Calculation of the temperature behavior features of electrical conductivity in $\text{GeTe}$, $\text{SnTe}$ and $A_{(x-1)}B_xC$ semiconductors – solutions of Tc near-structural phase transition

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Abstract. Temperature behavior calculation of the anomalous conductivity of the $A^4B^6$-type ferroelectric semiconductors ($\text{GeTe}$, $\text{SnTe}$ and $A_{(x-1)}B_xC$) near-phase transitions is carried out in the paper. The proposed integrable (analytical) model is applicable both for describing the temperature behavior of the conductivity of $\text{GeTe}$ multivalley semiconductors and $\text{SnTe}$-type systems. The influence of the structural phase transition on the systems’ conductivity is analyzed. The proposed analytical model of the conductivity behavior of ferroelectrics-semiconductors allows considering compounds with various spectra and compositions. The model is applicable both for the kinetic properties of multivalley semiconductors and for analyzing the effect of external influences on these properties: x composition and T temperature, as well as the presence of a structural phase transition in the system at Tc(x). It is shown that the graph can have the form of a break or the form of a smooth asymmetric maximum, depending on the value of the effective relaxation rate of carriers on soft phonons and the intervalley splitting of the anomalous conductivity near Tc in $A^4B^6$ systems. The calculation results are consistent with the experimental data. The dependence of the phase transition temperature Tc(x) on x composition is obtained.

1. Introduction

The electrical conductivity of solids is their most significant physical characteristic and its theory is represented in the papers of many authors. The proceedings of A.I. Anselm, G.L. Bir, G.E. Pikus and B.M. Askerov are widely known.

The approach, generalized to the case of real multivalley spectra, proposed by A.I. Anselm [1] is used in the paper [2]. The experimental data obtained in [3] are used.

2. Calculation and analysis

Consider the temperature dependence of electrical conductivity in the case of a real multivalley spectrum of the $A^4B^6$-type compounds. In these circumstances, the $\sigma_{\text{an}}(T)$ semiconductor conductivity, for instance, $\text{GeTe}$ is determined by the contributions’ sum of individual valleys [4, 5]
\[ \sigma_{\alpha\beta}(T) = \sum_{i=1}^{4} \sigma_{\alpha\beta}^{i}(T), \]

located on \([111],[1\, T],[T\, 1],[T\, 11]\) axes, respectively. The conductivity tensor of the \(i\)-th valley has the form of [1]:

\[ \sigma_{\alpha\beta}^{i}(T) = 2e^{2} \int_{0}^{\infty} \left(-\frac{\partial f_{i}}{\partial \varepsilon}\right) v_{\alpha}^{i}(\varepsilon)v_{\beta}^{j}(\varepsilon)\tau_{\alpha\beta}^{i}(\varepsilon, q_{i}^{F}, q_{i})d\varepsilon, \]

where \( f_{i}(x) = \left[\exp(x - \eta_{i} + 1)\right]^{-1} \) - electron distribution function, \( x = \varepsilon / k_{B}T \), \( \eta_{i} = \eta - \Delta \varepsilon_{i} \), \( \Delta \varepsilon_{i} = \Delta \varepsilon_{i}/k_{B}T \), \( \eta = \zeta / k_{B}T \), \( q_{i}^{F} = k_{F}^{i}/\sqrt{M_{ii}} \); \( \zeta \) and \( k_{F}^{i} \) - chemical potential and Fermi momentum; \( g_{i}(\varepsilon) \) - states density; \( \Delta \varepsilon \) - conduction band bottom shift; \( k_{B} \) - Boltzmann constant; \( T \) - absolute temperature; \( e \) - electron charge.

The inverse relaxation time of electrons in the \(i\)-th valley of a ferroelectric-semiconductor in the electron-phonon (or vibronic) model of the structural phase transition can be represented as [6,7]:

\[ \tau_{\alpha\beta}^{-1} = \left(kTM_{ii}/\hbar^{4}\rho\pi \left[\tilde{v}_{\alpha\alpha}\right]^{2} I_{\varepsilon} + \left[\tilde{v}_{\alpha\beta}\right]^{2} I_{ij}\right) \left(2e\{1 + \varepsilon / \varepsilon_{\alpha}^{F}\}^{0.5} \left(1 + 2\varepsilon / \varepsilon_{\alpha}^{F}\right)\right) \]

Here \( I_{\varepsilon} \) and \( I_{ij} \) are collision integrals, \( \rho \) - density, \( \left[\tilde{v}_{\alpha\alpha}\right]^{2} \), \( \left[\tilde{v}_{\alpha\beta}\right]^{2} \) - electron-phonon interaction coefficients, \( \hbar \) - Planck’s constant, \( M_{ii} \) - effective mass of the states density, \( \varepsilon_{\alpha} \) - energy of carriers in the \(i\)-th valley in the symmetric band model, \( \varepsilon_{\alpha}^{F}(x) = 2\varepsilon_{\alpha} - \Delta \varepsilon(x) \) - the band gap of the \(i\)-th valley is below \( T_{c} \) temperature of the structural phase transition, \( \Delta \varepsilon(x) \) - the seed gap between valence and conduction bands. The composition change of \( x=0.5+y \) for small \( y \) is set through \( \varepsilon_{\alpha}^{F}(x) \) in the form of

\[ \varepsilon_{\alpha}^{F}(x) = \varepsilon_{\alpha}^{F}(0)(1-\nu y) \]

with \( \nu=10 \) reasonable value for GeTe [8]. Thus, we obtain \( \rho(T) \) electrical resistance near \( T_{c} \) as a function of the different controlled composition for the \( Ge_{1-x}, Sn_{x}Te \)-type compounds.

The energy state of electrons in a solid forms almost continuous bands separated from each other by intervals of forbidden energy values, namely, band gaps. The valence band and the first band of excited states located above it, that is, the conduction band take part in the process of electrical conductivity. In our case, approximate equations are obtained for the energy band of the \(i\)-th valley in the symmetric bands model (Fig. 1) [2]:

Assume that \( n \) electrons are in the crystal conduction band of \( V \) volume. The electron concentration of \( N=n/V \) in the GeTe-type semiconductor is determined by \( \sum_{i=1}^{4} N_{i} \) ratio

For the electrons concentration in the \(i\)-th valley, we obtain

\[ N_{i}(\varepsilon) = 2\int_{0}^{\infty} f_{i}(\varepsilon)g_{i}(\varepsilon)d\varepsilon. \]

Applying the above equation in the case of a strongly degenerated semiconductor of \((T<T_{c})\), we detect

\[ N_{i} = B_{i} \eta_{i}^{3/2}(1 + \beta \eta_{i})^{3/2}, \]

in a nondegenerated case of \((T_{c}>T)\)
\[ N_i = \frac{3\sqrt{\pi}}{4} (1 + 1.5\beta_i)^{3/2} B_i \cdot \exp \eta_i, \quad B_i = \frac{(2M_n^0k_B T)^{3/2}}{3\pi^2 h^2 L_i}. \] (6)

Figure 1. Temperature dependence of the GeTe band gap in the model of symmetric (1) and parabolic (2) bands.

\[ \varepsilon_1 = T^2/24 \cdot 10^{-5} - 7T/24 \cdot 10^{-3} + 0.2, \quad \varepsilon_2 = -T^2/168 \cdot 10^{-5} - T/84 \cdot 10^{-3} + 0.5, \] (3)

\[ \Delta \varepsilon_i = \varepsilon_i - \Delta, \quad \varepsilon_{g1} = \Delta + 2\Delta \varepsilon_i, \quad \Delta \varepsilon_0 (T) = (\varepsilon_{g2} - \varepsilon_{g1})/2 - \text{intervalley splitting}. \]

Therefore, the reduced Fermi level in the model of symmetric bands is related to the concentration of conduction electrons as follows:

\[ \eta = -1 + \sqrt{1 + 4\beta_i (N_i / B_i)^{2/3}} + \frac{\Delta \varepsilon_i}{k_B T} \quad (T_c << T); \] (7)

\[ \eta = \ln \left( \frac{4N_i}{3\sqrt{\pi} B_i (1 + 1.5\beta_i)^{3/2}} + \frac{\Delta \varepsilon_i}{k_B T} \right) \quad (T << T_c). \] (8)

The temperature dependence graphs of the reduced Fermi level of \( \eta \) (Fig.2) and \( \rho_n^*(T) \) electrical resistance of the GeTe single crystal are constructed due to the last ratios and (6).

Figure 2. Temperature dependence comparison of the reduced \( \eta \) Fermi level in the integrable model of carrier mobility (2, 3) with the precise data (1) for \( \eta \) obtained on PC in GeTe.
At $T<T_c$, generalized Fermi integrals are calculated using the Dirac $\delta$-function. G-function is applied to calculate them and at $T>T_c$. Formulas 7 and 8 allow us to analytically calculate the conductivity behavior without using numerical methods.

The dependence of $\rho(T)$ for $\gamma = 300$ K calculated for GeTe is well consistent with the experiment. Fig. 3 (I).

We obtain $\Delta T \approx 10$ K for $\gamma = 100$ K values typical in SnTe. $\Delta T$ value as well as $\Delta T$ weak dependence on $T_c$ is confirmed by experience for Ge$_{1-x}$Sn$_x$. The calculation results are consistent with the experimental data. Fig. 3 (II).

Figure 3. I) Temperature dependence of the electrical resistivity of (a) GeTe single crystal. Dots and crosses are ($\rho||$) ($\rho\perp$) experimental values. Dash-dotted line – calculated values of ($\rho'^\parallel$) ($\rho'^\perp$) 1(2); II) Abnormal addition of SnTe electrical resistance. A solid line is a calculation at $\gamma_1 = 83$ K and $A = 1.25 \cdot 10^{-2}$ cm$^2$/s, $\Omega(q) = \omega_0 + Aq^2$; a dotted line – at $\gamma_2 = 20$ K and $B=1.63 \cdot 10^{12}$ cm$^2$/s$^2$, $\Omega^2(q) = \omega_0 + Bq^2$

According to the obtained results, $\Delta T$ temperature interval in GeTe is significantly larger than in SnTe, and the additional resistance of $\Delta \rho(T)$ decreases by half with distance from $T_c$. It is shown that the temperature half-width of the $\Delta T$ anomaly in SnTe is mainly defined by the relaxation rate of carriers, while in GeTe a significant contribution to $\Delta T$ is made by $T_c$ nonmonotonic change in the chemical potential of $\xi$ and anomalous scattering of carriers on LA- and TA-phonons. According to (1) and (5), the temperature half-width of $\Delta T$ anomaly is weakly dependent on $T_c$, but it increases significantly with a carrier concentration growth in strongly degenerated semiconductors of Pb$_{1-x}$Ge$_x$Te and SnTe. A weak dependence of $\Delta T$ on $T_c$ is confirmed by the experience.
3. The model of temperature nonlinear dependence of $T_{cx}$ structural phase transition of $\text{A}^4\text{B}^6$ – type compounds and $\text{A}_x\text{xB}_y\text{C}$ solid solutions.

The following is an explanation of $T_{cx}$ nonlinear behavior observed experimentally in [3, 6] on $x$ composition. In the papers, a strong increase in $T_{cx}$ phase transition temperature from $-60$ to $220 \, ^\circ\text{C}$ is observed with an increase in $x$ composition from $0$ to $1$, that is, components in solid solutions of $\text{A}_x\text{xB}_y\text{C}$-type.

In a simple two-band model of a ferroelectric-semiconductor, the phase transition at $T = T_c$ is associated with the interband electron-phonon interaction of $V(q)$ [1–4], whose momentum of $q$ coincides with the momentum of an active optical phonon of $\omega_q$ frequency (soft mode $\omega_0 \to 0$ at $q=0$ and $T = T_c$). In the model, in the case of an isotropic three-dimensional electronic spectrum (9) with the conduction band width of $E_0$ and $\Delta(x)$ and band gap, integrating on $d\vec{k}$, taking into account $q_0 = 0$, for the phase transition temperature of $T_c(x)$ at $E_{q_0}=0$ and $\Delta=\Delta(x)$ due to [2–4], we obtain:

$$T_c(x) = \frac{M\omega_0^2}{k_\beta A_0(0)} (\tau - 1), \quad (9)$$

$$\tau = \tau \left[1 - \frac{\Delta(x)}{E_0} \arctg \left( \frac{E_0}{\Delta(x)} \right) \right], \quad \tau = \frac{6V^2(0)}{M\omega_0^2 E_0}, \quad (10)$$

Here $\bar{A}(0) = \bar{A}(q \to 0)$ is renormalized phonon-phonon interaction constant, $M$– reduced mass of lattice atoms, $k_\beta$– Boltzmann constant. It is known from experience that the $\Delta(x)$ gap decreases linearly with $x$ increase in $\text{Pb}_1,\text{Ge}_2\text{Te}$ solutions, so that we can set $\Delta(x) = \delta_0 - ax$ and, according to (9), we obtain the nonlinear dependence of $T_c$ at $x=0$. However, in real values of the parameters of the $\bar{V}^2(0)=1.125$ (eV)$^2$, $E_0=17.45$(eV)$^2$, $m_0\omega_0^2 = 0.5$(eV)$^2$, and $\bar{A}(0) = 0.25A^{-2}$ (eV) at $a=2$ nonlinearity of $T(x)$ according to (9) is weakly expressed. At the same time, formula (9) with the specified parameters of the system ensures the growth of $T_c(x)$ from $-20$ to $220$ or $300$ $^\circ\text{C}$ (at $a=3$) when $x$ changes in $0 \leq x \leq 0.1$ area which is in general agreement with experiment.

4. Conclusion

Therefore, it has been shown that the conductivity anomaly near $T_c$ in $\text{A}^4\text{B}^6$ compounds can have both the form of an asymptotic peak (SnTe, Figure 3, II) and the form of a smooth asymmetric maximum (GeTe, Figure 4). The effective mass of the states density, the mass anisotropy coefficients, and the carrier relaxation rates have been determined for GeTe. The proposed analytical model can also be used to analyze the kinetic properties of significant solution systems such as Ge$_{1-x}$Sn$_x$Te-type. The parameters of the considered systems obtained in the paper can be applied for the development of elements in semiconductor electronics. The temperature of the structural phase transition as a function

![Figure 4. Dependence of the phase transition temperature in $\text{A}^4\text{B}^6(\text{A}_1,\text{B}_x\text{C})$ on $x$ composition.](image-url)
of x controlled composition and the temperature in $A_{1-x}B_xC$ solutions has been obtained in the research which is of great importance for the practical applications of these compounds.

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