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DISTORTIONS OF VACANCY COMPLEXES IN n-GaAs AND THEIR REORIENTATION UNDER UNIAXIAL STRESS

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Abstract. The results of piezospectroscopic studies of broad photoluminescence bands with the maximum near 1.18 eV for the $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, $V_{Ga}Si_{Ga}$ and $V_{Ga}S_{As}$ complexes in n-GaAs doped with Te, Sn, Si or S are presented. It has been found that in the emitting state the $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, and $V_{Ga}Si_{Ga}$ complexes have an additional (Jahn–Teller) distortion along one of the equivalent $\langle 111 \rangle$ directions. This distortion is a reorientable one and may become aligned under external uniaxial pressure at a temperature as low as 2 K. In the case of GaAs:S no reorientable distortion was observed. It is shown that the complexes related to a broad photoluminescence band with the maximum near 0.95 eV in GaAs doped with the same donors have reorientable distortions, too.

Key words: polarization of photoluminescence, Jahn–Teller effect, distortions of complexes, reorientation, alignment.

Complexes containing vacancies (V) are very common defects in semiconductors. These are generated during the growth, doping and thermal treatment of crystals or under irradiation. One type of such complexes – the ones containing a vacancy and a shallow donor (D) in adjacent sites of the crystal lattice – has been found in $A^{II}B^{VI}$, $A^{III}B^{V}$ semiconductors and Si long ago. The electron and space structures of these pairs in Si have been studied thoroughly by means of ESR and ENDOR [1–3]. It has been found that in a neutral state the initial trigonal symmetry of $(V_{Si}D_{Si})^0$ is lowered to a monoclinic one (C_{1h}) due to the Jahn–Teller effect. The lowering of the initial symmetry of similar defects in $A^{II}B^{VI}$ has also been observed ($V^{-}_{Zn}Cl^{+}_{S}$ complex in ZnS [4]). Recent investigations of CdTe [5] by means of ODMR, however, have shown no distortion of the initial point group of the symmetry for $V^{-}_{Cd}Cl^{+}_{Te}$ (trigonal symmetry) and $V^{-}_{Cd}In^{+}_{Cd}$ (monoclinic symmetry). The reasons for the

absence of this common manifestation of the Jahn–Teller effect in these complexes have not been discussed.

Vacancy-shallow donor complexes ($V_{Ga}Te_{As}$, $V_{Ga}S_{As}$, $V_{Ga}Sn_{Ga}$, $V_{Ga}Si_{Ga}$, etc.) have also been identified [6, 7] in n-GaAs through their intensive wide photoluminescence (PL) bands with the maximum at the photon energy ($\hbar\omega$) near 1.18 eV (at temperatures (T) of 2–77 K). However, the problems concerning the existence of the Jahn–Teller distortions in these complexes as well as the phenomena related to their reorientation have not been solved experimentally. The situation is complicated due to the lack of ESR signals from these complexes in n-GaAs. The first investigation of PL polarization diagrams for $V_{Ga}Sn_{Ga}$ and $V_{Ga}Te_{As}$ in n-GaAs led the authors of [8] to a conclusion that both of these complexes in the absorbing as well as in the emitting states have trigonal symmetry. However, it seems that the measurements [8] were carried out with relatively large experimental errors which could make the observing of the symmetry lowering impossible. Similar measurements performed by us later [9–11] have shown that complex symmetry is monoclinic or lower.

In this paper, we are presenting the results on distortions of these complexes in n-GaAs doped with Te, Sn, Si or S, which have been obtained from the investigations of the piezospectroscopic behaviour of their PL bands. In addition, we report the results on distortions in other vacancy complexes giving rise to a PL band with the maximum near 0.95 eV in n-GaAs.

The low-temperature spectra of PL bands near 1.18 eV for n-GaAs doped with Te, Sn, Si or S are shown in Fig. 1. The techniques of doping and the concentrations of uncompensated shallow donors are given in the Table. PL was generated by interband excitation.

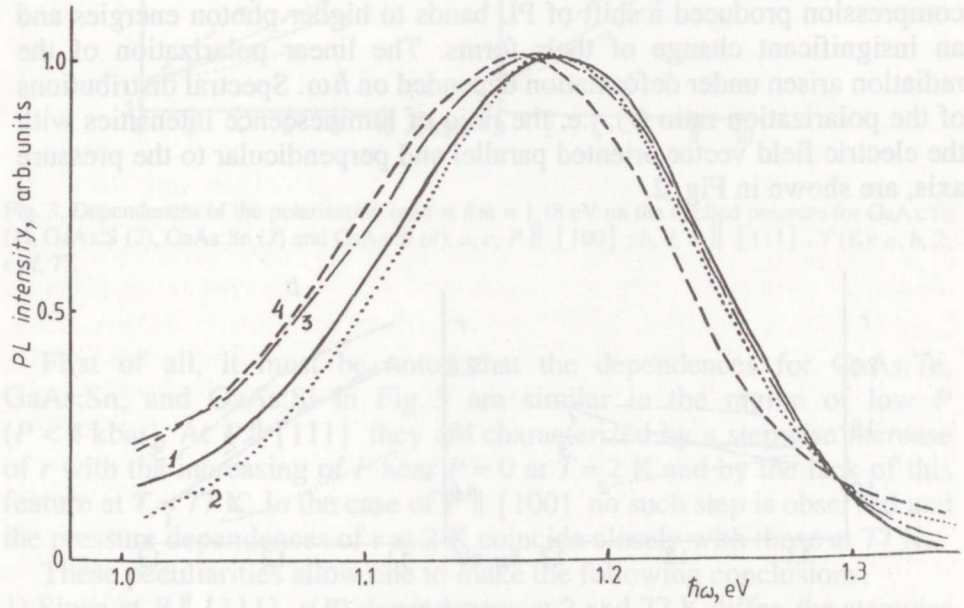

Fig. 1. Spectra of photoluminescence related to Ga vacancy-donor complexes in GaAs:Te (*1*), GaAs:S (*2*), GaAs:Sn (*3*), and GaAs:Si (*4*). $T = 2$ K.

Characterization of the samples under investigation

Shallow donor	Electron concentration at 300 K, cm^{-3}	Technique of doping
Te	$\sim 1\times10^{18}$	Doping of the melt during the process of growth by the Czochralski technique
Sn	$\sim 1.5\times10^{18}$	Doping of the melt during the process of growth by the Czochralski technique
Si	$\sim 1.5\times10^{18}$	Doping of the melt during the process of growth by the directed crystallization technique
S	$\sim 7\times10^{17}$	Diffusion from the vapour phase at 900°C in an evacuated ampoule

These bands for all types of shallow donors under investigation have nearly the same form and energy position. We have supposed [11] that the emitting and the ground state of these complexes are $(V_{Ga}^{2-}D^{+})^{-}$ and $(V_{Ga}^{3-}D^{+})^{2-}$, respectively. As already noted earlier [6], the PL peak energy for GaAs doped with group IV elements is by approximately 20 meV lower than for the one doped with group VI elements. This is due to the difference in the distance between the donor and the vacancy in $V_{Ga}D_{As}$ and $V_{Ga}D_{Ga}$ complexes.

In an attempt to observe the Jahn–Teller distortions of the complexes we studied the behaviour of their PL bands under uniaxial pressures (P) up to ~10 kbar at the temperatures of 2 and 77 K. In all instances uniaxial compression produced a shift of PL bands to higher photon energies and an insignificant change of their forms. The linear polarization of the radiation arisen under deformation depended on $\hbar\omega$. Spectral distributions of the polarization ratio (r), i.e. the ratio of luminescence intensities with the electric field vector oriented parallel and perpendicular to the pressure axis, are shown in Fig. 2.

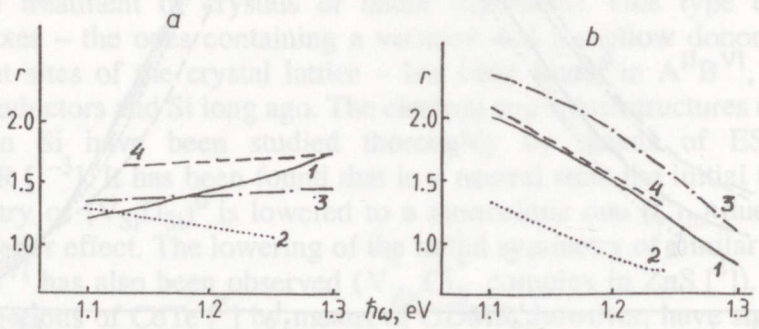

Fig. 2. Spectral dependences of the polarization ratio in the 1.18 eV-band of photoluminescence under uniaxial pressure for GaAs:Te (*1*), GaAs:S (*2*), GaAs:Sn (*3*), and GaAs:Si (*4*). $T = 2$ K. *a*, $P \parallel [100]$; *b*, $P \parallel [111]$. *P*: *1a, 2a, 3a, 4a, 4b* – 8 kbar; *1b, 2b, 3b* – 10 kbar.

Figure 3 presents the dependences of r at $\hbar\omega = 1.18$ eV on the value of pressure when $P \parallel [111]$ or $P \parallel [100]$ and $T = 2$ or 77 K. In the case of $P \parallel [110]$ the $r(P)$ dependences were qualitatively similar to those at $P \parallel [111]$. The dependences in Fig. 3 do not differ practically from the pressure dependences of the polarization ratio for the whole PL band (integrated polarization ratio r^*). The last one is governed by changes of the electron wave functions of the PL centres and/or of occupancy of their electron or configurational states due to uniaxial deformation.

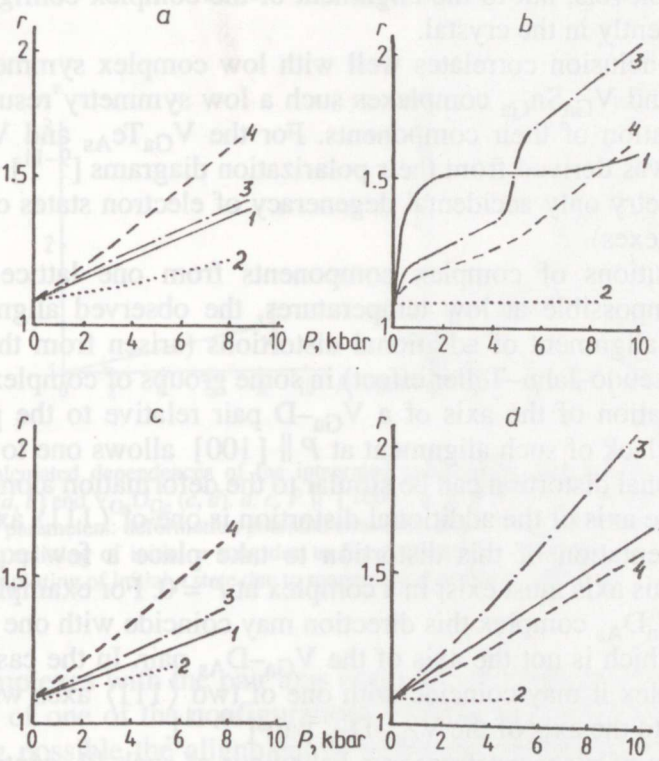

Fig. 3. Dependences of the polarization ratio at $\hbar\omega = 1.18$ eV on the applied pressure for GaAs:Te (*1*), GaAs:S (*2*), GaAs:Sn (*3*) and GaAs:Si (*4*). *a*, *c*, $P \parallel [100]$; *b*, *d*, $P \parallel [111]$. T (K): *a*, *b*, 2; *c*, *d*, 77.

First of all, it must be noted that the dependences for GaAs:Te, GaAs:Sn, and GaAs:Si in Fig. 3 are similar in the region of low P ($P < 4$ kbar). At $P \parallel [111]$ they are characterized by a stepwise increase of r with the increasing of P near $P = 0$ at $T = 2$ K and by the lack of this feature at $T = 77$ K. In the case of $P \parallel [100]$ no such step is observed and the pressure dependences of r at 2 K coincide closely with those at 77 K.

These peculiarities allow one to make the following conclusions:

1) Since at $P \parallel [111]$ $r(P)$ dependences at 2 and 77 K differ, the stepwise increase of r near $P = 0$ arises from the change of occupancy of split

electron sublevels or of space configurations of a complex in the emitting state which are equivalent at $P = 0$. This implies an alignment of some distortions of the complex.

2) Close coincidence of $r(P)$ dependences at 2 and 77 K in the case of $P \parallel [100]$ implies the lack of such occupancy changes. It seems likely that the smooth increase of r in this case is mainly related to the change of the electron wave functions of PL centres due to external deformation.

3) A strongly anisotropic piezospectroscopic behaviour of PL of the complex implies that the stepwise change of PL polarization observed at $P \parallel [111]$ (and $P \parallel [110]$) is related not to the change of the occupancy of electron sublevels, but to the alignment of the complex configurations oriented differently in the crystal.

The last conclusion correlates well with low complex symmetry. For the $V_{Ga}Si_{Ga}$ and $V_{Ga}Sn_{Ga}$ complexes such a low symmetry results from the initial location of their components. For the $V_{Ga}Te_{As}$ and $V_{Ga}Sn_{Ga}$ complexes it was derived from their polarization diagrams [9–11]. (Due to the low symmetry only accidental degeneracy of electron states can exist in these complexes).

Since transitions of complex components from one lattice site to another are impossible at low temperatures, the observed alignment is related to the alignment of additional distortions (arisen from the Jahn–Teller or the pseudo-Jahn–Teller effect) in some groups of complexes with definite orientation of the axis of a V_{Ga}–D pair relative to the pressure direction. The lack of such alignment at $P \parallel [100]$ allows one to suggest that the additional distortion can be similar to the deformation along one of $\langle 111 \rangle$ axes (the axis of the additional distortion is one of $\langle 111 \rangle$ axes).

For a reorientation of this distortion to take place a few equivalent directions of this axis must exist in a complex at $P = 0$. For example, in the case of the $V_{Ga}D_{As}$ complex this direction may coincide with one of three $\langle 111 \rangle$ axes, which is not the axis of the V_{Ga}–D_{As} pair. In the case of the $V_{Ga}D_{Ga}$ complex it may coincide with one of two $\langle 111 \rangle$ axes which are perpendicular to the axis of the V_{Ga}–D_{Ga} pair [10, 11].

Calculations of piezospectroscopic behaviour of such PL centres have been carried out in a simple model [10, 11]. These suggest that the initial wave functions of the emitting and the ground state of the centre are those of *p*- and *s*-type, respectively. The lowering of the centre symmetry due to complex formation (fixed distortion) and Jahn–Teller distortions (reorientable distortions) have been described as uniaxial deformations. This has given a qualitative agreement with experiment at reasonable values of the parameters describing distortions and the effect of uniaxial pressure (see, e.g., Fig. 4).

It should be noted that the additional distortion directed along one of the $\langle 111 \rangle$ axes may also explain the second step of the pressure dependence of the polarization ratio observed at $P \parallel [111]$ and $T = 2$ K for $V_{Ga}Sn_{Ga}$ (Fig. 3) [12]. It may be supposed that the complex configuration with the direction of the Jahn–Teller distortion not perpendicular to the pair axis is possible, in principle, but is unstable because it has higher total energy as shown in Fig. 5*c*, *d*. At $P \parallel [111]$ for

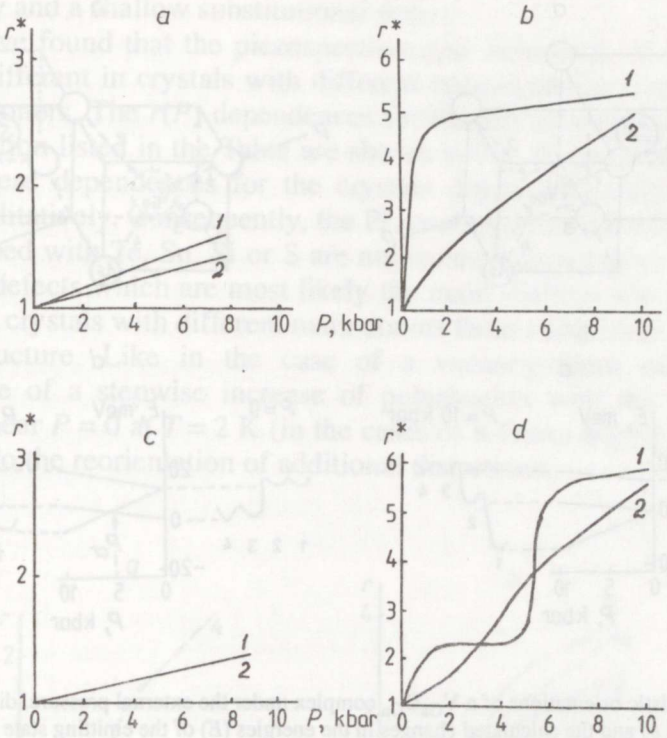

Fig. 4. Calculated dependences of the integrated polarization ratio on the applied pressure for $V_{Ga}D_{As}$ (*a*, *b*) and $V_{Ga}D_{Ga}$ (*c*, *d*). *a*, *c*, $P \parallel [100]$; *b*, *d*, $P \parallel [111]$. T (K): *1* – 6, *2* – 77. Values of parameters: deformation potential constants: $B = -0.8$ eV, $D = -2$ eV; spin–orbit splitting: 150 meV; splitting of initial p state due to fixed distortion: –38 meV for $V_{Ga}D_{As}$, –23 meV for $V_{Ga}D_{Ga}$; splitting of initial p state due to reorienting distortion: 150 meV.

the complexes with the pair axis normal to the pressure direction the total energy of one of the configurations existing at $P = 0$ decreases (Fig. 5*c*), making possible the alignment of additional distortions in such group of complexes. It gives rise to a stepwise increase of polarization near $P = 0$. For the complexes with the pair axis lying in the [110] plane passing through the pressure direction, two configurations realizable at $P = 0$ remain equivalent at the increase of P, but their total energy increases (Fig. 5*d*). At the same time, for these complexes the energy of one of the two configurations unstable at $P = 0$ decreases (Fig. 5*d*). When the value of pressure is higher than some P_{cr} value, the total energy of this configuration becomes the lowest one. It gives rise to the alignment of distortions in this group of complexes and to the second step in the $r(P)$ dependence (Fig. 3). As this takes place, the symmetry of this group of complexes improves from triclinic to monoclinic. The lack of the second step in the $r(P)$ dependence for the $V_{Ga}Te_{As}$ complexes up to 10 kbar in this model is explained by a stronger effect of the donor on the state of V_{Ga} (by the higher value of the splitting due to the fixed distortion for this complex).

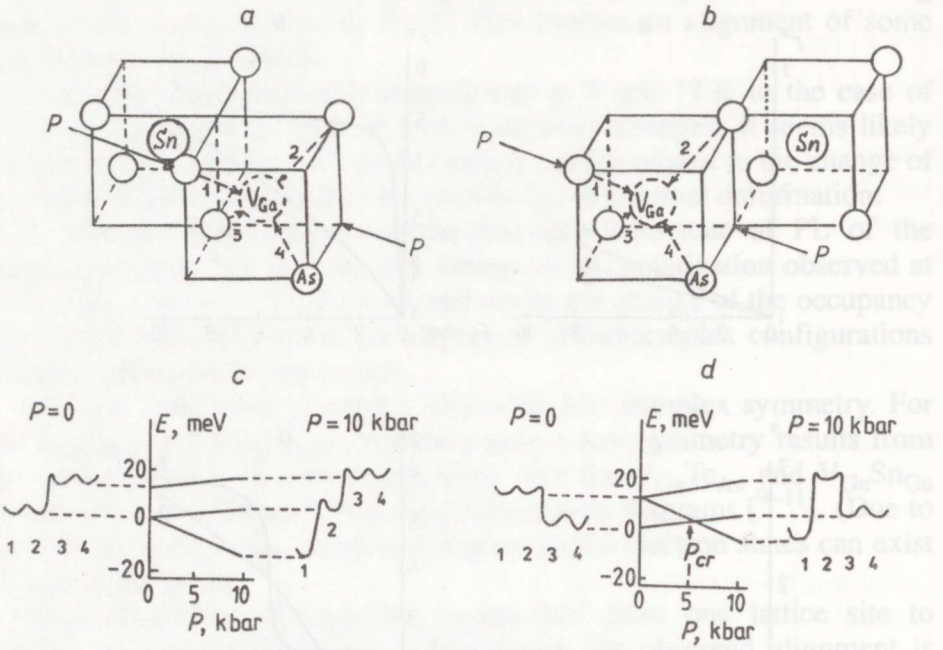

Fig. 5. Characteristic orientations of a $V_{Ga}D_{Ga}$ complex under the external pressure, directed along the [111] axis (*a*, *b*) and the calculated changes in the energies (*E*) of the emitting state for different complex configurations (*c*, *d*). The arrows 1–4 identify the directions of the reorientable distortion, related to adiabatic potential minima 1–4, shown schematically in 5*c* and 5*d* for $P = 0$ and $P = 10$ kbar. For the calculation of $E(P)$ for a $V_{Ga}D_{Ga}$ complex the values of complex parameters of Fig. 4 have been used.

Hence, the data presented above show that the centres giving rise to a broad PL band with the maximum at $\hbar\omega \sqsubset 1.18$ eV in n-GaAs doped with Te, Sn or Si ($V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, $V_{Ga}Si_{Ga}$ complexes) have an additional distortion in the emitting state. This distortion may have a few equivalent directions in a single complex. It is able to reorient itself at ~2 K, at least under the conditions of PL observation, and to become aligned under uniaxial pressure along [111] or [110] axis. Since in the $V_{Ga}^{2-}D^{+}$ complex electrons occupy vacancy-like orbitals, we suppose that the distortions of the $(V_{Ga}^{2-}D^{+})^{-}$ complexes arise from the distortion of the isolated V_{Ga}^{2-} which binds one hole.

Another complex involving vacancies in n-GaAs seems to be a defect responsible for a broad PL band at $\hbar\omega \sqsubset 0.95$ eV [13–16]. In the crystals with a moderate concentration of shallow donors ($N_D \leq 10^{17}$ cm^{-3}) this PL gives rise to an isolated band with the peak near ~0.95 eV, whereas in the crystals with a high donor concentration ($N_D \geq 10^{18}$ cm^{-3}) this PL manifests itself as a shoulder on the long-wave edge of the 1.18 eV-band (see, e.g., [17]). Proceeding from the PL intensity dependences of this and other PL bands on the conditions of the crystal growth, heat treatment and doping, several possible structures of this defect have been proposed. In particular, the authors of [13–15] have claimed this complex to be a

divacancy ($V_{Ga}V_{As}$). In a more recent paper [16] it has been related to a divacancy and a shallow substitutional donor.

We have found that the piezospectroscopic behaviour of the 0.95 eV-band is different in crystals with different concentrations and/or types of shallow donors. The $r(P)$ dependences for the samples with a high donor concentration listed in the Table are shown in Fig. 6. As illustrated in the figure, these dependences for the crystals doped with different donors differ qualitatively. Consequently, the PL centres under investigation in n-GaAs doped with Te, Sn, Si or S are not isolated divacancies but involve different defects which are most likely the main shallow donors. It seems that in the crystals with different main donors these complexes differ in the space structure. Like in the case of a vacancy-donor complex, the occurrence of a stepwise increase of polarization with the increase of pressure near $P = 0$ at $T = 2$ K (in the cases of n-GaAs doped with Te, Si, S) points to the reorientation of additional distortions.

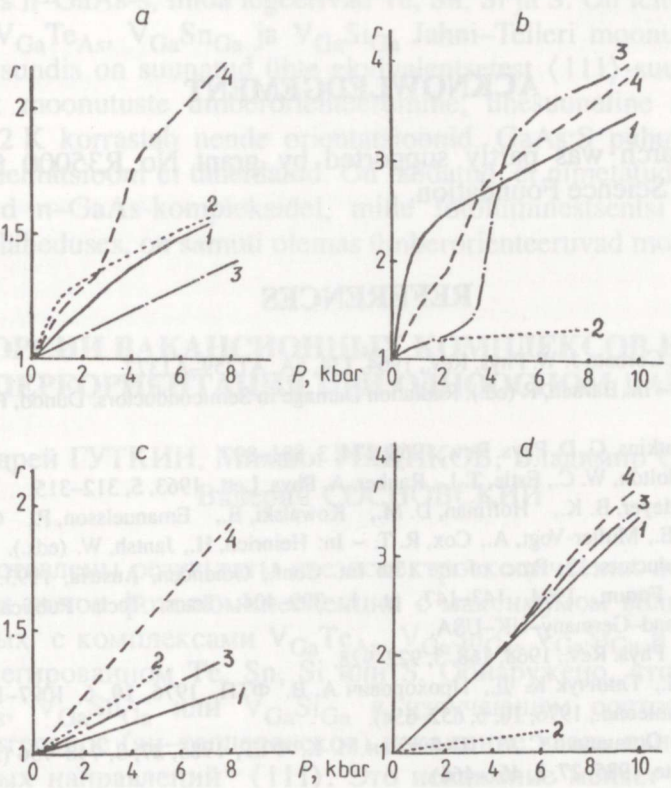

Fig. 6. Dependences of the polarization ratio at $\hbar\omega = 0.95$ eV on the applied pressure for GaAs:Te (*1*), GaAs:S (2), GaAs:Sn (*3*), and GaAs:Si (*4*). *a*, *c*, $P \parallel [100]$; *b*, *d*, $P \parallel [111]$. T (K): *a*, *b*, 2; *c*, *d*, 77.

For the complexes in n-GaAs:Te these distortions appear to be similar to those of the $V_{Ga}Te_{As}$ complexes, because their alignment at $P \parallel [100]$ has not been observed (Fig. 6) [17]. For the complexes in n-GaAs:Sn a

similar distortion directed along ⟨111⟩ axis is apparently not reorientable at $P = 0$, but it may become reorientable at $P = P_{cr}$ [17] (Fig. 6). For the complexes in n-GaAs:S and n-GaAs:Si the experimental results are complicated due to the existence of a stepwise increase of polarization near $P \sqsubset 0$ at $P \parallel [100]$ (see Fig. 6). However, this does not seem to rule out the presence of similar reorientable distortions.

Thus, the piezospectroscopic study of the broad PL bands related to the complexes involving vacancies and donors in n-GaAs, doped with Te, Sn, Si or S shows that most of these complexes in emitting states have an additional distortion. This distortion for the $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, and $V_{Ga}Si_{Ga}$ complexes appears to arise from the Jahn–Teller (or pseudo-Jahn–Teller) effect and has several equivalent orientations. It is similar to the deformation along one of the ⟨111⟩ axes. It is reorientable at liquid helium temperature and can be aligned under uniaxial pressures. Analogous reorientable distortions occur in the emitting states of the complexes related to a broad PL band at $\hbar\omega \sqsubset 0.95$ eV in n-GaAs doped with some group IV and group VI elements.

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VAKANTSKOMPLEKSIDE MOONUTUSED n–GaAs-s JA NENDE ÜMBERORIENTEERUMINE ÜHESUUNALISE RÕHU MÕJUL

Andrei GUTKIN, Mihhail REŠTŠIKOV, Vladimir SEDOV, Valeri SOSNOVSKI

Piesospektroskoopiliselt on uuritud komplekside $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, $V_{Ga}Si_{Ga}$ ja $V_{Ga}S_{As}$ fotoluminestsentsi laiu ribasid maksimumiga 1,18 eV läheduses n–GaAs-s, mida legeerivad Te, Sn, Si ja S. On leitud, et komplekside $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$ ja $V_{Ga}Si_{Ga}$ Jahni–Telleri moonutused ergastatud seisundis on suunatud ühte ekvivalentsetest ⟨111⟩-suundadest. On võimalik moonutuste ümberorienteerumine; ühesuunaline rõhk temperatuuril 2 K korrastab nende orientatsioonid. GaAs:S puhul moonutuse ümberorientatsiooni ei täheldatud. On näidatud, et nimetatud doonoritega legeeritud n–GaAs-kompleksidel, mille fotoluminestsentsi lai riba on 0,95 eV läheduses, on samuti olemas ümberorienteeruvad moonutused.

ДИСТОРСИИ ВАКАНСИОННЫХ КОМПЛЕКСОВ В n-GaAs И ИХ ПЕРЕОРИЕНТАЦИЯ ПРИ ОДНООСНОМ ДАВЛЕНИИ

Андрей ГУТКИН, Михаил РЕЩИКОВ, Владимир СЕДОВ, Валерий СОСНОВСКИЙ

Представлены результаты пьезоспектроскопических исследований широких полос фотолюминесценции с максимумом вблизи 1,18 эВ, связанных с комплексами $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$, $V_{Ga}Si_{Ga}$ и $V_{Ga}S_{As}$ в n-GaAs, легированном Te, Sn, Si или S. Обнаружено, что комплексы $V_{Ga}Te_{As}$, $V_{Ga}Sn_{Ga}$ или $V_{Ga}Si_{Ga}$ в излучающем состоянии имеют дополнительное (ян–теллеровское) искажение вдоль одного из эквивалентных направлений ⟨111⟩. Это искажение меняет ориентацию и может выстраиваться под влиянием одноосных давлений при температуре 2 K. В случае GaAs:S никакой переориентирующейся дисторсии не наблюдалось. Показано, что комплексы, вызывающие широкую полосу фотолюминесценции с максимумом вблизи 0,95 эВ в n-GaAs, легированном указанными выше донорами, также имеют переориентирующиеся дисторсии.