VIBRATIONAL MODES OF NATIVE DEFECTS IN A²B⁶ SEMICONDUCTORS[1]

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Peculiarities of the vibrational spectra of several A²B⁶ semiconductors with cation and anion vacancies and antisite defects are studied theoretically. The energy of vacancy resonance vibrations and local modes of antisite defects are determined for CdTe, ZnTe, ZnSe, ZnS.

Crystal defects are known to determine important characteristics of semiconductors and semiconductor devices. Numerous experimental data, as the rule, do not give the possibility to distinguish a native defect from other defects of crystals. Therefore, for identification of a defect, it is important to know its energy spectrum. In the present work, we studied theoretically peculiarities of the vibrational spectra of cation and anion vacancies and antisite defects in several semiconductors of A²B⁶ group. The vibrational properties were studied by the Green's function method [1]. For calculation of Green's functions of a crystal, we employ the rigid ion model with eleven parameters (RIM11) [2], that takes into account both long-range and short-range interactions. The model was used with great success in the theoretical studies of phonon dispersion curves of A²B⁶ semiconductors [1, 2]. The model parameters were deduced from available data for A²B⁶ semiconductors.

Defects of crystal structure give rise to new vibrations in the phonon spectrum of the crystal. If the energies of vibrations fall into the continuous phonon spectrum of the crystal, these vibrations are resonant, otherwise, if the energies lay in forbidden zones, the vibrations are local [1]. Vibrational spectra of point defects in cubic semiconductors were studied in [3]. It is assumed that atomic interactions are not strongly affected by the presence of a defect, therefore the effect can be described as a small perturbation arising from changes in atomic masses (the difference between the masses of host and substituent atoms) and nearest neighbour force constants [4]. Let $\hat{V}$ be the perturbation

matrix due to the defect and $\hat{G}$ - Green's function matrix of an ideal crystal. New states that arise due to the perturbation are determined by the condition

$$\text{Re}\{\det(I - \hat{G}\hat{V})\} = 0. \tag{1}$$

Equation (1) was solved in the basis of atomic displacements from equilibrium positions. The perturbation matrix has nonzero elements only in the "defect space" of size $3n \times 3n$, where n is the number of crystal sites directly perturbed by the defect. The dimension of determinant (1) is 3×3, if only mass changes are taken into account, and 15×15, if we also allow for a change in the force constants A and B which describe the interaction with four nearest neighbours. It is assumed that constants A and B are similarly affected by the presence of the defect. Then, we can characterize these changes by a single parameter $t = (f - f')/f$, where $f = A, B$. Solution of (1) is considerably simplified if the symmetry of the defect site is taken into account. The total representation of Γ_{def} in the 15-dimensional space can be decomposed into the irreducible representations A_1, E, F_1, F_2 of the point group T_d: $\Gamma_{def} = A_1 + E + F_1 + 3F_2$. These relationships specify the symmetry and number of vibrations associated with point defects in a zinc-blence structure crystal.

Taking into account the symmetry of the system the determinant $\det(I - \hat{G}\hat{V})$ can be decomposed into blocks corresponding to the irreducible representation of the group T_d:

$$\det(I - \hat{G}\hat{V}) = \prod_{\mu\Gamma}(\det(I - \hat{g}_{\mu\Gamma}\hat{v}_{\mu\Gamma}). \tag{2}$$

Here, $\hat{g}_{\mu\Gamma}$ is the Green's function of the perfect crystal projected on the defect space; $\hat{v}_{\mu\Gamma}$ - is the perturbation defect matrix for a given irreducible representation. Details about Green's function calculations can be found in [3, 4]. The change in atomic masses for the defect
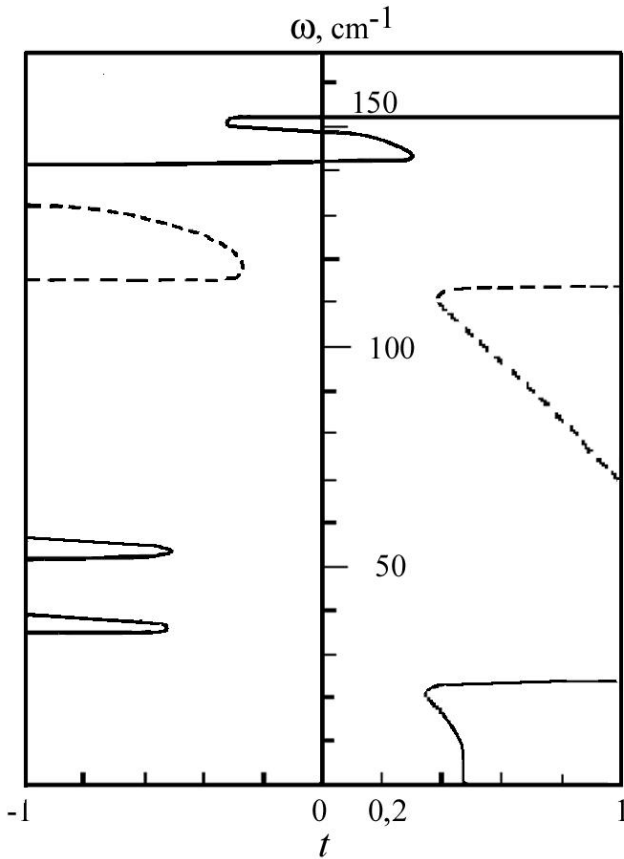

Fig. 1. Energy of resonance vibrations as the function of a change of the nearest neighbour force constants for a cation vacancy in CdTe. Solid lines — Γ_5 vibrations; dashed lines — Γ_1 vibrations

system can be taken exactly as the difference between the mass of host and substituent atoms, whereas the change of nearest neighbour force constants is considered as a parameter, in dependence of which the energy of vibrations and their half-width were studied.

The solutions of Eq. (1) that fall into the continuous phonon spectrum of the crystal give the energies of resonance vibrations. The presence of a resonance vibration results in a redistribution of the density of states within the continuous vibration spectrum of the crystal. Resonance vibrations, unlike local vibrations, have finite half-width which is given by relation

$$\gamma_r^\Gamma = \frac{1}{\omega_r}|\frac{Im(I - \hat{g}_{\mu\Gamma}\hat{v}_{\mu\Gamma})}{\frac{d}{d\omega^2}(Re(I - \hat{g}_{\mu\Gamma}\hat{v}_{\mu\Gamma}))}|_{\omega=\omega_r}, \qquad (3)$$

where ω_r is energy of resonance vibrations.

Performing the calculation of the energy of a localized state, caused by a vacancy, we put the mass of a defect to zero. Calculations show that, in the case of

a vacancy in A^2B^6 semiconductors, there are no local modes, whose energies lay above the maximum energy of the unperturbed phonon spectrum. Vacancies give resonance states of Γ_1 and Γ_5 symmetry. Γ_1 vibration involves the neighbouring atoms only in motion and is observed at a certain change of the force constants, whereas, for Γ_5 vibration, there is no restriction on t.

The calculated energies of resonant Γ_5 and Γ_1 vibrations for a cation vacancy in CdTe (as an example) are presented in Fig.1 as a function of the nearest neighbour force constants. It is worth to note that we take into account only vibrations, whose half-width is much less than the maximal energy of phonons in the unperturbed semiconductor. Cation vacancies in all semiconductors give a resonance state in the optical region of the crystal phonon spectrum between two peaks of the phonon density of states. Consider a vacancy in CdTe in more detail. As follows from the calculations, the energy of the vibration caused by a cation vacancy at $t = 0$ is equal to 148 cm^{-1}. With a change of the force constants within the limits $-0.33 < t < 0.31$, the energy of the vibration is not changed significantly: from 151 cm^{-1} at $t = -0.33$ to 144 cm^{-1} at $t = 0.33$, and, at $|t| > 0.35$, the vibration disappears. The same conclusions can be made for other semiconductors. The energy of the discussed above resonant vibration is: 178 cm^{-1} for ZnTe, 230 cm^{-1} for ZnSe, 334 cm^{-1} for ZnS. Besides, for ZnTe and ZnS, there are also Γ_5 resonant states in the region of transverse acoustic phonons (the energy of vibrations: 78 cm^{-1} for ZnTe and 133 cm^{-1} for ZnS). For all semiconductors, the low-energy vibration is observed, whose energy is lower than the energy position of the first peak of the phonon density of states. This state takes place at a quite great value of the parameter t.

An anion vacancy unlike a cation one does not give resonant Γ_5 states in the optical region of the phonon spectrum. For all semiconductors, vibrations in the region of longitudinal and transverse acoustic phonons are observed. For ZnS, the situation is opposite. The general picture of localized states due to cation and anion vacancies for ZnS differ from those for other semiconductors. It is caused by the fact that the

T a b l e. Energy of resonance Γ_5 vibrations ω_{Γ_5} (cm^{-1}) for cation and anion vacancy in A^2B^6 semiconductors ($t = 0$)

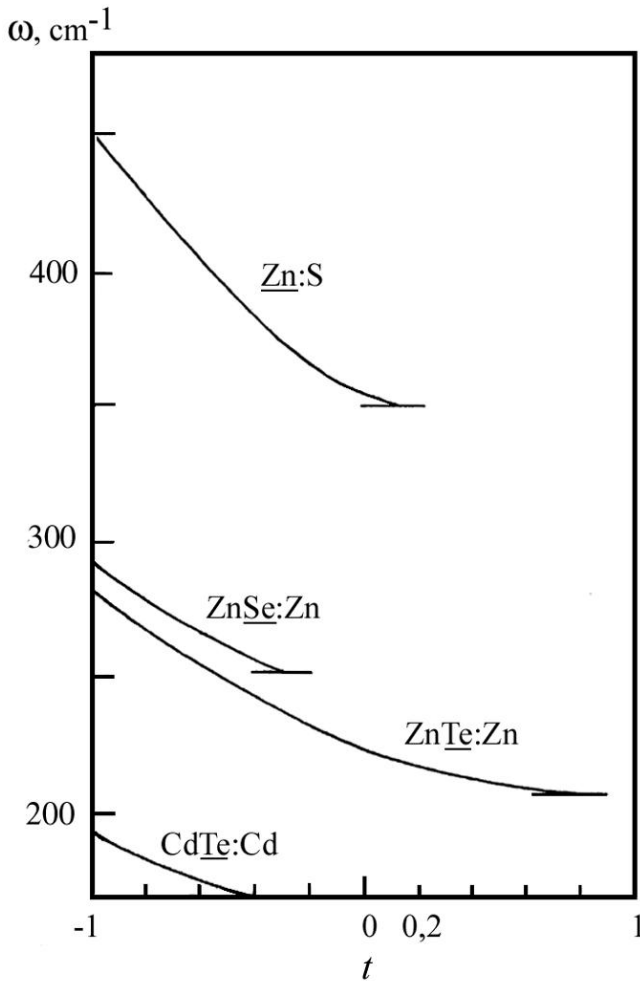| CdTe cation	CdTe anion	ZnTe cation	ZnTe anion	ZnSe cation	ZnSe anion	ZnS cation	ZnS anion
142	52	72	130	213	92	118	306
148	56	78	141	230	101	133	323
154	114	176	175	237	170	198	338
	126	178			188	260	
						334	

Fig. 2. Energy of local vibrations as the function of a change of the nearest neighbour force constants for antisite defects in A^2B^6 semiconductors.

where the mass of the substitution atom is less than the mass of the host atom. Therefore, for studied A^2B^6 semiconductors, local modes are observed in the case of an anion antisite defect in CdTe, ZnTe and ZnSe, and a cation antisite defect in ZnS. The energy of these vibrations as the function of a change of the force constants is presented in Fig.2. The vibrations are observed at negative values of the parameter t, which means that an enforcement of force constants takes place due to the defect. For CdTe, this enforcement is quite large for $t < -0.4$. For ZnTe practically at all values of the parameter t, one can expect the existence of a local mode due to the antisite defect.

Having an information about characteristic localized states above the continuous phonon spectrum and using the presented results, it is possible to identify the antisite defect in the semiconductor.

1. *Maradudin A.A., Montrall E.W., Weiss G.H., Ipatova I.P.* Theory of Lattice Dynamics in the Harmonic Approximation. – New York, 1971.

2. *Kunc K., Balkanski M., Nusimovici M.A.* // Phys. status solidi. (b). – 1975. – **71**. – N 1. – P. 341–349.

3. *Grimm A., Maradudin A.A., Ipatova I.P., Subashiev A.V.* // J. Phys. Chem. Solids. – 1972. – **33**. – N 4. – P. 775–796.

4. *Melnichuk S.V., Chernov V.M., Yurijchuk I.M.* // Fiz.Techn.Poluprov. – 1991. – **25**, N 6. – P. 876–879.

relation between the masses in ZnS is greater than unity, whereas, for CdTe, ZnTe and ZnSe, it is less than unity.

Resonant Γ_1 vibrations caused by a cation vacancy are observed only in the region of longitudinal acoustic phonons, and an anion vacancy gives Γ_1 vibrations in the region of optical and transverse acoustic phonons. For ZnS, the situation is again opposite. Note that Γ_1 vibrations take place, as the rule, at $|t| > 0.35$.

So, the obtained results give the energy regions where one can observe possible vacancy resonant vibrations. The change of the nearest neighbour force constants, which appears due to a vacancy, can also be estimated.

Antisite defects give rise to local vibrations whose energies lay above the continuous phonon spectrum of the crystal. These modes take place only in the case

КОЛИВАЛЬНІ СТАНИ ВЛАСНИХ ДЕФЕКТІВ
У НАПІВПРОВІДНИКАХ ГРУПИ A^2B^6

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Р е з ю м е

Теоретично досліджено особливості коливального спектра ряду напівпровідників групи A^2B^6 у випадку наявності в них ізольованих катіонних та аніонних вакансій, а також антивузлових дефектів. Визначено енергетичні області можливого виникнення в напівпровідниках CdTe, ZnTe, ZnSe, ZnS резонансних коливань, зумовлених наявністю вакансій, і локальних коливань, зумовлених антивузловими дефектами.

КОЛЕБАТЕЛЬНЫЕ СОСТОЯНИЯ СОБСТВЕННЫХ
ДЕФЕКТОВ В ПОЛУПРОВОДНИКАХ ГРУППЫ A^2B^6

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Р е з ю м е

Теоретически исследованы особенности колебательного спектра ряда полупроводников группы A^2B^6 в случае наличия в них изолированных катионных и анионных вакансий, а также антиузельных дефектов. Определены энергетические области возможного возникновения в полупроводниках CdTe, ZnTe, ZnSe, ZnS резонансных колебаний, обусловленных вакансиями, и локальных колебаний вследствие антиузельных дефектов.