ELECTRIC AND THERMOELECTRIC PROPERTIES OF p-Ag_2Te

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There have been investigated temperature dependencies of Hall-coefficient R, electric conductivity - σ and thermal EMF - α_0 in p-Ag_2Te in the temperature range 4-300 K. There have been observed feature: retardation $R(T)$ in the temperature range ≈ 200-300 K, minimum at ≈ 65 K and maximum at ≈200 K in $\sigma(T)$ and maxim in $\alpha_0(T)$ at ≈ 80 and 250 K. Obtained experimented data are rationalized semiempirically within the with two type model with regard to acceptor impurities placed from conduction band bottom by 0,030 eV. It is of electron and hole (U_n) at T < 65 K and generation of decrease acceptor electron concentration (n_a) at T > 65 K. Retardation $R(T)$ and decrease $\sigma(T)$ at T > 200 K at the expense of retro weakness of and decrease of $U_n(T)$. Maximum of $\alpha_0(T)$ at ≈270 K is accompanied by appearance of intrinsic conduction.

INTRODUCTION

Many papers [1-8] are concerned with the investigation of electrophysical and thermoelectric properties of Ag_2Te. Authors showed that the low of electron dispersion in n- Ag_2Te follows Kane model [1-2], electron interaction has nonelastic character [3], in the range 4-300 K the main scattering mechanism is the scattering on ionized impurities and optic phonons [1-4].

Unlike n-Ag_2Te electric and thermoelectric properties in p-Ag_2Te have the features that are not observed in peculiar narrow-band semiconductors.

So their analyses require knowledge of energy spectra of charge carriers in p-Ag_2Te. In spite of series of papers, dedicated to investigation of energy spectra of charge carriers in p-Ag_2Te [4-8] one cannot treat this task solved.

So, this paper deals with the investigation of temperature dependence $R(T)$,$\sigma(T)$ and $\alpha_0(T)$ to establish energy spectrum of charge carriers p- Ag_2Te.

EXPERIMENTAL DATA

In Fig. 1.1 temperature dependence R is presented. It is shown that $R(T)$ up to ≈ 45 K does not depend on T, then reduces and at ≈ 65 K it changes the sign for negative one, reaching the maximum at ≈ 80 K, then reduces continuously and in the range ≈ 200-300 K heavily weakens.

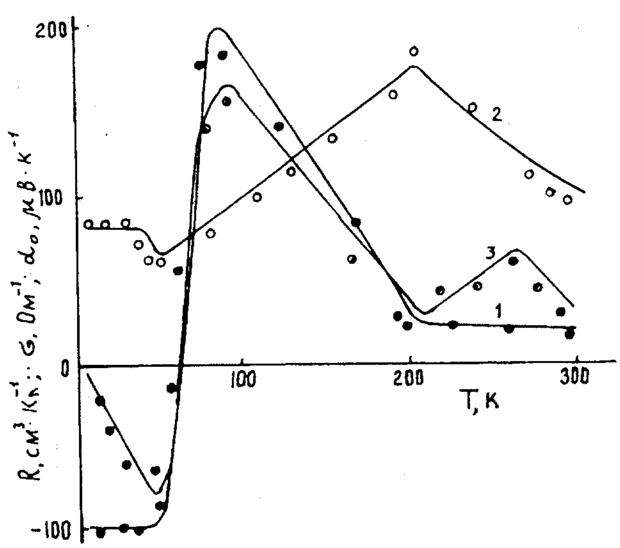

Fig. 1. Temperature dependence: Hall coefficient (1), electric conductivity (2) and thermal EMF (3).
Solid lines – calculated.

In Fig. 1.2 the temperature dependence is shown. From comparing $\sigma(T)$ and $R(T)$ it is shown that $\sigma(T)$ at $T \lesssim 45$ K follow $R(T)$, and T ≈ 65 K corresponding the temperature of sign inversion R, passes through the minimum, then with the temperature rise it increases and at ≈200 K passes through maximum. In Fig.1.3 the temperature dependence α_0 is shown. $\alpha_0(T)$ increases linearly up to $T \leq 45$ K, and then changes the sign p for n, and at ≈ 80 and 270 K passes through maximum.

DISCUSSION OR OBTAINED DATA

Temperature dependence $\sigma(T)$, $R(T)$ and $\alpha_0(T)$ have been discussed in various papers [5-8]. Authors try to explain observed plateau on dependence $R(T)$ in the range ≈ 230-300 K. From slope of $R(T)$ (after ≈ 80 K) there have been estimated activization energy 0,04±0,01 eV, supposing that local energy levels are taken place in band gap. The presume of plateau in $R(T)$ is due to exhaustion of these energy levels, and activization energy is the ionization energy of these levels [5]. Authors [6] concluded that in the range of intrinsic conduction in charge concentration follows exponential function $P_i, n_i \approx T^3$, corresponding to electron activation between the lauds with highly non-parabolic spectrum of electron and holes. According to experimental $R(T)$ and $\sigma(T)$ they have determined ε_i < 6 MeV and have supposed that in Ag_2Te gapless state is taken place at low temperatures. As to the authors point of new [6] sharp retardation of electron concentration increase (or plateau in $R(T)$) in the range ≈ 250-300 K is due to the presence of additional valence band with high state density.

Author [7] supposed that the presence of conduction maximum and some anomaly of thermal EMF in the range ≈ 248-283 K could be connected with possible phase transition. Decrease of α_0 above 283 K is more characteristic for impurity conduction, and increase of α_0 with the reduction of temperature in connected with the change of scattering mechanism and phonon increase of electrons. Authors of papers [8] showed that in temperature range 140-200 K $\alpha_0(T)$ behaves the low $|\alpha_0| \approx T^3$ and in this range there have taken place increase of electrons by phonons.

As it is shown authors [5-8] it makes false conclusions from low-temperature investigation R, σ and α_0 temperature dependence of band parameters. For revealing given problem one must carry out complex analysis with regard to dispersion law, with broad temperature dependence of experimental data, band parameters and mechanism of scattering.

Such kind of analysis is carried out as following:

For calculation of $R(T), \sigma(T)$ and $\alpha_0(T)$ we use the following formulas:

$$R = \frac{1}{N_a e} \frac{(1-c)(1-b^2c)}{(1+bc)^2} , \quad (1)$$

$$\sigma = N_a e U_n \frac{1+bc}{b(1-c)} , \quad (2)$$

$$\alpha_0 = \frac{\alpha_{op}\sigma_p - \alpha_{on}\sigma_n}{\sigma_p + \sigma_n} , \quad (3)$$

where N_a - acceptor concentration, $b=U_n/U_p$ relation of electron mobility to hole mobility, $c=n/p$ relation of electron concentration to hole concentration, $\sigma_p, \sigma_n, \alpha_{op}$ and α_{on} are partial of electroconductivity and thermal EMF and holes, respectively. For analysis of obtained data it is necessary to determine $n(T), U_n(T)$ and $U_p(T)$ by dependence, and for their determination one must know energy of acceptor activation (ε_a) and temperature dependence of Fermi level as a whole. At low value of band gap $\varepsilon_g = (0{,}035 - 7\cdot10^{-5}\ T\cdot K^{-1})$ eV [9] and at high value of Na it is impossible to determine the value of ε_a for p-Ag_2Te. ε_a can be determined as follows: it is known, that thermal EMF(α_p) of any degree of degeneration of hole gas with standard band is defined as follows [10],

$$\alpha = -\frac{k}{e}\left[\frac{F_{r+2}(\mu_p^*)}{F_{r+1}(\mu_p^*)} - \mu_p^*\right] , \quad (4)$$

where $\mu_p^* = \mu/KT$ - reducible chemical potential, μ and F level and Fermi integral. From formulas (4) μ at $T \approx 20$ K is determined. Of one knows μ, N_a and μ_p^*, ε_a can be found with formula [10]:

$$\mu = -\frac{1}{2}(\varepsilon_g - \varepsilon_a) - \frac{kT}{2} \ln\left[\frac{8\pi^{3/2}\hbar^3 N_a}{(2m_p^* kT)^{3/2}}\right] \quad (5)$$

At values $N_a = 6{,}25\cdot10^{16}$ cm^{-3}, $m_p^* = 0{,}12$ [4] and $T = 20$ K it is bound that $\varepsilon_a = 0{,}030$ eV (reading against conduction band bottom). If values ε_a and μ, are known electron concentration on acceptor level [10] can be determined:

$$n_a = N_a\left[1 + \frac{1}{2}\exp - \frac{\varepsilon_a + \mu}{kT}\right]^{-1} . \quad (6)$$

Obtained values for $n_a(T)$ are shown in Fig.2.1.

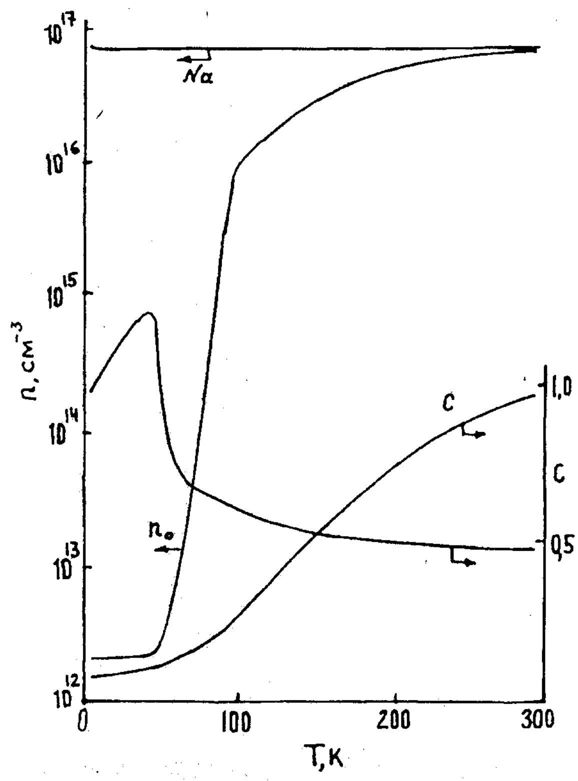

Fig.2. Temperature dependence of concentration (1) and relation of electron mobility b and c to holes (2).

Now let's define $b(T)$. Value b at T ≤ 65 K, where conduction is far from intrinsic conduction ($n \ll p$) it is impossible to derive from formula:

$$b = \frac{P_r}{n_i} \frac{\frac{n_i}{N_a} + \sqrt{1 + \frac{P_r}{N_a}}}{1 - \frac{n_i^2}{P_r N_a}} , \quad (7)$$

where $P_r = P - n$, $n_i^2 = Pn$, $P = N_a + n$ and $n = n_a + n_i$.

At inversion R, $b = 1/\sqrt{c}$ and at maximum (≈ 80 K):

$$R_{max} = \frac{(1-b)}{4beN_a} , \quad (8)$$

where N_a can be does not depend on temperature. Above 80 K b is matched so that the calculated values R coincide with experimental data (Fig.1.1 and 2.2).

If $b(T)$ known, with (2) and according to $\sigma(T)$ (Fig.1.2) one can determine $U_n(T)$ and $U_p(T) = U_n(T)/b(T)$ (fig.3). For theoretical determination $U_n(T)$ there have been carried out calculations as following: as it is noted in paper [2] at high degeneration and Kane law of dispersion at scattering on ionized impurities and acoustic oscillations of lattice the charge carrier mobility are expressed in the following formulas:

$$U'_{ion} = \frac{3\pi\hbar^3\varepsilon^2}{2em_0^{*2}}\frac{1}{f_{ion}} , \quad (9)$$

$$U'_{ak} = \left(\frac{\pi}{3}\right)^{1/3}\frac{e\rho V_L^2\hbar^3 n^{-1/3}}{EKTm_0^{*2}}\frac{1}{f_{ak}} , \quad (10)$$

where f - factor taking account the influence of non-parabolity on probability of scattering, ρ - crystal density, V_L - speed of sound in crystal, E - constant of deformation potential and ε - dielectric constant. Values ρ, V_L, ε and E are given from [11]. $U'(T)$ results are shown in Fig.3.

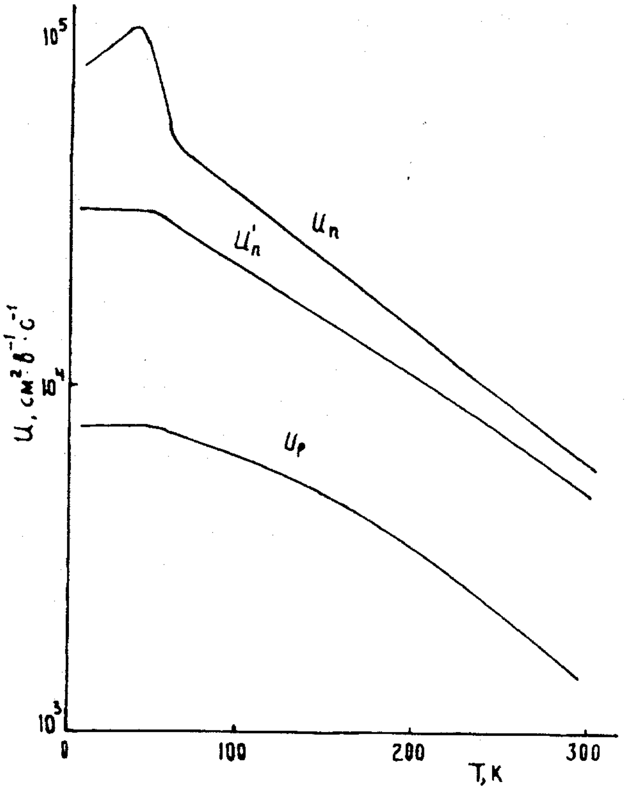

Fig.3. Temperature dependence of electron mobility (U_n and U'_n) and holes (U_p).

Calculations show that at low temperatures conduction is completely due to holes, i.e. at $T \leq 40$ K acceptor concentration is very high comparing with electron concentration. So R and σ must be change with temperature, and α_0 must be increased linearly.

As it is seen from Fig.3 hole mobility U_p at $T \leq 40$ K depends on temperature, if any, but electron mobility U_n increases with temperature, i.e. charge carriers are scattered on ionized impurities. After $T > 40$ K scattering occurs on acoustic oscillations of lattice, due which U_p and U_n reduce with the temperature leading to decrease of $\sigma(T)$. Calculations show that at the expense of decrease of $U_p(T)$ $\sigma(T)$ reduces approximately by 7 %. From Fig.1.2 it is seen that $\sigma(T)$ at $\approx$ 65 K is reduced approximately by 12 %, i.e. the decrease of $\sigma(T)$ occurs at the expense of high decrease of U_n in the range 50-65 K.The cause of high change of $U_n(T)$ at $T < 65$ K is probably connected with following circumstance: unlike $U_n(T)$ the design curve $U'_n(T)$ does not depend on T at 50 K, after 50 K it decreases approximately as the law $U'_n(T) \approx T^{-0,8}$. The matter is to reveal the cause of high change U_n with the temperature rise: at low temperatures electrons are scattered on acceptor impurities where average thermal energy is much less than energy of acceptor level ($\Delta\varepsilon_a$=5 MeV) i.e. with the temperature rise electron captures on acceptors increase, that brings about decrease of band electrons and increase of U_n at $T < 40$ K. High decrease of $U_n(T)$ in the temperature range 50-65 K can be caused by additional resonance electron scattering on acceptor levels, where Fermi levels are placed in narrow vicinity near $\Delta\varepsilon_a$.

Now we can analyze increase of $\sigma(T)$ and change of sign R and α_0 at $T > 65$ K. Calculation shows that at $T < 65$ K Fermi level is some less than main state of acceptor $\Delta\varepsilon_a$ and n_a remains constant. At further temperature rise (where $KT > \Delta\varepsilon_a$) number of vacant places on acceptors are exhausted, i.e. generation n_a and process of electron excitation form valent band into conduction band is started. As it is shown from Fig.2 $n_a >> n_i$, i.e. concentration N_a plays an important role in conduction, which at $T < 65$ K increases as the law $n_a \approx T^{2,7}$, leading to increase of σ and change R, α_0.

Decrease of σ, retardation R and maximum α_0 in the temperature range $\approx$ 200-300 K. As it is shown from Fig.2 at $T > 200$ K $n_a(T)$ retards highly, but b does not practically depend on temperature as formula (2) σ depends on U_n, i.e. with the temperature rise U_n is decreased approximately for $U_n \approx T^{-1,2}$ and σ is also decreased. In this temperature range contribution of electron in conduction is more than of holes, i.e. $n_a U_n^2$ or $R \approx -1/1n_a$.It is seen from Fig.2 that at $T > 200$ K $n_a(T)$ retards highly, that brings about high attenuation of $R(T)$ decrease of $\alpha_0(T)$. Since $c \approx 270$ K decrease of $\alpha_0(T)$ is accompanied by occurrence of intrinsic conduction.

One can conclude from above-mentioned, that suggested model, i.e. interpretation of data within with two type models with the regard to acceptor impurities placed from conduction band zone by 0,030 eV, completely describes electric and thermoelectric properties of p-Ag_2Te.

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p-Ag_2Te KRİSTALININ ELEKTRİK VƏ TERMOELEKTRİK XASSƏSİ

Məqalədə p-Ag_2Te kristalının Holl əmsalı - R, elektrikkeçirmə - σ və termoelektrik əmsalı - α_0 4-300 K temperatur intervalında tədqiq olunmuşdur. Təcrübədə $R(T)$-nin 200-300 K intervalında zəif asılılığı, $\sigma(T)$-nin ≈65 K və ≈200 K minimum və maksimumu, $\alpha_0(T)$-nin isə ≈270 K-də maksimumu müşahidə olunmuşdur. Alınan nəticələr iki tip yukdaşiyıcı və keçirici zonanın dibindən 0,030 eV məsafədə olan aşqar səviyyəsinin varlığı ilə izah olunmuşdur. Müəyyən olunmuşdur ki, $\sigma(T)$-nin ≈65 K - dəki minimumu T<65 K-də elektron və deşiklərin yürüklüyünün azalması və T>65 K-də elektronların akseptor səviyyəsindən generasiyası ilə əlaqədardır. $R(T)$-nin 200-300 K temperatur intervalında zəifləməsi və $\alpha_0(T)$-nin xətti artması $n_a(T)$-nin zəifləməsi, $\alpha_0(T)$-nin isə ≈270 K-dən sonra azalması məxsusi keçiriciliyinin başlaması ilə əlaqədardır.

Ф.Ф. Алиев

ЭЛЕКТРИЧЕСКИЕ И ТЕРМОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА p-Ag_2Te

Исследованы температурные зависимости коэффициента Холла – R, электропроводности – σ и термоэ.д.с. – α_0 в p-Ag_2Te в интервале температур 4-300 К. Наблюдаются особенности: замедление $R(T)$ в интервале температур ≈200-300 К, минимум при ≈65 К и максимум при ≈200 К в $\sigma(T)$, и максимумы $\alpha_0(T)$ при ≈80 и ≈270 К. Полученные экспериментальные данные интерпретированы в рамках модели с двумя типами носителей тока с учетом акцепторных уровней, расположенных от дна зоны проводимости на 0,030 эВ. Установлено, что минимум $\sigma(T)$ при ≈65 К обусловлен уменьшением подвижности электронов (U_n) и дырок (U_p) при T < 65 К и генерацией акцепторных электронов (n_a) при T > 65 К. Замедление $R(T)$ и уменьшение $\sigma(T)$ при T >200 К происходят за счет ослабления $n_a(T)$ и уменьшения $U_n(T)$. Максимум $\alpha_0(T)$ при ≈270 К связан с проявлением собственной проводимости.

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