

Plasmon – two phonon interaction in PbMnTe and PbTeS alloys

JELENA TRAJIĆ^{1*}, NEBOJŠA ROMČEVIĆ¹, MAJA ROMČEVIĆ¹
and VLADIMIR N. NIKIFOROV²

¹*Institute of Physics, Department for Solid State Physics and New Materials, P. O. Box 68,
11001 Belgrade, Serbia and* ²*Department of Low-Temperature Physics,
Moscow State University, Moscow, Russia*

(Received 18 December 2006)

Abstract: In this work far-infrared spectroscopy over a wide temperature range was used to investigate the vibration properties of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ ($x \leq 0.12$) and $\text{PbTe}_{1-x}\text{S}_x$ ($x \leq 0.05$) single crystals. In the analysis of the experimental results, a dielectric function which in advance takes into account the existence of plasmon – two phonon interaction was employed. As a result of the best fit, the three frequencies of the coupled modes were obtained and then the values for the two LO modes and the plasma frequency (ω_p) were calculated. It was found that the phonons in $\text{PbTe}_{1-x}\text{S}_x$ and $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ showed two-mode behavior (each TO–LO mode pair for the end members degenerates to an impurity mode).

Keywords: semimagnetic semiconductors; far-infrared spectroscopy; vibration properties; phonon behavior.

INTRODUCTION

The lead telluride family of the IV–VI compounds are narrow-band gap semiconductors. Depending on the composition, their band gap can vary from almost zero to 0.30 eV.^{1–5} Lead telluride and its solid solutions are used for active and passive devices. Namely, it is well known³ that in lead chalcogenides electrically active native point defects (vacancies and interstitial atoms) produce energy states lying either above the bottom of the conduction band (donor defects) or below the top of the valence band (acceptors). This leads to high charge carrier concentrations in undoped crystals because of the deviation of the composition from stoichiometry. Furthermore, neither cooling nor a magnetic field has been observed to have a freeze-out effect on the charge carriers.

Solid solution $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ are semimagnetic semiconductors which have not been sufficiently studied.^{6–9} Their crystal structure is cubic (NaCl-type), the lattice parameter changes linearly with the content of manganese concentration.

*Corresponding author. E-mail: jelena@phy.bg.ac.yu
doi: 10.2298/JSC0803369T

If the manganese concentration is less than 20 at. %, Mn enters the PbTe lattice as Mn^{2+} , and is not an electroactive dopant. Doping of PbTe with Mn increases the band gap at the rate $\partial E_g / \partial x \cong 38\text{--}48 \text{ meV}/\% \text{ MnTe}^{10}$ but does not provide for the appearance of local or quasi-local levels in the vicinity of the actual bands.⁷

$\text{PbTe}_{1-x}\text{S}_x$ is a narrow band gap semiconductor with a direct band gap in the infrared region.⁴ Recent experimental studies^{11,12} indicate that there is a second-order phase transition in the $\text{PbTe}_{1-x}\text{S}_x$ system. The phonon properties of $\text{PbTe}_{1-x}\text{S}_x$ have not yet been studied. Nevertheless, it is obvious that $\text{PbTe}_{1-x}\text{S}_x$ alloys cannot be treated by simply interpolating the phonon behavior between the two end-point materials. In addition, the subject of the former investigations was a mixed crystal with a relatively high concentration of sculpture.¹² Far-infrared spectroscopy is a powerful technique for investigation in this field.

In this paper, the results obtained using far infrared spectroscopy (FIR) to study the optical properties of $\text{PbMn}_{1-x}\text{Te}_x$ and $\text{PbTe}_{1-x}\text{S}_x$ mixed crystals are presented.

EXPERIMENTAL

The synthesis procedure for the preparation of single crystals of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ has already been described in previous papers.¹³⁻¹⁵ Briefly, single crystals of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ were grown by a modified Bridgman method with a lowered rate of $1.0^\circ\text{mm h}^{-1}$. The sample was obtained from the elements of high purity. The chemical composition of the samples was checked by an electron microprobe, which revealed good chemical homogeneity of the material.

The chemical composition of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ crystals were determined by the XRD technique.^{13,14} All the samples were examined under the same conditions using a Philips PW 1729 X-ray generator, a Philips 1710 diffractometer and original APD software.

Single crystals of $\text{PbTe}_{1-x}\text{S}_x$ alloys were grown by the vapor-liquid-solid (VLS) technique, using metal and chalcogenide atoms of high purity as the source materials. The chemical composition of the sample was controlled by X-ray microprobe investigation. Far-infrared reflection spectra were measured between 10 K and 300 K on a BOMEM DA8 spectrometer.

Reflectivity analysis and fitting procedure

The theoretical model for the bulk dielectric function has been discussed by several authors.^{16,17} It should be noticed briefly that the low-frequency dielectric properties of PbTe and related compounds have been described with not less than two classical oscillators ($l \geq 2$) corresponding to the TO-modes, superimposed by a Drude part, which takes into account the contribution of free carriers:¹⁸

$$\varepsilon_S(\omega) = \varepsilon_\infty + \sum_{k=1}^l \frac{\varepsilon_\infty(\omega_{LOk}^2 - \omega_{TOk}^2)}{\omega_{TOk}^2 - \omega^2 - i\gamma_{TOk}\omega} - \frac{\varepsilon_\infty\omega_p^2}{\omega(\omega + i\gamma_p)} \quad (1)$$

where ε_∞ is the bound charge contribution and is considered as a constant, ω_{LOk} and ω_{TOk} are the longitudinal and transverse optical-phonon frequencies, respectively, ω_p is the plasma frequency, γ_{TOk} and γ_p are the phonon and plasma damping, respectively. In the PbTe-based systems, the pure LO-modes ($\omega_{LO, \text{PbTe}}$) of the lattice are strongly influenced by the plasmon mode (ω_p) of free carriers. As a result, combined plasmon-LO phonon modes ($\omega_\pm$) were observed.¹⁹

Bearing this in mind, in the analysis of the reflectivity spectra of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ and $\text{PbTe}_{1-x}\text{S}_x$, it was decided to use a dielectric function which takes into account the existence of plasmon-LO phonon interaction in advance:²⁰

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\prod_{j=1}^{m+n} (\omega^2 + i\gamma_{lj}\omega - \omega_{lj}^2)}{\omega^m \prod_{i=1}^m (\omega + i\gamma_{pi}) \prod_{i=1}^n (\omega^2 + i\gamma_{ti}\omega - \omega_{ti}^2)} \prod_{k=1}^s \frac{\omega^2 + i\gamma_{kLO} - \omega_{kLO}^2}{\omega^2 + i\gamma_{kTO} - \omega_{kTO}^2} \quad (2)$$

The first term in Eq. (2) represents the coupling of m plasmons and n phonons, and the second term represents uncoupled modes of the crystal (s), also $l = n + s$. The ω_{lj} and γ_{lj} parameters of the first numerator are eigenfrequencies and damping coefficients of the longitudinal plasmon – n phonon waves. The parameters of the first denominator correspond to the corresponding characteristics of the transverse (TO) vibrations. In the second term ω_{LO} and ω_{TO} are the longitudinal and transverse frequencies, respectively, and γ_{LO} and γ_{TO} are damping. Therefore, the determinations of the LO-mode and plasma frequency are connected with a decoupled procedure.

A situation which considers the coupling of one plasmon and one phonon is explained in detail in the literature.²⁰ In this work, when the existence of this interaction in cases of $\text{Pb}_{0.98}\text{Mn}_{0.02}\text{Te}$ and $\text{PbTe}_{0.95}\text{S}_{0.05}$ alloys was taken into account and then the influence of free carrier eliminated, satisfactory results were not obtained. Considering this fact, it was decided to use a dielectric function which takes into account the existence of plasmon-two LO phonon interactions in the analysis of reflectivity spectra of $\text{Pb}_{0.98}\text{Mn}_{0.02}\text{Te}$ and $\text{PbTe}_{0.95}\text{S}_{0.05}$ alloys. This corresponds to $l = 2$ in dielectric function given by Eq. (1). The positions of the coupled modes are defined as the solutions of the real part of Eq. (1) ($\text{Re}\{\varepsilon_S\} = 0$). In this case, there are three coupled modes, which can be calculated by solving the Equations:

$$\omega^6 - A\omega^4 - B\omega^2 - C = 0 \quad (3)$$

$$A = \omega_{LO1}^2 + \omega_{LO2}^2 + \omega_P^2, \quad B = \omega_{LO1}^2 \omega_{LO2}^2 + \omega_P^2 (\omega_{LO1}^2 + \omega_{LO2}^2), \quad C = \omega_{LO1}^2 \omega_{LO2}^2 \omega_P^2 \quad (4)$$

If the dielectric function defined by Eq. (2) is used, the values of the initial ω_{LO1} , ω_{LO2} and ω_P modes can be determined by:

$$\omega_P = \frac{\omega_{l1}\omega_{l2}\omega_{l3}}{\omega_{t1}\omega_{t2}} \quad (5)$$

$$\omega_{LO1,2}^2 = \frac{1}{2}(\omega_{l1}^2 + \omega_{l2}^2 + \omega_{l3}^2 - \omega_P^2) \pm \sqrt{\frac{1}{4}(\omega_{l1}^2 + \omega_{l2}^2 + \omega_{l3}^2 - \omega_P^2)^2 - \omega_{l1}^2 \omega_{l2}^2 - \omega_{l1}^2 \omega_{l3}^2 - \omega_{l2}^2 \omega_{l3}^2 + \omega_P^2 (\omega_{l1}^2 + \omega_{l2}^2)} \quad (6)$$

The parameters adjustment was performed automatically by means of the least-square fitting of the theoretical (R) and experimental (R_e) reflection coefficients at k points arbitrarily chosen:

$$\chi = \sqrt{\frac{1}{k} \sum_{j=1}^k (R_{ej} - R_j)^2}, \quad R = \left| \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right|^2 \quad (7)$$

where ε is given by Eq. (1) or (2). The value of χ was minimized until it become comparable with the usual experimental error. Practically, for all samples the determined errors of the eigenfrequencies and damping coefficients were about 3–6 % and 10–15 %, respectively.

RESULTS AND DISCUSSION

Pb_{0.98}Mn_{0.02}Te single crystal

The far-infrared reflection spectra of the Pb_{0.98}Mn_{0.02}Te single crystal sample are shown in Fig. 1. The experimental data are presented with circles. The solid lines in Fig. 1 were obtained using the dielectric function from Eq. (2). An oscillator of weak intensity, at about 70 cm⁻¹ (denoted by * in Fig. 1), is a Brillouin zone edge mode because the phonon density of PbTe has a maximum at these frequencies.²¹

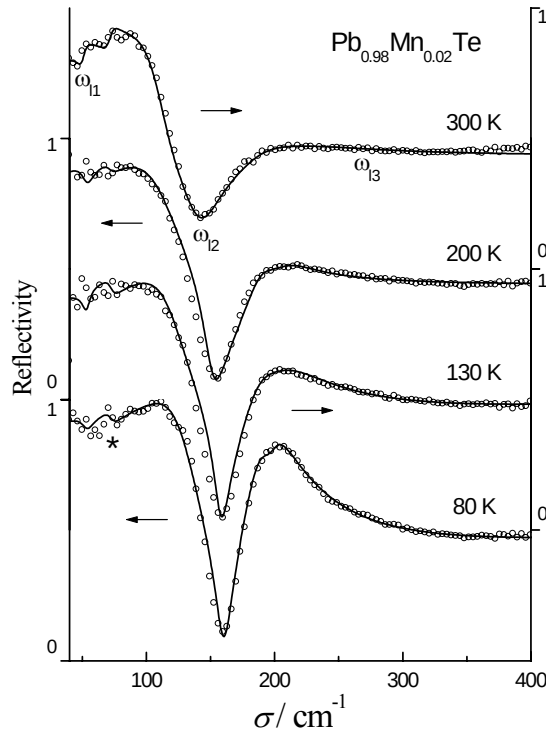


Fig.1. Far-infrared reflection spectra of Pb_{0.98}Mn_{0.02}Te single crystal. Experimental spectra are presented by circles. The solid lines are calculated spectra obtained by a fitting procedure based on the model given by Eq. (2).

From the best fit, the frequencies of the coupled modes (ω_1 , ω_2 and ω_3), marked in Fig. 1, and then the values for ω_{LO1} , ω_{LO2} and ω_P were calculated in the way described above. The characteristic parameters obtained in this way are shown in Fig. 2.

In Fig. 2, the solid circles (●) refer to the eigenfrequency spectra ω_j obtained by Eq. (2). The solid lines in Fig. 2 were obtained by application of Eq. (3). The agreement of the plasmon – two LO phonon mode frequencies calculated in such a way with the experimentally determined values is very good. The open circles (○) in Fig. 2 represent the calculated values for ω_{LO1} and ω_{LO2} (Eq. (6)) and the experimentally determined values for ω_{TO1} and ω_{TO2} are denoted by

stars (*). The values determined in this way are in excellent agreement with calculated values based on the Genzel model,²² mentioned above. The obtained results presented in Fig. 2 are the best demonstration of the fact that use of the dielectric function given by Eq. (2) is justifiable. Also, the results shown in Fig. 2 suggest that the optical phonons in $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ mixed crystals (Fig. 3) exhibit the well-known two-mode behavior (each TO–LO mode pair of the end members degenerates to an impurity mode), according to the notation of Genzel.²² The behavior of the optical phonon modes is presented in Fig. 3. The solid lines were obtained employing the Genzel model. The experimental values are indicated by the same marks as used in Fig. 2.

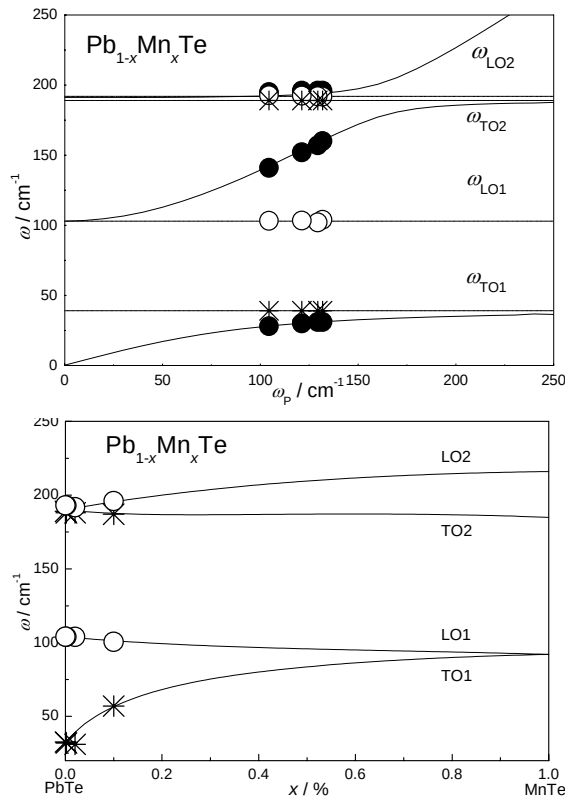


Fig. 2. The eigenfrequencies of the plasmon – two LO phonon modes (solid lines – Eq.(3)); • – eigenfrequency spectra ω_j obtained by Eq. (2); ○ – calculated values for $\omega_{\text{LO}i}$ (Eq. (6)) and * – experimentally determined values for $\omega_{\text{TO}i}$.

Fig. 3. Concentration dependence of the optical mode frequencies of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ mixed crystal. ○ – calculated values for $\omega_{\text{LO}1}$ and $\omega_{\text{LO}2}$ (Eq. (6)); * – ω_{TO} .

$\text{PbTe}_{0.95}\text{S}_{0.05}\text{Te}$ single crystal

The far-infrared reflection spectra of the $\text{PbTe}_{0.95}\text{S}_{0.05}$ single crystal sample are shown in Fig. 4, with the same notation as in the case of the $\text{Pb}_{0.98}\text{Mn}_{0.02}\text{Te}$ alloy described above.

The calculated values for $\omega_{\text{LO}1}$ and $\omega_{\text{LO}2}$ from Eq. (6) and the experimentally determined values for $\omega_{\text{TO}1}$ and $\omega_{\text{TO}2}$ (Eq. (2)) for the $\text{PbTe}_{0.95}\text{S}_{0.05}$ single

crystal are presented in Fig. 5. As can be seen, the agreement of the plasmon – two LO phonon mode frequencies calculated using Eq. (3) (solid line) with the experimentally determined values for ω_{l1} , ω_{l2} and ω_{l3} (Eq. 2) is very good.

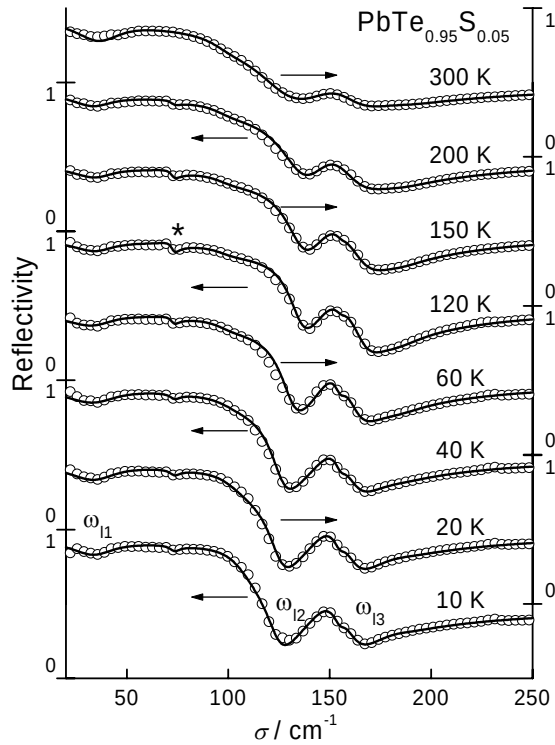


Fig.4. Far-infrared reflection spectra of a $\text{PbTe}_{0.95}\text{S}_{0.05}$ single crystal. Experimental spectra are presented by circles. The solid lines are calculated spectra obtained by a fitting procedure based on the model given by Eq. (2).

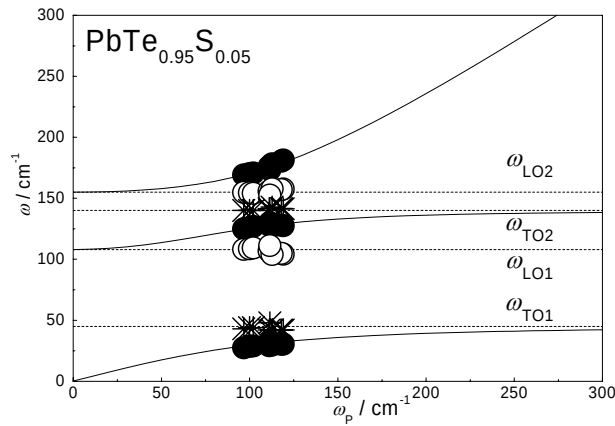


Fig.5. The eigenfrequencies of the plasmon – two LO phonon modes (solid lines – Eq. (3)); • – eigenfrequency spectra ω_j obtained using Eq. (2); o – calculated values for $\omega_{\text{LO}i}$ (Eq. (6)) and * – experimentally determined values for $\omega_{\text{TO}i}$.

The mode frequencies determined on this way suggest that the optical phonons in $\text{PbTe}_{1-x}\text{S}_x$ mixed crystals exhibit a two-mode behavior according to Genzel notation,²² which is presented in Fig. 6.

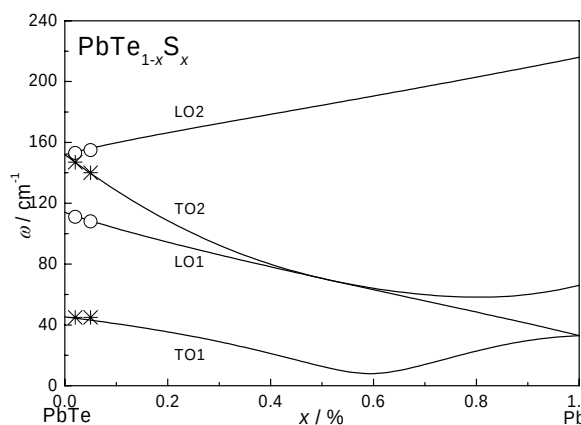


Fig.6. Concentration dependence of the optical mode frequencies of $\text{PbTe}_{1-x}\text{S}_x$ mixed crystals. $\circ$ – calculated values for ω_{LO1} and ω_{LO2} (Eq. (6)); $*$ – ω_{TO} .

CONCLUSION

As a method for investigating the phonon properties of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ and $\text{PbTe}_{1-x}\text{S}_x$ mixed crystals, far-infrared spectroscopy was employed. In spite of the strong plasmon – two LO phonon interaction, it was found that the long wavelength optical phonon modes of these mixed crystals exhibited a two-mode behavior.

Acknowledgements. This work was supported by Serbian Ministry of Science under Project 141028B.

ИЗВОД

ПЛАЗМОН – ДВО ФОНОН ИНТЕРАКЦИЈА КОД PbMnTe И PbTeS ЛЕГУРА

ЈЕЛЕНА ТРАЈИЋ¹, НЕБОЈША РОМЧЕВИЋ¹, МАЈА РОМЧЕВИЋ¹ И ВЛАДИМИР Н. НИКИФОРОВ²

¹Институт за физику, Центар за физику чврстог стања и нове материјале, бр. 68, 11001 Београд и

²Department of Low-Temperature Physics, Moscow State University, Moscow, Russia

У овом раду су представљени резултати проучавања вибрационих својстава монокристала $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ ($x \leq 0,12$) и $\text{PbTe}_{1-x}\text{S}_x$ ($x \leq 0,05$) применом далеке инфрацрвене спектроскопије. Приликом анализе експерименталних резултата коришћена је диелектрична функција која унапред узима у обзир постојање плазмон – дво фонон интеракције. Као резултат најбољег фита, добијају се три учестаности спрегнутих модова и онда израчунавају вредности учестаности два LO мода и плазма учестаност (ω_p). Установили смо да оптички фонони у $\text{PbTe}_{1-x}\text{S}_x$ и $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ испољавају дво-модни тип понашања (сваки TO–LO пар мода се дегенерише у примесни мод).

(Примљено 18. децембра 2006)

REFERENCES

1. M. E. Lines, A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, The Int. Series of Monographs on Physics, Clarendon, Oxford, 1977
2. H. Kawamura, in *Narrow-Gap Semiconductors, Physics and Applications*, Lecture Notes in Physics, Vol. 33, W. Zawadski, Ed., Springer, Berlin, 1980

3. B. A. Volkov, L. I. Ryabova, D. R. Khokhlov, *Uspekhi Fizicheskikh Nauk*, Russian Academy of Science **8** (2002) 875 [*Physics – Uspekhi* **8** (2002) 819]
4. T. Shimada, Kh. I. Kobayasi, Y. Katayama, K. F. Komatsubara, *Phys. Rev. Lett.* **39** (1977) 143
5. W. Jantsch, A. Lopez-Ortego, G. Bauer, *Infrared Phys.* **18** (1978) 877
6. D. G. Adrianov, C. A. Belokon, C. O. Klimonskii, V. M. Lakeenkov, *Fiz. Tekh. Poluprovodn.* **22** (1988) 670
7. J. Niewodniczanska-Zawadzka, G. Elsinger, L. Pametshofer, *Physica B&C* **C117** (1983) 458
8. A. V. Brodovoi, G. V. Lashkarev, M. B. Radchenko, E. I. Sl'inko, K. D. Tovstuk, *Fiz. Tekh. Poluprovodn.* **18** (1984) 1547 [*Sov. Phys. Semicond.* **18** (1984) 970]
9. J. Nuerwirth, W. Jantsch, L. Palmetchhofer, W. Zulehner, *J. Phys. C* **19** (1986) 2475
10. Z. Korczak, M. Subotowicz, *Phys. Stat. Sol. (a)* **77** (1983) 497
11. Kh. A. Abdulin, A. I. Lebedev, A. M. Gas'kov, V. N. Demin, V. P. Zlomanov, *Pi'ma Zh. Eksp. Teor. Fiz.* **40** 229 (1984) [*JETP Lett.* **40** (1984) 998]
12. Z. Vang, B. A. Bunker, *Phys. Rev. B* **46** (1992) 11277
13. A. Golubović, S. Nikolić, J. Trajić, S. Đurić, N. Romčević, M. Romčević, A. J. Nadolny, B. Taliashvili, V. Domukhovski, V. N. Nikiforov, *Mat. Sci. Forum* **453** (2004) 99
14. N. Romčević, A. Golubović, M. Romčević, J. Trajić, S. Nikolić, S. Đurić, V. N. Nikiforov, *J. Alloys Comp.* **402** (2005) 36
15. J. Trajić, M. Romčević, N. Romčević, S. Nikolić, A. Golubović, S. Đurić, V. N. Nikiforov, *J. Alloys Comp.* **365** (2004) 89
16. E. Burstein, A. Pinczuk, R. F. Wallis, in *The Physics of Semimetals and Narrow-Gap Semiconductors*, D. L. Carter, R. T. Bate, Eds., Pergamon, New York, 1971, p. 251.
17. M. A. Kinch, D. D. Buss, *Solid State Commun.* **11** (1972) 319
18. V. Gopal, *Infrared Phys.* **18** (1978) 121
19. S. Takaoka, T. Hamaguchi, S. Shimomura, K. Murase, *Solid State Commun.* **54** (1985) 99
20. A. A. Kuharskii, *Solid State Commun.* **8** (1970) 1275
21. W. Cochran, R. A. Cowley, G. Dolling, M. M. Elcombe, *Proc. Royal. Soc.* **A293** (1966) 433
22. L. Genzel, T. P. Martin, C. H. Perry, *Phys. Status Solidi (b)* **62** (1974) 83.