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Raman spectroscopy of impurity states in gallium-doped PbTe

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Abstract. We present Raman spectra and results of galvanomagnetic measurements of PbTe single crystals, doped with gallium, between 10 and 300 K. The effect of persistent photoconductivity depends on the gallium concentration. In all samples well-resolved peaks were observed at about 104 cm^{-1} (impurity-induced PbTe LO mode) and 166 cm^{-1} at all temperatures. Another mode appears at about 117 cm^{-1} at temperature below 250 K. One additional mode, at about 188 cm^{-1}, is observed in PbTe + 0.4 at% Ga. These modes are discussed in terms of local vibrations of impurities corresponding to different Ga charge states.

1. Introduction

Doped narrow-band semiconductors are very important materials as they are widely used in microelectronics, computer and communications industries. Therefore, studying the nature of disorder in these solids is of much significance. To be more exact, a better understanding of their physical properties, lattice dynamics in particular, is quite relevant. The vibration properties of a crystal are all affected by the inclusion of point defects in the lattice. Point defects are most often empty places in a crystal lattice, atoms in the intermediate position and impurity atoms in positions of the atoms of the main crystal. The results of the experiments prove that such defects change the vibrational properties of a crystal [1–3].

Impurity vibrations can be observed clearly only when an impurity vibrates with a frequency that the host crystal cannot follow, that is, such that the density of vibrational states of the host crystal is either small or zero. The energies where such an effect can be expected are, therefore: (a) at frequencies above the highest host lattice frequency (localized mode); (b) in a gap (if one exists) between the acoustic and optical modes of the host lattice (gap mode); (c) in the low-frequency tail of the host lattice acoustic mode (resonance mode). Impurity-induced modes could be expected in the regions where the host lattice has a high density of vibrational states, where the contribution of the impurity 'in band' mode would be shared out with the rest of the lattice, i.e. tightly coupled to the host lattice modes of similar energy. Whether or not any or all of these effects are observed for a particular impurity in a given crystal will depend essentially on the mass of the impurity with relation to that of the host crystal components, and on the force constants that bind the impurity into the site [2, 4], or their appearance may be caused by a more complex mechanism of electron–phonon interaction [5].

Lead tellurid is a particularly well known material used in infrared optoelectronics. Using group III-doped lead tellurides provides some new opportunities, arising from the appearance

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of completely new physical properties of the doped material (Fermi level pinning [6] and persistent photoconductivity effect [7] at low temperature).

The solubility of Ga in PbTe is low. When the concentration of Ga increases, starting from a PbTe p-type sample, the hole concentration decreases linearly. This drives the crystal to an uncompensated state at $N_{Ga} \sim 0.1$ at%. Upon further doping (up to $N_{Ga} = 0.3$ at%) the samples remain in the semiconducting state. The Fermi level pinning position is inside the gap, which results in a semiconductor behaviour [8]. Above this region, there is a p–n inversion and the concentration of electrons in the n-region increases rapidly. In this situation the donor action of Ga becomes unstable with respect to the external factors, such as hydrostatic pressure or temperature [9]. Indeed, in PbTe(Ga) a decrease of the free electron concentration under pressure has been detected [9, 10]. Lowering the temperature has the same effect as the application of pressure [10], and a model has been proposed where the ability of Ga to act as a donor was assumed to be strongly coupled to the lattice [11]. Theoretical estimates based on the evaluation of ionic radii for different impurity atoms in the PbTe lattice have shown that the donor action of Ga atoms depends critically on the lattice parameter. Even minor changes of this parameter may lead to a transition from an electrically active to a neutral Ga state [11]. This paper analyses the influence of the degree of doping on the Raman spectra of PbTe(Ga) and, in this way, clarifies the behaviour of the impurity centres in these systems.

2. Experiment

Single crystals of PbTe doped with gallium were grown by the Czockhralski method. The gallium impurity was introduced into the liquid zone. The concentration of gallium was between 0.4 and 0.5 at%, so that the regime of the unstable donor action of Ga was realized.

The galvanomagnetic coefficients were determined from Hall effect measurement with van der Pauw contact geometry. The size of the samples was about 5 mm in diameter, with a thickness of about 0.75 mm. The magnetic field strength and the current through the samples were 0.45 T and 10 mA, respectively. The samples were installed in a special low-temperature chamber, cooled with liquid helium. In this arrangement the sample was completely screened from external radiation. Controlled illumination was performed using a photodiode ($\lambda \sim 1\ \mu$m) at an energy greater than the width of the forbidden gap. The electrical resistivity and Hall coefficient were measured in the temperature interval of 20–290 K, under conditions of 'darkness' and controlled illumination.

The Raman spectra were excited by the 488 and 514.5 mm lines of an argon laser (the average power was about 100 mW) in the back-scattering geometry. We used a Jobin Yvon model U-1000 monochromator, with a conventional photocounting system. The samples were held in a closed-cycle cryostat, equipped with a low-temperature controller and evacuated by a turbopump. In order to attain a better signal-to-noise ratio, approximately 40 low-temperature spectra were averaged at a given temperature.

3. Results and analysis

The temperature dependence of the free carrier concentration $N(T)$, resistivity $\rho(T)$ and mobility $\mu(T)$ measured under the conditions of 'darkness' and controlled infrared illumination are shown in figure 1.

The sample with $N_{Ga} = 0.4$ at% is highly resistant. The temperature dependence of the electrical resistivity and free carrier concentration has, for an illuminated sample, an activation

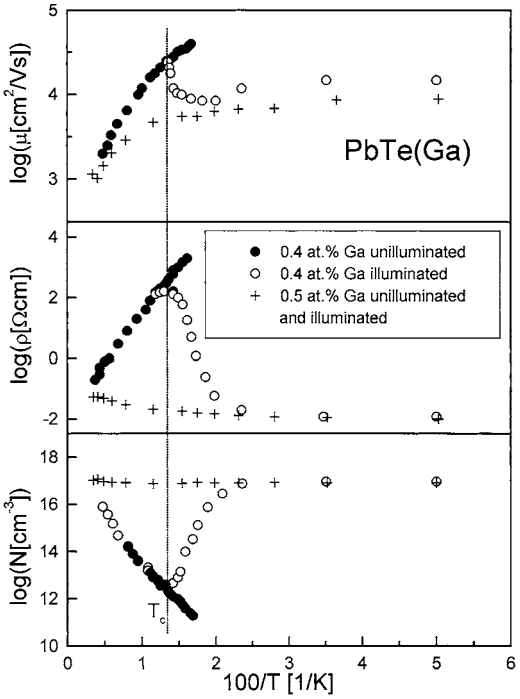

Figure 1. Temperature dependence of the free carrier concentration $N(T)$, resistivity $\rho(T)$ and mobility $\mu(T)$ for illuminated and unilluminated PbTe(Ga).

character ($\rho \sim \exp(E_a/kT)$) [12] with $E_a = 140$ meV. At liquid nitrogen temperature the concentration of free carriers amounts to about 10^{12} cm^{-3}. When it is illuminated with a photodiode a considerable photoresponse is registered at $T < 80$ K. This is one of the characteristics of the persistent photoconductivity effect, registered in other lead-telluride systems doped with group III elements [6]. This also appears in highly-resistant samples of n-type PbTe(Ga) obtained by other methods [10, 13, 14]. Above $T_c = 80$ K, $\mu(T)$ varies similarly to $\sim T^n$ with $n = (-2 \pm 0.3)$, as is expected for lead telluride [15]. Under infrared illumination, peculiarities appear on $\mu(T)$. They are connected with the effect of persistent photoconductivity.

For the sample with 0.5 at% Ga, the temperature dependence of the electrical resistivity shows a metallic character. The free carrier concentration is relatively high and amounts to approximately 10^{17} cm^{-3} in the entire temperature range. In this case, the photoresponse is not registered; that is, illumination does not influence the transport properties. The mobility of free carriers has a degree form with $n \approx -0.3$.

The unpolarized Raman spectra of PbTe and PbTe(Ga) in the spectral range of 80–210 cm^{-1}, at temperatures between 13 and 300 K, are shown in figure 2. In all samples, the modes at 126 and 146 cm^{-1} are clearly observed. These modes, which are also observed in other telluride compounds, originate from TeO_2 vibrations, a very thin layer of which is regularly created on the surface of the sample [16, 17]. In order to demonstrate this fact, the sample PbTe + 0.5 at% Ga was polished just before measurement in order to prevent the formation of the TeO_2 layer. The intensity of these modes is very low. In addition the polishing would remove other oxides, such as PbO and Ga_2O_3, from the surface of the sample. However, in the spectra recorded some days later only modes that originate from the TeO_2

appeared, therefore we conclude that either there are no other oxides on the surface or their modes are not Raman active. This phenomenon is discussed in full detail in [18]. In the doped samples, well resolved peaks appear at about 104 and 166 cm^{-1}. They were observed at all temperatures. Below 250 K another mode appears at about 117 cm^{-1}. Finally, one additional mode at 188 cm^{-1} is observed in PbTe + 0.4 at% Ga. Raman scattering spectra are often analysed with the help of a Lorentzian function or by the convolution of a Lorentzian and Gaussian curve [19, 20]. As the quality of the spectra in figure 2 is such that it allows only a qualitative analysis with a partial discussion of the trend, we take that all the lines are of the Lorentzian type. A typical line shape obtained in this way is shown in figure 3. The results of the analysis are given in figures 4 and 5. The position of modes (ω_c) at 104, 117, 166 and 188 cm^{-1} does not depend on temperature.

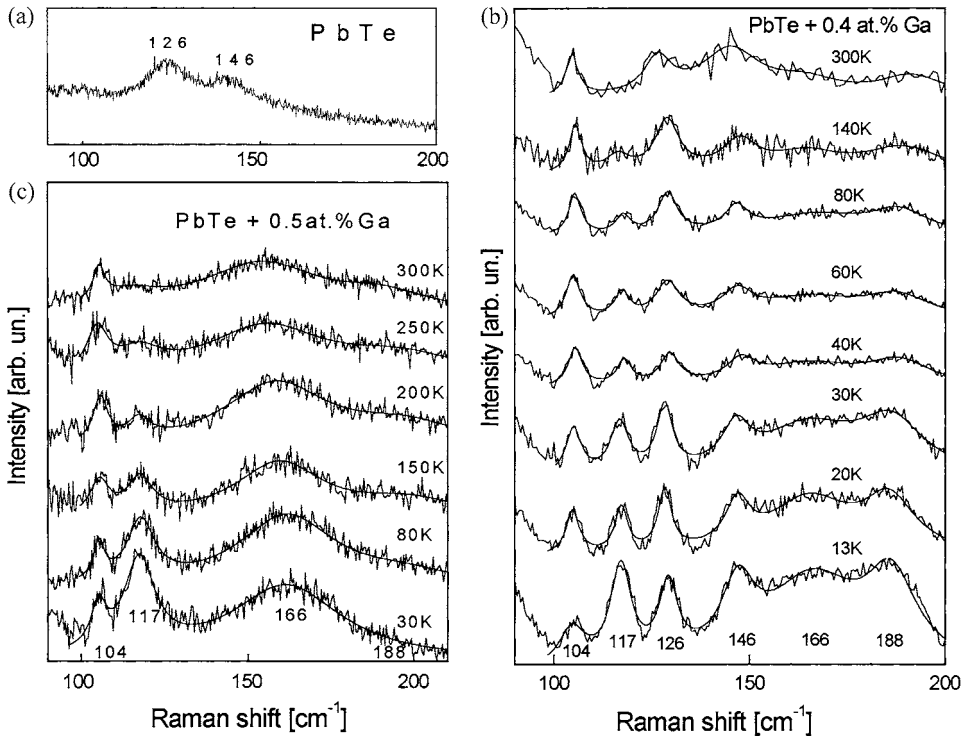

Figure 2. Unpolarized Raman spectra of (a) PbTe, (b) 0.4 at% and (c) 0.5 at% gallium-doped PbTe at different temperatures.

Figure 4 shows the temperature changes of the half-width (W) obtained by the deconvolution technique. Two distinct types of the line half-width are clearly seen:

(a) at 104 and 117 cm^{-1}, we find narrow phonon lines whose half-width practically does not change with temperature;

(b) at 166 and 188 cm^{-1}, some broader phonon lines are observed, the half-width increases for the 166 cm^{-1} line and decreases for the 188 cm^{-1} one with the lowering of the temperature.

The relative error in determining the half-width of the modes at 104 and 117 cm^{-1} is about 5%. However, the modes at 166 and 188 cm^{-1} form a common structure, consequently at high temperatures the error is 30%. At low temperatures the relative error is lower and amounts

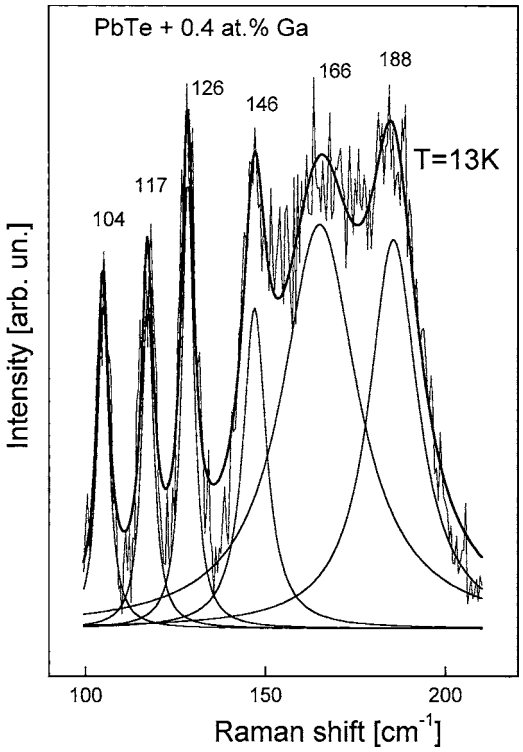

Figure 3. The result of the application of the deconvolution on the spectrum of the PbTe + 0.4 at% Ga sample at $T = 13$ K.

to about 15%. This fact makes the quantitative analysis of the spectra more difficult in many aspects.

The temperature change of the line intensities $I(\omega_c)$ is shown in figure 5. In all PbTe(Ga) samples, the mode at 104 cm^{-1} has a relatively low intensity (almost independent of temperature). With the decrease of the temperature, the intensity of the mode at 117 cm^{-1} (PbTe + 0.5 at% Ga) increases rapidly. The mode at 166 cm^{-1} also increases when the temperature is lowered. In PbTe + 0.4 at% Ga, the intensity of the modes at 117, 166 and 188 cm^{-1} increases rapidly at temperatures below 60 K.

The relative error in determining the line intensity is directly connected with the level of the noise of the experimental results and ranges from 10% at high temperatures to 5% at low temperatures.

4. Discussion

The properties of the registered modes can only be explained by the direct connection of these modes with the effect of persistent photoconductivity and the mixed valence of gallium in these systems. As is well known, PbTe crystallizes in the cubic structure of the NaCl type (O_h space group symmetry), and the first-order Raman modes are not active. If the concentration of Ga is less than 1 at%, then Ga enters the Pb sublattice. As a consequence of gallium as a substitutional impurity ion, every ion in PbTe is no longer in the centre of inversion symmetry, and PbTe vibrational modes could be Raman active (the impurity ion is still in the centre of

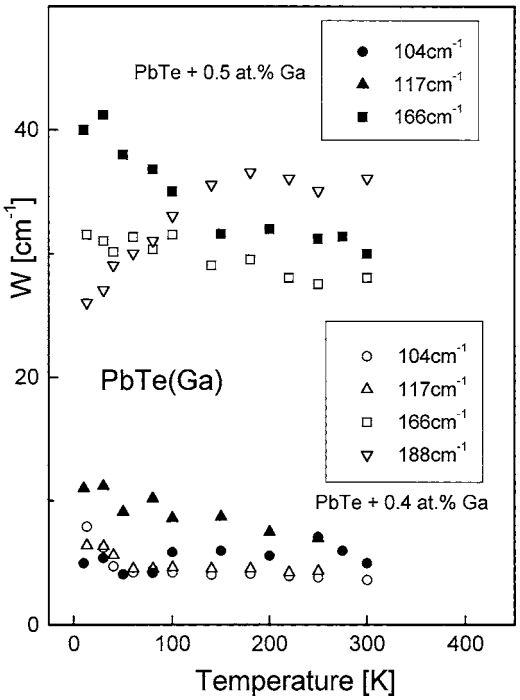

Figure 4. The temperature dependence of half-widths (W).

the inversion, but its six nearest neighbours are not). Thus, the mode at 104 cm^{-1} represents the well known LO mode of PbTe [21] due to impurities.

The modes at 117, 166 and 188 cm^{-1} are connected to excitations of local phonon modes in the vicinity of an impurity atom for the following reasons. Lead telluride grows with a rather high concentration of internal defects (vacancies in the Te place), which results in the weakening of selection rules. On the other hand, if the semiconductor (in this case PbTe) is doped with a substitution impurity [22] (gallium), and the heavier mass (Pb) is substituted by a lighter impurity, two modes are obtained: a local mode situated above the optical band, and a gap mode situated above the acoustic band, but below the optical band of the host lattice. In our case, the additional mode has frequencies over the optical range of PbTe (104 cm^{-1}).

A question naturally arises here: why do three local modes of Ga appear? It is known that the neutral state of gallium in the lattice PbTe(Ga^{2+}) is unstable [7, 23], and according to equation

$$2Ga^{2+} = Ga^{+}Ga^{3+} \tag{1}$$

changes to the two-electron stable state (Ga^{+}), which is energy-wise more favourable than the metastable single electron (Ga^{2+}) state and the state of an empty centre (Ga^{3+}). This means that the effective energy of the interaction of an impurity is negative (negative U-centres) [23, 24]. This behaviour of impurities leads to an effect of the Fermi level stabilization on a level that corresponds to an equilibrium of the total energy between the states Ga^{+} and Ga^{3+} [24].

In addition to this, it is known [25] that a change of electronic state of impurity centres leads to a change of the force constant between an impurity and the lattice. This means that in these systems the isotopic effect is not satisfied: that is, the mode position does not depend only on the mass of an added impurity. These results were checked on the PbTe(B) sample [26].

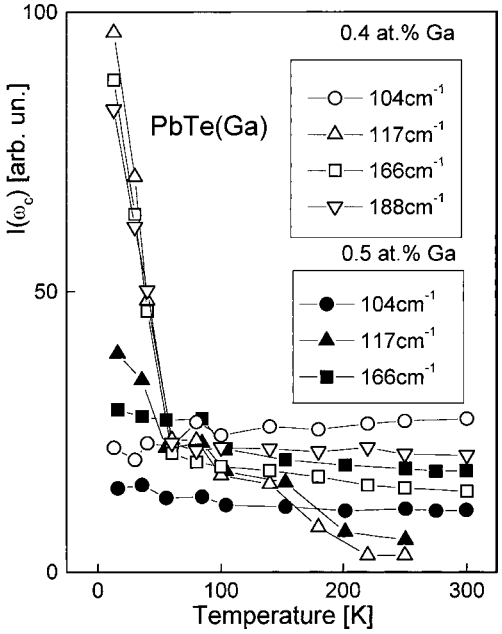

Figure 5. The temperature dependence of intensity.

Three local boron modes were noticed at 156, 210 and 260 cm^{-1}. As compared to PbTe(Ga) the position of these modes is shifted to a higher frequency, but the shift does not satisfy the isotopic effect. This means that there is a strong correlation between an impurity and the lattice.

The registered temperature change of the mode intensity in figure 5 is directly connected with the persistent photoconductivity effect. Namely, as can be seen in figure 1 under the irradiation of the PbTe+0.4 at% Ga sample, a significant photoresponse at $T < 80$ K was found. The photoresponse was missing in PbTe + 0.5 at% Ga. The registered effect is reproducible, and its appearance is directly conditioned by the unstable behaviour of Ga as a donor [24]. It appears that at relatively higher concentrations of gallium ($N_{Ga} \geqslant 0.4$ at%) a non-homogenic dispersion of the impurity in the volume of the sample takes place [27, 28], which can lead to the widening of some phonon lines, as registered in figure 4 for the mode at 166 and 188 cm^{-1}. This case is discussed in more detail in [29]. Naturally, the widening of these lines may be brought about by a number of other effects like that of local strain [29] and a more complicated mechanism of electron–phonon interaction [5].

In materials with 0.5 at% Ga, we have clearly seen only the 166 cm^{-1} mode. This mode corresponds to the empty impurity centres (Ga^{3+}) because it is a conducting material with a high concentration of free carriers. The excitations at 117 cm^{-1} have very short lifetimes and the occupation of states responsible for scattering increases with a lowering of the temperature. Since the intensity of this mode increases with a lowering of the temperature (see figure 5) it can be concluded that the 117 cm^{-1} mode corresponds to the impurity centre which is in an unstable one-electron state of Ga^{2+}. Below T_c there is an abrupt increase of the mode intensity. Thus we conclude that the 188 cm^{-1} mode for 0.4 at% Ga corresponds to impurity centres of Ga with two electrons (Ga^{+}). The temperature T_c depends on E_g—the barrier in the configuration space, which separates a metastable impurity state from the two-electron ground state of Ga^{+}.

5. Conclusions

In this paper we have shown Raman spectra of gallium-doped PbTe single crystals, together with the results of galvanomagnetic measurement, at temperatures between 10 and 300 K. Together with impurity-induced PbTe LO mode we registered three impurity local modes of gallium. The position of these local modes depends on the impurity centre charge. The effect of persistent photoconductivity has been registered for $N_{Ga} = 0.4$ at% with an increase of the Ga concentration, at $N_{Ga} = 0.5$ at% this effect disappears.

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