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Hopping conductivity in GaSe monocrystals at low temperatures

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Abstract. The paper represents results of investigation in the wide temperature interval (4.2...300) K of hopping conductivity in GaSe single crystals doped by cadmium impurities (0.01 and 0.1 atomic percent) during crystal growing. Specific resistance of GaSe doped by cadmium at room temperature is equal to 31 and 250.0 ohm·cm, concentration of impurities is 10^{15} and 2.0×10^{16} cm⁻³, mobilities are equal to 25.0 and 12.0 cm²/V·sec, respectively. It is ascertained that specific resistance weakly depends on temperature at (5...33)K, activation energy of this conductivity is 1.2×10^{-3} eV, and it is determined by hopping mechanism of charge transfer. At temperatures (33...100)K, activation energy of conductivity is 7.8×10^{-2} eV, and it is connected with hole transfer in empty band.

Keywords: conductivity, temperature, hopping conductivity, activation energy, specific resistance, concentration, mobility, lamellar monocrystals, phonon.

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Experimental results

Up to now, an electrical conduction in lamellar monocrystals of GaSe was investigated in the wide range of temperatures (70...700) K [1, 2, 3, 4]. First, we studied an electrical conduction of GaSe from helium temperatures up to the room ones (4.2...300) K.

The experiments have been carried out using GaSe monocrystals grown by Bridgman method and doped by cadmium impurities (0.01 and 0.1 atomic percents) during their growth.

p-type GaSe samples with dimensions of $1.4 \times 0.4 \times 0.02$ cm³ and $0.9 \times 0.35 \times 0.023$ cm³ were made in the parallelepiped form. Indium contacts were fused in vacuum at temperatures from 350 to 400°C for an hour, and they were used as ohmic contacts. Specific resistances of GaSe samples doped by cadmium at room temperature are 31.0 and 250.0 ohm·cm. It is known [4] that the elements of the Periodic Table second group are acceptor dopants in GaSe, and therefore the decrease of a specific resistance by four orders as a result of doping by cadmium enabled us to carry out measurements nearby helium temperatures. Impurity concentration N_A determined

from measurements of the Hall effect at room temperatures for both samples is 10^{15} cm⁻³ and 2.0×10^{16} cm⁻³, and mobilities are equal to 25.0 and 12.0 cm²/V·sec, respectively. Temperature dependencies of a specific resistance for GaSe samples in the temperature interval 4.2–100 K are shown in Fig. 1. Two sections can be marked on the temperature dependence curve $\rho(T)$ (curve 1): low temperature section 5–33 K ($kT \ll E_A$) and high temperature section 33–100 K ($kT > E_A$), where E_A is *p*-type ionization energy. In the first temperature range, the dependence ρ on T is weak, and activation energy of this conductivity is $\varepsilon_3 = 1.2 \times 10^{-3}$ eV ($\rho = \rho_3 e^{-\varepsilon_3/kT}$). This energy is conditioned by hopping mechanism of charge transfer with further saturation (transfer temperature is $T = 11$ K). Hopping conductivity ε_3 with saturation was determined experimentally in low-doped and compensated samples $N_A a^3 \ll 1$, where N_A is the concentration of majority impurities; a is the localization length of a wave function in Ge samples [7, 8], and it was also theoretically described in [5]. As shown in [5], the reason of saturation of hopping resistance is connected with a temperature dependence of electron concentration on the *n*-type impurities ($n = N_D \exp(-\varepsilon_3/kT)$), and the saturation appears at the

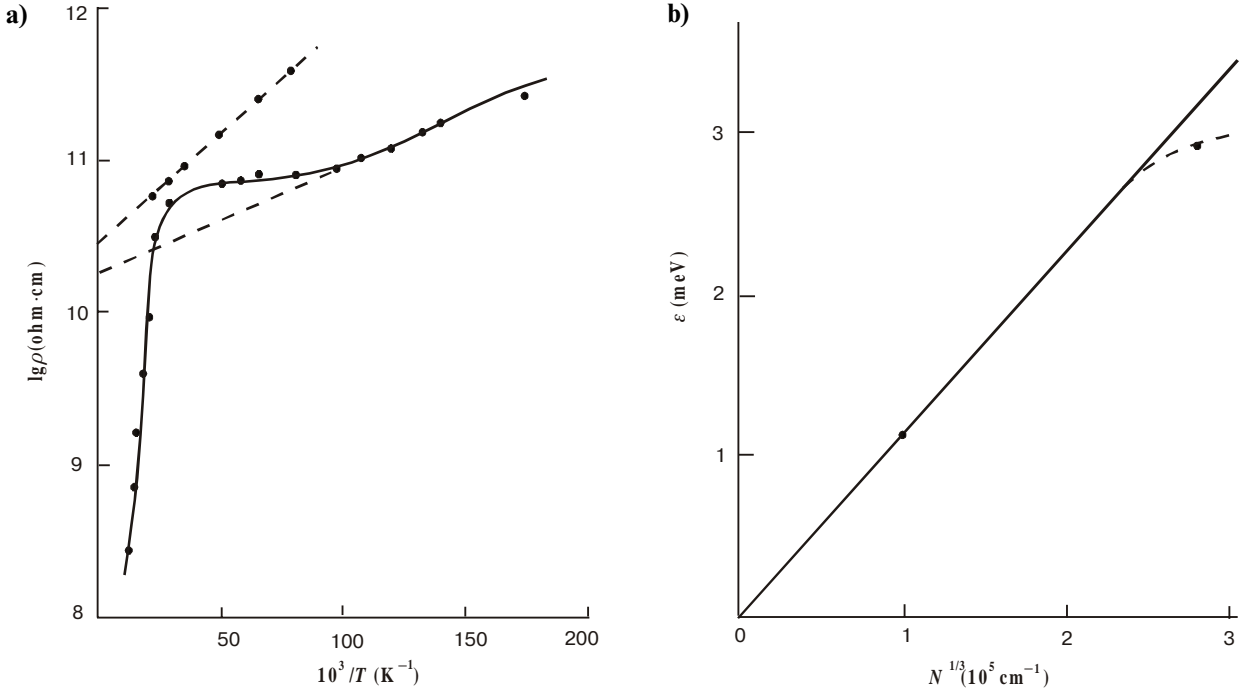


Fig. 1. Temperature dependencies of specific resistance (a) and concentration dependencies of activation energy of hopping conductivity (b) for GaSe samples.

temperature $T_0 = \epsilon_3 \ln^{-1}(N_A/N_D)$. Knowing transfer temperature T_0 and value of activation energy for hopping conductivity ϵ_3 we can determine the compensation $k = N_D/N_A$ of majority impurities and it is equal to 0.31. As shown in [5], the value of k can be also determined in the presence of almost horizontal section of saturation by the value of preexponential factor ρ_3 and by the value of hopping resistance ρ_{sat} as their ratio: $k = \rho_3 / \rho_{\text{sat}}$. It is seen from Fig.1 that $\rho_3 = 2.08 \times 10^{10}$ ohm·cm, $\rho_{\text{sat}} = 6.3 \times 10^{10}$ ohm·cm, then $k = 0.32$, and it is in well accord with previous determination regarding transfer temperature T_0 . Knowing compensation value for GaSe sample ($N_A - N_D = 10^{15}$ cm⁻³) we can determine concentration of majority impurities equal to $1.4 \cdot 10^{15}$ cm⁻³.

The concentrations of majority impurities estimated by the energy activation value ϵ_3 ($\epsilon_3 = 0.99 \frac{e^2 N^{1/3}}{\chi} \times (1 - 0.3k^{-1/3})$, where χ is a capacitivity of GaSe sample and χ is 10.6) equal to 10^{15} cm⁻³ and $2 \cdot 10^{16}$ cm⁻³. These results are in well accord with values of N_A , determined from the Hall effect.

The estimation of state radius a from experimental data f_3 and pre-exponential factor of the hopping resistance ρ_0 ($\rho_3 = \rho_0 e^{2N^{1/3}} / a$) for GaSe gives a value equal 31 \AA . The value ρ_0 was determined by the following formula: $\rho_0 = Ca^3(N_D^{1/3}a)^\delta$, at $\delta = 0$ and it was $4 \cdot 10^7$ ohm·cm,

[6], where $C = \frac{9\pi}{8} \frac{\hbar^4}{\epsilon^6} \frac{d\chi^2 v^5}{\epsilon}$, where d is a density of substance, v is a velocity of longitudinal sound wave, ϵ is a constant of deformation potential.

The dependence ϵ_3 from the concentration of impurities for GaSe samples ($N_A = 10^{15}$ cm⁻³ and $N_A = 2 \cdot 10^{16}$ cm⁻³) has been shown in Fig. 1b. It is seen that the value of ϵ_3^{exp} coincides with theoretical line, subject to large-scale fluctuation of potential at $k = 0.3$ for the sample with $N_A = 10^{15}$ cm⁻³. The value of for GaSe sample with $N_A = 2 \cdot 10^{16}$ cm⁻³ deviates from the theoretical line and the deviation value is $\frac{1}{2} \Omega = 10^{-4}$ eV and it indicates the formation of quantum impurity band conditioned by the overlapping of wave functions from neighboring impurity centers.

At the second section of the curve $\rho(T)$ the activation energy of conductivity is $7.8 \cdot 10^{-2}$ eV and connected with transfer of holes into the empty band. The conductivity $\rho(T)$ in the zone of ϵ_1 is mainly determined by the concentration of free holes ($\rho = N_A \exp(-\frac{\epsilon_1}{kT})$) in the valence band and their mobility $\mu(T)$.

The temperature dependencies of mobility, which was recalculated from $\rho(T)$ (points) at the values $N_A = 10^{15}$ cm⁻³ and $\epsilon_1 = 7.8 \cdot 10^{-2}$ eV as well as estimated mobility $\mu(T)$ (full curve) in the case of scattering on non-polar optic phonons with energy $\hbar\omega = 18$ MeV are shown in Fig. 2.

The calculation results of charge carrier mobility for two-dimensional energy-band structure [1, 4] were used for construction of $\mu(T)$ curve. Availability of strong gradient of deformation potential in lamellar crystals stipulates dominating role of hole scattering on non-polar optic phonons in comparison with acoustic phonons.

Authors [1, 4] got the following expression in case of short-range potential for mobility along a layer:

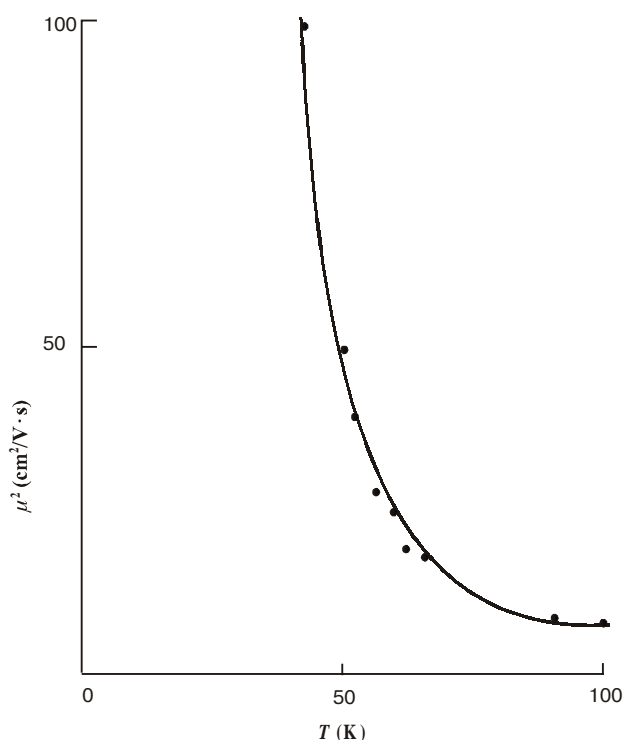


Fig. 2. Experimental (points) and calculated (full line) temperature dependencies of hole mobility in GaSe.

$$\mu_{xx} = \mu_{xx}^+ \left\{ 1 - \frac{1 - \exp(-\frac{\hbar\omega}{kT})}{2 - \exp(-\frac{\hbar\omega}{kT})} \left(1 + \frac{\hbar\omega}{kT} \right) \exp(-\frac{\hbar\omega}{kT}) \right\} \quad (1)$$

where

$$\mu_{xx}^+ = \frac{9}{g^2 \hbar \omega} \frac{m_0}{m_x} \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right] \quad (2)$$

and $m_x = 0.8m_0$ – mass of free holes along the layer; $g^2 = 0.24$ – bond constant of holes with optic phonons [2].

From comparison of (1) and experimental results (Fig. 2), authors came to conclusion that main contribution in $\mu(T)$ is caused by hole scattering on lattice vibrations with phonon absorption (2). The calculation of hole scattering with phonon emitting $\mu(T)$ does not practically change the results of comparison with experiment. These experimental data are in accord with results obtained by authors [4], who measured $\mu(T)$ in GaSe within the temperature range between 80 to 700 K. Thus, we may ob-

tain the following expression by comparison of [2] with experimental data

$$\mu = \mu_0 \left(\frac{T}{T_0} \right)^{-2.1} \quad (3)$$

where $T_0 = 300\text{K}$, $m_0 = 50 \text{ cm}^2/\text{Vsec}$.

Application of two-dimensional model for explanation of temperature dependence of mobility justified with the following: firstly, although electronic states in GaSe are three-dimensional [9] because of allocation of electron density «incoming» into interlayer space, availability of inhomogeneity caused by the packing of layers and accumulation of impurities around such defects the conductivity is essentially anisotropic; secondly, temperature dependence of mobility points to the scattering on low-frequency oscillations of a lattice, which are conditioned by strong anisotropy of elastic constants due to different bonding force perpendicular and across the layers.

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