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Colossal tuning of an energy gap in $\text{Sn}_2\text{P}_2\text{S}_6$ under pressure

Vladimir V. Shchennikov,¹ Natalia V. Morozova,¹ Iryna Tyagur,² Yuriy Tyagur,³
and Sergey V. Ovsyannikov^{4,a)}

¹High-Pressure Group, Institute of Metal Physics of Russian Academy of Sciences, Urals Division,
18 S. Kovalevskaya Str., Yekaterinburg 620041, Russia

²International Center for Piezoelectric research, Technical University of Liberec, Halkova 6,
461 17 Liberec 1, Czech Republic

³Uzhgorod National University, Pidhirna 46, 88000 Uzhgorod, Ukraine

⁴Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95447 Bayreuth, Germany

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We report results of investigation of electrical and thermoelectric properties of $\text{Sn}_2\text{P}_2\text{S}_6$ under strong compression up to 20 GPa. An “insulator-metal”(I-M)-type transition was discovered by a monotonic and reversible lowering of electrical resistivity by 9–10 orders. The energy gap ($E_g = 2.3$ eV) was estimated to decrease to ~ 0.25 – 0.3 eV at 20 GPa. X-ray diffraction and Raman studies on samples recovered from the high pressure experiments confirm a conservation of the original monoclinic lattice. Thus, a colossal “band-gap engineering” potential is revealed in this optical material. $\text{Sn}_2\text{P}_2\text{S}_6$ is a potential candidate for emergent multi-functional switches, between transparent “insulator” state and conducting state with magneto-dependent properties. © 2011 American Institute of Physics. [doi:10.1063/1.3662926]

Materials with properties which may be significantly altered in a controlled manner by some external factor (i.e., “smart” materials) are very promising for industrial applications, e.g., in micro-(nano)-opto-electro-mechanical systems (M(N)OEMS). Stress-(pressure)-related effects have a great technological potential.¹ For instance, stresses in thin films permit band-gap E_g tuning.² Nanoindentation load may be used for surface modification;³ it is applied, e.g., in “writing electrically conductive zones” on Si,⁵ and in data recording in IBM memory devices of ultrahigh storage density.⁴ “Insulator-metal”(I-M)-type transitions under moderate pressures (<20–30 GPa) open possibilities for various switches.⁵ However, well-controlled and reversible tuning of E_g and its closure are achieved only in some narrow-gap semiconductors with $E_g < 0.3$ eV (e.g., PbTe, PbSe).⁶ Shrinkage of E_g in wide-gap materials under pressure is usually concurrent with reconstructive transition (e.g., ZnTe),⁷ which can lead to sample damage. Smooth closure of E_g (e.g., in I_2 , some iodides, Se)⁷ is a rare phenomenon, and corresponding changes in electrical properties are smeared and partly irreversible. Thus, no material seemed to be suitable for “I-M” switches operating in the visible range.

In this work, we show that electrical resistivity of $\text{Sn}_2\text{P}_2\text{S}_6$ ($E_g = 2.3$ eV)⁸ is gradually and reversibly decreased ten orders of magnitude by pressurizing up to 20 GPa. Hence, it is a promising candidate for “opto-electrical” switches. $\text{Sn}_2\text{P}_2\text{S}_6$ exhibits excellent optical characteristics and it is particular important for photorefractive applications.⁹ In addition, it possesses ferroelectric (piezoelectric) properties¹⁰ and could find applications in tunable capacitances, non-volatile memory elements, and various sensor devices.¹¹ Above ~ 0.2 – 0.5 GPa, it shows a second-order

transition from the monoclinic Pn lattice¹² to a paraelectric phase with a $P2_1/n$ lattice.^{13,14}

The measurements of electrical resistivity and thermopower were carried out at an automated high-pressure setup.¹⁵ The experimental details are similar to previous works^{15,16} and are described in the supplementary materials.¹⁷ Two samples of $\text{Sn}_2\text{P}_2\text{S}_6$ were measured, each for five compression-decompression cycles up to ~ 20 GPa. Before and after the measurements, the samples were examined by x-ray diffraction (XRD), Raman and optical absorption studies, using Rigaku diffractometer (wavelength $\lambda = 0.7108$ Å), LabRam spectrometer with a He-Ne laser ($\lambda = 632.8$ nm), and Bruker IFS 120 Fourier transform spectrometer, respectively.¹⁸

The pressure dependencies of electrical resistance, R of $\text{Sn}_2\text{P}_2\text{S}_6$ indicate a gradual and reversible “I-M”-type transition (Fig. 1(a)). Direct thermopower, S measurements were possible only beyond 12 GPa, when, R was lowered substantially (Fig. 1(b)). In the sample #2, we determined thermopower values from the linear dependencies of the thermoelectric current vs temperature difference, ΔT on the sample at 9.6 and 10.7 GPa, as $S \sim +1.65$ and $+1.2$ mV/K, respectively (Fig. 1(b), inset). Thus, S also diminishes monotonically with pressure. Such behavior of R and S unambiguously suggests a strong narrowing in E_g . The positive sign of S suggests that the hole conductivity is dominant.

For nearly intrinsic semiconductors, an expression for thermopower (S) is as follows:¹⁹

$$S = -\frac{k}{|e|} \left[\frac{b-1}{b+1} \cdot \frac{E_g}{2kT} + \left(r_n + \frac{5}{2} \right) \frac{b}{b+1} - \left(r_p + \frac{5}{2} \right) \frac{1}{b+1} - \frac{3}{4} \ln \frac{m_p^*}{m_n^*} \right], \quad (1)$$

where k the Boltzmann’s constant, e the electron charge, $b = \sigma_n/\sigma_p$ is the ratio of partial conductivities of electrons and holes, T is the temperature, and $r_n(r_p)$ and $m_n^*(m_p^*)$ are the

^{a)}Present address: Dr. Sergey V. Ovsyannikov, Research Professor, Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95447 Bayreuth, Germany. Electronic mail: sergey.ovsyannikov@uni-bayreuth.de.

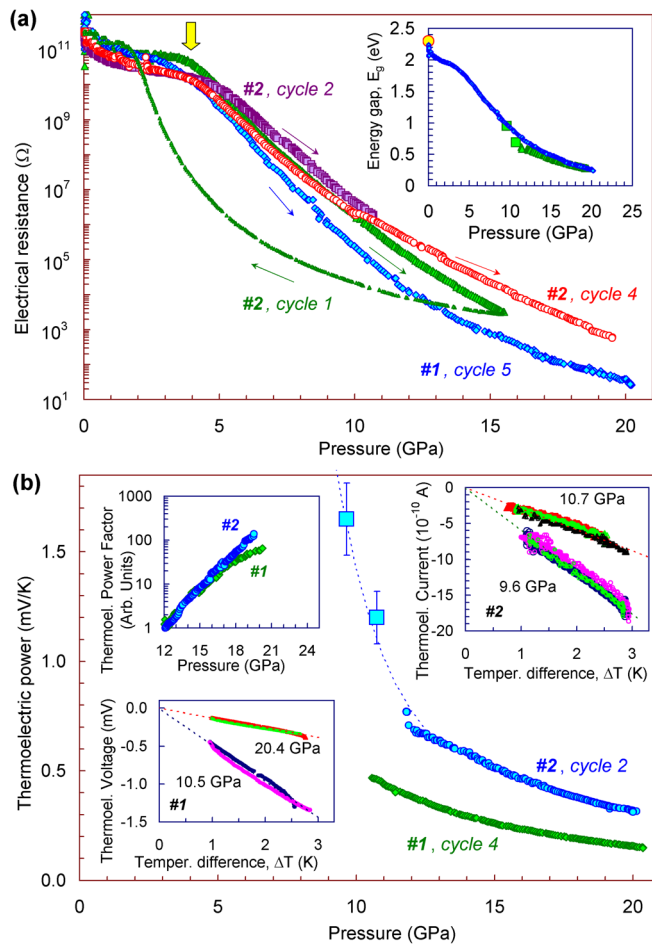


FIG. 1. (Color online) The pressure dependencies of the electrical resistance (a) and the thermoelectric power (b) of $\text{Sn}_2\text{P}_2\text{S}_6$ at room temperature. The labels #1-#2 mark different samples. The inset in (a) shows a pressure variation of the energy gap, found by the data of (a) and (b) plots. The lower and right insets in (b) show examples of thermopower determination from linear slopes of dependencies of the thermoelectric voltage (V) or the current (I) on the temperature difference along a sample (ΔT). The upper left inset in (b) shows a pressure variation of the thermoelectric power factor, normalized to 12 GPa.

scattering parameter and the effective mass of density of states of electrons (holes), respectively. Equation (1) is a linear function of E_g and expressing E_g through electrical resistivity ρ ($\rho = \rho_0 \exp[E_g/(2kT)]$),¹⁹ a relation between S and ρ may be found as follows: $S \approx -(k/e)[(b-1)/(b+1)](\ln \rho - \ln \rho_0)$. Then, from “ R vs S ” curves, one can determine the parameter b from a linear slope. Since the pressure dependence of ρ_0 is much weaker than ρ , the former could be neglected. For the range of 12–20 GPa, we find average, $b \sim 0.4$ (~ 0.2) in the sample #1 (#2) (Fig. 2); a calculated “ R vs S ” curve for $b = 0$ is shown in Fig. 2 also.

For the constants $k/e \approx -86.4 \mu\text{V/K}$ and $2kT = 50 \text{ meV}$, the above-estimated b (Fig. 2) and dS/dP coefficients found from Fig. 1(b) ($dS/dP \sim -30$ (-50) ($\mu\text{V/K})/\text{GPa}$ for the sample #1 (#2)), Eq. (1) gives $dE_g/dP \sim -41$ (-43) meV/GPa for the sample #1(#2). Notice that the thermopower data suggest a bowing in the dE_g/dP coefficient. It seems that $\text{Sn}_2\text{P}_2\text{S}_6$ could reach a (semi-) metal state beyond $\sim 30 \text{ GPa}$. Since, compounds of VI-VII Groups are usually superconducting in their metal phases, one could expect similar behavior in $\text{Sn}_2\text{P}_2\text{S}_6$. A value of E_g in the sample #1 (#2) at 20 GPa may be estimated to be $E_g \sim 0.25$ (0.3) eV. A proposed pressure

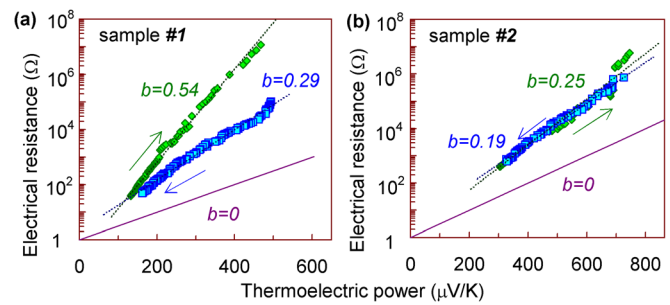


FIG. 2. (Color online) The examples of the parametric dependencies “Electrical resistance vs Thermopower” for $\text{Sn}_2\text{P}_2\text{S}_6$, for samples #1 (cycles 2 and 4) and #2 (cycles 2 and 3). The arrows show the directions of pressure-driven changes. Values b are determined from the linear slopes using Eq. (1).

dependence of E_g is shown in inset in Fig. 1(a). A study on a pressure-driven shift of the absorption edge of $\text{Sn}_2\text{P}_2\text{S}_6$ up to 1 GPa found $dE_g/dP = -580$ and -80 meV/GPa , in the ferroelectric and paraelectric phases (above 0.2 GPa), respectively.¹⁴ The former has a correspondence with a strong reduction in R at very low pressures (Fig. 1(a)), while the latter agrees with our $E_g(P)$ curve in the range of 0–20 GPa (Fig. 1(a), inset).

Hole concentration p and mobility μ_p in model of one-band conductivity may be determined as follows:¹⁹ $p = [2 \times (2\pi m^* kT)^{3/2} / h^3] \times \exp(-E_g/(2kT))$ and $\mu_p = 1/(\rho |e| p)$, where h the Planck’s constant. For rough estimation, m^* may be put to be equal to the free electron mass, m_0 (band structure calculations of the paraelectric phase found $m_p^* \sim (0.8-2)m_0$).²⁰ At 20 GPa for $E_g \sim 0.25$ (0.3) eV, we find $p \sim 1.7$ (0.6) $\times 10^{17} \text{ cm}^{-3}$. We estimate $\rho \sim 0.2 \Omega \times \text{cm}$ for the sample #1 at 20 GPa, and hence, $\mu_p \sim 180 \text{ cm}^2/(\text{Vs})$, which corresponds to a covalent semiconductor with direct E_g . The thermoelectric power factor ($\alpha = S^2/\rho$) which characterizes the thermoelectric performance, increases with pressure (Fig. 1(b), inset) and reaches values of $\sim 10^{-6} \text{ W/(K}^2\text{cm)}$ at 20 GPa. This is about two orders lower, than those in good thermoelectrics;²¹ however, a further narrowing in E_g could enhance it.

The electrical resistance data show a perfect reversibility and a reproducibility of the pressure-driven changes (Fig. 1(a)). Besides, they show an anomaly around 3.5–5 GPa that could be due either to a crossover between extrinsic and intrinsic conductivities or to some minor structural modification. XRD and Raman studies on the original and recovered samples confirm a conservation of the initial Pn structure (Figs. 3(a) and 3(b)).¹² This is in contrast to irreversible changes in SnP_2S_6 subjected to compression to 40 GPa.²² Both the original and the recovered samples have the same unit cell parameters ($a = 9.372(4) \text{ \AA}$, $b = 7.464(4) \text{ \AA}$, $c = 6.528(6) \text{ \AA}$, and $\beta = 91.15^\circ$) that are very similar to the literature data.¹² Our Raman spectra (Fig. 3(b)) agree well with previous works.²³ The recovered samples show a new peak at 411 cm^{-1} . This could be a local phonon mode related to pressure-induced defects. Optical spectra demonstrate both an abrupt absorption edge in the original crystal near $E_g \sim 2.3 \text{ eV}$ ⁸ and its smoothing in the recovered samples (Fig. 3(c)). This observation is corroborated by a color change to dark red in the recovered samples (Fig. 3(c), insets).

Thus, $\text{Sn}_2\text{P}_2\text{S}_6$ is a unique optical material that exhibits a reversible and well-reproducible ten-order tuning in

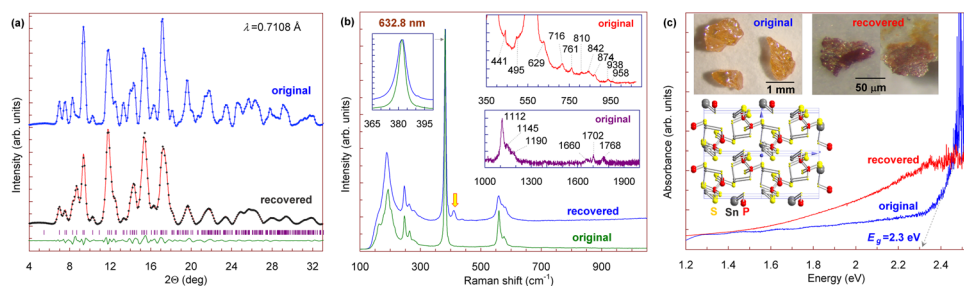


FIG. 3. (Color online) The x-ray diffraction patterns (a), Raman (b), and optical absorbance spectra (c) of the original and recovered from high-pressure samples of $\text{Sn}_2\text{P}_2\text{S}_6$. Plot (a): the both patterns correspond to the monoclinic Pn lattice. A full-profile Rietveld refinement of the pattern for the recovered sample is shown as an example; a model determined in Ref. 12 was used (see supplementary material).¹⁷ The tick marks—calculated peak positions for the Pn space group, the lowermost curve—the difference between the experimental (points) and the calculated (line) profiles. Plot (b): the both spectra show the main features at $\sim 163, 179, 192, 203, 216, 247, 264, 280, 382, 391, 560, 567, 577$, and 582 cm^{-1} ; other wave numbers are given at the insets. A new peak in the recovered sample at 411 cm^{-1} is pointed by an arrow. Plot (c): the original sample has an abrupt absorption edge near 2.3 eV , while the recovered one shows its smoothing down to 1.5 eV . The photographs of the samples and the crystal lattice of $\text{Sn}_2\text{P}_2\text{S}_6$ are shown as insets.

conductivity to 20 GPa, while retaining its structural properties. “Hard” wide-gap materials predominantly show positive or minor dE_g/dP coefficients.²⁴ While, in some “soft” materials (e.g., S, Se, I_2 , some iodides), E_g might decrease rapidly with pressure.^{7,25} The relatively high mobility of holes found in $\text{Sn}_2\text{P}_2\text{S}_6$ at 20 GPa suggests direct E_g and strong sensitivity to magnetic field. Therefore, $\text{Sn}_2\text{P}_2\text{S}_6$ is capable of exhibiting of new physical properties. For instance, it is likely to exhibit large magnetoresistance (MR) and magnetothermopower effects (they both are functions of μ^2),¹⁹ which might be enhanced with pressure (for direct E_g : $\mu \sim 1/E_g$).¹⁹ Optical properties of $\text{Sn}_2\text{P}_2\text{S}_6$ are also expected to be strongly tuned with pressure, e.g., a large modification of its photoconductivity is anticipated.⁹ Since, E_g in $\text{Sn}_2\text{P}_2\text{S}_6$ is mainly formed by sp -hybridization of S and P orbitals, it is the most sensitive to the S-sub-lattice.^{8,9} In pure sulfur, indirect E_g of $\sim 3\text{ eV}$ decreases to $\sim 1\text{ eV}$ upon compression to 25 GPa.²⁵ However, sulfur itself compressed to 25 GPa shows very low μ and electrical conductivity and tiny MR effect.²⁶

Thus, $\text{Sn}_2\text{P}_2\text{S}_6$ is a good candidate for multi-functional “opto-electrical” switches. Similar effects are expected in other $\text{M}_2\text{P}_2\text{X}_6$ ($M = \text{Sn, Pb}$ and $X = \text{S, Se}$) materials. Pressure effects may be simulated *in-situ* e.g., by stresses in thin films² or by electro-mechanically driven nanoindenter.^{3,4}

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¹S. Kwon, S. Choi, H. J. Chung, H. Yang, S. Seo, S.-H. Jhi, and J. Y. Park, *Appl. Phys. Lett.* **99**, 013110 (2011).

²A. Kadir, T. Ganguli, R. Kumar, M. R. Gokhale, A. P. Shah, S. Ghosh, B. M. Arora, and A. Bhattacharya, *Appl. Phys. Lett.* **91**, 111913 (2007).

³S. Ruffell, K. Sears, J. E. Bradby, and J. S. Williams, *Appl. Phys. Lett.* **98**, 052105 (2011).

⁴P. Vettiger, G. Cross, M. Despont, U. Drechsler, U. Durig, B. Gotsmann, W. Haberle, M. A. Lantz, H. E. Rothuizen, R. Stutz, and G. K. Binnig, *IEEE Trans. Nanotechnol.* **1**, 39 (2002); M. I. Lutwyche, M. Despont, U. Drechsler, U. Durig, W. Haberle, H. Rothuizen, R. Stutz, R. Widmer, G. K. Binnig, and P. Vettiger, *Appl. Phys. Lett.* **77**, 3299 (2000).

⁵H. T. Yi, T. Choi, and S.-W. Cheong, *Appl. Phys. Lett.* **95**, 063509 (2009).

⁶V. V. Shchennikov and S. V. Ovsyannikov, *Solid State Commun.* **126**, 373 (2003).

⁷G. A. Samara and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 457 (1962); B. M. Riggelman and H. G. Drickamer, *J. Chem. Phys.* **38**, 2721 (1963); F. P. Bundy and K. J. Dunn, *J. Chem. Phys.* **71**, 1550 (1979).

⁸A. Ruediger, O. Schirmer, S. Odoulov, A. Shumelyuk, and A. Grabar, *Opt. Mater.* **18**, 123 (2001); K. Kuepper, B. Schneider, V. Caciuc, M. Neumann, A. V. Postnikov, A. Ruediger, A. A. Grabar, and Yu. M. Vysochanskii, *Phys. Rev. B* **67**, 115101 (2003); R. V. Gamernyuk, Yu. P. Gnatenko, P. M. Bukivskij, P. A. Skubenko, and V. Yu. Slivka, *J. Phys.: Condens. Matter* **18**, 5323 (2006).

⁹*Photorefractive Materials and Their Applications: Materials*, edited by, P. Günter and J.-P. Huignard (Springer, New York, 2007); S. G. Odoulov, A. N. Shumelyuk, G. A. Brost, and K. M. Magde, *Appl. Phys. Lett.* **69**, 3665 (1996); A. Shumelyuk, S. Odoulov, G. Cook, and D. R. Evans, *Opt. Lett.* **34**, 2126 (2009).

¹⁰C. D. Carpentier and R. Nitsche, *Mater. Res. Bull.* **9**, 1097 (1974); K. Z. Rushchanskii, Y. M. Vysochanskii, and D. Strauch, *Phys. Rev. Lett.* **99**, 207601 (2007); I. Tyagur, *Funct. Mater. Lett.* **2**, 95 (2009).

¹¹M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).

¹²G. Dittmar and H. Schaefer, *Zeitschrift fuer Naturforschung, Teil B. Anorganische Chemie, Organische Chemie* **29**, 312 (1979); B. Scott, M. Pressprich, R. D. Willet, and D. A. Cleary, *J. Solid. State Chem.* **96**, 294 (1992).

¹³Y. I. Tyagur and E. I. Gerzanich, *Sov. Phys. Crystallogr.* **29**, 563 (1984); Y. Tyagur and I. Tyagur, *High Press. Res.* **28**, 607 (2008); O. Andersson, O. Chobal, I. Rizak, and V. Rizak, *Phys. Rev. B* **80**, 174107 (2009); O. Andersson, O. Chobal, I. Rizak, V. Rizak, and V. Sabadosh, *Phys. Rev. B* **83**, 134121 (2011).

¹⁴A. G. Slivka, *Ukr. J. Phys. Opt.* **2**, 171 (2001).

¹⁵V. V. Shchennikov, S. V. Ovsyannikov, A. Y. Derevskov, and V. V. Shchennikov, Jr., *J. Phys. Chem. Solids* **67**, 2203 (2006); V. V. Shchennikov, S. V. Ovsyannikov, and A. Y. Manakov, *J. Phys. Chem. Solids* **71**, 1168 (2010).

¹⁶S. V. Ovsyannikov and V. V. Shchennikov, *Appl. Phys. Lett.* **90**, 122103 (2007); S. V. Ovsyannikov, V. V. Shchennikov, A. E. Karkin, A. Polian, O. Briot, S. Ruffenach, B. Gil, and M. Moret, *Appl. Phys. Lett.* **97**, 032105 (2010); S. V. Ovsyannikov, V. V. Shchennikov, M. A. Shvetsova, L. S. Dubrovinsky, and A. Polian, *Phys. Rev. B* **81**, 060101 (2010).

¹⁷See supplementary material at <http://dx.doi.org/10.1063/1.3662926> for details of the experiments and the crystal structure refinement.

¹⁸S. V. Ovsyannikov, X. Wu, V. V. Shchennikov, A. E. Karkin, N. Dubrovinskaya, G. Garbarino, and L. Dubrovinsky, *J. Phys.: Condens. Matter* **22**, 375402 (2010).

¹⁹K. Seeger, *Semiconductor Physics* (Springer, Wien, NY, 1973).

²⁰D. M. Bercha, A. A. Grabar, L. Y. Kharkhalis, O. B. Mitin, and A. I. Bercha, *Phys. Solid State* **39**, 1081 (1997).

²¹S. V. Ovsyannikov and V. V. Shchennikov, *Chem. Mater.* **22**, 635 (2010); S. V. Ovsyannikov, V. V. Shchennikov, G. V. Vorontsov, A. Y. Manakov, A. Y. Likhacheva, and V. A. Kulbachinskii, *J. Appl. Phys.* **104**, 053713 (2008).

²²K. Z. Rushchanskii, Yu. M. Vysochanskii, V. B. Cajipe, and X. Bourdon, *Phys. Rev. B* **73**, 115115 (2006).

²³V. Gomonnai, Yu. M. Azhniuk, Yu. M. Vysochanskii, A. A. Kikineshi, M. Kis-Varga, L. Daroczy, I. P. Prits, and I. M. Voynarovych, *J. Phys.: Condens. Matter* **15**, 6381 (2003).

²⁴S. H. Wei and A. Zunger, *Phys. Rev. B* **60**, 5404 (1999).

²⁵H. Luo, S. Desgreniers, Y. K. Vohra, and A. L. Ruoff, *Phys. Rev. Lett.* **67**, 2998 (1991).

²⁶V. V. Shchennikov and S. V. Ovsyannikov, *Phys. Status Solidi B* **239**, 399 (2003).