



Raman spectroscopy of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ (In) single crystals

N. Romčević^{a,*}, D. Stojanović^a, M. Romčević^a, D.R. Khokhlov^b

^a Institute of Physics, P.O. Box 68, 11080 Belgrade, Serbia

^b Physics Department, Moscow State University, Moscow 119899, Russia

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ABSTRACT

Raman scattering spectra of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($x = 0, 0.15$ and 0.25) doped with Indium in the temperature range 10–300 K are presented. Three local modes of Indium at about 115, 155 and 190 cm^{-1} are registered. These modes are discussed in terms of local vibrations of impurities corresponding to different In charge states. The position of these lines is independent of alloy compound, temperature and amount of added In.

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1. Introduction

The doping of lead-telluride based alloys with the III-group impurities as In, Ga, Tl substantially modifies the electronic spectrum of the semiconductor. In $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ (In) solid solutions Fermi level is pinned at some position that does not depend on N_{In} [1,2]. The pinned Fermi level moves continuously from the conduction band to the valence band with increasing SnTe content, passing the band gap in the composition range $0.22 \leq x \leq 0.28$ at $T = 4.2\text{ K}$ [3,4]. It shows metal (n-type)–insulator–metal (p-type) transition owing to x at low temperature.

External IR illumination leads to substantial increment in material conductivity at $T < 25\text{ K}$ independently on the Fermi level pinning position. If the pinned level lies within the band gap, the relative conductivity change is much higher. The high amplitude of photoresponse at low temperatures is a consequence of the persistent photoconductivity (PPC) effect [2]: if the permanent radiation flux illuminates the sample, the photoresponse increases linearly in time, and when the light is switched off, the conductivity value remains stable (photomemory), i.e. photoconductivity persists after the removal of photoexcitation.

The nature of this PPC is not well understood. Inhomogeneous mixed-valence models for In and other group III impurities have been proposed to explain several experimental data [5,6]. In these models In impurities exist in two valence states, one trivalent and the other monovalent (divalent impurity state is an excited state), stabilized by strong electronic and ionic relaxation. One of these

mechanisms is in some way connected with some deep donors, known as DX-like centers. DX center is a negatively charged and highly localized defect center resulting from a large lattice distortion. In the ground state, DX center is a deep donor that is negatively charged and photoexcitation changes the DX into a shallow state. This excited state is metastable, hence a barrier to recombination is originated by the structural relaxation required to return to the DX state. At low temperatures the photogenerated electrons remain in the conduction band indefinitely and the PPC is observed.

In spite of that, ab initio electronic structure calculations [7,8] indicate that all the impurities have the same electronic configurations, two electrons occupy a localized state whose energy is below the valence-band minimum and one electron occupies a localized state in the gap (homogeneous mixed-valence picture).

2. Raman measurements and discussion

The samples studied were In-doped $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($x = 0, 0.15$ and 0.25) single crystals grown by the modified Bridgeman method. The Raman spectra were excited by the 488 and 514.5 nm line of an Ar laser (the average power was about 50 mW) in the back-scattering geometry. We used Jobin Yvon model U-1000 monochromator, with a conventional photcounting system.

Raman spectra (Figs. 1–3) of $\text{PbTe} + 0.4\text{ at.}\% \text{In}$, $\text{Pb}_{0.85}\text{Sn}_{0.15}\text{Te} + 1\text{ at.}\% \text{In}$ and $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te} + 1.2\text{ at.}\% \text{In}$, respectively, are shown in the spectral range between 20 and 300, 330, 620 cm^{-1} , respectively, at temperatures between 10 and 300 K. For $\text{PbTe}(\text{In})$ sample in spectral range of 28–104 cm^{-1} modes at 28, 42, 47, 59, 75 and 95 cm^{-1} are registered. In the same range for sample $\text{Pb}_{0.85}\text{Sn}_{0.15}\text{Te}(\text{In})$ modes at 42 and 73 cm^{-1} are registered, while for sample $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te}(\text{In})$ these types of lines are not registered.

* Corresponding author. Tel.: +381 113160346; fax: +381 113160531.
E-mail address: romcevi@phy.bg.ac.yu (N. Romčević).

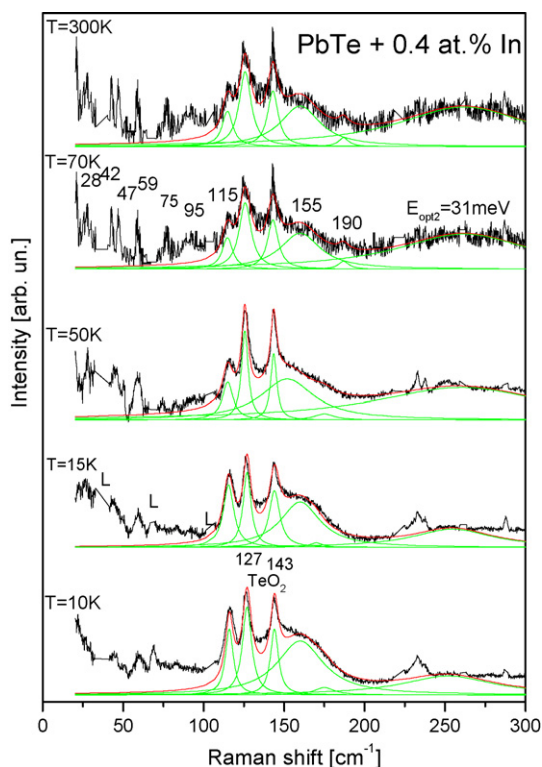


Fig. 1. Unpolarized Raman spectra of PbTe + 0.4 at.% In at different temperatures and the results of the deconvolution, applied on this spectra.

These oscillators are an edge Brillouin zone mode (the density of states of PbTe [9] has maximum at about these frequencies) which becomes Raman active due to impurity induced disorder. For sample Pb_{0.75}Sn_{0.25}Te(In) this weak feature is probably overlaid by the other mode.

Mode appearing on Raman spectra Pb_{1-x}Sn_xTe(In) can be explained this way: PbTe crystallizes in the cubic structure of the NaCl type (O_h space group symmetry). Each lead atom is ambient with six tellurium atoms and vice versa. Lead telluride grows with a rather high concentration of internal defects (vacancies in the Te place) and lead atom is substituted by In atom [10]. Impurity atom is surrounded with six tellurium atoms. However, adding impurity disturbs lattice symmetry. Tellurium atom, in vicinity of In atom is not in the center of inversion and becomes Raman active. In this way impurities induce additional mode on Raman spectra.

At frequency above 104 cm⁻¹ (ω_{LO} PbTe) the situation is more complicated. Raman scattering spectra are often analyzed with the help of a Lorentzian function or by the convolution of a Lorentzian and Gaussian curves. As the quality of the spectra in Figs. 1–3 is such that it allows only a qualitative analysis with a partial discussion of the trend, we assume that all lines are of the Lorentzian type. A typical line shape obtained in this way is also shown. As first, in Figs. 1 and 2 modes at 127 and 143 cm⁻¹ are registered. From literature [11] it is known that these modes originate from the TeO₂, which is always formed on the sample surface. The intensity of these modes can be very low if they are polished just before measurement but their existence do not effect spectra because the light progression depth is more than the depth of TeO₂ which is clearly seen. As in a previous case these mode are hidden in Fig. 3.

Two types of lines are registered above the top of the optical range:

- (1) phonon lines at about $\omega_1 = 115$ cm⁻¹, $\omega_2 = 155$ cm⁻¹ and $\omega_3 = 190$ cm⁻¹. In Fig. 3 there are first and second harmonic

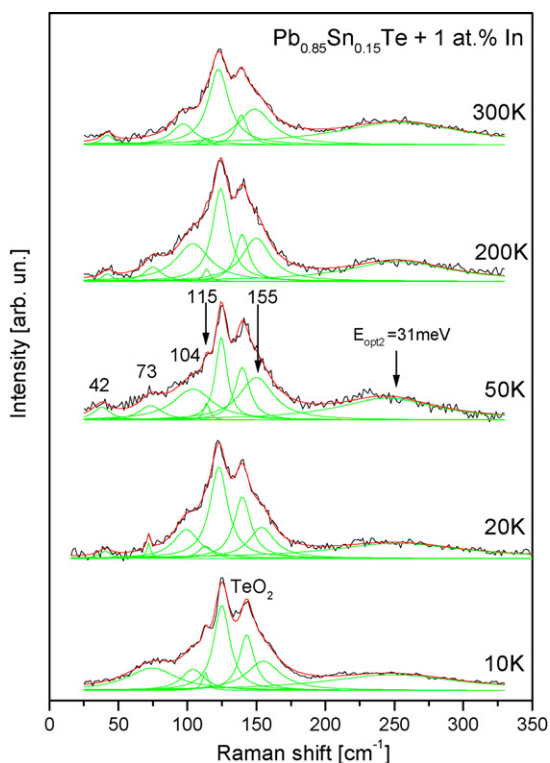


Fig. 2. Unpolarized Raman spectra of Pb_{0.85}Sn_{0.15}Te + 1 at.% In at different temperatures, and the results of the deconvolution, applied on this spectra.

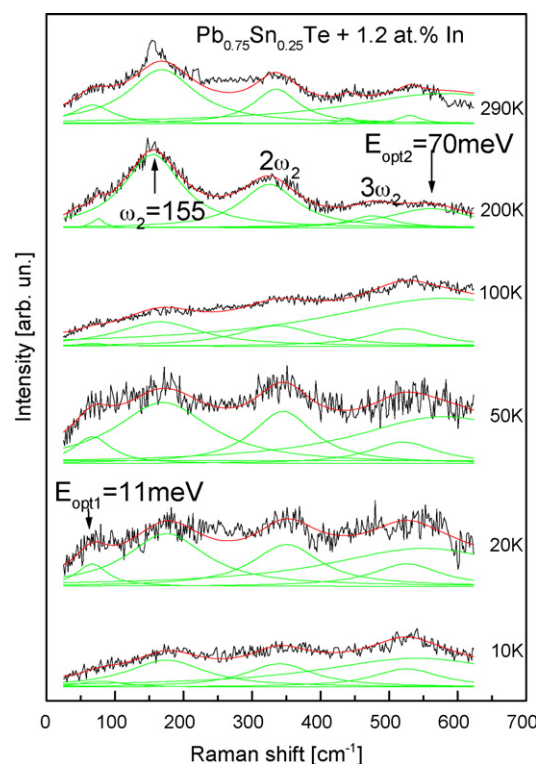


Fig. 3. Unpolarized Raman spectra of Pb_{0.75}Sn_{0.25}Te + 1.2 at.% In at different temperatures, and the results of the deconvolution, applied on this spectra.

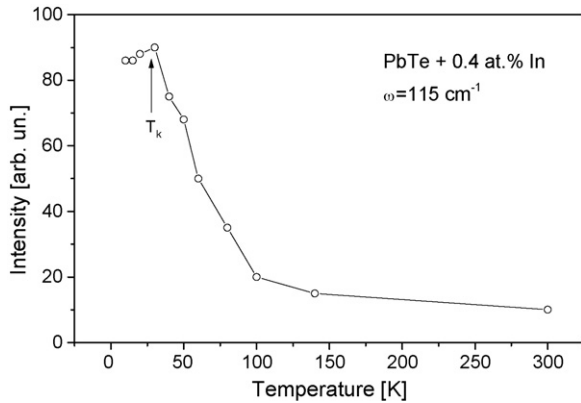


Fig. 4. The temperature dependence mode intensity at $\omega_1 = 115 \text{ cm}^{-1}$ at PbTe(In).

of local phonon mode at 155 cm^{-1} . While line ω_1 is narrow ($W \approx 6 \text{ cm}^{-1}$), other lines are considerably broad ($W \approx 30 \text{ cm}^{-1}$). Position of these lines is independent of alloy compound, temperature and amount of In added.

The registered temperature change of the mode intensity at $\omega_1 = 115 \text{ cm}^{-1}$ for PbTe(In) is presented in Fig. 4. There is weak intensity rise with the lowering of the temperature from room to temperature about 50 K. Rapid intensity rise is at about $T \approx 20 \text{ K}$ and when temperature is decreasing there is no change of intensity. Also, temperature varying like this is evidenced for $\text{Pb}_{0.85}\text{Sn}_{0.15}\text{Te}(\text{In})$ sample.

Mode intensity at 190 cm^{-1} is weak and it can be seen that it decreased when temperature decreased. Mode intensity at 155 cm^{-1} is temperature independent.

Naturally, owing to complicated spectra and broad line at 155 cm^{-1} this part of discussion must be taken heedfully.

- (2) electron transitions between impurity levels (E_{OPT2}) and impurity and band states (E_{OPT1}). These lines are broad and their positions depend on alloy compound.

The mode at about 115 , 155 and 190 cm^{-1} are connected to excitations of local phonon mode in the vicinity of an impurity atom In. If the semiconductor (in this case PbTe) is doped with substitution impurity (indium), 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

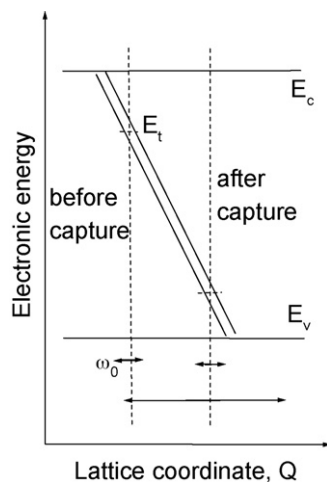


Fig. 5. Diagram illustrating how capture of an electron take place. The smaller arrows represent the amplitudes of the thermal vibrations (T_0). The large arrow represents the amplitude of the lattice vibrations.

the host lattice. In our case, the additional mode has frequencies over the optical range of PbTe (104 cm^{-1}).

In addition to this, it is known [12] that a change of electronic state of impurity centers leads to a change of the force constant between an impurity and a 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(Ga) and PbTe(B) samples [13,14]. Three local modes were noticed at 156 , 210 and 260 cm^{-1} for boron and 117 , 166 and 188 cm^{-1} for gallium. As compared to PbTe(In) 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.

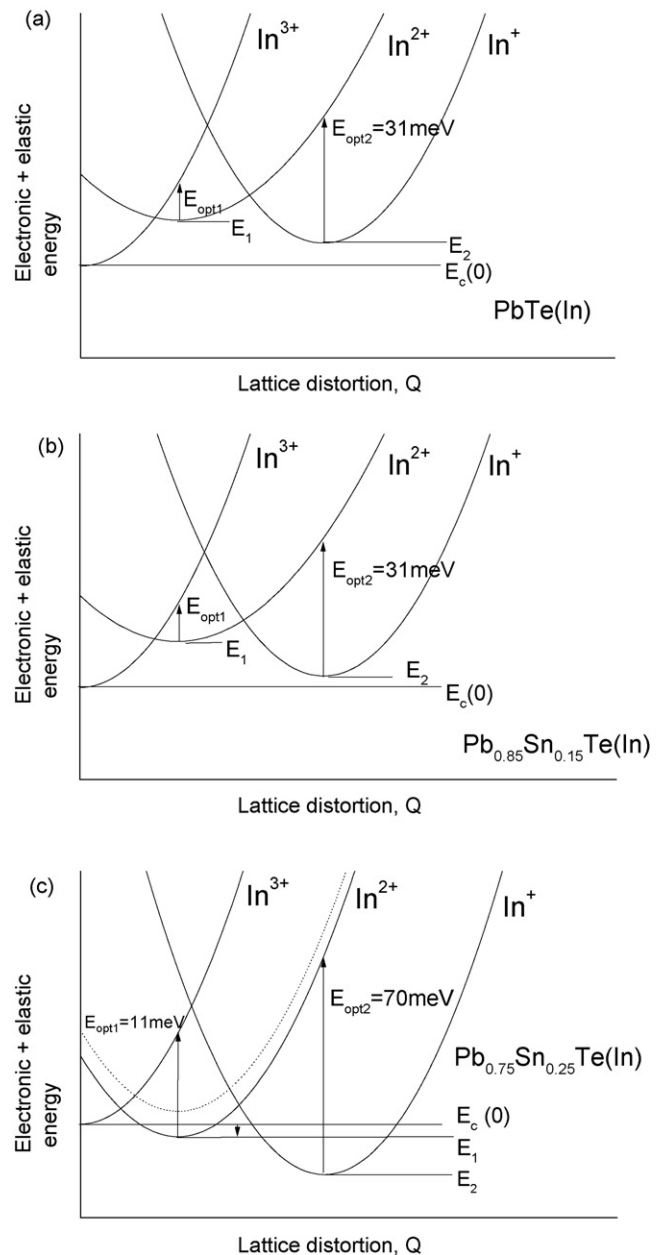


Fig. 6. Schematic total energy diagram as a function of the local displacement (Q) of a substitutional donor for the ionized In^{3+} state (E_c), the neutral donor In^{2+} state (E_1) and a negative, according to the lattice, two-electron donor state In^+ (E_2) in PbTe + 0.4 at.% In (a), $\text{Pb}_{0.85}\text{Sn}_{0.15}\text{Te} + 1 \text{ at.}\%$ (b) and $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te} + 1.2 \text{ at.}\%$ In (c).

Modes at about 310 and 470 cm^{-1} (see Fig. 3.) are harmonics of local phonon mode at about 155 cm^{-1} (In^+ state) [15] and mode at 570 cm^{-1} are registered here according multiphonon emission process MPE. Namely, in the $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te}(\text{In})$, the equilibrium position of the ground donor level before the electron capture is in the upper half of the gap [16]. After capture of the electron the lattice near the defect relaxes in such a way as to lower the equilibrium position of the level in the energy gap. Immediately after capture of the electron the lattice is displaced far from the new equilibrium position and there will be a violent lattice vibration at the defect. The vibration will rapidly damp down to the amplitude of the thermal vibrations (ω_0) after a small number of vibration periods. During the damping, the localized energy propagates away from the defect as phonons. This justifies calling this process nonradiative capture by multiphonon emission process [17]. This situation is schematically presented in Fig. 5.

Fig. 6 shows a suggested configuration coordinate diagram which describes In behavior in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system. Electron transitions which are registered in Figs. 1–3 are signified. Electronic spectrum of indium in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system is composed of two-electron ground state (E_2 is the average energy per electron of the In^+ state), metastable one-electron state (E_1 is the average energy per electron of the In^{2+} state) and conduction band (E_c). A “configuration” diagram [5,6], such as those shown in Fig. 6, are useful in describing the donor–acceptor states in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}(\text{In})$. The total energy is given as a function of the configuration parameter Q which describes the displacement of the substitutional donor. The three given curves correspond to an ionized donor (In^{3+}) at the bottom of the conduction band (E_c), the neutral donor (In^{2+}) and the negatively charged In^+ state, respectively. As follows from Fig. 6 the energy E_2 of the indium impurity level (In^+) in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}(\text{In})$ in relation to the tin content x changes linearly with x from 80 meV ($x=0$) in the conduction band to 22 meV ($x=0.25$) [18,19] in the forbidden band.

Also, a few experimental results [16,20] show that the In^+ and In^{3+} impurity states, which correspond to two electrons localized at the impurity and at the empty center, respectively, correspond

to a centrally symmetric position of the impurity atom, whereas, for the metastable state In^{2+} , which corresponds to one localized electron, the impurity atom is displaced from the inversion center. Consequently, the ionization of each of the electrons from the two-electron impurity ground state results in a displacement of the impurity atom first to an interstitial position, and then back into a substitutional center (Fig. 7). The In^{2+} atom position is not central but lattice is in normal state while the lattice is spread or expanded depending on whether indium is in In^+ or In^{3+} state. As a result, barriers are formed in a configuration space between all the states of the system with different numbers of localized electrons.

The registered MPE, and effects connected with them, are of fundamental importance. Namely, it gives us the direct proof that electron capture on impurity level results in a displacement of the impurity center from equilibrium position. As a result, barriers are formed in configuration space between all the states of the systems with different number of electrons. Because of that, for DX-like center in IV–VI compound, it allows nonequilibrium charge carriers to accumulate in metastable impurity state at low temperatures and produces a whole series of strong nonequilibrium effects: persistent photoconductivity effect, giant negative magnetoresistance and other effects [16].

3. Conclusion

In this paper we have performed a study of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ ($x=0, 0.15$ and 0.25) doped with In by Raman spectroscopy. There are three local mode of indium at about 115, 155 and 190 cm^{-1} . These modes are discussed in terms of local vibrations of impurities corresponding to different In charge states. Position of these lines is independent of alloy compound, temperature and amount of In added. A model connected with some deep donors, known as DX-like centers, describes the experimental data well.

The existence of energy barriers between one-electron metastable state and ground state In^+ and In^{3+} is a condition for appearing of persistent photoconductivity effect and long-time relaxation processes in III group doped PbTe base alloys.

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References

- [1] V.I. Kaidanov, R.B. Mel'nik, Chernik, Fiz. Tekh. Poluprov. 7 (1973) 759.
- [2] V.I. Kaidanov, Yu.I. Ravich, UFN 145 (1985) 51.
- [3] D.R. Khokhlov, I.I. Ivanchik, S.N. Raines, D.M. Watson, J.L. Pipher, Appl. Phys. Lett. 76 (2000) 2835.
- [4] K.G. Kristovskii, A.E. Kozhanov, D.E. Dolzhenko, I.I. Ivanchik, D. Watson, D.R. Khokhlov, Phys. Solid State 46 (2004) 122.
- [5] D.R. Khokhlov, Phys. Usp. 49 (2006) 955.
- [6] L.I. Ryabova, D.R. Khokhlov, JETP Lett. 80 (2004) 133.
- [7] S. Ahmad, S.D. Mahanti, K. Hoang, M.G. Kanatzidis, Phys. Rev. B 74 (2006) 155205.
- [8] S. Ahmad, K. Hoang, S.D. Mahanti, Phys. Rev. Lett. 96 (2006) 056403.
- [9] Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology, in: Semiconductors, vol. 17, Springer, Berlin/Heidelberg/Tokyo, 1983.
- [10] A.M. Gaskov, N.G. Lisina, V.P. Zlomanova, A.V. Novoselova, Pokladi Akademii nauka SSSR, ser. Hemija 261 (1981) 95.
- [11] J.H. Cappe, L.G. Halle, W.E. Tannet, Surf. Sci. 62 (1979) 639.
- [12] P.M. Mooney, J. Appl. Phys. 67 (1990) R1.
- [13] P.M. Nikolić, N. Romčević, K. Radulović, S.S. Vujatović, S. Djurić, V. Blagojević, S. Mihajlović, D. Siapakas, T.T. Zorba, Sci. Sinter. 31 (1999) 125.
- [14] M. Romčević, N. Romčević, D.R. Khokhlov, I.I. Ivanchik, J. Phys.: Condes. Matter 12 (2000) 8737–8744.
- [15] S. Takaoka, S. Shimomura, H. Takahashi, K. Murase, Phys. Rev. B 40 (1989) 5642.

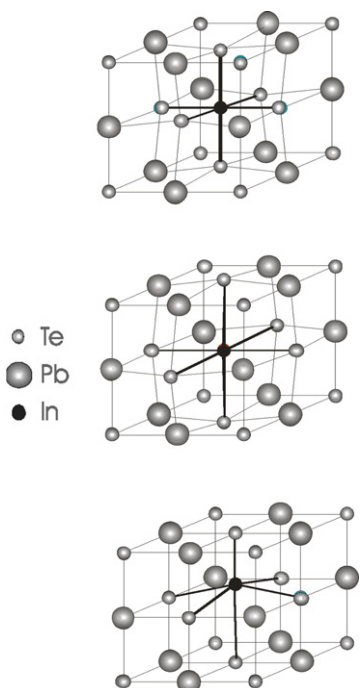


Fig. 7. Lattice in the vicinity of a different charge In center.

- [16] D.R. Khokhlov, B.A. Volkov, in: M. Scaffler, R. Zimmermann (Eds.), *Proceedings of the Twenty-Third International Conference on the Physics of Semiconductors* vol. 4, Berlin, Germany, July 21–26, 1996, World Scientific, Singapore, 1996, p. 2941.
- [17] C.H. Henry, D.V. Lang, *Phys. Rev. B* 15 (1977) 989.
- [18] N. Romčević, D. Stojanović, M. Romčević, D.R. Khokhlov, B. Hadžić, A.V. Nikorich, *J. Alloys Compd.* 436 (2007) 38–42.
- [19] A.N. Veis, *Semiconductors* 36 (2002) 176.
- [20] I. Ivanchik, D.R. Khokhlov, A.I. Belogorokhov, Z.V. Popović, N. Romčević, *Semiconductors* 32 (1998) 608.