Proc. Estonian Acad. Sci. Phys. Math., 1995, 44, 2/3, 187–193
https://doi.org/10.3176/phys.math.1995.2/3.07

EQUILIBRIUM DISTORTIONS OF A DEFECT WITH AN INITIAL ELECTRON STATE OF t_2 SYMMETRY: ROLES OF THE NONLINEARITY OF ELASTIC FORCES AND OF STATE OCCUPANCY

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Received 30 August 1994, accepted 17 April 1995

Abstract. It is shown that for the initial T_d symmetry of a defect complex the anharmonicity of elastic forces may lead to an equilibrium configuration formed by the interaction of electrons in the t_2 state simultaneously with both E and F_2 vibrations. The calculations have been carried through within one-particle approximation, taking into account the anharmonicity of the E mode by adding a term αQ_E^4 only. The relative contribution of αQ_E^4 to the total elastic energy of this equilibrium configuration depends on the relative efficiency of the interaction between the electrons trapped by the defect and E, F_2 modes. The filling of the initial t_2 state with 2–5 electrons decreases the value of α required for the transition to the configuration caused by E and F_2 vibrations. This may give a qualitative explanation of the experimental data for a vacancy in silicon.

Key words: Jahn–Teller effect, vacancy, many-particle effects.

It is well known that the initial electron wave functions of many single-point defects in cubic semiconductors have t_2 symmetry. The symmetry is broken by various internal interactions such as spin–orbit, electron–electron or electron–phonon (the Jahn–Teller effect) interaction. In the last case the initial T_d symmetry of a complex including a point defect and surrounding lattice atoms is lowered. One of such defects in diamond-like semiconductors (Ge, Si, A_3B_5) is a vacancy which has been studied both experimentally [1–3] and theoretically [4, 5] for many years. The vacancy in Si has been investigated most thoroughly. Namely, the initial T_d symmetry has been experimentally established to be altering due to the Jahn–Teller effect (JTE) for the charge states V^+, V^- [1, 2]. The equilibrium configuration of V^+ turns out to be determined by the interaction of the electron located in the t_2 state with the E vibronic mode only and the defect has tetragonal symmetry. In other words, one can say that the F_2 modes of the T_d complex are inactive. With the increasing of

the number of electrons located at the vacancy up to five (i.e. for the V^- case) the equilibrium symmetry of the vacancy becomes orthorhombic, C_{2v}. It means that the equilibrium distortions of the vacancy are formed by simultaneous interaction of these electrons with E and F_2 complex vibrations.

The first essential numerical calculations [4, 5] based on the local density approximation demonstrated a possibility of the existence of the local symmetry distortion observed experimentally for V^+ and V^- in silicon. However, these calculations do not give a clear physical explanation of the reasons and factors determining these distortions and their change with the vacancy charge. This gap is partially filled in [6]. This paper shows that the complicated character of the V^- distortion cannot be explained within the frame of a simple model supposing that electron–phonon interaction exceeds sufficiently the exchange interaction between bound electrons in the t_2 state. In an opposite case no linear JTE takes place, hence, this defect has to have T_d symmetry. The reason of the equilibrium C_{2v} symmetry of V^- may be the pseudo-JTE in case the exchange interaction is comparable with linear electron–phonon interaction.

However, there is another possibility for the appearance of absolute minima on the adiabatic potential surface due to simultaneous interaction of electrons with the E and the F_2 mode. This takes place if a nonlinear term is added to the defect elastic energy [7]. An early study of such a defect has been made with an electron state of e symmetry in cubic crystals [7]. The aim of this report is to consider the actual case for a vacancy in cubic semiconductors, when the initial single-electron state has t_2 symmetry and can be filled by one to six electrons. The exchange interaction will be neglected, i.e. we suppose that the electron–phonon interaction is considerably stronger than the exchange one. It implies that the inclusion of multi-particle effects reduces to the consideration of the Pauli principle.

Briefly speaking, the main result can be presented as follows. To qualitatively account for the experimental data for Si we have to add the term $\alpha(Q_2^2+Q_3^2)^2$ in the elastic energy U_0 where Q_2 and Q_3 are generalized coordinates of the E vibronic mode and α is a constant. When α is equal to zero and an electron occupies the t_2 state, the adiabatic potential minima have the energies [8]

$$W_E = -\frac{b'^2}{2k_E},\quad W_F = -\frac{2d'^2}{3k_F},\quad W_{E,F} = -\frac{b'^2}{8k_E} - \frac{d'^2}{2k_F},$$

where b' and d' are the coupling constants of an electron with the E and the F_2 mode, respectively, k_E and k_F are the elastic coefficients for the E and the F_2 vibration, respectively. If $\eta = \frac{4k_E}{3k_F}\frac{d'^2}{b'^2} < 1$, the inequality

$W_E < W_{E,F} < W_F$ takes place. It means that the defect in the equilibrium state is subjected to solely tetragonal distortion and the electron interacts with the E mode only (i.e. the generalized coordinates of F_2 modes are equal to zero). When $\eta > 1$, the equilibrium configuration of the complex is formed due to the interaction with the F_2 mode. Thus, in the case of $\alpha = 0$ the equilibrium configuration of the defect corresponds to the interaction with one of the vibronic modes only. The nonlinearity of the elastic force results in the increase of the effective coefficient of elasticity. This increase depends on the values of both Q_2, Q_3, and α. Since the extreme values, W_E, $W_{E,F}$, and W_F, are reached at different values of Q_2 and Q_3, the effective enhancement of k_E will be different at the different extrema of the adiabatic potential (AP). This may result in the $W_{E,F}$ minimum of AP becoming the absolute one if the condition $\eta < 1$ is fulfilled.

So, the equilibrium configuration of the defect will be formed by a simultaneous interaction with the E and the F_2 mode. In this case the vacancy has the C_{2v} point symmetry. The same situation can exist when several electrons occupy the t_2 state. The increase of the number of electrons gives the effective enhancement of the coupling constants b' and d'. Namely, in the case of two particles b' and d' are doubled. The increase of b' equals to the factor $\sqrt{3}$ for three electrons in the t_2 state. The enhancement of b' leads to the increase of the generalized coordinates Q_2 and Q_3 corresponding to the W_E and $W_{E,F}$ minima. Because of this, $W_{E,F}$ can become the absolute minimum at smaller values of α. This may give rise to the change of the type of equilibrium distortions with the increase of the number of bound electrons.

To illustrate this idea, we have considered the $t_2 \otimes (E + F_2)$ problem. A vacancy in a cubic semiconductor produces two single particle states. The ground one with a_1 symmetry lies usually in the valence band and is filled by two electrons. The other state, having t_2 symmetry, lies in the forbidden gap and can be occupied by several electrons. Hence the $t_2 \otimes (E + F_2)$ problem is topical for a vacancy in cubic semiconductors.

The Hamiltonian describing the linear JTE has the form

$$H_{lp} = -\frac{b'}{2}\left[(3L_z^2 - L^2)\,Q_3 + \sqrt{3}\,(L_x^2 - L_y^2)\,Q_2\right] - \\ - 2d'\left[[L_xL_y]\,Q_4 + [L_xL_z]\,Q_5 + [L_yL_z]\,Q_6\right]. \qquad (1)$$

Here L_i is the operator of the angular momentum projection for $L = 1$, Q_i is a generalized coordinate, $[L_iL_j] = (L_iL_j + L_jL_i)/2$. The elastic energy of the defect (U_0) is written as follows:

$$U_0 = \frac{k_E}{2}(Q_2^2 + Q_3^2) + \alpha(Q_2^2 + Q_3^2)^2 + \frac{k_F}{2}(Q_4^2 + Q_5^2 + Q_6^2). \qquad (2)$$

The adiabatic potential of the vacancy binding one electron is defined as sum of U_0 and the eigenvalues of the H_{lp}. As mentioned above, we have reduced the many-particle effects to the consideration of the Pauli principle. We have found four types of the AP extrema. Two of them (W_E, W_F) are formed by interaction between electrons and either the E mode or the F_2 mode. Others ($W^{(1)}_{E,F}$, $W^{(2)}_{E,F}$) are due to interaction between bound electrons and both the E and the F_2 mode simultaneously. The results of our calculations are shown in Figs. 1–3. The equilibrium state of the defect at any value of t corresponds to the lowest value of AP. Note, firstly, that within our simple model the case of one electron in t_2 state is similar to that of five electrons; the two-electron case is equivalent to the four-electron one. There is no linear JTE for the defect having zero or six electrons in the t_2 state. Secondly, Figs. 1–3 point clearly out the effective enhancement or b' for two and three bound electrons in comparison with the case of one electron. Our results (see Figs. 1–3) demonstrate the possibility of changing the symmetry of the defect with the degree of the t_2 state filling. We would like to emphasize that the change of complex symmetry requires no changes of the constants characterizing the interaction of a single bound electron with the phonons or changes of lattice elastic forces. For instance, let us study a case where $\eta = 0.5$ and $t = 0.3$. According to Fig. 1, the defect which has trapped one electron in the t_2 state will have tetragonal symmetry. According to our supposition for two electrons located at the defect in the t_2 state, the values of b', d', k_E, k_F and α are held constant and hence t and η are kept the same too. Then (Fig. 2) the symmetry of this defect reduces. A comparison of Figs. 1 and 2 shows that at $t = 0.3$ the stabilization energy of the C_2-axis for this defect is approximately equal to the stabilization energy of the S_4-axis direction for the tetragonal complex with one electron. When three particles are trapped by the defect (Fig. 3), the JTE becomes dynamic for all generalized coordinates if $t = 0.3$. However, the nonlinear electron–phonon interaction may result in the stabilization of some complex configurations. Coherent interaction of bound electrons with the E and the F_2 mode can be shown to set up the orthorhombic symmetry of the complex with three particles in the triplet state. (Note that the same effect may originate from anharmonism of elastic forces [7].)

Thus, we have demonstrated that the symmetry of a complex containing a vacancy and nearest lattice atoms can vary with the varying of the number of electrons trapped by the vacancy in the t_2 state only. This is a qualitative explanation of the symmetry observed in Si [1, 2] for V^+ (one trapped electron in the t_2 state) and for V^- (having three electrons in this state). It should be noted that this change of symmetry has to take place with the changing of the number of electrons from one to two in the t_2 state, i.e. with the transition from V^+ to V^0 in silicon. As can be seen from Figs. 1–3, in the case of $\eta = 0.5$ a defect's symmetry break may take place for $0.25 < t < 0.75$. An estimation shows that the relative contribution of the anharmonic term to the total elastic energy at the absolute $W_{E,F}$ minima of AP is less than 1/3 at $\eta = 0.5$ and decreases when η increases up to 1.

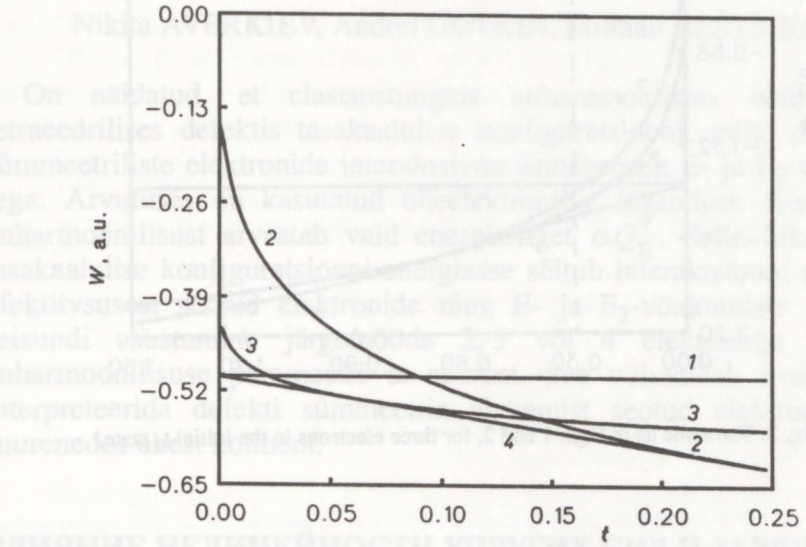

Fig. 1. Dependences of the extremum energies of the adiabatic potential for a defect with one trapped electron in the initial t_2 state on the parameter of nonlinear elastic forces $t = k_E^3 / 4\alpha b'^2$, $\eta = 0.5$. *1*, W_F; *2*, W_E; *3*, $W_{E,F}^{(1)}$, *4*, $W_{E,F}^{(2)}$.

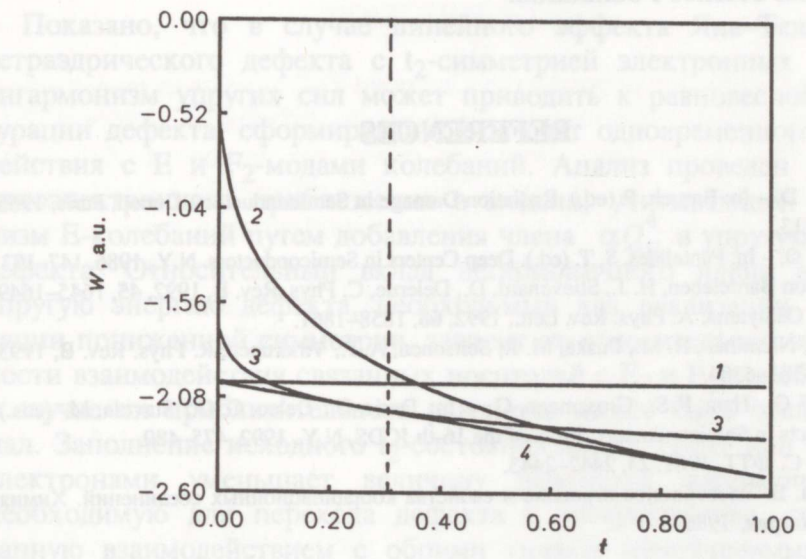

Fig. 2. The same as in Fig. 1, for two electrons in the initial t_2 state. The vertical line corresponds to $t = 0.3$.

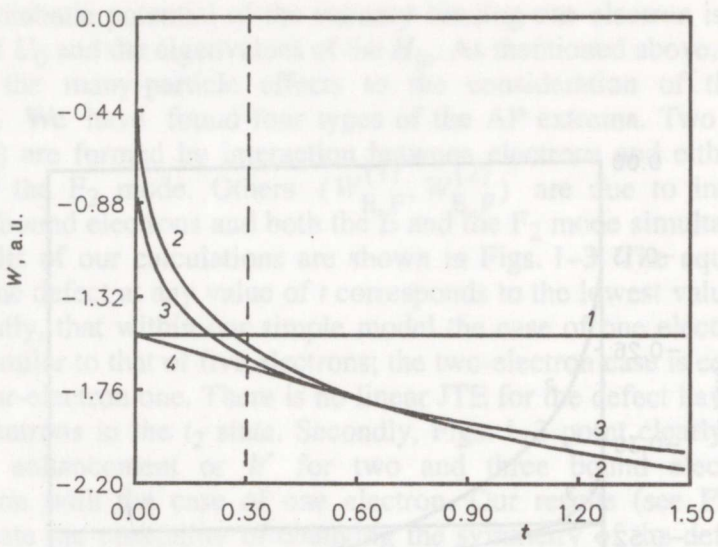

Fig. 3. The same as in Figs. 1 and 2, for three electrons in the initial t_2 state.

ACKNOWLEDGEMENTS

The authors would like to thank A. M. Monakhov for the help with the numerical calculations and M. J. Puska, R. M. Nieminen, and V. V. Emtsev for useful discussions.

The research was in part made possible by grant No. R35000 from the International Science Foundation.

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ELASTSUSTUNGIDE MITTELINEAARSUSE JA LAENGU SUURUSE ROLL t_2-SÜMMEETRILISE ALGELEKTRONOLEKUGA DEFEKTI TASAKAALULISTES MOONUTUSTES

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On näidatud, et elastsustungide anharmoonilisus võib tekitada tetraeedrilises defektis tasakaalulise konfiguratsiooni, mille määrab t_2-sümmeetriliste elektronide interaktsioon samaaegselt E- ja F_2-võnkumistega. Arvutuses on kasutatud üheelektronilist lähendust. E-võnkumise anharmoonilisust arvestab vaid energialiiget αQ_E^4. Selle liikme panus tasakaalulise konfiguratsiooni energiasse sõltub interaktsiooni suhtelisest efektiivsusest seotud elektronide ning E- ja F_2-võnkumiste vahel. t_2-seisundi asustamine järgemööda 2, 3 või 4 elektroniga vähendab anharmoonilisuse parameetri α suurust. See võimaldab kvalitatiivselt interpreteerida defekti sümmeetria alanemist seotud elektronide arvu suurenedes ühest kolmeni.

ВЛИЯНИЕ НЕЛИНЕЙНОСТИ УПРУГИХ СИЛ И ЗАРЯДОВОГО СОСТОЯНИЯ НА ТИП РАВНОВЕСНЫХ ИСКАЖЕНИЙ ДЕФЕКТОВ С t_2 -СИММЕТРИЕЙ ИСХОДНОГО ЭЛЕКТРОННОГО УРОВНЯ

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Показано, что в случае линейного эффекта Яна–Теллера для тетраэдрического дефекта с t_2-симметрией электронных функций ангармонизм упругих сил может приводить к равновесной конфигурации дефекта, сформированной за счет одновременного взаимодействия с E и F_2-модами колебаний. Анализ проведен в рамках одноэлектронного приближения в модели, учитывающей ангармонизм E-колебаний путем добавления члена αQ_E^4 в упругую энергию дефекта. Относительный вклад негармоничного члена в полную упругую энергию дефекта, необходимый для реализации конфигурации пониженной симметрии, зависит от относительной эффективности взаимодействия связанных носителей с E- и F_2-колебаниями и в случае их приблизительного равенства может быть сравнительно мал. Заполнение исходного t_2-состояния двумя, тремя или четырьмя электронами уменьшает величину параметра ангармонизма α, необходимую для перехода дефекта в конфигурацию, сформированную взаимодействием с обоими типами неполносимметричных колебаний. Это позволяет качественно объяснить последовательное понижение симметрии дефекта с исходным t_2-состоянием при изменении числа захваченных им электронов от 1 до 3, аналогичное наблюдавшемуся для вакансии в кремнии.