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Convergence of plasmon and electron transition energies in crystal $Bi_{0.6}Sb_{1.4}Te_3$

© N.P. Stepanov

Trans-Baikal State University, Baikal State University,
672036 Chita, Russia

E-mail: np-stepanov@mail.ru

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The temperature dependences of the reflection coefficient spectra in the range of effects caused by the resonant behavior of the plasma of free charge carriers of the $Bi_{0.6}Sb_{1.4}Te_3$ crystal, in the temperature dependences of the magnetic susceptibility of which features are observed, are investigated. A change in the shape of the plasma edge and the resulting splitting of the peak of the energy loss function were detected, which allows us to conclude that an electron-plasmon interaction affecting the state of the electronic system has been observed.

Keywords: bismuth and antimony tellurides, plasma reflection, plasmon, electron-plasmon interaction.

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1. Introduction

Single crystals of solid solutions $Bi_2Te_3-Sb_2Te_3$ continue to be intensively studied. Their bulk properties are of interest, which affect the thermoelectric efficiency [1,2], films made from them [3,4] and nanomaterials [5]. All this predetermines the importance of studying elementary excitations of the electronic system and their interactions, which can affect the physical properties of $Bi_2Te_3-Sb_2Te_3$ single crystals. Such excitations include plasma oscillations, or longitudinal oscillations of free charge carriers relative to the ion core, the natural frequency of which depends on their concentration. Plasma responds to external electromagnetic influence, and the plasma resonance of free charge carriers is clearly observed at room and even higher temperatures. In this case, the value of the natural frequency, and therefore the energy of the plasmon E_p — quantum of plasma oscillations, changes depending on the amount and type of dopant, pressure, and temperature. In $Bi_2Te_3-Sb_2Te_3$ crystals, a sufficiently high concentration of charge carriers can be created by violating the stoichiometry, as a result of which there will be plasma resonance in the mid-infrared region of the spectrum. Other well-known excitations of the electronic system are interband and intraband transitions. The work [6] shows that in crystals $Bi_2Te_3-Sb_2Te_3$ *p*-type the plasmon energy E_p is close to the energy ΔE of single-particle excitation of the electronic system — electron transition from the subband of heavy holes to the subband of light ones. The specificity of this transition is that due to its effect, which increases with increasing temperature, the concentration of light holes, which make the main contribution to kinetic phenomena, decreases. This, in particular, predetermines the existence of an anomalous temperature dependence of the Hall coefficient in crystals of $Bi_2Te_3-Sb_2Te_3$ *p*-type [7]. A decrease in the concentration of light holes with increasing temperature also leads to a decrease in the plasmon energy, while the energy of the ΔE transition increases, since the level of chemical potential that responds to a decrease in the concentration of light holes shifts toward the top of the valence band. This counter change in the plasmon and electronic transition energies creates favorable opportunities for their approach and, thus, the observation of electron-plasmon interaction (EPI) in $Bi_2Te_3-Sb_2Te_3$ crystals.

The consequences of the convergence of the energies of the collective excitation of the electronic system — plasmon and the single-particle interband transition, accompanied by an increase in the electron wave effect, were considered in a number of theoretical works [8–10]. It was demonstrated that plasmons can participate in the processes of generation and recombination of free charge carriers, and also lead to the appearance of a bound state of electrons [11].

A fundamental opportunity for observing electron-plasmon interaction exists in semimetals and narrow-gap semiconductors. However, the observation of EPI, for example, in the semimetal bismuth, requires an optical experiment in the long-wave infrared region at low temperatures, which is due to the small value of the energy gap at the *L*-point of the Brillouin zone. In connection with this, the problem of studying electron-plasmon interaction in a sufficiently thoroughly studied narrow-gap semiconductor $Bi_2Te_3-Sb_2Te_3$ was formulated, which differs from bismuth in having a larger band gap, which shifts the range of observation of EPI to the more accessible mid-infrared region. Solving this problem required a study of the plasma resonance of free charge carriers depending on the composition of the $Be_2Te_3-Sb_2Te_3$ solid solution and temperature [12].

In addition, the question remained open as to whether the interaction of thermal plasmons and electronic transitions could affect the physical properties of the material. Therefore, the magnetic properties of $Be_2Te_3-Sb_2Te_3$ crystals were also studied. The emphasis on the study of magnetic properties was made for a number of reasons. On the one hand, magnetic susceptibility as an equilibrium thermodynamic parameter does not depend on the intensity of relaxation processes, the complexity of interpretation of which makes it difficult to use them to detect and isolate the contribution of the electron-plasmon interaction, and on the other hand, the use of sensitive SQUID magnetometers allows to monitor changes in the state of the electron systems of the material being studied. Indeed, during the study, features were discovered in the behavior of the temperature dependences of the magnetic susceptibility of $Be_2Te_3-Sb_2Te_3$ crystals, described in the work [6]. Their analysis showed that they are observed in the case of approach of E_p and ΔE. It is important to note that the results of experimental studies presented in the work [6] indicate the convergence of E_p and ΔE in Bi_2Te_3 crystals at a temperature of $\approx 300\,K$. However, the thermal chaotization in this case turns out to be great, which makes the electron-plasmon interaction practically undetectable. During the analysis performed in the work [6], it was also shown that the features discovered in the behavior of the temperature dependence of the magnetic susceptibility of the $Bi_{0.6}Sb_{1.4}Te_3$ crystal are due to the convergence of E_p and ΔE in the low temperature region, which creates a favorable opportunity for the experimental detection of electron-plasmon interaction. In connection with this, the task was set to experimentally study the reflectance spectra in the range of manifestations of effects caused by the resonant behavior of the plasma of free charge carriers in the $Bi_{0.6}Sb_{1.4}Te_3$ crystal.

2. Experimental procedure

We studied a single crystal $Bi_{0.6}Sb_{1.4}Te_3$ grown by the Czochralski method at the A.A. Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences. The reflectance spectra of the crystal $Bi_{0.6}Sb_{1.4}Te_3$ were obtained on an infrared Fourier spectrometer IFS-113V (Bruker) at fixed temperatures. The angle of incidence of electromagnetic radiation on the mirror cleavage of the crystal along the plane perpendicular to the optical axis C_3 was equal to 7°. When carrying out temperature measurements, temperature stabilization was carried out with an accuracy of 2 K. The experimental methodology and technique are described in more detail in the work [12].

3. Experimental results and discussion

The results of the study are presented in Figure 1, from which it is clear that the spectra of the reflectance $R(\nu)$ have a form characteristic of the resonance interaction of an electromagnetic wave and a plasma of free charge carriers As the temperature decreases, the minimum of the reflectance shifts to the region of high energies, and the plasma edge is deformed, an inflection point appears on it, the presence of which indicates that the plasma of free charge carriers is influenced by another process occurring in the crystal. Moreover, its effect, which increases with decreasing temperature, leads to splitting of the peak of the energy loss function $-\mathrm{Im}\,\varepsilon^{-1}(\nu)$, which characterizes the rate of energy dissipation in the crystal, the temperature dependences of which are presented in Figure 2. The spectral dependences of the value

$$-\mathrm{Im}\,\varepsilon^{-1} = \varepsilon_2(\varepsilon_1^2 + \varepsilon_2^2)^{-1} \tag{1}$$

were calculated from the reflection spectra $R(\nu)$ shown in Figure 1 using the Kramers–Kronig relations, which make it possible to calculate the frequency dependence of the phase angle of the reflected radiation from the frequency dependence of the reflectance, and then reconstruct the spectral dependences of the real ε_1 and imaginary ε_2 parts of the dielectric permittivity constant function that are included in the expression (1) [12].

Thus, the data presented in Figure 1 and 2 indicate that as the temperature decreases, the resonant frequency of plasma oscillations of free charge carriers approaches the resonant frequency of another mechanism of interaction between electromagnetic radiation and the crystal. We use the results presented in Figure 1 and 2. for a qualitative description of the observed phenomenon. First, we note that, as can be seen from Figure 1, as the temperature decreases, the reflectance in the plasma minimum decreases and the angle of inclination of the plasma edge increases. This indicates an increase in the optical relaxation time, which characterizes the intensity of the damping of plasma oscillations with decreasing temperature. As can be seen from Figure 1, the value of the reflectance in the high-frequency region of the studied spectral range R_∞ practically does not change with temperature, which also indicates the invariance of the high-frequency dielectric permittivity ε_∞, since the empirical rule

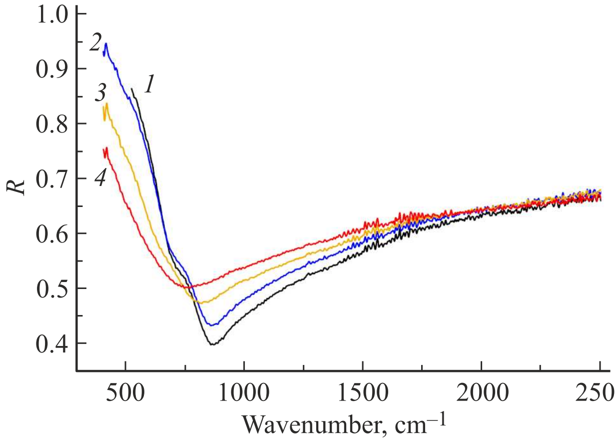

Figure 1. Reflectance R spectra of the $Bi_{0.6}Sb_{1.4}Te_3$ crystal measured at various temperatures, K: *1* — 78, *2* — 101, *3* — 173, *4* — 292. (The colored version of the figure is available on-line).

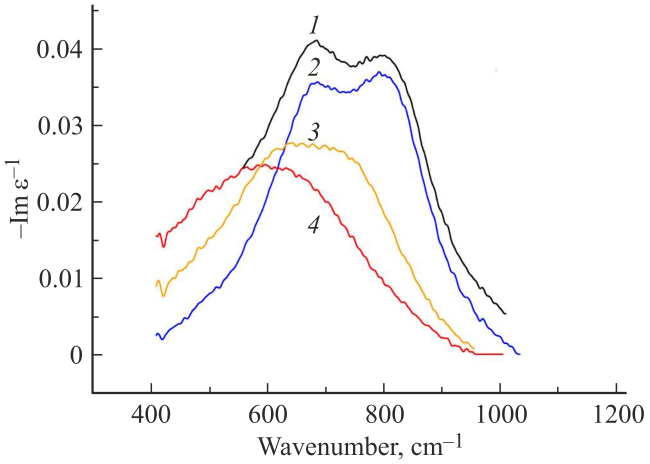

Figure 2. Spectral dependences of the energy loss function $-\mathrm{Im}\,\varepsilon^{-1}$ at different temperatures, K: *1* — 78, *2* — 101, *3* — 173, *4* — 292.

is known, according to which a $\omega \to \infty$

$$R \to \left(((\varepsilon_\infty)^{1/2} - 1)/((\varepsilon_\infty)^{1/2} + 1)\right)^2.$$

The high-frequency dielectric constant ε_∞ is included in the expression that determines the value of the plasma frequency ω_p:

$$\omega_p^2 = \frac{pe^2}{m^* \cdot \varepsilon_0} \cdot \frac{1}{\varepsilon_\infty}, \qquad (2)$$

which, in addition to the electron charge e, also includes the dielectric constant ε_0, the concentration of holes p and their effective mass m^*. In accordance with expression(2), the constancy of ε_∞ indicates that the increase in the plasma frequency with decreasing temperature is due to an increase in the ratio p/m^*.

From Figure 2 it is clear that at a temperature of 292 K the peak of the energy loss function, the spectral position of which determines the plasma frequency, has one well-pronounced maximum at a frequency of 597 cm^{-1}, which corresponds to the plasmon energy equal to 74 meV. As the temperature decreases to 173 K, the form of the energy loss function $-\mathrm{Im}\,\varepsilon^{-1}$ changes significantly, and instead of a clearly expressed maximum, there is an almost flat top. This indicates that energy losses are caused not only by plasmons, but also by some other, additional mechanism of interaction between radiation and crystal. Moreover, the low-frequency part of the $\mathrm{Im}\,\varepsilon^{-1}(\nu)$ plateau corresponds to an energy of 79 meV, and the high-frequency part corresponds to an energy of 92 meV. It can be assumed that the low-frequency excitation corresponds to the plasmon energy E_p, and the high-frequency excitation corresponds to the energy of the electronic transition ΔE, which manifests itself precisely in the high-frequency region of the spectrum relative to the plasma frequency. This is attributable to the specificity of the polarization response of the plasma, due to which the real part of the dielectric permittivity constant function ε_1 passes through zero at the plasma frequency. Therefore, near the plasma frequency, the polarization effect of electronic transitions, usually weak compared to free charge carriers, is manifested in the spectra of optical functions, including the behavior of $-\mathrm{Im}\,\varepsilon^{-1}(\nu)$, calculated in accordance with expression (1), in which ε_1 is included in the denominator.

The assumption that the high-frequency perturbation is caused by electron transitions between hole subbands in the valence band can also be justified by the fact that the band gap in the crystal under study is significantly greater than 92 meV and amounts to $\sim$ 160–180 meV. In addition, it is known that in crystals of the Be_2Te_3–Sb_2Te_3 *p*-type there are no other similar energy transitions and mechanisms of interaction with electromagnetic radiation that would manifest themselves in the course of comprehensive studies of these materials. Accordingly, it can be argued that a decrease in temperature from 292 to 173 K led to an increase in the plasmon energy and its approach to the electronic transition energy ΔE.

A further decrease in temperature to 101 K, as can be seen from Figure 2, leads to a splitting of the peak of the energy loss function and an increase in its absolute values. Moreover, the manifested structure of the $-\mathrm{Im}\,\varepsilon^{-1}(\nu)$ function is repeated at a temperature of 78 K, and the energy position of the peaks ceases to depend on temperature. In this case, the energy of the low-frequency peak turns out to be equal to 85 meV, and the high-frequency peak is 98 meV. Based on the foregoing, it can be assumed that the observed structure of the energy loss function and its insensitivity to temperature changes is most likely the result of the convergence of the plasmon energies and the electronic transition, which affects the concentration of light holes and, accordingly, the plasmon energy. Indeed, if the plasmon energy is equal to the energy ΔE required for the transfer of electrons from the heavy hole subband to the light hole subband, the appearance of an additional mechanism for reducing the concentration of light holes, additional to the direct thermal surges, will contribute to the formation of a specific state of the electronic system. The reason for this is that, accelerating the process of reducing the concentration of light holes, plasmons, in accordance with expression (2), simultaneously reduce the intrinsic energy. This, in turn, will lead to a decrease in the intensity of electron transitions under the influence of plasmons, and the concentration of light holes, which make the main contribution to the plasma frequency, will increase, which will contribute to an increase in the plasmon energy and the intensity of electron-plasmon interaction. Thus, a state of the electronic system will be formed in which the concentration of free charge carriers will periodically change, which is the reason for the appearance of an inflection point at the plasma edge, and two peaks in the spectra of the $-\mathrm{Im}\,\varepsilon^{-1}(\nu)$ function. The dominance of the described process is the most likely reason for the temperature stabilization of the peaks of the energy loss function.

In the work [10] the stimulated plasma resonance in a narrow-gap semiconductor placed in an external alternating electric field was theoretically reviewed. It was shown that, under certain conditions, a section with hysteresis may appear on the resonance curve, corresponding to the presence of two stable states of the electronic system. This is possible when the plasmon energy is sufficient to cause impact ionization. Then an increase in the electron concentration in accordance with expression (2) will lead to an increase in the plasma frequency, and, consequently, to the system leaving resonance and the termination of the impact ionization process. The process of recombination of the non-equilibrium concentration of free charge carriers will reduce the plasma frequency and plasmon energy, which will contribute to increased ionization by plasmons.

Thus, regardless of the specificity of the electronic transition in $Be_2Te_3-Sb_2Te$ type crystals, which leads not to an increase in the concentration of light, mobile charge carriers, but to its decrease, the convergence of its energy with the energy of an optically excited plasmon causes an effect similar theoretically considered in the work [10].

4. Conclusion

In conclusion, we note that the experimental observation of electron-plasmon interaction in the $Bi_{0.6}Sb_{1.4}Te_3$ crystal, in which a sharp decrease in diamagnetic susceptibility was detected in the same temperature range, confirms the assumption that its cause is a decrease in the concentration of light diamagnetic holes due to thermal interaction excited plasmons and electronic transition [6].

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Conflict of interest

The author declares that he has no conflict of interest.

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