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The Grasshopper Effect in the Diamond Lattice

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The earlier notion of point defects in diamond-like crystals has by now undergone changes. The models of isolated vacancies and interstitials often prove inadequate for the interpretation of radiation effects /1, 2/. Theoretical and experimental results reveal new metastable configurations of point defects /3, 5/.

A thorough investigation was carried out of the metastable configuration /4, 5/ of point defects in silicon by means of the quantum-chemical simulation method /6/. The cluster computation was carried out by an US-1020 computer. The accuracy of energy estimation is 0.1 eV. The cluster model was selected with regard to solving dynamic problems /7/ and constructing the potential pattern /6/. A composite (quantum-classical) model of the diamond lattice cluster was elaborated. Two inner coordination spheres (17 atoms) were described quantum-mechanically in the two-centre approximation. Two external spheres (91 atoms in the cluster altogether) were described by means of classical potentials of the Morse type.[1)]

To provide most compact calculations the peculiarities of the defect zone geometry were taken into consideration while describing the "quantum nucleus" of the cluster. For instance for the displacement of atom A to the position A^{I}, i groups of equivalent bonds can be singled out, with j bonds within each group (Fig. 1). The cluster energy can be presented as

$$E = \sum_{ij} \langle \Psi_{ij} |\hat{H}| \Psi_{ij} \rangle + \sum_{ij} U_{ij} , \qquad (1)$$

where Ψ_{ij} is the molecular orbital of bonds j in group i, $\hat{H}$ two-centre Hamiltonian, U_{ij} potential function of the Morse type, describing the interaction of atoms in the cluster peripheral part (beyond the cluster nucleus).

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1) The volumetric size of the classical part of the cluster could be enlarged if required. The configurations investigated were to be found in the "quantum nucleus" of the cluster. Boundary conditions are provided by the dissipative forces acting on boundary atoms /7/.

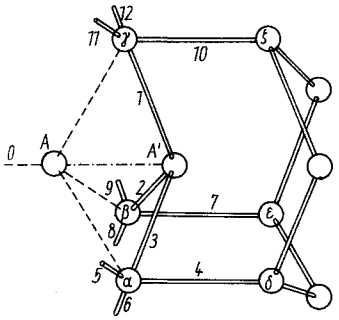

Fig. 1. Fragment of a diamond lattice cluster. Groups of equivalent bonds (1, 2, 3), (4, 7, 10), (5, 6, 8, 9, 11, 12). The cluster made up of 17 atoms includes two coordination spheres around atom A: Atoms α, β, γ of the first coordination sphere and atoms δ, ε, ξ of the second coordination sphere are shown

In order to construct the potential pattern for the atomic displacement during defect formation it proves necessary to exceed the limits of harmonic and adiabatic approximations. Therefore the procedure of finding the radial wave functions in the unharmonic region was applied, which is based on definite estimates /8/. Slater functions with variable orbital exponent $\alpha(R)$ were taken as initial ones. The angular part of wave functions was presented as

$$Y_i = \sum_{j=1}^{4} a_{ij} Y_j \ , \tag{2}$$

where Y_j stands for the angular part of s- and p-functions, a_{ij} for the hybrid coefficients, which for distorted structures are determined by the conditions of orthonormalization and maximum overlap of the hybrid orbitals of neighbouring atoms.

The calculation of the potential pattern was carried out in the following way. Atom A was displaced some distance towards A^{I} (Fig. 1). For this position of atom A the relaxed coordinates are calculated by means of the gradient method /7/. Relaxation was effected sequentially for all groups of equivalent bonds with iterative cycles, since each group i of equivalent bonds has its particular step in the method of fastest down grade. This means that at first the relaxations were calculated for i = 1 at fixed position of bonds with i = 1; then for i = 2 with the remaining bonds fixed, etc.

The essential fact is that the hybrid coefficients are calculated before each subsequent relaxation step, and the forces determining "the fastest down grade" at the given relaxation step are calculated with regard to the modified state of the electron sub-system, related to the cluster configuration of the preceding

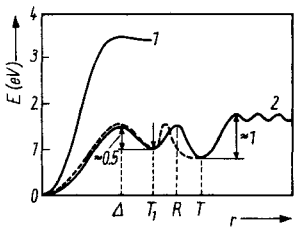

Fig. 2. Potential pattern for the non-adiabatic (1) and adiabatic (2) displacement of a Si atom in the <111> direction. T_1 metastable interstitial configuration. Beyond position T_1 the construction of the potential pattern is carried out qualitatively. T natural interstitial. R point of bond re-hybridization /10/

step. Relaxation of all groups of equivalent bonds being carried out, the process begins anew with i = 1. Iterative cycles are terminated when the final relaxation of the entire system meets the precision required; then atom A is displaced to another position.

The algorithm described here enables one to construct the potential pattern taking constantly into account the interference of the electron and lattice subsystems. This approach makes it possible to exceed the limits of the adiabatic approximation and regard the energy transition from the electron to the lattice sub-system and vice versa. The potential pattern is constructed as a function of the total electronic energy of the system depending on the position of atom A (Fig. 2).

The variation of Morse potential parameters in the classical region permits an optimization of the terminal conditions for the quantum nucleus of the cluster. Prior to investigations of defect configurations an ideal lattice was regarded (interatomic distance $R_o \approx 2.2$ Å, bond angle $\beta \approx 109^o$). Then the potential pattern was constructed for a displacement of the Si atom towards the T-interstitial (Fig. 2). In the vicinity of T two types of metastable states are to be found: a) for the non-relaxed system (curve 1) and b) for the system which underwent certain relaxation after arrival of atom A at the area T (curve 2). The atomic configuration corresponding to the metastable state of the second type is shown in Fig. 3.

A shift of the system to the metastable states, shown in Fig. 2, proved also possible as a result of pulsing atom A (Fig. 1). The dynamic calculation was carried out with the help of Vineyard's method /7/. Calculation of forces and the account of electron-lattice interactions were done similarly to those constructing the potential pattern.

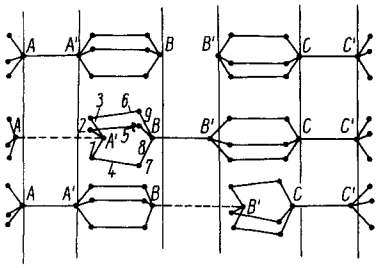

Fig. 3. Grasshopper configuration. Bonds 1 to 3: recovery results in both atom B and defect area shift

For certain impulse values atom A is displaced beyond the point T_1 (curve 1 in Fig. 2 shows the potential pattern for the non-adiabatic displacement), and afterwards the free evolution of the system in dynamic calculations resulted in a reconstruction of atomic configurations, shown in Fig. 3.

The recovery of the defect configuration in the vicinity of B results in a rightward displacement of atom B and in the appearance of analogous defect configurations in the vicinity of B. There occurs a "jump-over" of the area with turned-about bonds (Fig. 3), resembling the jump of a grasshopper ("grasshopper effect").

The grasshopper effect points to another possibility of migration of defect configurations in the diamond lattice. The migration of this kind is not long-range and cannot be regarded as ordinary traditional point defect. Nevertheless, this effect can be used for the interpretation of radiation-enhanced diffusion /2/, migration of sub-threshold defects /1/, and certain phenomena observed at Si implantation /9/.

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