n\text{-Ag}_2\text{Te}$  with the excess of Ag 0.10 and 0.12 at.% are presented on fig.2.

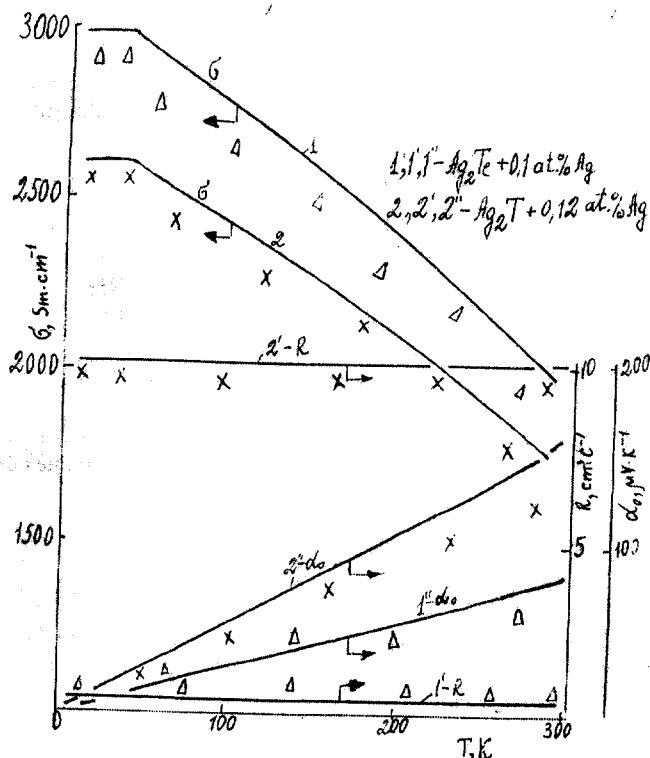


Fig.2 Temperature dependence of the Hall coefficient  $R$  (at  $H=12\text{KE}$ ) electroconductivity  $\sigma$  and thermoelectromotive force  $\alpha_0$ . Solid lines are calculated.

It is seen that for both samples the behavior of  $R(T)$ ,  $\sigma(T)$  and  $\alpha_0(T)$  is characteristic for semiconductors with one kind of charge carriers in the degenerate state and Cane's law of dispersion [4]. In spite of essential distinction of their concentrations, qualitative distinctions are not observed in them. Authors [5] suggested that in Ag chalcogenides Ag can be two-electron donor giving two electrons into the conduction

band ( $\text{Ag}^+ \rightarrow \text{Ag}^{3+} + 2e^-$ ). Then the forming two-electron state is located either at the expense of strong interaction with the lattice or strong interaction with vacancies and other defects. Our experimental data on samples with Ag content up to 0.10at.% (fig.1) confirm hypothesis of authors [5]. Starting with the excess of Ag 0.12 at.%, the electron concentration rises proportionally to Ag content, i.e. in this case the excess of Ag plays a role of one-electron donors.

In paper [6] it is noted, that there are two structurally different types of Ag atoms in  $\text{Ag}_2\text{Te}$ .  $\text{Ag}_1$  atom is surrounded by four Te atoms on distances 2.87; 2.91; 3.04 and 2.99 Å;  $\text{Ag}_2$  atom has five nearest neighbours on the distances 3.04; 3.01; 2.95; 2.90 and 2.85 Å. In both positions the cell has 4 ( $\text{Ag}_2\text{Te}$ ) and all atoms occupy the disposition of 4 order. Thus Ag atoms form 2 sublattices of Ag atoms in the structure. CPT takes place at the transition from the first position ( $\text{Ag}_1$ ) to the second one ( $\text{Ag}_2$ ).

$\text{Ag}_2\text{Te}$  relates to the class of compensated semiconductors [7,8]. Thus Te atoms create acceptor levels disposed on the distance  $(0.03 \cdot 7 \cdot 10^{-5} \text{T} \cdot \text{K}^{-1}) \text{eV}$  from the conduction bottom [4], and Ag atoms in the forbidden band create local energy donor levels [9].

In literature an activation energy value of donors  $E_d$  is absent. Experimental determination of  $E_d$  at the small value of band gap  $E_g = (0.03 \cdot 7 \cdot 10^{-5} \text{T} \cdot \text{K}^{-1}) \text{eV}$  and the high value of the donor concentration  $N_d$  is very difficult. In this situation the following method is suggested [4]. At any degree of the electron gas degeneration with a nonstandard band thermal, EME forces are expressed according to [10].

$$\alpha_0 = - \frac{K_0}{e} \left[ \frac{I_{r+1.2}^1(\mu^*, \beta)}{I_{r+1.2}^0(\mu, \beta)} - \mu^* \right] \quad (1)$$

where  $\mu^* = \mu / K_0 T$  is the reduced chemical potential,  $\mu$  and  $I_{n,k}^m$  are the Fermi level and two - parametric Fermi integral,  $\beta = K_0 T / E_g$  is the parameter specifying a non-parabolic of the band. From (1)  $\mu E_d$  values have been determined at  $T=15 \text{ K}$ . If  $\mu$ ,  $N_d$  and  $m_n$  [4] magnitudes ( $m_n$  is the effective electron mass on the Fermi level) are known, you can define  $E_d$  according to [10]:

$$E_d = K_0 T / n \left[ \frac{2\pi^{3/2} \hbar N_d}{(2m_n K_0 T)^{3/2}} \right] - 2\mu \quad (2)$$

Magnitudes  $E_{d_0}$  have been calculated (at  $T=0\text{K}$ ) taking into account the dependence  $E_g(T)$  [4]:  $E_{d_0} \approx 2\text{meV}$  (at  $N_d = (1.1 \div 50) \cdot 10^{18} \text{sm}^{-3}$ ) and  $E_{d_0} \approx 5\text{meV}$  (at  $N_d = (1.1 \div 6.25) \cdot 10^{17} \text{sm}^{-3}$ ) (counting from the bottom of the conduction band) (fig.3).

If you take into consideration that weak compensation goes in the concentration interval  $N_d = (1.1 \div 5.0) \cdot 10^{18} \text{sm}^{-3}$ , and high compensation goes in the interval  $N_d = (1.1 \div 6.25) \cdot 10^{17} \text{sm}^{-3}$ , then the state density in both cases are expressed, respectively [11]:

$$\rho(\varepsilon) = \frac{N_d}{Y\sqrt{\pi}} \exp(-\varepsilon^2/Y^2) \text{ and } \rho(\varepsilon) = \frac{3E_d^3}{2\varepsilon^4} N_d, \quad (3)$$

$$\text{where } y=0, 26E_d' (N_a/N_d)^{1/4}, E_d' = \left( \frac{4\pi}{3} N_d \right)^{1/3} \frac{e^2}{\chi} \quad [11],$$

$N_a$  is the acceptor impurity concentration,  $\chi$  is the dielectric constant of the crystal. Chemical potential in the first case is calculated from (2), and in the second case is calculated according to [11]:

$$\mu = - \frac{E_d'}{2^{1/3} (1 - N_a/N_d)} \quad (4)$$

If the value  $\mu$  is known, then the concentration can be presented as

$$n = \int_{-E_d'}^{\mu} \nu(\varepsilon) d\varepsilon \quad (5)$$

and temperature dependence of thermoelectromotive forces as (1),  $R$  and  $\sigma$  as

$$R = \frac{1}{en}, \quad \sigma = enU_n(T). \quad (6)$$

Temperature dependence of the electron mobility  $U_n(T)$  at any degree of electron gas degeneration for a non-standard band has been determined earlier.

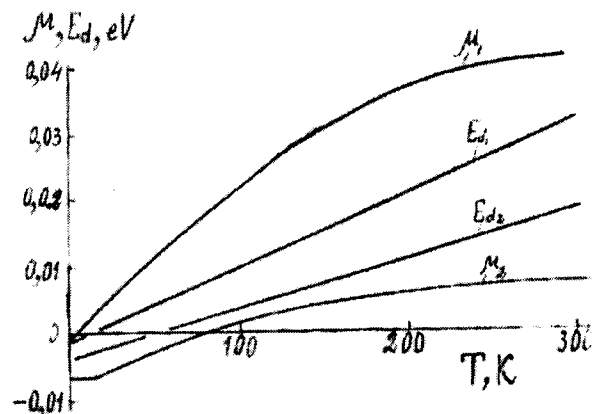


Fig.3. Temperature dependences of the chemical potential ( $\mu$ ) and activation energy of donors ( $E_d$ ).  $\mu_1 E$  and  $\mu_2 E$  are calculated in  $\text{Ag}_2\text{Te}$  with the excess of Ag 0.10 and 0.12 at %, respectively.

Calculated data are presented on fig.1,2. As it is seen, calculated curves  $n$  to CPT are below. The reason is due to the error of the application field of the formula (3). Agreement of calculated and experimental curves  $R$ ,  $\sigma$  and  $\alpha_0$  confirms the assumption, that  $N_d \text{Ag}_2\text{Te}$  is weakly and highly compensated semiconductor in corresponding above mentioned intervals. It offers the scope for understanding of the origin of CPT in  $\text{Ag}_2\text{Te}$ . New sublattice Ag (position  $\text{Ag}_2$ ) is formed in the cell  $\text{Ag}_2\text{Te}$  starting with the excess of Ag 0.12 at %. In this case the crystal is highly compensated at the expense of interaction with vacancies and other defects. Then the electron concentration, localized in donors  $n = N_d - N_a$ , is much less than the donor concentration. Thus at all temperatures all electrons can be arranged in donors, whose energy levels are significantly reduced by the potential of neighbour

charged impurities. As a result,  $\mu$  is below than the level of the isolated impurity (fig.3). The less electron concentration of  $n$  the deeper  $\mu$  is arranged.

If we do not take into consideration Hauss fluctuations [11] it can be suggested that another positively charge donor can appear in the vicinity of some donors on the distance  $r \ll N_d^{-1/3}$ , where  $\mu$  is above the impurity state. At  $r \gg \alpha$  ( $\alpha$  - is the effective Bohr radius) the correction of  $E$  to the energy

level in the first donor is defined only by the Coulomb potential of the second donor, i.e.  $E = -e^2/xr$ . In this case it is suggested that the second donor is empty. Band energy of the second electron in the couple of donors is close to  $R E_d^1$ . Therefore at the high compensation, when  $\mu$  is below the donor impurity level and is into the impurity state (fig.3), only one electron can correspond to the couple of close donors.

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## Ag<sub>2</sub>Te KRİSTALININ Ag ARTIQLIĞINDA KONSENTRASIYA FAZA KEÇİDİ

Ag<sub>2</sub>Te kristalında 0.25 at.% Ag artıqlığı ilə olan nümunələrin elektrik və termoelektrik xassələri tədqiq olunmuşdur. Ag artıqlığının 0.1±0.12at.%-də konsentrasiya faza keçidi (KFK) aşkar olunmuşdur. Keçid yeni alt qəfəsin Ag artıqlığının hesabına yaranması ilə əlaqələnməmişdir.

Ф.Ф. АЛИЕВ

## КОНЦЕНТРАЦИОННЫЙ ФАЗОВЫЙ ПЕРЕХОД В Ag<sub>2</sub>Te С ИЗБЫТКОМ Ag

При исследовании концентрационных и температурных зависимостей электрических и термоэлектрических свойств Ag<sub>2</sub>Te обнаружен концентрационный фазовый переход (КФП) в образцах с избытком Ag>0.01at.%. Предполагается, что появление КФП связано с образованием новой подрешетки Ag в Ag<sub>2</sub>Te начиная с избытка ~ 0.01 at.%. Показано, что первая подрешетка атома Ag<sub>1</sub> создает двухэлектронный донор, а вторая – (Ag<sub>2</sub>) - одноэлектронный донор. Последнее связано с нахождением уровня Ферми ниже или внутри примесного состояния.