Local Lattice Mode - Induced Far-Infrared Selective Photoconductivity in PbTe(Ga)

A. I. Belogorokhov[a], I. I. Ivanchik[b], D. R. Khokhlov[b], S. Ponomarev[b]

[a]*Institute of Rare Metals, Moscow, Russia;*

[b]*Physics Department, Moscow State University, Russia*

We have measured the spectral characteristics of photoresponse in PbTe(Ga). The photoconductivity has been detected in two spectral regions: in the middle- and in the far-infrared. Response in the middle-infrared consists of the ordinary fundamental band and a superimposed resonance - like structure at the energy just below the bandgap value. The resonance amplitude is much higher than that of the fundamental part. The photoresponse in the far-infrared is an analogous resonance - like structure with an energy close to the LO-phonon one. The maximal photosignal corresponds to ~75 K in the middle-infrared and to ~60 K in the far-infrared. The photoresponse characteristic time is $< 10\,\mu s$. This unusual photoresponse is believed to be due to the excitation of a local lattice mode corresponding to the metastable impurity center. Activation of this mode allows the transfer of electrons localized on the metastable impurity states to the conduction band.

I. Introduction

The IV-VI semiconductors are extensively used in the infrared optoelectronics. Some of their features, such as direct energy gap, high radiation recombination output, possibility of the gap value variation in a wide range - make them especially attractive for the construction of infrared lasers[1]. The application of IV-VI semiconductors as infrared photodetectors is restricted by the high free carrier concentration originating from a large number of growth defects in the as-grown materials.

Doping is one of the main tools providing variation of the free carrier concentration in semiconductors. However doping of the lead telluride-based alloys with some of the group III impurities results also in the appearance of features that are not observed in the undoped material, such as Fermi level pinning and persistent photoconductivity effects[2].

Gallium is one of the dopants of the above-mentioned kind. Generally it acts as a donor in the lead telluride. However in some range of a gallium concentration the Fermi level becomes pinned at ~70 meV be-

low the bottom of the conduction band. In this regime the impurity centers reveal some of the features of DX-centers in III-V and II-VI materials, for instance, the persistent photoconductivity is observed at the temperatures $T < T_c = 80$ K [3].

At the same time there is a considerable difference from the case of the DX-centers in III-V and II-VI. The kinetics of the photoconductivity is quite complicated and consists of two parts: the relatively fast and the slow ones[3]. The characteristic time of the slow part of the photoresponse varies from $> 10^4$ s at T = 4.2 K to 10 ms at T = 77 K [3]. The amplitude of the fast part of photoresponse does not depend on the sample conductivity if the latter is high enough, i.e. if a somewhat considerable amount of free electrons is accumulated in the conduction band.

II. Experiments

The spectral measurements of the slow part of the photoresponse are very uneasy to do. Indeed, since the characteristic energies of the energy spectrum of PbTe are quite small, the background infrared radiation present in any standard spectrophotometer would

lead to the accumulation of electrons in the conduction band so that one would not be able to start measurements from the initial "darkness" state.

We have measured the fast part of the photoconductivity spectra of PbTe(Ga) in the wavenumber range (10 - 5000) cm^{-1} at the temperatures (45 - 100) K. At T < 45 K the changes in the photoconductivity that are due to the fast processes are not noticeable on the background of a high concentration of free electrons accumulated in the conduction band due to the slow processes. The spectra have been taken using a Fourier-transform spectrophotometer "Bruker IFS-113v".

The samples were grown by Chokhralski technique. The indium contacts used were ohmic at all temperatures. The measurements of the photoconductivity have been done using the 4-probe technique.

III. Results

The photoconductivity has been detected in two spectral regions. The typical spectra taken in the wavenumber range (1000 - 5000) cm^{-1} at the different temperatures are shown in Fig. 1. The spectra consist of a resonant-like structure at the energy that is very close to the gap value in the undoped PbTe superimposed on the rather flat broad band with a pronounced red cutoff wavelength. The position of the photoconductivity peak ω_{max} shifts with the temperature coefficient $\partial\omega_{max}/\partial T \approx 3 \mathrm{cm}^{-1}/\mathrm{K}$ that is equal to the temperature coefficient of the energy gap in PbTe. The amplitude of the peak reaches maximum at T = (75 - 80) K.
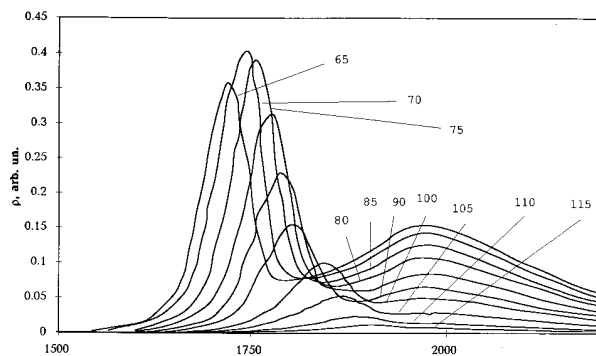

Figure 1. PbTe(Ga) photoconductivity spectra taken in the middle-infrared. Figures near the curves correspond to the temperature in K.

The amplitude of the photoconductivity peak A_{max} compared to the amplitude of the broad "background"

A_{bg} does not depend on the temperature, but changes from sample to sample. In most of the cases the ratio $A_{max}/A_{bg} > 1$.

The photoconductivity spectrum taken in the far-infrared region consists of a narrow resonance-like structure at $\omega \approx 155$ cm^{-1} (Fig. 2). In most of the cases this line is resolved only in a very narrow temperature range (57-63) K with the maximum at 60 K. Sometimes the photoconductivity resonance is not resolved at all, in some cases it exists in a more wide region of temperatures. In the latter situation not only the main peak is observed, but also some additional photoconductivity resonances at the multiple frequencies. The amplitude of the main peak is maximal just after the sample is cooled down to 60 K. If then the temperature is fixed, the photoresponse gradually decreases and eventually disappears in ~40 min. Whenever the temperature is changed even for 10 K in any direction and then returned back, the main photoconductivity line at ~155 cm^{-1} appears again.
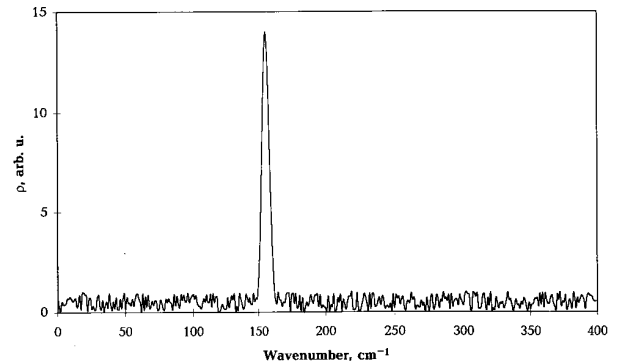

Figure 2. PbTe(Ga) photoconductivity spectrum in the far-infrared taken at T = 60 K.

IV. Discussion

According to the commonly accepted point of view, gallium forms a negative-U center in the lead telluride[4]. Therefore the ground impurity state E2 corresponds to two electrons localized on an impurity. At the same time there exists a metastable one-electron local state E_1, separated by a barrier in the configuration-coordinate space from the states of a system with two and zero localized electrons[5]. All the states of the system with two, one and zero electrons localized on an impurity are separated by barriers in the configuration-coordinate space (Fig. 3). It should

be noted here that though the impurity centers in IV-VI are in many respects analogous to the DX-centers in III-V, the last point makes a substantial difference. In the III-V's the metastable impurity states are shallow and are not separated by a barrier from the state of a system with the delocalized electrons[6].
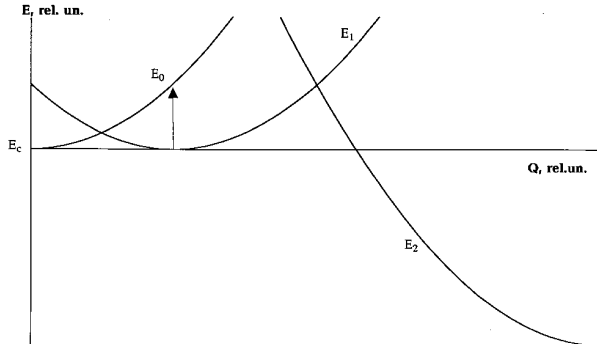

Figure 3. Configuration-coordinate diagram of PbTe(Ga). E_c - bottom of the conduction band. The curves E_n (n = 0,1,2) correspond to the states of a system with n electrons localized on the impurity center. The arrow correspond to the possible optical transition from E_1 to E_0 - state.

The first amazing feature of the photoresponse spectra in PbTe(Ga) is the absence of the impurity photoconductivity at the energies well below the gap even though the galvanomagnetic measurements show unambiguously that there exists an impurity level providing the Fermi level pinning at ~70 meV below the bottom of the conduction band[3]. It means that the transitions from the ground two-electron state to the conduction band most likely correspond to the slow part of the photoresponse, whereas the fast part that we measure originates from the transitions between allowed bands and the excited local state. This explanation however does not give an answer to the question, why there is no sub-bandgap photoconductivity. Indeed, the excited local level should lie higher in energy than the ground one, therefore the energy of transitions between the excited local state and the conduction band should be much smaller than the gap.

The possible resolution of this discrepancy is the following. The metastable one-electron local states E_1 are much less localized than the ground ones E_2, therefore their wavefunctions spread over many lattice periods. Consequently, the hydrogen-like contribution to the energy of this state may be predominant, despite it is separated by a small barrier in the configuration-coordinate space from the conduction band and there-

fore is localized. Since the dielectric constant is extremely high in PbTe $\epsilon \sim 1500$ [7] and the effective masses ofthe free carriers are only $\sim 0.01\ m_0$ [8], the binding energy of the hydrogen-like state is very small < 0.1 meV, so the ordinary hydrogen-like states would be delocalized at all reasonable temperatures.

The metastable E_1 - states keep many features of the hydrogen-like states. The near-bandgap resonant-like structure is most likely due to the transitions from the valence band to the E_1 state. Indeed, if this state is hydrogen-like, then its wavefunction originates mainly from the states of the conduction band bottom. Since the wavevector does not change in the optical transitions, their energy should be close to the energy gap value, and the photoresponse will have the resonant-like structure. Optical transitions of electrons lying rather deep in the valence band to the E_1 - state are strongly damped because of the momentum conservation law. The density of E_1 - states is of the order of magnitude of the overall gallium concentration and may be much higher than the density of states at the bottom of the conduction band. The latter value is quite small because of the small effective electron mass. As a result, the amplitude of photoconductivity due to the valence band - E_1 - level transitions may be considerably higher than the photoresponse due to the fundamental absorption.

Optical transitions from the E_1 - state to the conduction band are strongly-damped because of two reasons. First of all, it is the momentum conservation law mentioned above allowing only the transitions that are direct in the configuration-coordinate space. Besides that, the probability of the optical transitions is maximal if the initial and the final electron states have different parity. The transitions from the valence band to the E_1 - state satisfy this condition since the E_1 - states originate from the conduction band wavefunctions and conduction and valence bands have different parities in PbTe. At the same time the parity is not changed in E_1 - state - conduction band transitions.

One could consider the far-infrared photoresponse at $\omega = 155\ \mathrm{cm}^{-1}$ to be originated from the optical excitation from the E_1 - state to the conduction band. This possibility however seems to us to be not very likely. Indeed, as one can see from the photoconductivity spectra in the bandgap region, the position of the E_1 - level is

extremely close to the bottom of the conduction band, and the shift of 155 cm^{-1} would be quite noticeable. On the other hand one cannot completely exclude the above- mentioned possibility since the optical E_1 - conduction band transitions should occur without changing the impurity crystalline surrounding, i.e. they are direct in the configuration-coordinate space. Therefore the energy of this transition may exceed the energy difference between the E_1 - level and the conduction band bottom (see Fig. 3).

However in our opinion the far-infrared photoresponse has another origin. The frequency of $\omega = 155$ cm^{-1} directly corresponds to the frequency of an additional oscillator revealing itself in the infrared reflection spectra of PbTe(Ga) at the temperatures T < 80 K [9]. An analogous oscillator at the frequency $\omega = 115$ cm^{-1} has been observed in the infrared reflection spectra of Pb$_{0.75}$Sn$_{0.25}$Te(In) alloy[10] and in the Raman spectra of PbTe(In)[11] at T < 25 K. These materials reveal the persistent photoconductivity effect as well as PbTe(Ga), but at a lower temperatures $T < T_c = 25$ K. The frequencies of all these oscillators are quite close to, but somewhat higher than the frequency of the LO-phonon mode in PbTe $\omega_{LO} = 110$ cm^{-1} in PbTe [12]. Therefore it is natural to assume that these oscillators originate from the local lattice vibrations corresponding to the E_1 - state. Indeed, gallium and indium atoms are more light than lead that they substitute in the lattice, therefore the respective local mode should have the frequency higher than the LO-phonon one. Moreover, if one considers only the mass effect, the frequencies of the oscillators corresponding to In- and Ga- doped materials should satisfy a simple relation

$$\frac{\omega(\mathrm{Ga})}{\omega(\mathrm{In})} = \sqrt{\frac{m_{\mathrm{In}}}{m_{\mathrm{Ga}}}}$$

It is easy to calculate that this relation is approximately valid for the oscillator frequencies of In- and Ga- doped alloys.

The experimental data[9−11] show that the oscillator strength in both Ga - and In - doped alloys grows rapidly at $T < T_c$ - temperature of appearance of the persistent photoconductivity effect. In this temperature region the barrier between the E_0 and E_1 states is likely to appear[11], and the metastable local E_1 - states start to be populated, so the respective local modes pro-

duce the oscillator in the reflection and in the Raman spectra.

Coincidence of the frequency of the far-infrared photoconductivity with the oscillator frequency in the reflection spectra seems to be symptomatic. It means that the far-infrared photoresponse is most likely due to the optical excitation of a local vibration mode. The mechanism of the photoresponse could be the following. The background radiation excites one electron from the ground two-electron impurity state, and the impurity center is transferred to the metastable one- electron local state lying nearby the bottom of the conduction band. If then the local vibration mode is excited by the incident far-infrared radiation, the electron localized on a metastable impurity state may overcome small barriers separating it from the conduction band and thus may take part in the photoconductivity. As the excitation of a local mode is resonant in frequency, the photoresponse should be resonant, too.

The recent magnetization experiments[13] give some additional evidence to our hypothesis. A strong enhancement of paramagnetism has been observed in PbTe(Ga) at $\sim$ 60 K that is just the temperature at which maximal far-infrared photoresponse is detected in our experiments. Paramagnetism may arise in PbTe(Ga) only when the Ga atoms are in the paramagnetic E_1 state since all other charge states of Ga are diamagnetic, as well as the PbTe lattice itself. In view of these data it becomes evident that the far-infrared photoconductivity is strongly related to the population of the E_1 states. This population however depends not only on the temperature, but also on how was this temperature reached. By the way, this conclusion is supported not only by our experiments, but by the magnetization data, too: the paramagnetic response was defined not only by the temperature, but by the temperature dynamics. The reason for such a complicated behaviour of the E_1 - states population is not clear at the moment.

V. Summary

The resonance-like photoconductivity spectrum in the middle- and in the far-infrared has been observed in PbTe(Ga). In the middle infrared the resonant structure corresponds to the optical transitions from the valence band to the "quasi-shallow" one-electron local

state lying close to the conduction band bottom. Selective photoconductivity originates from the optical excitation of a local vibration mode providing transfer of electrons from the metastable one-electron local state to the conduction band.

Acknowledgments

References

1. A. Lambrecht, H. Boettner, M. Ange, R. Kurbel, A. Fach, B. Halford, U. Sciessl and M. Tacke, Semicond. Sci. Technol. **8**, S334 (1993).

2. B. A. Akimov, A. V. Dmitriev, D. R. Khokhlov and L. I. Ryabova, Phys. Stat. Sol. (a) **137**, 9 (1993).

3. B. A. Akimov, N. B. Brandt, A. M. Gas'kov, V. P. Zlomanov, L. I. Ryabova and D. R. Khokhlov, Fiz. Tekh. Poluprovodn. **17**, 87 (1983) [Sov. Phys. Semicond. **17**, 53 (1983)].

4. I. A. Drabkin and B. Ya. Moizhes Fiz. Tekh. Poluprovodn. **17**, 969 (1983) [Sov. Phys. Semicond. **17**, 611 (1983)].

5. I. I. Zasavitskiy, B. N. Matsonashvili, O. A. Pankratov and V. T. Trofimov, Pis'ma v Zh. Eksp. Teor. Fiz. **42**, 3 (1985) [JETP Lett. **42**, 1 (1985)].

6. P. M. Mooney, J. Appl. Phys., **67**, R1 (1990).

7. *Narrow-Gap Semiconductors.* Berlin etc: Springer, 1983. (G.Nimtz, B.Schlicht - Narrow Gap Lead Salts), eds. G. Hohler.

8. B. A. Akimov, N. B. Brandt, L. I. Ryabova, V. V. Sorovishin and S. M. Chudinov, Journ. of Low Temp. Phys. **51**, 9 (1983).

9. A. I. Belogorokhov, S. A. Belokon', I. I. Ivanchik and D. R. Khokhlov, Fiz. Tverd. Tela **34**, 1651 (1992) [Sov. Phys. Solid State **34**, 873 (1992)].

10. N. Romcevic, Z. V. Popovic, D. Khokhlov, A. V. Nikorich and W. Konig, Phys. Rev. **B43**, 6712 (1991).

11. N. Romcevic, Z. V. Popovic and D. R. Khokhlov, Journ. of Phys. C: Condensed Matter, in press.

12. M. A. Kinch and D. D. Buss. Solid State Comm. **11**, 319 (1972).

13. A. N. Vasil'ev, B. A. Volkov, T. N. Voloshok and S. V. Kuvshinnikov, Pis'ma v Zh. Eksp. Teor. Fiz. **61**, 768 (1995).