Research Article

DC-Electrical Properties of TlGaTe_2 Single Crystals under Hydrostatic Pressure

Solmaz N. Mustafaeva, Shafag G. Gasymov, Elmira M. Kerimova, and MirSalim M. Asadov

Institute of Physics, National Academy of Sciences of Azerbaijan, G. Javid Avenue 33, Baku 1143, Azerbaijan

Correspondence should be addressed to Solmaz N. Mustafaeva, solmust@gmail.com

Received 9 September 2010; Accepted 9 February 2011

Academic Editor: Z. Mao

Copyright © 2011 Solmaz N. Mustafaeva et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The effect of hydrostatic pressure (up to 0.82 GPa) on the electric properties of chain TlGaTe_2 single crystals has been investigated in the temperature range 77–296 K. It has been shown that pressure leads to a considerable increase of conductivity ($\sigma_{\perp}$) across the chains of TlGaTe_2 single crystals. Parameters of localized states in the band gap of TlGaTe_2 single crystal according to the low-temperature electrical measurements were obtained at various pressures.

1. Introduction

TlGaTe_2 single crystals are typical representatives of chain-layered semiconductors and attract a lot of attention due to their interesting physical properties. These properties include strong anisotropy of the electric parameters related to special features in the crystalline structure. Chain and layered crystals usually contain structural defects, such as vacancies and dislocations. The presence of these defects results in a high density of localized states near the Fermi level. The states localized in the band gap are responsible for most electronic processes occurring in semiconductors. Both dc and ac charge transport in thallium-gallium chalcogenides proceeds via these localized states [1–3]. Measurements of temperature-dependent conduction of a crystal can give valuable information on the localized states. The physical properties of TlGaTe_2 single crystals are very sensitive to external actions, such as temperature, dc and ac electric fields, laser light, ionizing irradiations, and pressure. Room-temperature study of the effect of hydrostatic pressure up to 0.9 GPa on the electrical conductivity and Hall coefficient for the TlGaTe_2 crystals have been made in [4].

The work [5] deals with the results of experimental investigation of the effect of hydrostatic pressure up to 0.9 GPa on the kinetic properties of the TlGaTe_2 crystals

over temperature range 220 to 295 K. The aim of this work is to study the influence of hydrostatic pressure on the dc-electrical properties of TlGaTe_2 single crystals over the temperature range from 77 to 296 K.

2. Experimental

The crystals used for our study were grown by the Bridgman method and have tetragonal structure of the TlSe type with space group $I4/mcm$ and lattice parameters: $a = (8.430 \pm 0.002) \text{ \AA}$, $b = (6.858 \pm 0.004) \text{ \AA}$ at room temperature. The samples for electrical measurements had the shape of rectangular plates. Indium was used as a contact material to the TlGaTe_2 samples. Dc-electric field from Ohmic region of current-voltage characteristic was applied crosswise to the natural chains of a TlGaTe_2 single crystal.

The measurements under pressure (up to 0.82 GPa) were performed in a conventional copper-beryllium vessel with a mixture of dehydrated transformer oil and kerosene (1 : 4) as a pressure transmitting media. This fluid did not cause any irreversible changes in the samples. Pressure was measured with a calibrated manganine gauge with an accuracy not less than 1%.

FIGURE 1: Temperature dependences of the conductivity of a TlGaTe₂ single crystal measured at various values of the pressure P : (1) 0, (2) $3.1 \cdot 10^8$, (3) $5.1 \cdot 10^8$, and (4) $7.1 \cdot 10^8$ Pa.

3. Results and Discussions

The temperature dependences of electrical conductivity of TlGaTe₂ across the chains ($\sigma_{\perp}$) measured at different pressures in the interval 0–0.71 GPa are shown in Figure 1.

It is evident from Figure 1 that high-temperature branches of $\log \sigma_{\perp}(1/T)$ dependences are exponential in the temperature range 230–296 K. In this temperature range, the conduction of thermally generated impurity charge carriers in the allowed zone is dominated. The activation energies of impurity charge carriers (E_t) estimated from the slopes of the curves $\log \sigma_{\perp}(1/T)$ under various pressures, are presented in the last column of Table 1. The activation energy at $P = 0$ and $3.1 \cdot 10^8$ Pa for TlGaTe₂ $E_t = 0.29$ eV is in satisfactory agreement with that presented in [6] ($E_t = 0.26$ eV).

The characteristic feature is that at $T < 230$ K, the slope of $\log \sigma_{\perp} = f(1/T)$ curves plotted on a semilogarithmic scale is not constant; the activation energy of conductivity decreases monotonically with decreasing temperature. As the pressure increases, the $\log \sigma_{\perp}(1/T)$ dependence becomes flatter and, at $P = 7.1 \cdot 10^8$ Pa and $T < 130$ K, the low-temperature conductivity increases with decreasing temperature (Figure 1, curve 4).

The above experimental facts indicate that, in the temperature range 130–220 K, the TlGaTe₂ single crystals exhibit variable range hopping conduction over states lying in a narrow energy band (of width ΔE) near the Fermi level. Such type of hopping conductivity in TlGaTe₂ was observed also in [6]. With this type of conductivity, the $\ln \sigma_{\perp} = f(T^{-1/4})$ dependence should be a straight line with a slope T_0 [7]:

$$\sigma \sim \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right], \quad (1)$$

$$T_0 = \frac{16}{(N_F \cdot k a^3)}, \quad (2)$$

FIGURE 2: Temperature dependences of the low-temperature conductivity of a TlGaTe₂ single crystal plotted in Mott coordinates: (1) 0, (2) $3.1 \cdot 10^8$, (3) $5.1 \cdot 10^8$, and (4) $7.1 \cdot 10^8$ Pa.

where N_F is the density of states near the Fermi level, k is the Boltzmann constant, and a is the localization radius.

Figure 2 displays the $\log \sigma_{\perp} = f(T^{-1/4})$ dependences for a TlGaTe₂ single crystal at various values of the pressure. The measured values of T_0 at different pressures are presented in Table 1, from which it follows that, as the pressure increases, the T_0 value also increases.

Using (2), we estimated the density of states near the Fermi level. When calculating N_F , the localization length for the TlGaTe₂ single crystal was taken as $a = 25$ Å by analogy with binary gallium telluride [8]. The values of N_F at different pressures are also listed in Table 1. It can be seen that, as the pressure increases, the density of localized states N_F decreases. The $N_F(P)$ dependence plotted on a semilogarithmic scale is shown in Figure 3(a). It is obvious that this dependence is exponential.

From the formula [7],

$$R(T) = \left(\frac{3}{8} \right) a \left(\frac{T_0}{T} \right)^{1/4}, \quad (3)$$

one can calculate the carrier jump distance. We found average values of R at temperature interval 130–220 K under various hydrostatic pressures. The obtained values of R_{av} are presented in Table 1. As the pressure increases, R_{av} also increases. From Figure 3(b), it is obvious that dependence $R_{av}(P)$ is linear. As is seen, the average jump distance $R_{av}(T)$ in the TlGaTe₂ single crystal substantially exceeds the distance between the carrier localization centers.

From the condition [7],

$$\left(\frac{4}{3} \right) \pi R^3 N_F \left(\frac{\Delta E}{2} \right) = 1, \quad (4)$$

we determined the scatter of trap states near the Fermi level (ΔE). The values of ΔE under different pressures are also listed in Table 1. It can be seen that, as the pressure increases, the range of ΔE energies becomes wider. The dependence $\Delta E(P)$ (Figure 3(c)) is linear.

FIGURE 3: (a) Density of states near the Fermi level, (b) average hopping distance, (c) scatter of trap states near the Fermi level, and (d) jump activation energy in TlGaTe₂ single crystal as a function of pressure.

TABLE 1: Parameters of localized states in the band gap of the TlGaTe₂ single crystal according to the temperature electrical measurements at various pressures.

P (10^8 Pa)	T_0 (K)	N_F ($\text{eV}^{-1} \cdot \text{cm}^{-3}$)	R_{av} ($\text{\AA}$)	ΔE (eV)	ΔW (eV)	N_t (cm^{-3})	E_t (eV)
0	$1.4 \cdot 10^5$	$8.6 \cdot 10^{19}$	50	0.04	0.03	$3.4 \cdot 10^{18}$	0.29
3.1	$1.5 \cdot 10^6$	$8.0 \cdot 10^{18}$	90	0.08	0.05	$6.4 \cdot 10^{17}$	0.29
5.1	$4.7 \cdot 10^6$	$2.6 \cdot 10^{18}$	119	0.11	0.07	$2.9 \cdot 10^{17}$	0.15
7.1	$9.4 \cdot 10^6$	$1.3 \cdot 10^{18}$	140	0.13	0.09	$1.7 \cdot 10^{17}$	0.15

Charge carrier jumps occur exactly in this narrow energy band. The temperature dependence of activation energy of hopping conductivity is described by relation [9]:

$$\Delta W(T) = \frac{(kT)^{3/4}}{(N_F \cdot a^3)^{1/4}}. \quad (5)$$

The $\Delta W(T)$ values for TlGaTe₂ calculated at $T = 130$ K and under various pressures from 0 to $7.1 \cdot 10^8$ Pa are presented in Table 1. It is seen from Figure 3(d) that ΔW

linearly increases with pressure. The table also presents the concentrations of trapping states in TlGaTe₂ under different pressures, which were calculated according to the formula

$$N_t = N_F \cdot \Delta E. \quad (6)$$

Since the concentration of localized states in the band gap of TlGaTe₂ is rather high, the energy band structure of the crystals under consideration is similar to that of amorphous semiconductors. The amorphous state is characterized by

FIGURE 4: Conductivity $\sigma_{\perp}$ as a function of pressure for TlGaTe₂ single crystal at room temperature.

the presence of strongly deformed or even broken chemical bonds, which have a tendency toward manifestation of acceptor properties. These defects play an especially important role in layered and chain crystals, such as TlGaTe₂ single crystals. The generation of new defects under pressure does not make a significant contribution against the background of the initially high concentration of localized states in the band gap of TlGaTe₂ due to the presence of different types of defects. It seems that the decreasing of N_F and N_t values in TlGaTe₂ due to pressure is caused by the partial healing of defects. Hydrostatic pressure stimulates also the redistribution of already existing defects in the TlGaTe₂ single crystal, which apparently leads to a spreading of the energy distribution of localized states.

Figure 4 represents the pressure dependence of the conductivity of TlGaTe₂ single crystal at room temperature. The characteristic feature of the pressure behavior of the conductivity $\sigma_{\perp}$ may be described as follows: the conductivity increases with increasing pressure from $2 \cdot 10^{-3}$ to $5.43 \cdot 10^{-2} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$. Measurements permitted to evaluate the pressure behavior of $\sigma_{\perp}$, which may be written as

$$\ln \sigma_{\perp}(P) = \ln \sigma_{\perp}(0) + \beta P, \quad (7)$$

where $\beta = d \ln \sigma_{\perp}(P) / dP = 4.02 \text{ GPa}^{-1}$.

Assuming that the electrical conductivity changes with pressure according to the equation

$$\sigma_{\perp}(P) = \sigma_{\perp}(0) \exp\left(\frac{-\gamma P}{2kT}\right), \quad (8)$$

where $\gamma = dE_g^i/dP$ is the pressure coefficient of the indirect band gap, one can easily find that

$$\gamma = 2kT\beta. \quad (9)$$

One can see that since $\beta > 0$ then it follows from (9) that γ should be negative to satisfy (8). Hence, with increasing pressure, the forbidden band gap of TlGaTe₂

should decrease. We found that the dependence of the band gap of TlGaTe₂ on pressure may be written as $E_g^i(P) = E_g^i(0) - |\gamma|P$, where $|\gamma| = 0.207 \text{ eV/GPa}$. Analogical results have been obtained by us for chain TlInSe₂ single crystals [10], where $dE_g^i/dP = -0.175 \text{ eV/GPa}$.

As it was shown above in TlGaTe₂ single crystal, the anomaly on $\log \sigma_{\perp}(1/T)$ —dependence (Figure 1, curve 4) is observed at low temperatures ($T < 130 \text{ K}$) and high pressure (0.71 GPa). It seems to be due to phase transition stimulated by high pressure. About phase transition in TlGaTe₂ at 98.5, 121 and 130 K, it was reported in [11–14] from investigation of electrical, optical, and thermal properties of these single crystals. The pressure-induced phase transition at $P \approx 0.72 \text{ GPa}$ has been observed by us also in TlInSe_{1-x}S_x crystals [10].

4. Conclusions

The effect of hydrostatic pressure (up to 0.82 GPa) on the electric properties of chain TlGaTe₂ single crystals has been investigated in the temperature range 77–296 K. It has been shown that pressure leads to a considerable increase of conductivity ($\sigma_{\perp}$) across the chains of TlGaTe₂ single crystals. The increase of conductivity with pressure is described by the formula $\sigma_{\perp}(P) = \sigma_{\perp}(0) \exp(-\gamma P/2kT)$, and the pressure coefficient of the indirect band gap $\gamma = dE_g^i/dP$ was found to be -0.207 eV/GPa .

Parameters of localized states in the band gap of TlGaTe₂ single crystal according to the low-temperature electrical measurements were obtained at various pressures. It has been established that, as the pressure increases, the density of localized states near the Fermi level decreases exponentially, but average jump distance, energy spread of localized states, and activation energy of hopping conduction in TlGaTe₂ increase linearly.

References

- [1] S. N. Mustafaeva, V. A. Aliev, and M. M. Asadov, “Anisotropy of the hopping conductivity in TlGaSe₂ single crystals,” *Physics of the Solid State*, vol. 40, no. 1, pp. 41–44, 1998.
- [2] S. N. Mustafaeva, V. A. Aliev, and M. M. Asadov, “DC hopping conduction in TlGaS₂ and TlInS₂ single crystals,” *Physics of the Solid State*, vol. 40, no. 4, pp. 612–615, 1998.
- [3] S. N. Mustafaeva, “Dielectric dispersion in TlGaS₂ layered crystals,” *Physics of the Solid State*, vol. 46, no. 6, pp. 979–981, 2004.
- [4] K. R. Allakhverdiev, Sh. G. Gasymov, T. G. Mamedov, E. Yu. Salaev, A. M. Shirokov, and A. N. Tolmachev, “Effect of hydrostatic pressure on kinetic properties of TlSe and TlGaTe₂ crystals,” *Fiz. Tekh. Poluprov.*, vol. 16, no. 7, p. 1916, 1982.
- [5] K. R. Allakhverdiev, Sh. G. Gasymov, and T. G. Mamedov, “Effect of hydrostatic pressure on the electrical conductivity and Hall coefficient of TlGaTe₂ crystals,” *Physica Status Solidi A*, vol. 94, no. 2, pp. k143–k146, 1986.
- [6] R. M. Sardarly, O. A. Samedov, A. P. Abdullaev, A. A. Bayramov, F. T. Salmanov, and G. R. Safarova, “Hopping conduction and Pool-Frenkel effect in TlGaTe₂,” *Fizika (Baku)*, vol. 15, no. 2, pp. 91–95, 2009.

- [7] N. Mott and E. Davis, *Electronic Processes in Non-Crystalline Materials*, Oxford University Press, 1977.
- [8] S. N. Mustafaeva, *Thesis of Institute of Physics*, Doc. of Sciences thesis, NASA, Baku, Azerbaijan, 1990.
- [9] B. I. Shklovsky and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Nauka, Moscow, Russia, 1979.
- [10] E. Kerimova, S. Mustafaeva, D. Guseinova et al., "Influence of hydrostatic pressure on the electrical conductivity and optical properties of chain-layered TlInSe_2 and TlInSe_2 - TlInS_2 solid solutions," *Physica Status Solidi*, vol. 179, no. 1, pp. 199–203, 2000.
- [11] H. Hahn and B. Weltman, "Über-ternare chalkogenide des thalliums mit gallium und indium," *Naturwissenschaften*, B 2, no. 1, pp. 42–45, 1967.
- [12] N. M. Gasanly, A. F. Goncharov, B. M. Dzhavadov, N. N. Melnik, V. I. Tagirov, and E. A. Vinogradov, "Vibrational spectra of TlGaTe_2 , TlInTe_2 , and TlInSe_2 layer single crystals," *Physica Status Solidi B*, vol. 97, no. 1, pp. 367–377, 1980.
- [13] V. A. Aliev, M. A. Aldjanov, and S. N. Aliev, "Incommensurate phase transition in TlGaTe_2 ," *Pisma v JETF*, vol. 45, no. 9, pp. 418–420, 1987.
- [14] A. U. Sheleg, V. G. Gurtovoy, S. N. Mustafaeva, and E. M. Kerimova, "Influence of ionizing radiation on dielectric characteristics of TlInSe_2 and TlInTe_2 single crystals," *Fizika Tverdogo Tela*, vol. 53, no. 3, pp. 443–445, 2011.