SINGLE-CRYSTALLINE QUATERNARY CHALCOQENIDE COMPOUNDS $AgCd_2GaS_4$ AND THEIR PHYSICAL PROPERTIES

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Little-studied single-crystalline compounds of the content $AgCd_2GaS_4$, which crystallize by forming the rhombic structure (space group $Pmn2_1$), have been studied. The violation of sample stoichiometry and the stochastic occupation of the cation sublattice by Ag and Ga ions result in the violation of long-range order and make $AgCd_2GaS_4$ compounds more similar to disordered systems. On the basis of studying the temperature dependence of the electrical conductivity and the spectra of thermally induced conductivity, the energy levels of defect centers in the semiconductor energy gap have been determined. The experimental results obtained were used to develop a qualitative model for the distribution of the electron density of states in $AgCd_2GaS_4$ semiconductors.

1. Introduction

An important task of the modern technology of semiconducting materials is the fabrication of new multicomponent compounds with low symmetry, which can expand the range of traditional use of classical semiconducting materials in electronic and optoelectronic engineering and nonlinear optics. In this respect, promising are little-studied complex chalcogenide compounds, because, in this case, the attention was mainly paid to studying their structural parameters. Such compounds involve, in particular, quaternary single crystals $AgCd_2GaS_4$, the electronic analogs of cadmium sulfide single crystals.

In this work, we report the results of our researches dealing with the temperature dependences of the electrical conductivity and thermally induced conductivity of $AgCd_2GaS_4$ single crystals fabricated at the Faculty of Chemistry of the Lesya Ukrainka Volyn National University.

X-ray diffraction studies showed that $AgCd_2GaS_4$ compounds crystallize by forming the rhombic structure (space group $Pmn2_1$) with the following lattice parameters: $a = 0.81459$ nm, $b = 0.68989$ nm, and $c = 0.65932$ nm. More detailed information can be found in works [1–5]. Cations of Cd atoms occupy predetermined crystallographic positions, while Ag and Ga atoms are located stochastically in the cation sublattice. The structure of the $AgCd_2GaS_4$ compound can be described as the densest packing of chalcogenide atoms, where a half of tetrahedral voids are filled with cations of Ag, Cd, and Ga atoms. Every anion S^- is surrounded by four cations, and, vice versa, every cation is surrounded by S^--anions. The statistical character of the occupation of crystal lattice sites by Ag and Ga cations gives rise to the violation of electron potential energy periodicity in the lattice, which imparts some features of disordered systems to the $AgCd_2GaS_4$ compound and, as a result, leads to the emergence of the tails of the electron density of states in the energy gap [6, 7]. Other defects make an additional contribution to the violation of the long-range order as well.

2. Experimental Results and Their Discussion

For physical researches, specimens were fabricated in the form of regular parallelepipeds $(0.15 \div 0.4) \times (1 \div 2) \times (3 \div 5)$ cm^3 in dimensions, depending on the research character. The surfaces of specimens were ground and polished with diamond pastes. In some cases (thin crystals), the surfaces were additionally etched in an HNO_3 solution with adding 10% of H_2O_2. As contacts at electric measurements, there served copper wires welded to the surface making use of a spark discharger. Alternatively, the contacts were prepared of gallium–indium eutectic alloy, by rubbing the latter into an as-treated surface. The ohmic character of contacts remained valid in a wide range of temperatures and voltages (up to $5 \div 10$ V).

All studied specimens, according to the sign of their thermal emf, had conductivity of the n-type. The dark conductivity σ of specimens at room temperature $T \approx 292$ K amounted to $\sigma \approx 10^{-6}\ \Omega^{-1}\text{cm}^{-1}$. Complex semiconductor compounds, which $AgCd_2GaS_4$ single crystals belong to, differ from elementary and binary semiconductors by a higher concentration of various structural defects. In addition, the results of microprobe

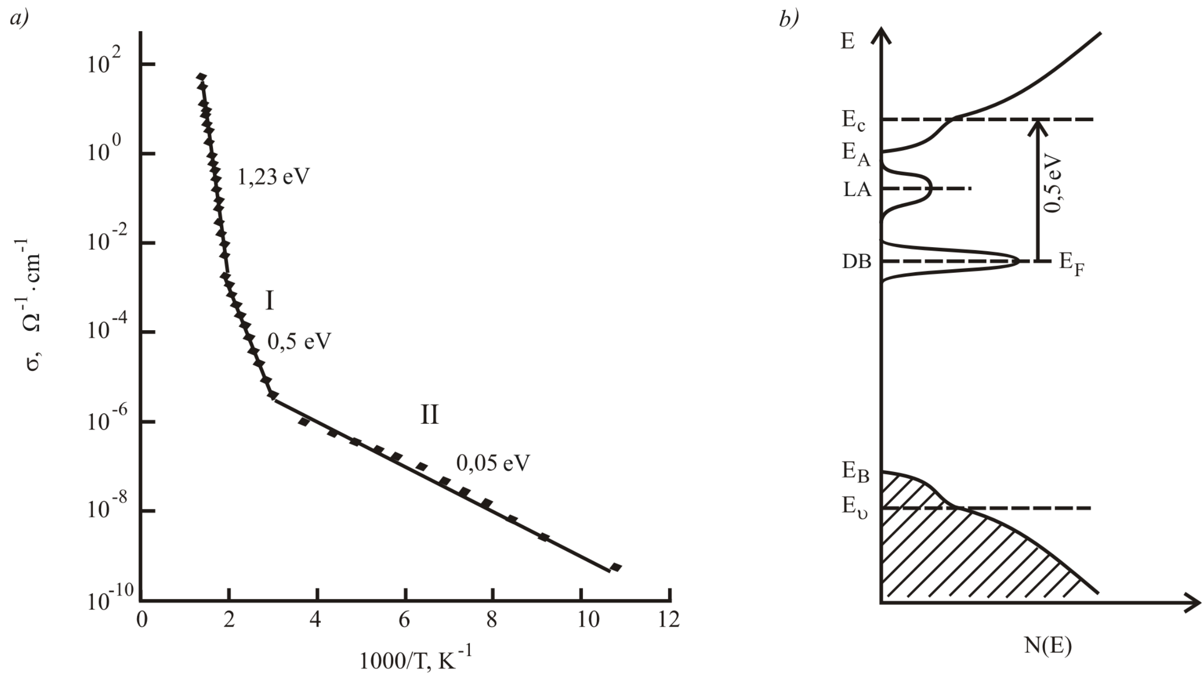

Fig. 1. *a* – Temperature dependence of the electrical conductivity of $AgCd_2GaS_4$ single crystals. *b* – Dependence of the electron density of states on the energy in defect semiconductors: E_c and E_v are the percolation levels for electrons and holes in the conduction and valence bands, respectively; E_A and E_B are the tail edges of the density of states adjacent to the conduction and valence bands, respectively

analysis testify that $AgCd_2GaS_4$ single crystals are nonstoichiometric by a few percent with respect to cadmium, i.e. they are enriched by cadmium vacancies (V_{Cd}) [3,4]. Some V_{Cd} sites can evidently can be occupied by Ag and Ga atoms, whose ionic radii are close to that of a cadmium atom ($r_{Ag^+} = 0.113$ nm, $r_{Ga^+} = 0.062$ nm, and $r_{Cd} = 0.099$ nm) and which possess close values of electronegativity, namely, 1.9, 1.6, and 1.7 for Ag, Ga, and Cd atoms, respectively. Such a substitution results in the emergency of both the acceptor Ag_{Cd} and donor Ga_{Cd} centers, with V_{Cd} being the acceptor center. A hypothesis concerning the existence of antistructural defects in complex semiconductor compounds was confirmed in a plenty of scientific works. For instance, the authors of works [8–10] reported about the formation of antistructural defects of the A_B and B_A types in $A^{II}B_2^{III}C_4^{VI}$ crystals.

Hence, $AgCd_2GaS_4$ single crystals are compensated defect semiconductors with a high concentration of acceptors (these are V_{Cd} and Ag_{Cd}) and donor centers (Ga_{Cd}) which compensate the charge of acceptors. In addition, other defects of a technological origin, both donors – in particular, these are interstitial silver (Ag_i) and gallium (Ga_i) atoms – and acceptors, should not be excluded from consideration. If the number of charged defects in a compensated semiconductor is large, the fluctuations of their concentration can also give rise to the violation of the long-range order and the appearance of a random electric field, which is responsible for the emergence of localized- and delocalized-state bands in the energy gap of a compound.

The temperature dependence of the electrical conductivity of $AgCd_2GaS_4$ single crystals reveals features that are typical of disordered semiconductors (Fig. 1,*a*); it is described by the formula [7]

$$\sigma = \sigma_0 \exp\left(-\frac{E_0}{kT}\right) + \sigma \exp\left(-\frac{E}{kT}\right). \quad (1)$$

The first term in the $\sigma(T)$ dependence (see section *I* in Fig. 1,*a*) has an exponential character with the activation energy $E_0 \approx (0.5 \pm 0.02)$ eV. The multiplier σ_0 is equal to $200 - 300\ \Omega^{-1}\text{cm}^{-1}$ for various specimens, which is typical of disordered systems [7] for the electron transition from the defect band (DB) of localized states, which includes the Fermi level E_F, onto the percolation level E_c in the conduction band (Fig. 1,*b*).

Wide section *II* in the dependence $\sigma(T)$ (Fig. 1,*a*), which is described by the second term in Eq. (1), is

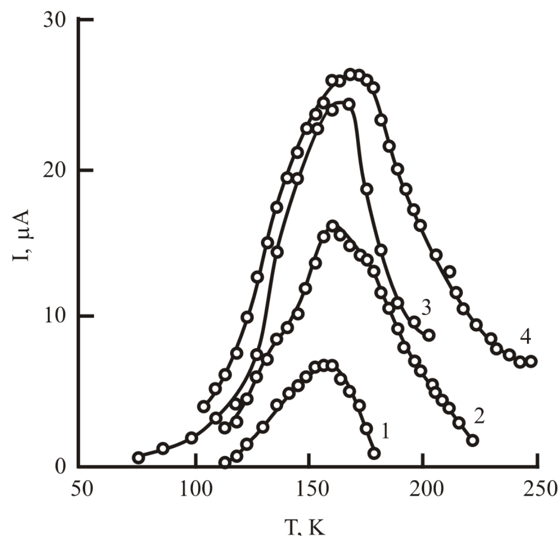

Fig. 2. TIC spectra of $AgCd_2GaS_4$ single crystals measured at various heating rates of a specimen: *1* – 0.035, *2* – 0.05, *3* – 0.086, and 4 – 0.11 K/s

characterized by the activation energy $E \approx 0.05 \div 0.06$ eV (for different specimens) and the electrical conductivity $\sigma \approx 10^{-4}\ \Omega^{-1}\text{cm}^{-1} \ll \sigma_0$. Such parameters are characteristic of the conductivity through the impurity-defect band [7], which is caused by the hopping of thermally activated electrons between localized states in the vicinity of the level E_F in this band (Fig. 1,*b*). In this case, the hopping activation energy E is close to the halfwidth of the defect band ΔE; in particular, for our specimens, $\Delta E \approx 0.1$ eV.

In work [7], the value of ΔE was estimated for the temperature $T \approx 300$ K, the average distance between defects $R = 60$ Å, and $\alpha^{-1} = 8$ Å, where the parameter α determines the integral of wave function overlapping. The value $\Delta E \approx 0.1$ eV, which coincides with the width of the impurity-defect band in $AgCd_2GaS_4$ single crystals, was obtained. Taking into account that $R = 1/\sqrt[3]{N}$, we can estimate the concentration of defects. It turned out to be $N \approx 5 \times 10^{18}$ cm^{-3}, which is lower than the concentration $N_\text{Cd} \approx 10^{20}$ cm^{-3} of V_Cd defects in thecadmium sublattice, stemming from the nonstoichiometry of the compound, according to the results of microprobe analysis. The role of defects that are responsible for the impurity band, which is located in the upper half of the energy gap, can be played by donor centers Ga_Cd which compensate the charge of acceptors (V_Cd and Ag_Cd).

At temperatures higher than $T_2 = 500$ K, the electrical conductivity $\sigma(T)$ of $AgCd_2GaS_4$ single crystals is described by an exponential dependence with the activation energy $E_a \approx 1.23$ eV, which corresponds to the position of the Fermi level E_F near the midpoint of the energy gap and testifies to the beginning of the own conductivity of the semiconductor. The thermal width of the energy gap in the $AgCd_2GaS_4$ semiconductor compound, which was evaluated from the given dependence, turned out equal to $E_g \approx 2E_a \approx 2.46$ eV, which is confirmed by other researches.

It is known [7] that the thermal emf of disordered semiconductors obeys the formula

$$S = \frac{k}{e}\left(\frac{E_\text{F}}{kT} + A\right). \qquad (2)$$

The parameter A depends on the mechanism of electron scattering. For crystalline semiconductors – formula (2) is also valid for them – the value of A, as a rule, falls within the limits of $2 \div 4$. For disordered semiconductors in the case where the charge is transferred by electrons in delocalized states (at the percolation level E_c), the parameter A acquires a value which is close to unity or, in the case of electrons in localized states (in the tail of the *c*-band), much less than unity.

The measurements of thermal emf for $AgCd_2GaS_4$ single crystals at temperatures close to room one (under this condition, the energy of thermal ionization $E_0 \approx 0.5$ eV) gave the value $S = 1.2 \times 10^{-3}$ V/K, which corresponds to $A \approx 1.5$. The result obtained confirms a conclusion made earlier about the energy of conductivity activation $E_0 \approx 0.5$ eV [formula (1)], which corresponds to the transitions of electrons from the energy states in the vicinity of E_F onto the percolation level in the conduction band.

Donor centers located near the bottom of the conduction band, when having lost electrons in a compensated semiconductor, can play the role of traps or sticking centers for free charge carriers. Such centers can be filled with electrons by illuminating a photosensitive semiconductor with light from the intrinsic absorption range at a certain low temperature, at which the probability of thermal excitation of an electron from the trap into the band is insignificant. Heating the specimen which was activated in such a manner in dark should result in the removal of electrons from traps at definite temperatures and in the emergence of peaks on the curve of thermally induced conductivity (TIC) [11].

In order to obtain the information about centers, whose energy position is located near the bottom of the conduction band, we studied the spectra of TIC of $AgCd_2GaS_4$ single crystals (Fig. 2). A broad width of the TIC peak (Fig. 2) is evidently caused by the existence of a band of

quasicontinuous energy states of shallow electron traps in the semiconductor energy gap. For the analysis of TIC spectra, we, similarly to the authors of work [12], used the formula

$$I(T) = I_0 \exp\left(-\frac{E_t}{kT}\right) \times$$

$$\times \exp\left[-\frac{\vartheta N_{ef} S_t}{\beta}\left(\frac{kT^2}{E_t}\right)\exp\left(-\frac{E_t}{kT}\right)\left(1+\frac{4kT}{E_t}\right)\right]. \quad (3)$$

At the initial stage of the trap thermal ionization, the contribution made by the first term in Eq. (3) to the dependence $I(T)$ dominates, i.e.,

$$\ln I(T) \approx \ln I_0 - \frac{E_t}{kT}. \quad (4)$$

Taking advantage of formula (4) which is valid for both slow and fast traps [11, 12], we estimated – by the slope of the dependence $\ln I$ versus T^{-1} – the energy depth E_t of electron traps in $AgCd_2GaS_4$ single crystals. Taking into account the fact that electron traps are distributed within some energy interval, we decomposed, by applying the "thermal refinement" method, the smeared TIC peak into curves which are associated with thermal ionization of electrons from individual traps [13] (Fig. 3).

While repeating the heating–cooling cycle [13], the slope of the initial TIC section at the heating stage increases within the interval from 0.07 to 0.18 eV, which evidences for the existence of an impurity band of sticking levels in the interval $0.07 \div 0.18$ eV in $AgCd_2GaS_4$ single crystals (Fig. 1,*b*). In the formation of the sticking level band, there can be engaged the energy levels of shallow donors – these are Ag_i, Cd_i, and Ga_i interstitial atoms at various interstitial sites, – as well as sulfur vacancies V_S which are always present in multicomponent defect semiconductors.

3. Conclusions

Single crystals of chalcogenide compounds $AgCd_2GaS_4$, owing to the defect structure of their crystal lattice, reveal some features of disordered systems with their conductivity of the *n*-type. On the basis of analysis of the temperature dependence of electrical conductivity, the width of the energy gap of $AgCd_2GaS_4$ single crystals at a temperature of 292 K has been estimated. The qualitative model for the distribution of the electron density of states in the energy gap of the $AgCd_2GaS_4$ semiconductor has been proposed. Single-crystalline quaternary chalcogenide compounds $AgCd_2GaS_4$, being characterized by a low symmetry of their crystal lattice and wide transparency windows, can be practically used in nonlinear optics and other domains of optoelectronic engineering.

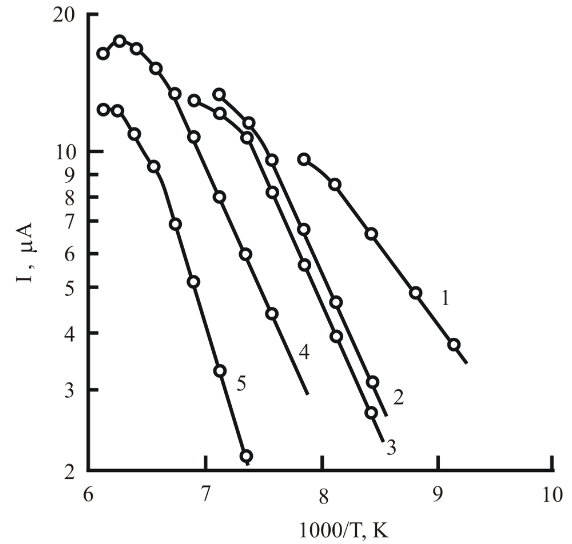

Fig. 3. TIC curves resolved by the "thermal refinement" method (one to five consecutive heatings at the rate $\beta \approx 0.11$ K/s)

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ХАЛЬКОГЕНІДНІ ПОЧЕТВЕРЕНІ МОНОКРИСТАЛІЧНІ СПОЛУКИ $AgCd_2GaS_4$ ТА ЇХ ФІЗИЧНІ ВЛАСТИВОСТІ

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Р е з ю м е

Досліджено маловивчені монокристалічні сполуки $AgCd_2GaS_4$, які кристалізуються в ромбічній структурі (просторова група $Pmn2_1$). Порушення стехіометрії зразків і статистичне заповнення іонами Ag^+ і Ga^+ катіонної підґратки веде до порушення далекого порядку і наближає сполуку $AgCd_2GaS_4$ до невпорядкованих систем. На основі дослідження температурної залежності питомої електропровідності і спектрів термостимульованої провідності визначено енергетичне положення дефектних центрів в забороненій зоні напівпровідника. З врахуванням експериментальних результатів була розроблена якісна модель розподілу щільності електронних станів в напівпровідниках $AgCd_2GaS_4$.