

Breathing-mode relaxation around tetrahedral interstitial 3d impurities in silicon

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The symmetric relaxation of nine shells of host atoms around the tetrahedral interstitial Cr, Mn, Fe, Co, and Ni impurities in silicon are predicted from the self-consistent charge-density displacement and a host-crystal force field. A unique relaxation pattern is predicted (first shell moves out, second shell moves in) yielding an unusual molecular species: an approximately tenfold-coordinated transition metal. It is explained in terms of the nature of the transition-metal silicide bond.

Transition-metal (TM) atoms form a unique class of impurities in silicon^{1,2}. Having highly localized *d* orbitals unmatched by the *sp* bonded host crystal, they form deep impurity states that couple literally to thousands of host bands³ and, in sharp contrast to isolated TM ions, they can sustain a multitude of stable spin and charge states in a relatively narrow energy range^{2,4} (the Si band gap). This is accomplished without forming ionic bonds, but rather through an intra-atomic population inversion $s^m d^n \rightarrow d^{n+m}$ and a polarization of the valence band.³ The ability of these impurities to accommodate themselves electronically to the host crystal (electrical self-regulating response⁴) despite profound chemical dissimilarities to Si, raises the question of their ability to accommodate themselves structurally (lattice relaxation). Electron paramagnetic resonance (EPR) studies^{1,2} suggest that under normal preparation conditions most TM impurities occupy in Si the tetrahedral interstitial sites (coordination number of four), preserving the cubic symmetry of the host crystal (i.e., no symmetry breaking static Jahn-Teller distortions). Symmetry-conserving distortions (i.e., breathing mode) were not studied experimentally.

In this Rapid Communication we report the first theoretical prediction of lattice relaxation around interstitial TM impurities in a semiconductor. Previous calculations on TM-induced relaxation were specialized to ionic solids⁵ and were based on wave-functionless models with phenomenological pair potentials. We have calculated self-consistently the electronic structure of undistorted Si:TM for TM = Cr, Mn, Fe, Co, and Ni using in the local density formalism and the quasi-band-crystal-field (QBCF) Green's function method.⁶ We obtained the *ab initio* impurity-induced forces using the pseudopotential Hellmann-Feynman theorem^{7,8} and calculated the breathing distortions of the first 9 shells (82 atoms) by using an empirical Si force field.⁷ We find that for all impurities studied the first shell of nearest neighbors (1NN) containing four Si atoms moves *away* from the impurity, whereas the second nearest neighbor shell (2NN) containing six Si atoms moves *towards* the impurity. This deformation pattern tends to equalize the TM-Si bonds to 2.4–2.6 Å, producing a rare molecular species of an approximately tenfold coordinated TM. Interestingly, the Coulombic part of the host pseudopotential, $-8/r$ predicts a *reverse* (i.e., inward) motion of the 1NN but the repulsive part

$V_R(r)$ of the pseudopotential reverses the trend. We explain the unique displacement pattern in terms of the structural significance of the non-Coulombic part of the pseudopotential, the $s \rightarrow d$ population inversion, and the shape of the impurity-induced charge-density fluctuation reflecting the effective impurity size.

An impurity (*I*) with an electronic density perturbation $\Delta n(\vec{r}) = n_I(\vec{r}) - n_H(\vec{r})$ around it and a valence difference $\Delta Z = Z_I - Z_H$ relative to the host (*H*) atom it replaces, exerts a change $\Delta \vec{F}^{(p)}$ in the Hellmann-Feynman force^{7,8} acting on the *p*th host atom at \vec{R}_p , given by

$$\Delta \vec{F}^{(p)} = \Delta \vec{F}_e^{(p)} + \Delta \vec{F}_{cc}^{(p)}. \quad (1)$$

The electronic (*e*) force is given in terms of the gradient of the local host pseudopotential $v_{ps}(r) = -2Z_H/r + V_R(r)$ and the projection $\Delta \vec{\rho}_{l-1}^{(p)}(r)$ of the impurity-centered $\Delta n(\vec{r})$ on the *p*th host site as

$$\Delta \vec{F}_e^{(p)} = - \int_0^\infty [r^2 dv_{ps}(r)/dr] \Delta \vec{\rho}_{l-1}^{(p)}(r) dr, \quad (2)$$

whereas the core-core (cc) force exerted by all other cores on the one at \vec{R}_p is

$$\Delta \vec{F}_{cc}^{(p)} = \frac{Z_H \Delta Z}{|\vec{R}_p - \vec{R}_0|^3} (\vec{R}_p - \vec{R}_0). \quad (3)$$

The projected density $\Delta \vec{\rho}_{l-1}^{(p)}(r)$ is a vector function whose components $\Delta \rho_{l-1,\alpha}^{(p)}(r)$ for $\alpha = x, y,$ and z are the radial parts of the three partners of the $l=1$ term in the t_2 cubic harmonics expansion of the charge-density perturbation $\Delta n(\vec{r})$ around the *p*th host atom. This rigorous impurity-induced force formula (for local host potentials⁷), shows that both the isotropic ($l=0$) and the anisotropic ($l=3, 4, \dots$) components of the impurity-centered density perturbation $\Delta n_l(r)$ contribute to the magnitude $\Delta \rho_{l-1}^{(p)}(r)$ of the projected density $\Delta \vec{\rho}_{l-1}^{(p)}(r)$ around the host site and hence to the force. The electronic force represents the interaction of a displacement $\Delta \vec{\rho}_{l-1}^{(p)}(r)$ in the electronic charge with the effective core charge [given by the square brackets in (2)].

A quantum-mechanical force calculation can be computationally difficult since the error in the density appears as a *first-order* error in the force.⁹ The two leading corrections are the basis set incompleteness and the non-self-

consistency errors.⁹ The first correction measures the amount by which a wave function fails to be an eigensolution to the Hamiltonian. Sufficient variational flexibility is achieved here by using a large set (192 s , p , d , f , and g) of optimized orbitals.⁶ Since in the QBCF method⁶ all orbitals are chosen to be impurity centered, the explicit basis set incompleteness error vanishes (i.e., no gradients of basis orbitals are needed). The second correction measures the departure of the potential from self-consistency; its minimization requires a self-consistency tolerance that is about an order of magnitude more stringent than what is normally needed in total energy calculations. We calculate the equilibrium configuration $\bar{Q} = \bar{Q}^*$ of the first nine shells of atoms surrounding the impurity from the condition that the total force $\bar{F}(\bar{Q}) = \bar{F}_0(\bar{Q}) + \Delta\bar{F}(\bar{Q})$ vanishes simultaneously at all sites. This is achieved efficiently using the Jacobian update method where the Cartesian force gradients (force constants) are used to locate iteratively the equilibrium structure.^{6,7,9} We use the approximation that the impurity-centered charge fluctuation $\Delta n(\bar{r})$ does not vary with \bar{Q} (however, the forces $\Delta\bar{F}_e$ and $\Delta\bar{F}_{cc}$ both depend on \bar{R}_p); this is a good approximation for a highly localized $\Delta n(\bar{r})$ characteristic of weakly interacting TM impurities. We evaluate the restoring force \bar{F}_0 of the pure host from an accurate force field fitted to the phonon spectra.⁷ Hence, in this anharmonic model we assume that the forces inducing the displacements are short ranged but that the displacements can extend to a large range.

Figure 1 depicts the predicted breathing-mode distortions of the 82 Si atoms belonging to the 9 shells nearest the impurity. We find a strong coupling between the displacements

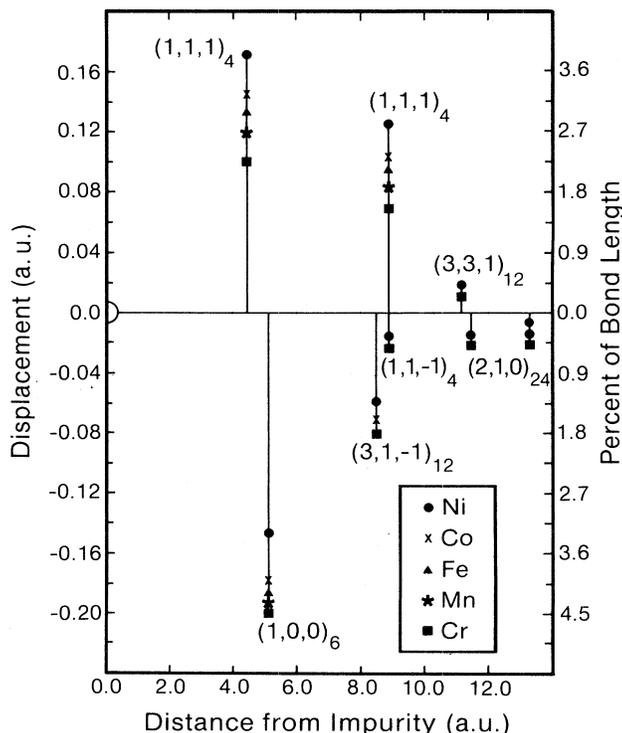


FIG. 1. Predicted breathing-mode relaxations of the $(h,k,l)_I$ silicon shells (containing I atoms) surrounding the neutral tetrahedral interstitial TM impurity (at the origin).

of the first two shells and the rest of the crystal: if all but the first two shells are frozen, the former relax only about $\frac{2}{3}$ of their unconstrained relaxation. Integrating the forces over the lattice space, we find that the energy gained by relaxation is approximately 0.4 ± 0.05 eV for all impurities. The major relaxation pattern near the impurity consists of an outward movement of the 1NN shell and an inward movement of the 2NN shell, leading to an approximately tenfold coordinated TM, a molecular species that is rare in covalent coordination chemistry of $3d$ elements.¹⁰ Intriguingly, all three metallic disilicide structure types—the TiSi_2 group (orthorhombic), the CrSi_2 group (hexagonal), and the MoSi_2 group (tetragonal) are known to (inexplicably¹⁰) avoid the conventional close-packed coordination of 12 and exhibit a variety of unique stacking sequences, all leading to an approximate coordination number 10 around the TM. Our analysis suggests that the Si:TM system maintains a universal relaxation pattern despite the variations in the band filling, electronegativities, and ground-state configurations due to $s \rightarrow d$ population inversion.⁶ This process places all of the bonding s electrons in the d shell, producing nearly identically weak bonds for all TM.

Figure 2 analyzes the relaxation pattern in terms of the force formula in Eqs. (1)–(3). The pseudopotential gradient [Fig. 2(a)] has a strongly repulsive part $2Z_H/r^2$ due to the point-core of $v_{ps}(r)$. However, the non-Coulombic part of the pseudopotential (a consequence of core-valence orthogonality, or, “kinetic energy cancellation”) strongly reduces the gradient inside the core. This general feature is shared both by the “soft” potential used here³ (curve 1) as well as by the “hard-core” pseudopotentials¹¹ (curve 2). The actual pattern of lattice deformation will differ from that induced by point-cores due to this non-Coulombic effect. The impurity-centered charge perturbation $\Delta n(\bar{r})$ [insert to Fig. 2(b)] has a positive region (the bonding region, where the impurity has more charge than the host), followed by a negative domain with a minimum near the 1NN at $R_M \cong 4.5$ a.u. (the antibonding region). The antibonding region, a consequence of the impurity wave functions being orthogonal at the ligand sites (hence, absent in semiclassical wave-functionless models³), penetrates the core of the host atoms. When projected relative to the 2NN atom (located at $R > R_M$), it produces a density $\Delta \bar{\rho}_{l-1}^{(P)(r)}$ that has a negative portion, whereas when projected relative to the 1NN (located at $R < R_M$), $\Delta \bar{\rho}_{l-1}^{(P)(r)}$ is purely positive. These features control the opposite displacement patterns of the 1NN and the 2NN. Figure 2(c) depicts the integrand of Eq. (2); the area under this curve gives the electronic force acting on the respective host atom in the undistorted position. Integrating it from $r = \infty$ to the Si core radius produces the same attractive electronic force both for the point-core ($V_R = 0$, dashed line) and for the pseudized core ($V_R \neq 0$, solid line). Inside the core, however, the Coulombic part of v_{ps} makes a further negative contribution whereas the non-Coulombic (pseudized) core, having a weaker gradient [Fig. 2(a)], reduces the attractiveness of the electronic force. As a result, the strongly negative ΔF_e for the point-core overwhelms the positive ΔF_{cc} , producing a net *inward* relaxation, whereas the weaker ΔF_e of the pseudized core is overwhelmed by ΔF_{cc} , producing a net *outward* relaxation. Since $\Delta \bar{\rho}_{l-1}^{(P)(r)}$ for the 2NN has the opposite sign of that for the 1NN inside the core, the non-Coulombic part of the pseudopotential has just the opposite effect, in-

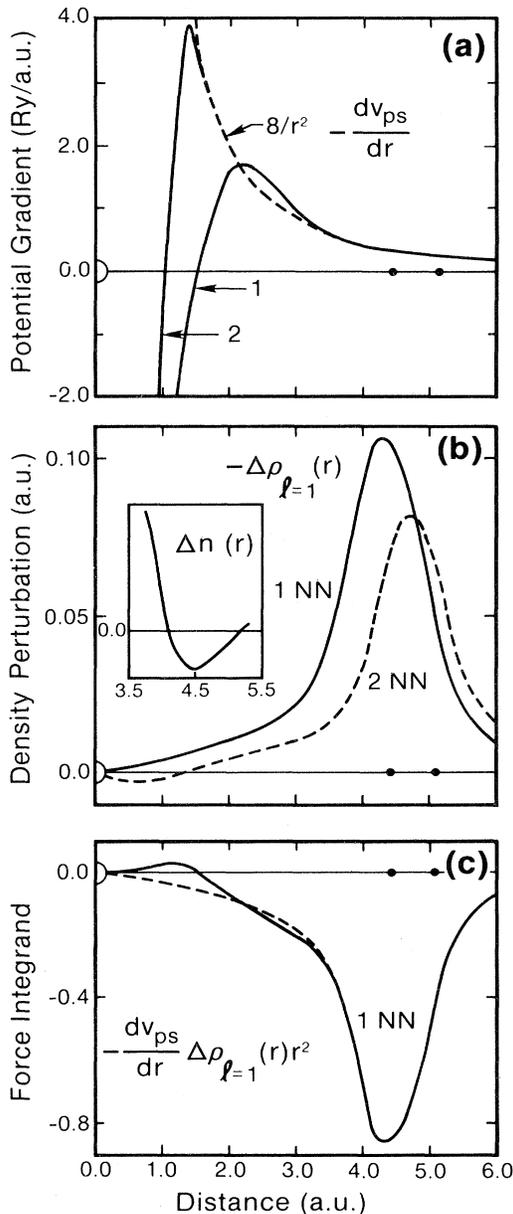


FIG. 2. (a) Host pseudopotential gradients for a point-core (---), a soft pseudopotential (Ref. 3) (1), and a hard pseudopotential (Ref. 11) (2). (b) Magnitude of projected Si-centered density displacement $\Delta\bar{\rho}_{l=1}^{(p)}(r)$ for Si:Fe. The insert shows the spherically symmetric impurity-centered $\Delta n(r)$. (c) The integrand of the electronic force [Eq. (2)] acting on the 1NN atom in Si:Fe for a point core (---), and a pseudopotential core (—). The two solid circles represent the position of the impurity relative to the 1NN and 2NN Si atom (at the origin).

creasing the attractiveness of ΔF_e , leading thereby to an inward relaxation. We conclude that the relaxation pattern of a given host atom is dictated by its relative position in the region where the impurity-induced electronic charge (reflecting the impurity size) overlaps the non-Coulombic part of the host pseudopotential (reflecting the size of the host atom). The chemical trends for a fixed host are hence dictated by the magnitude of the bonding and the antibonding

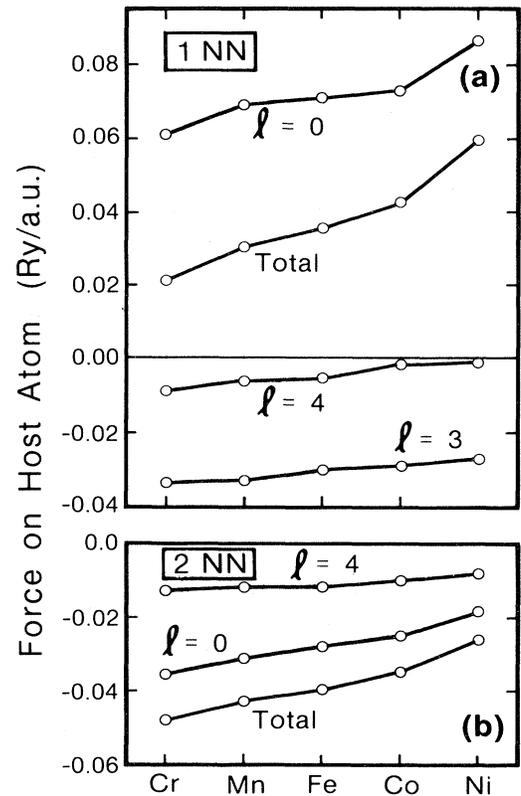


FIG. 3. Spherical ($l=0$) and nonspherical ($l \neq 0$) contributions to the forces acting on the undistorted first two Si shells around a TM impurity.

parts of $\Delta n(r)$: the heaviest impurity (Ni) induces the largest outward displacement of the 1NN but the smallest inward displacement of the 2NN, whereas the lightest impurity (Cr) does just the opposite (Fig. 1). These trends reflect the fact³ that in going from Cr to Ni the bonding area increases in magnitude whereas the antibonding area decreases. The predicted trend with the host crystal is that all other things being equal, diamond (with $V_R=0$ as its valence $2p$ orbitals have no counterpart in the core) will favor an inward relaxation.

The introduction of an impurity into the host crystal induces both spherical ($l=0$) charge displacements $\Delta n_{l=0}(r)$ reflecting the overall depletion or accumulation of bond charge, as well as nonspherical $l \neq 0$ displacements reflecting perturbations in bond anisotropy (broken covalency). Both can contribute to the electronic force through $\Delta\bar{\rho}_{l=1}^{(p)}$ in Eq. (2). Figure 3 depicts the contributions to the force on the 1NN [Fig. 3(a)] and 2NN [Fig. 3(b)] due to isotropic and anisotropic charge displacements. Since an interstitial TM forms weak directional bonds which did not exist in the unperturbed host crystal, the charge anisotropy produces for all TM forces which tend to shorten (stabilize) the bonds. In contrast, substitutional TM impurities disrupt the directed covalency which existed in the unperturbed crystal³ by replacing a Si atom with an element that is less able to bond to Si. The charge anisotropy hence tends to increase (destabilize) the bonds, causing an overall outward relaxation both for the 1NN and the 2NN shells.⁷

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