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Effect of Entrainment of Ions by Electrons and Onset of Electrodiffusion Potential in n-Ag₂S and p-Cu_{1-x}Ag_xS (x=0; 0,4)

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First, in the course of temperature heating of binary and triple polycrystal silver sulphide (n-Ag₂S, p-CuAgS and Cu_{0.6}Ag_{0.4}S-alloy) it was found that for lack of temperature gradient and no other external influence there are the potential difference of the order of some millivolts in the samples and its inversion.

The onset of electrodiffusion potential (EDP) is observed with temperature rise of samples from 300 K at specific range.

The onset the EDP and thereof temperature dependence similar to EDP, stipulated an entrainment of ions by electrons (or alternatively). As the true ionic mobility exponential depends upon the temperature, the temperature dependence effective mobility has unusual nature. The course of the EDP with temperature rise follows from effective mobility course.

For this crystals the necessary condition for the entrainment phenomenon is the existence of metastable substructure between high-and low temperature modifications, plays a role a perturbing factor in its place of external influence. Within a narrow temperature interval the conductivity of samples increases by a factor of 10⁴ ÷ 10⁵. Just in this temperature range there is the onset the EDP in studded crystals.

Key words: the onset, the electrodiffusion, potential, entrainment

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Onset of electrodiffusion potential (EDP) with entrainment ions by electrons, defect and by influence temperature or concentration gradient, perturbing of the electron system is described in [1].

The entrainment of free carriers by photons and inversion of the effective mobility sign, as a result of electron entrainment was observed experimentally by Ryvkin, Jaroshetsky [2-3]. An EDP of the order of microvolts occurs in liquid metals [4]. The entrainment effect in the semiconductors was predicted by Fiks [5].

First, onset an EDP of the order of some millivolts in the binary and triple silver sulfide with no external influence (electric field, temperature gradient etc) was observed by us.

Within the range, where the significant entrainment effects, all factors, changing an electron concentration (additional impurities, photon radiation, thermal effect etc) may change not only the value, but also a sign of effective ion mobility, wherein a temperature dependence has a rather original character [5].

The binary n-Ag₂S and triple silver sulfide p-CuAgS proved an as control sample for detection an EDP. The potential difference of the order of some millivolts at the specimen under test developed upon heating.

The n- Ag₂S crystallized in monoclinic lattice with space group symmetry C_{2h}⁵ and with lattice parameters:

The phase transition from the low-temperature mono-

$$a = 4,231 \text{ \AA}; b = 6,930 \text{ \AA}; c = 9,526 \text{ \AA}; \beta = 125^{\circ}29'$$

clinic to the high temperature cubic modification in n-Ag₂S` arises through intermediate metastability tetragonal phase .

Low-temperature modification of p-CuAgS is crystallized in rhombic lattice with parameters:

The phase transition in p-CuAgS takes place at 373÷378K.

$$a = 4,02 \text{ \AA}; b = 6,68 \text{ \AA}; c = 7,99 \text{ \AA}$$

The polycrystal samples in the form of thick rectangular plates (1x5x5)mm³ are polished and glued on the substrate.

the holder, volume of which was pumped up to ~10⁻⁴ mmHg.

Heating of the mica with crystal is taken a course from 300K to 500K at the rate of 2.0÷3.0 grade per minute.

The thermocouple is taken reading of temperature directly on the crystal/ the electrodes are presses to border of the sample and are connected to the double scale X-Y recorder.

The onset of an EDP in n-Ag₂S, p-CuAgS and Cu_{0.6}Ag_{0.4}S are shown on figures 1-3, respectively. The X-axis is scale of temperature and Y-axis is scale of

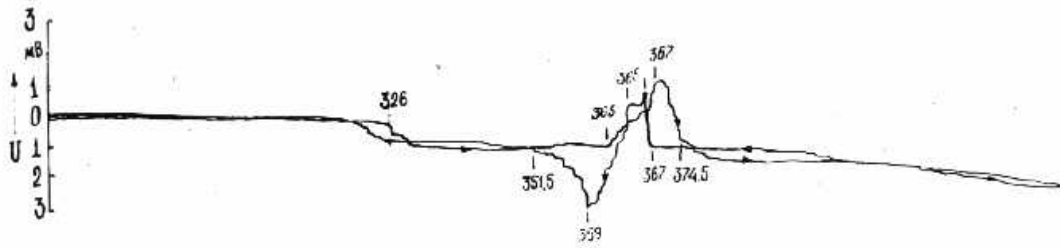


Fig1. The onset EDP in n-Ag₂S.

anEDP.

The origin of X-axis corresponds to 300K, and the origin of Y-axis corresponds to zero. On fig.1 is shown an onset of the EDP in n-Ag₂S. First the step of the order of (-1.0mV) arises on the interval (326÷363,5)K. On the temperature interval (363,5÷367,0)K the EDP increases up to (+2,5mV). At the 375 K the EDP passes through zero and its sign changes by negative. Then, the EDP keeps minus (1,0÷1,2) mV up to 435 K. The shape of a curve EDP with decrease of temperature is seen by an arrow in opposite direction. Practically, curves are copying their courses at cooling of sample.

The fig.2 shows onset of an EDP in p-CuAgS. At first, the recording pen moves on zero level up to 339 K. In range (346÷355) K the step of the order of plus one millivolt makes its appearance. The EDP spike of order of (1.0÷1.5) mV arises at 379 K. In the temperature range (382÷391) K the EDP is of the order of plus 3,0 mV. With increase of temperature up to 400,3 K the EDP drops to zero and inversion sign of EDP occurs. Then, the EDP reaches to minus 7,0 mV at 410,5 K and falls to zero at 414,5 K.

On fig. 3 is shown an onset of the EDP in the Cu_{0,6}Ag_{0,4}S. This crystal involves an intense concentrated and compensated alloy with the resistivity of the order of 10¹³÷10¹⁴ Ohm.cm. Onset of the EDP in Cu_{0,6}Ag_{0,4}S in comparison previous samples have more intricate form. From now, an EDP ever increasing monotonically up to 309K then abrupt changes to minus 7,5 mV (326 K) and in the range (326÷335) K abrupt changes to plus 6,0 mV (335 K). Further, the EDP passes through zero (340 K) and increases to minus 6,6 mV (342 K). In a range (345÷404) K the EDP keeps minus 2,0mV and then in-

creases sharply to minus 28 mV (422 K). In the course of heating, the EDP decreases to minus 12 mV (446,5 K).

The reverse motion of the EDP (with decreases of temperature) is shown on the fig.3 by needle. The process of onset the EDP in Cu_{0,6}Ag_{0,4}S have more complicated temperature dependence and more intensity of an EDP in comparison with n-Ag₂S and p-CuAgS. It is results from high degree of compensation of Cu_{0,6}Ag_{0,4}S alloy. It is known, that by increase a degree of compensation the screen radius and the amplitude of large-scale fluctuations increases. The presence of double-grade carriers causes the relative rise of entertainment effect [1].

An intermediate tetragonal substructure, arising in these crystals near of phase transition offers a great concentration of current carriers are stipulated high defects. This equated a perturbation of distribution function from out.

Such perturbation has separated direction. The anisotropy of distribution function causes electrical current or compensating it's a potential difference. The electric field arises as result of an ion's entertainment by an electron flow. In its place of external field disturbed of electronic system, the disturbing factor is a formation of metastable phase, in which the concentration of carriers are rather more, than in α and β modification of specimens under test.

All factors, changing a concentration of charge carriers are changing not only value, but also sign of ionic mobility. The polarity inversion of the EDP is stipulated by inversion of sign an effective ionic mobility.

The formation of substructure with differed volume resistivity between low-and high modifications in like

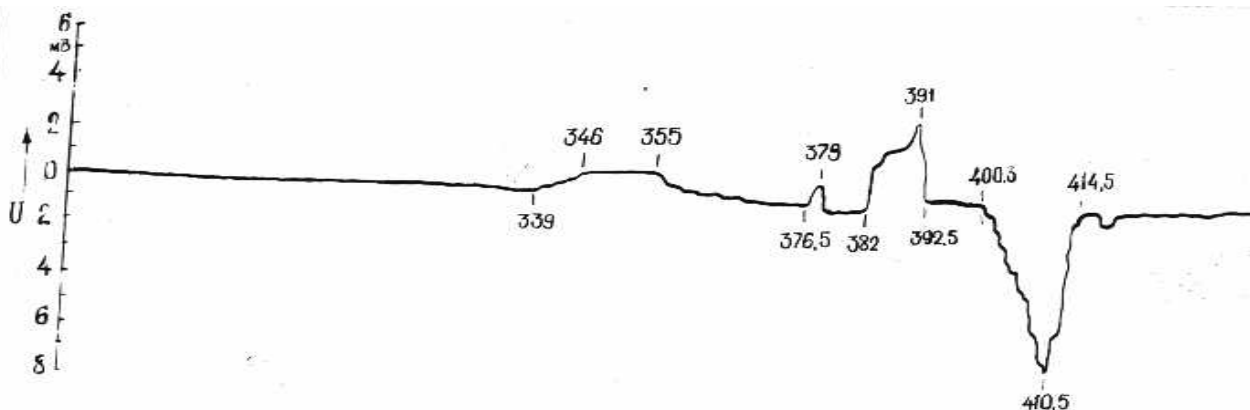


Fig 2. The onset EDP in p-CuAgS.

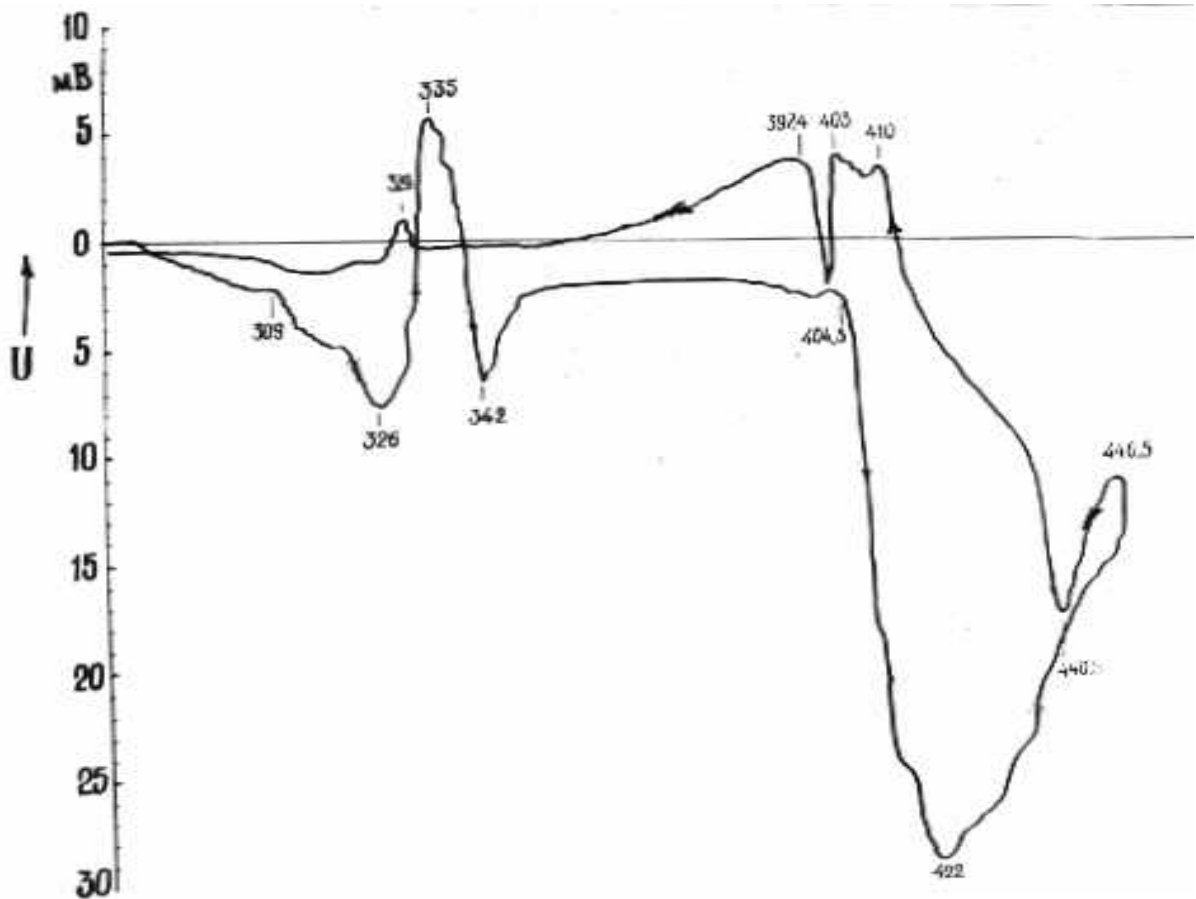


Fig 3. The onset EDP in $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{S}$.

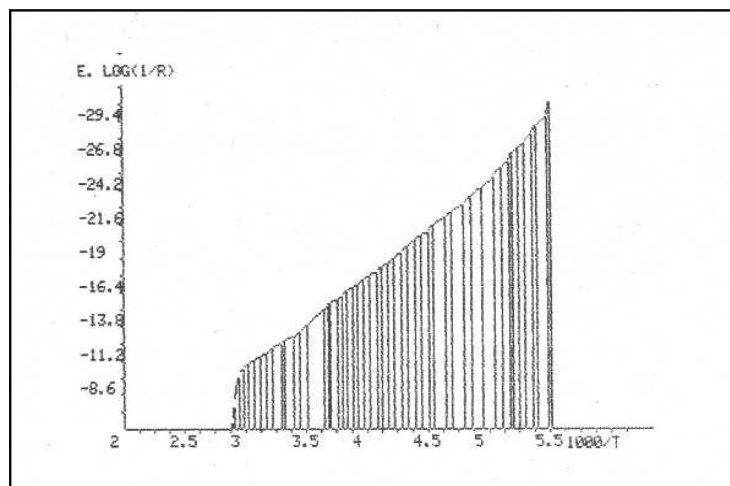


Fig. 4. The temperature dependence of resistivity of p-CuAgS.

crystal allowed observing the onset of diode state near phase transition [6]. Also, the investigation of temperature dependence of resistance this samples is convinced unequivocally. Fig. 4 shows $R \sim f\left(\frac{1}{T}\right)$ for p-CuAgS.

Just in range (339÷345) K (cf. Fig.2) the resistivity falls from 10^5 Ohm-cm to a few ohm.

In this manner, due to specific features of the studied crystals: high ionic conductivity, formation intermediate metastable substructure with differed widely volume

conductivity are perturbed of elastic anisotropy of function distribution and the entertainment ions by electrons and as result the onset EDP are stipulated.

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Ефект захоплення іонів електронами та виникнення електродифузного потенціалу в n-Ag₂S і p-Cu_{1-x}Ag_xS (x-0; 0,4)

Вперше, без температурного градієнта і зовнішнього електричного поля в бінарному та потрійному сульфіді срібла (n-Ag₂S, p-CuAgS, Cu_{0,6}Ag_{0,4}S) при підігріві зразків від 300 до 450 К, виявлено утворення електродифузного потенціалу (ЕДП) порядку кількох мілівольт і інверсія його знаку. Встановлено, що ЕДП виникає у вузькому температурному інтервалі існування метастабільної фази у цих кристалах, провідність

якої значно більша, ніж провідність α і β фази. Це підтверджується дослідженням залежності $R \sim f\left(\frac{1}{T}\right)$,

де у вузькому інтервалі температур спостерігається різкий скачок провідності у $10^4 \div 10^5$ раз. Отже, замість зовнішніх сил, збуджуючих електронну систему і супроводжуючому цьому ефекту захоплення, збуджуючим фактором виступає метастабільна тетрагональна фаза значно більшої провідності.