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Raman scattering spectra of indium-doped PbTe

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Abstract. The non-polarized Raman scattering spectra of indium-doped PbTe single crystals were measured in the temperature range between 10 and 300 K. Well resolved peaks at about 68, 126 and 143 cm^{-1} were observed for all temperatures. An additional mode appears at about 115 cm^{-1} for temperatures below 100 K. The intensity of this mode increases sharply when the temperature is lowered below 25 K, the temperature where a persistent photoconductivity effect in PbTe(In) appears. This mode is assigned as a local In impurity mode and represents a population of metastable states due to the transfer of electrons from two-electron to one-electron metastable impurity states.

The curious behaviour of the group III elements in the IV–VI narrow-gap semiconductors has been investigated intensively over the last two decades [1–4]. Indium impurity effects in these semiconductors were studied in more detail because of the persistent photoconductivity [5] and other interesting properties [6].

As is well known, PbTe crystallizes in the cubic structure of NaCl type. Doping with indium up to a concentration of 20 at.% does not cause a change in the crystal structure.

A single crystal of PbTe, grown by the Bridgman technique, was used in this study. An indium impurity was introduced into the liquid zone in the same way as for $Pb_{1-x}Sn_xTe$(In) [1]. The In concentrations in the sample used here were 0.2 and 0.4 at.%. The Raman spectra were excited by the 488 and 514.5 nm lines of an argon laser (the average power was about 100 mW). For measurement of the Raman spectra we used both a Jobin–Yvon model U-1000 monochromator with a conventional photon-counting system and a Dilor monochromator equipped with a charge-coupled device detector. The samples were held in a closed-cycle cryostat, equipped with a low-temperature controller and evacuated with a turbopump. In order to attain a better signal-to-noise ratio, using a classical photon-counting system (in the case of the 0.4 at.% sample) we averaged approximately 40 low-temperature spectra at each temperature.

The non-polarized Raman spectra of a PbTe (0.4 at.% In) single crystal, at temperatures between 300 and 10 K, are given in figure 1. At room temperature the modes at 68, 126 and 143 cm^{-1} are clearly observed. These modes are also observed in other telluride compounds and originate from the vibrations of TeO_2, a very thin layer regularly created on the surface of the sample. However, these modes are not considered here since this effect has been well examined in [7, 8].

The first-order Raman modes are not active in the NaCl-type crystal structure (O_h space group symmetry). Nevertheless, under certain conditions, it was possible to measure the Raman spectra of PbTe, such as the Jahn–Teller instability [9], and the scattering by longitudinal phonons with a finite wavevector ($q \neq 0$) [10], i.e. scattering induced by an

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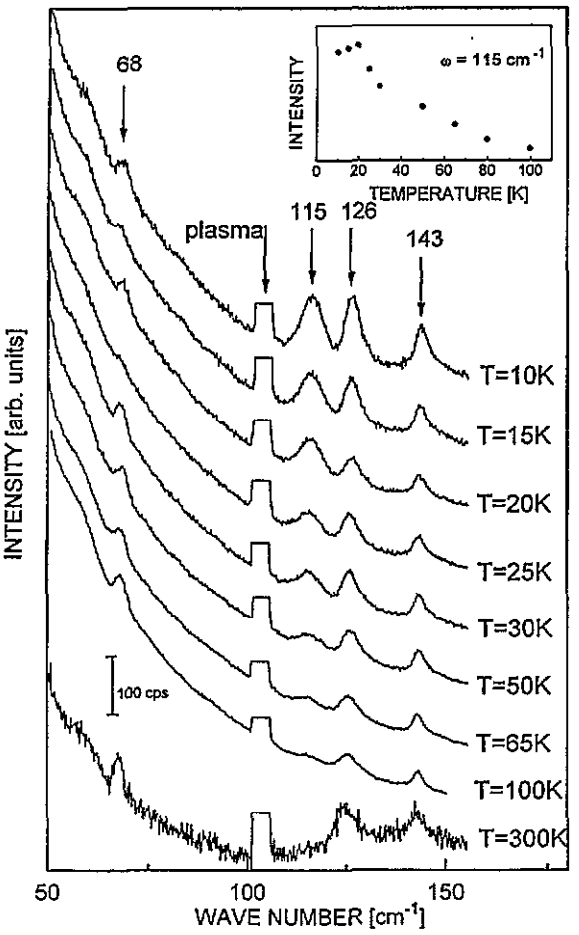

Figure 1. Non-polarized Raman spectra of 0.4 at.% In-doped PbTe at different temperatures measured using the 488 nm line of an Ar-ion laser. The inset shows the integrated intensity temperature dependence of the Raman peak at 115 cm^{-1}.

external electric field or by an electric field induced at the metal–semiconductor junction [11]. The frequencies of transverse and longitudinal modes are determined to be about 32 cm^{-1} and 105 cm^{-1}, respectively. In the spectra shown in figure 1, we were unable to observe these modes of PbTe either because of the high level of elastically scattered light, or because of the existence of the plasma line at 103 cm^{-1}. The dominant mode in the spectra in figure 1 is the mode at 115 cm^{-1}, whose intensity sharply increases as the temperature decreases. We have concluded that this mode is the indium impurity local mode for the following reasons.

Lead telluride grows with rather a high concentration of internal defects (vacancies on Te sites). Indium in PbTe substitutes for Pb or occupies the Te vacant site, which leads to a significant reduction in the free-carrier concentration and the appearance of persistent photoconductivity [5], at temperatures lower than 25 K. Indium is a substitution impurity ion because every ion in PbTe is no longer at the centre of inversion symmetry and PbTe vibrational modes could be Raman active (the impurity ion is still at the centre of inversion, but its six nearest neighbours are not). The impurity mode can arise simply owing to

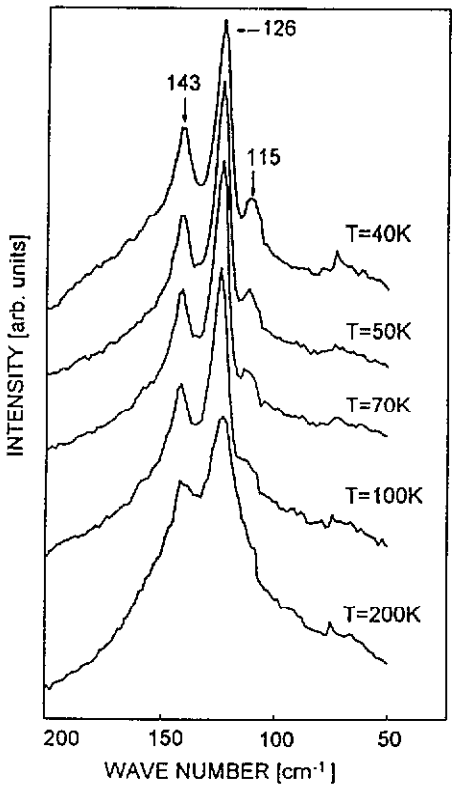

Figure 2. Non-polarized Raman spectra of 0.2 at.% In-doped PbTe at different temperatures measured with the 514.5 nm line of an Ar-ion laser.

the difference between the masses and force constants of the impurity ion and the ion of the host material [12], or their appearance can be caused by more complex mechanisms of electron–phonon interaction [13]. In our case, taking into consideration only the mass effect, it is shown that the mode at 115 cm^{-1} could be an In impurity mode. That is, if the semiconductor is doped with a substitution impurity [14] (in this case In), when substitution is made on the light mass (in this case Te), a lighter impurity gives a localized mode which rises out of the top of the optical band; when substitution of the heavier mass (Pb) is made by a lighter impurity, one gets two modes: 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 the first case the mass ratio $(m_{Te}/m_{In})^{1/2}$ is 1.05, which for the frequency of the In impurity mode gives $\omega_{In} = \omega_{(PbTe)}(m_{Te}/m_{In})^{1/2} = 111$ cm^{-1}. In the case of of Pb–In substitution, the frequency of the local mode is $\omega_{In} = 139$ cm^{-1}. These frequency values are very close to the experimentally observed value of 115 cm^{-1} (see figure 1).

In order to check our conclusion and eliminate, as a possible explanation, the resonance effect, we measure the Raman spectra of the same sample with the $\lambda_L = 514.5$ nm laser line. The spectra obtained are completely the same as the spectra presented in figure 1. We also measured the sample with 0.2 at.% In and these results are shown in figure 2. The 115 cm^{-1} mode is again seen in the spectra for temperatures below 100 K. In this case the intensity of the 115 cm^{-1} mode is lower, corresponding to phonon TeO_2 modes, than in the 0.4 at.% In sample. This effect is a consequence of the lower In concentration in the sample.

Our conclusion that the Raman mode at 115 cm^{-1} (IR mode at 122 cm^{-1}) is an In impurity local mode was tested in the case of PbTe doped with gallium. Considering only

the mass effect, in this case we obtained $\omega_{Ga} = \omega_{In}(m_{In}/m_{Ga})^{1/2} = 150$ cm^{-1} which is in excellent agreement with experimental findings [15].

The integrated intensity temperature dependence of the 115 cm^{-1} mode is given in the inset of figure 1. This mode is clearly extracted from the background only for temperatures lower than 100 K. By decreasing the temperature, the integrated intensity increases and a sharp rise occurs at a temperature of about 25 K. This temperature is the critical temperautre for the appearance of the persistent photoconductivity effect in PbTe(In) [5]. The temperature dependence of the mode intensity shown in the inset of figure 1 is also very similar to the oscillator strength temeprature dependence of the corresponding infrared-active indium impurity mode observed in all $Pb_{1-x}Sn_xTe$(In) [16] ($x < 0.22$) and $Pb_{1-x}Mn_xTe$(In) [17] ($x < 0.05$) samples. Furthermore, in these materials the Fermi level is pinned in the conduction band [1], and by lowering the temperature the concentration of the free carriers increases. As a consequence ω_P is shifted towards higher wavelengths in the IR spectra [15]. In these spectra, as well as in the spectra of $Pb_{0.75}Sn_{0.25}Te$(In) [18], we observe a new structure at about 122 cm^{-1}, with a temperature dependence of the oscillator 'strength' similar to the behaviour shown in the inset of figure 1. Thus we conclude that these modes have the same origin. As we previously showed [17, 18], the additional oscillator at about 122 cm^{-1} in the IR spectra of $Pb_{1-x}Sn_xTe$(In) and $Pb_{1-x}Mn_xTe$(In) represents an optical transition between the ground two-electron In impurity states that pin the Fermi level and the metastable one-electron impurity states. The oscillator strength is defined by the occupancy of the metastable state which is, in turn, related to the height of a barrier between the metastable and the ground states in configuration-coordinate space [18]. Since, at $T = 25$ K, owing to the persistent photoconductivity effect, the population of the ground impurity states decreases and the population of the one-electron metastable states increases, we concluded that the Raman mode at about 115 cm^{-1} is an In impurity local mode which represents a population of metastable In impurity states due to the transfer of electrons from two-electron to one-electron impurity states.

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