

Quadrupole Susceptibility and Elastic Softening due to a Vacancy in Silicon Crystal

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We investigate the electronic states around a single vacancy in silicon crystal by using the Green's function approach. The triply degenerate vacancy states within the band gap are found to be extended over a large distance $\sim 20 \text{ \AA}$ from the vacancy site and contribute to the reciprocal temperature dependence of the quadrupole susceptibility resulting in the elastic softening at low temperature. The Curie constant of the quadrupole susceptibility for the trigonal mode (O_{yz}, O_{zx}, O_{xy}) is largely enhanced as compared to that for the tetragonal mode (O_2^0, O_2^2). The obtained results are consistent with the recent ultrasonic experiments in silicon crystal down to 20 mK. We also calculate the dipole and octupole susceptibilities and find that the octupole susceptibilities are extremely enhanced for a specific mode.

KEYWORDS: silicon, vacancy, softening, quadrupole, elastic constant

1. Introduction

The recent discovery of low temperature elastic softening in silicon (Si) crystal¹⁾ has stimulated much interest in the investigations not only for physical properties but also for industrial applications as the softening is closely related to the Si vacancy concentration.²⁾ The elastic constants of the both $(C_{11} - C_{12})/2$ and C_{44} modes show reciprocal temperature dependence below 20 K down to 20 mK, which implies the existence of triply degenerate groundstates which couple to the strain caused by the ultrasound.¹⁾ The softening of non-doped Si is independent of the external magnetic fields up to 10 T and is attributed to the vacancy with the non-magnetic neutral charge state V^0 , while that of boron (B)-doped Si is suppressed by the external magnetic fields of the order of 1 T and is attributed to the vacancy state V^+ with the valence +1 and the spin $1/2$.¹⁾

A huge number of researches on the single vacancy in Si crystal have been done in the both experimental³⁻⁶⁾ and theoretical⁷⁻¹⁰⁾ viewpoints. Early experiments of the electron paramagnetic resonance (EPR)³⁾ revealed the local lattice distortion around the positive charge state V^+ and negative charge state V^- . Schlüter *et al.*^{9,10)} predicted that the negative- U effect due to the Jahn-Teller distortion results in the V^{++} groundstate with the excited V^+ state; which is the well-known standard theory of the single vacancy in Si crystal and is experimentally confirmed by Watkins and Troxell.⁴⁾ The negative charge state V^- with the Jahn-Teller distortion has also been confirmed by the EPR³⁾ and the electron nuclear double resonance (ENDOR)⁵⁾ measurements. Recent first-principle calculations¹¹⁻¹⁴⁾ with supercells up to 1000-atoms have showed that the calculated symmetry of the relaxed vacancy state depends on computational details such as supercell size and k-point sampling. Although the detailed symmetry of the charge state is still controversial issue, the first-principle calculations have concluded that the degeneracies of the charge states are resolved due to the Jahn-Teller distortions except the doubly positive

charge state V^{++} .¹⁴⁾ More recently, the elastic properties in a Si vacancy have also been discussed by using the first-principle calculations.^{15,16)}

In the EPR experiments,³⁾ the vacancies were intentionally created by electron-beam and γ -ray irradiations, and then, the observed local distortions in the EPR are considered to be caused by the cooperative Jahn-Teller effect among the highly irradiated vacancies being strongly coupled each other.¹⁾ Such vacancies are well described by the first-principle calculations with supercells where the vacancy concentration is $\sim 1/1000$. In the ultrasonic experiments, however, the charge state of the thermally created vacancies with the extremely low concentration in the FZ Si crystal, which is believed less than 10^{15} cm^{-3} , shows no sign of the local distortion, although a small inter-vacancy coupling $\sim 2 \text{ K}$ is also observed.¹⁾

When only a single vacancy exists in the infinite Si crystal, T_d -point symmetry should be preserved against the Jahn-Teller distortions and the 3-fold orbital degeneracy should remain in the vacancy groundstates. Even in the case with a finite vacancy concentration, such a single vacancy state without the Jahn-Teller distortions is expected to be a good starting point to describe the properties for finite temperature, where the cooperative Jahn-Teller effects due to the small inter-vacancy coupling are not significant. Such situation is realized in the FZ Si crystal above at least 20 mK and are observed in the ultrasonic experiments. Therefore we need a theoretical study for a single vacancy in infinite Si crystal without the Jahn-Teller distortions to describe the low temperature elastic softening in the FZ Si crystal.

The similar elastic softenings have been widely observed in the $4f$ electron systems,^{17,18)} where the Curie-like behavior of the quadrupole susceptibilities due to the orbital (quadrupole) degeneracy of the $4f$ electrons are responsible for the elastic softenings via the quadrupole-strain coupling. Similarly to the $4f$ electron systems, the orbital degeneracy of the localized vacancy states in the Si crystal is expected to result in the low temperature softenings observed in the ultrasonic experi-

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ments. Recently, Matsuura and Miyake¹⁹⁾ have studied the quadrupole susceptibility due to a Si vacancy on the basis of a cluster model for the dangling-bond orbitals in the Si vacancy.¹⁾ Yamakawa *et al.*^{20,21)} have studied the effect of the coupling between the electrons of the dangling-bonds and the Jahn-Teller distortions by using the exact diagonalization for the cluster model developed by Schlüter *et al.*^{9,10)} and have revealed that the degeneracy of the vacancy state remains against the Jahn-Teller effect because of the strong quantum fluctuation due to the non-adiabatic effect, in contrast to the case with the adiabatic approximation.^{9,10)} However, the effect of the spatial extension of the vacancy state, which is important to determine the absolute value of the elastic softening, has not been discussed in above cluster models. The experimental group¹⁾ has claimed that the widely extended vacancy state with the effective radius¹⁰⁾ $a \sim 5 \text{ \AA}$ is responsible for the huge quadrupole susceptibility in proportion to a^4 which contributes to the elastic constant via the quadrupole-strain coupling.

In this study, we focus on the V^0 charge state which has non-magnetic groundstate and is realized in the non-doped Si as confirmed by the ultrasonic experiment.¹⁾ In this case, the spin-orbit interaction, which is crucial for the magnetic groundstates in the V^+ and V^- states, is irrelevant. In the groundstate of V^0 , the two electrons are occupied in the 3-fold degenerate orbital states with intra-orbital and inter-orbital spin-singlet configurations which are responsible for the electric multipole susceptibilities such as the quadrupole and octupole.

The purpose of this paper is to clarify the effect of the spatial extension of the vacancy state on the quadrupole susceptibility which contributes to the elastic constant at low temperature. For this purpose, we determine the electronic state around a single vacancy in the infinite Si crystal by using the Green's function approach.^{22,23)} By virtue of this approach, we can discuss the electronic state up to 30 \AA from the vacancy site, where more than 4000 Si atoms are included. Using the obtained Green's functions, we calculate the quadrupole susceptibility on the basis of the linear response theory.

2. Model and Formulation

The model Hamiltonian consists of the tight-binding Hamiltonian H_0 and a vacancy potential H_v given by

$$H = H_0 + H_v, \quad (1)$$

$$H_0 = \sum_{ij} \sum_{\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} = \sum_{\mathbf{k}} \sum_{m=1}^8 \epsilon_{\mathbf{k}m} c_{\mathbf{k}m}^\dagger c_{\mathbf{k}m}, \quad (2)$$

$$H_v = \Delta \sum_{\alpha} c_{0\alpha}^\dagger c_{0\alpha}, \quad (3)$$

where $c_{i\alpha}^\dagger$ is a creation operator for an electron at site i and orbital α ($= s, p_x, p_y, p_z$), and $c_{\mathbf{k}m}^\dagger$ is that for wave vector \mathbf{k} and band m ($= 1 \sim 8$). In eq. (2), the tight-binding parameters $t_{ij}^{\alpha\beta}$ are written by the Slater-Koster parameters and determined so as to fit the tight-binding band energies $\epsilon_{\mathbf{k}m}$ to the LDA band energies²⁴⁾ for the Si crystal as shown in Fig. 1. The explicit values of the parameters are as follows: atomic levels $\epsilon_s =$

-4.778 eV , $\epsilon_p = 1.218 \text{ eV}$, 1st-neighbor hopping integrals $t_{ss1} = -2.104 \text{ eV}$, $t_{sp1} = -1.788 \text{ eV}$, $t_{pp\sigma1} = -2.810 \text{ eV}$, $t_{pp\pi1} = -0.743 \text{ eV}$, 2nd-neighbor hopping integrals, which gives hopping between the dangling bonds, $t_{ss2} = 0.092 \text{ eV}$, $t_{sp2} = 0.112 \text{ eV}$, $t_{pp\sigma2} = -0.386 \text{ eV}$, $t_{pp\pi2} = -0.116 \text{ eV}$. The vacancy potential H_v excludes electrons from the vacancy site by raising the energy levels Δ for the orbitals belong to the vacancy site. For $\Delta \rightarrow \infty$, no electron exists at the vacancy site and then an effective vacancy state is realized.

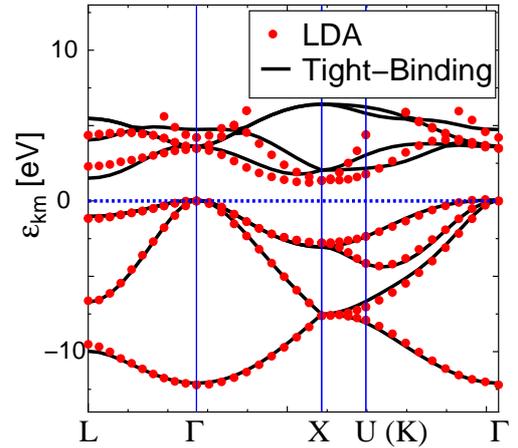


Fig. 1. The band structure for the Si crystal calculated from the LDA²⁴⁾ (closed circles) and from the tight-binding model (solid lines).

In the absence of the vacancy ($\Delta = 0$), the Green's function for the perfect crystal is described as

$$G_{ij}^{0\alpha\beta}(z) = \sum_{\mathbf{k}m} \frac{u_{\alpha m}(\mathbf{k}) u_{\beta m}^*(\mathbf{k})}{z - \epsilon_{\mathbf{k}m}} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \quad (4)$$

where $u_{\alpha m}(\mathbf{k})$ is the eigenvector for the energy band $\epsilon_{\mathbf{k}m}$ and orbital α given in eq. (2). In the presence of the vacancy ($\Delta \neq 0$), the Green's function is obtained by solving the Dyson's equations which can be written in the 4×4 matrix representation as

$$\mathbf{G}_{ij} = \mathbf{G}_{ij}^0 + \mathbf{G}_{i0}^0 \Delta \mathbf{G}_{0j}, \quad (5)$$

with the vacancy potential matrix $(\Delta)_{\alpha\beta} = \Delta \delta_{\alpha\beta}$, where $(\mathbf{G}_{ij}^0)_{\alpha\beta} = G_{ij}^{0\alpha\beta}$ is the Green's function for $\Delta = 0$ given in eq. (4) and $(\mathbf{G}_{ij})_{\alpha\beta} = G_{ij}^{\alpha\beta}$ is the corresponding Green's function for $\Delta \neq 0$. In the limit $\Delta \rightarrow \infty$, $\mathbf{G}_{ij} \rightarrow 0$ with $i = 0$ and/or $j = 0$, and then

$$\mathbf{G}_{0j}^0 + \mathbf{G}_{00}^0 \Delta \mathbf{G}_{0j} \rightarrow 0. \quad (6)$$

By using eq. (6) in eq. (5), \mathbf{G}_{ij} is obtained by \mathbf{G}^0 as

$$\mathbf{G}_{ij} = \mathbf{G}_{ij}^0 - \mathbf{G}_{i0}^0 (\mathbf{G}_{00}^0)^{-1} \mathbf{G}_{0j}^0. \quad (7)$$

According to the Lehmann representation, $G_{ij}^{\alpha\beta}$ is described by using the spectral function $A_{i\alpha j\beta}^l$ and the excitation energy E_l , as

$$G_{ij}^{\alpha\beta}(z) = \sum_l \frac{A_{i\alpha j\beta}^l}{z - E_l}. \quad (8)$$

3. Results

3.1 Density of States

Now, we calculate $G_{ij}^{0\alpha\beta}$ in eq. (4) by performing the \mathbf{k} summation with $20 \times 20 \times 10 = 4000$ mesh points, and substitute it into eq. (7) to obtain $G_{ij}^{\alpha\beta}$ which yields $A_{i\alpha j\beta}^l$ and E_l in eq. (8). By using the obtained values of $A_{i\alpha j\beta}^l$ and E_l , we calculate the local density of states (DOS) at site i in the presence of the vacancy, $\rho_i(\omega) = \sum_{l\alpha} A_{i\alpha i\alpha}^l \delta(\omega - E_l)$. Fig. 2 shows $\rho_i(\omega)$ together with the DOS for the perfect crystal without vacancy, where the top of the valence band is set to the energy origin. We find two remarkable localized levels: one sits in the band gap and the other sits in the valence band. By summing the contribution to each level from all sites, the total weight of each state is 3 for the former level and 1 for the latter level. Therefore, we find that the former and the latter levels correspond to T_2 triplet states with the energy $E_{T_2} = 0.44$ eV and A_1 singlet state with the energy $E_{A_1} = -0.12$ eV, respectively. These localized levels are occupied by 4 electrons in the V^0 state and by 3 electrons in the V^+ state, respectively. In the both cases, the chemical potential μ is close to the T_2 level at low temperature. Then in the following, we focus on the T_2 triplet states which exclusively contribute to thermodynamic quantities such as the quadrupole susceptibilities at low temperature.

The inset of Fig. 3 shows the local DOS for the T_2 triplet states at site i , $N_{T_2}^i = \sum_{\alpha} A_{i\alpha i\alpha}^{T_2}$, as a function of the distance R_i from the vacancy site. We can see that, with increasing R , $N_{T_2}^i$ exponentially decreases with decay length ξ of several \AA accompanied by a complicated oscillation. We also calculate the integrated local DOS for T_2 triplet states up to the radius R_c from the vacancy site, $N_{T_2} = \sum_i^{R_c} N_{T_2}^i$, which is plotted as a function of R_c in Fig. 3. When $R_c \rightarrow \infty$, we can see $N_{T_2} \rightarrow 3$ as expected. We note that a large part ($\sim 80\%$) of T_2 triplet states is concentrated on the region $R < 5 \text{ \AA}$ with 34 atoms, but a small part ($\sim 20\%$) of the widely extended vacancy states $R = 5 \sim 20 \text{ \AA}$ with $\sim 10^3$ atoms play crucial roles for thermodynamic quantities such as the quadrupole susceptibilities as will be shown later.

3.2 Quadrupole susceptibility

The low temperature elastic softening is considered to be caused by the interaction between the electric quadrupole and the elastic strain,¹⁾ which is explicitly given by

$$H_{QS}(t) = - \sum_{\Gamma} g_{\Gamma} \tau_{\Gamma} \epsilon_{\Gamma}(t) \quad (9)$$

with a quadrupole-strain coupling constant g_{Γ} . Here, $\epsilon_{\Gamma}(t)$ is a strain with mode Γ excited by the ultrasonic wave and couples to a quadrupole operator,

$$\tau_{\Gamma} = e \sum_{ij} \sum_{\alpha\beta} \langle i\alpha | \phi_{\Gamma}(\mathbf{r}) | j\beta \rangle c_{i\alpha}^{\dagger} c_{j\beta}, \quad (10)$$

with $\phi_{\Gamma}(\mathbf{r})$, given by

$$\phi_{\Gamma}(\mathbf{r}) \equiv \begin{cases} (3z^2 - r^2)/\sqrt{3} & \text{for } \tau_{\Gamma} = O_2^0 (\epsilon_u) \\ x^2 - y^2 & \text{for } \tau_{\Gamma} = O_2^2 (\epsilon_v), \end{cases}$$

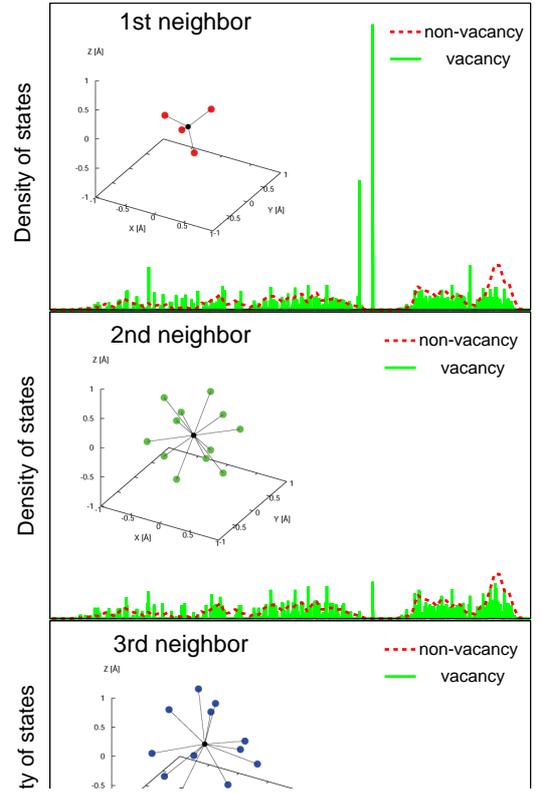


Fig. 2. The local density of states in the presence of the vacancy (solid lines) together with those for the perfect crystal without vacancy (broken lines) at 1st (top), 2nd (middle) and 3rd (bottom) neighbor Si sites from the vacancy site.

$$\phi_{\Gamma}(\mathbf{r}) \equiv \begin{cases} yz & \text{for } \tau_{\Gamma} = O_{yz} (\epsilon_{yz}) \\ zx & \text{for } \tau_{\Gamma} = O_{zx} (\epsilon_{zx}) \\ xy & \text{for } \tau_{\Gamma} = O_{xy} (\epsilon_{xy}), \end{cases}$$

where the electric quadrupoles of O_2^0, O_2^2 couple to the tetragonal strain ϵ_u, ϵ_v and O_{yz}, O_{zx}, O_{xy} couple to the trigonal strain $\epsilon_{yz}, \epsilon_{zx}, \epsilon_{xy}$, respectively. Since the radius of the atomic orbital of each Si atom at site i is smaller than the distance R_i from the vacancy site to the Si atom, we can approximate $\langle i\alpha | \phi_{\Gamma}(\mathbf{r}) | j\beta \rangle \approx \phi_{\Gamma}(\mathbf{r}_i) \delta_{ij} \delta_{\alpha\beta}$, and then eq. (9) is rewritten as

$$H_{QS}(t) = -g_{\Gamma} e \epsilon_{\Gamma}(t) \sum_{i\alpha} \phi_{\Gamma}(\mathbf{r}_i) c_{i\alpha}^{\dagger} c_{i\alpha}. \quad (11)$$

The relationship between the elastic constant $C_{\Gamma}(T)$ and the quadrupole susceptibility $\chi_{\Gamma}(T)$ at temperature T is given in the second order perturbation w.r.t. g_{Γ} :

$$C_{\Gamma}(T) = C_{\Gamma}^0 - N_v g_{\Gamma}^2 \chi_{\Gamma}(T), \quad (12)$$

where C_{Γ}^0 is the background of the elastic constant and N_v is the number of vacancies. We note that the quadrupole susceptibilities of O_2^0, O_2^2 contribute to the elastic constant of $(C_{11} - C_{12})/2$, while those of O_{yz}, O_{zx}, O_{xy} contribute to C_{44} . In the linear response

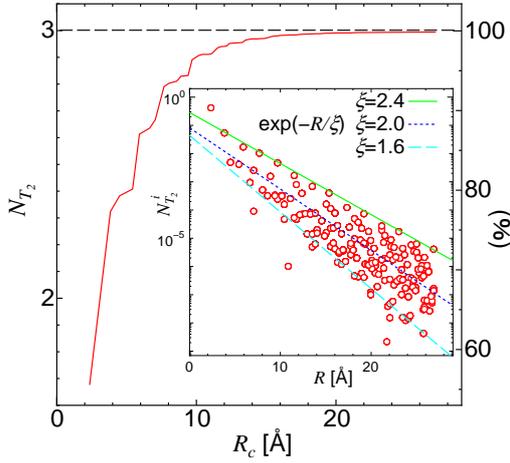


Fig. 3. The integrated local DOS for T_2 triplet states up to the radius R_c from the vacancy site. The inset shows the local DOS for the T_2 triplet states as a function of the distance R from the vacancy site. The solid, dot and dashed lines are functions $\exp(-R/\xi)$ with $\xi = 2.4$, $\xi = 2.0$ and $\xi = 1.6$, respectively.

theory, the quadrupole susceptibility is given by

$$\begin{aligned} \chi_\Gamma(T) &= \text{Re} \int_0^\infty dt e^{-0^+t} \langle [\tau_\Gamma^\dagger(t), \tau_\Gamma] \rangle \\ &= -e^2 \sum_{l'} \sum_{ij\alpha\beta} \phi_\Gamma(\mathbf{r}_i) \phi_\Gamma(\mathbf{r}_j) A_{i\alpha j\beta}^l A'_{j\beta i\alpha} \frac{f(E_l) - f(E_{l'})}{E_l - E_{l'}} \end{aligned}$$

with the fermi distribution function $f(E) = 1/(e^{\beta(E-\mu)} + 1)$, where $\chi_\Gamma(T)$ consists of the Curie term ($E_l = E_{l'}$) and the Van-Vleck term ($E_l \neq E_{l'}$). As the Van-Vleck term is almost T -independent at low temperature, we focus only on the Curie term due to the degenerate T_2 triplet states ($E_l = E_{l'} = E_{T_2}$), which is explicitly given by

$$\begin{aligned} \chi_\Gamma(T) &= e^2 \sum_{ij\alpha\beta} \phi_\Gamma(\mathbf{r}_i) \phi_\Gamma(\mathbf{r}_j) A_{i\alpha j\beta}^{T_2} A_{j\beta i\alpha}^{T_2} \frac{f(E_{T_2})f(-E_{T_2})}{T} \\ &= \frac{K_\Gamma}{T} F(n) \end{aligned} \quad (13)$$

with $F(n) = n(6-n)/36$, where $n = 6f(E_{T_2})$ is the occupation number of electrons in the T_2 triplet states, and $n = 2$ for the V^0 state. Substituting eq. (13) into eq. (12), we obtain the elastic constant which shows the reciprocal T dependence, $C_\Gamma(T) \propto -N_v g_\Gamma^2 K_\Gamma F(n)/T$, where the absolute value of the elastic softening is determined by the Curie constant of the quadrupole susceptibility given by

$$K_\Gamma = e^2 \sum_{ij} \sum_{\alpha\beta} \phi_\Gamma(\mathbf{r}_i) \phi_\Gamma(\mathbf{r}_j) A_{i\alpha j\beta}^{T_2} A_{j\beta i\alpha}^{T_2}. \quad (14)$$

By using eq. (14), we calculate K_Γ with the site summation (i, j) up to the distance R_c from the vacancy site as done for the calculation of N_{T_2} , where K_Γ consists of the site diagonal contribution ($i = j$) and the site off-diagonal contribution ($i \neq j$). Fig. 4 shows K_Γ together with the site diagonal and site off-diagonal contributions for K_Γ as functions of R_c . To estimate the $R_c \rightarrow \infty$ extrapolated value of K_Γ , we assume a fitting function $K_\Gamma(R_c) \approx K_\Gamma(\infty)[1 - \{R_c^2/(2\xi_\Gamma^2) + R_c/\xi_\Gamma + 1\}e^{-R_c/\xi_\Gamma}]$.²⁵⁾

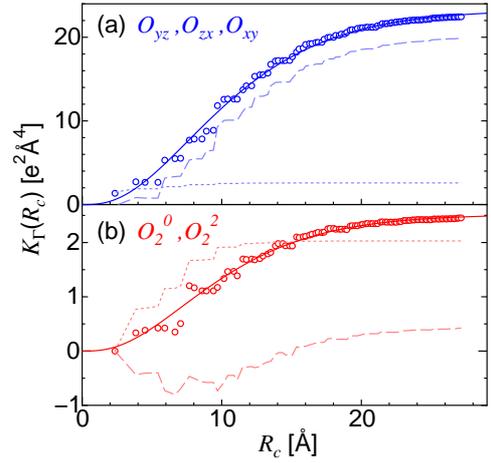


Fig. 4. The Curie constant K_Γ for the trigonal mode (O_{yz}, O_{zx}, O_{xy}) (a) and the tetragonal mode (O_2^0, O_2^2) (b) as functions of R_c . The open circles, dotted and dashed lines correspond to the total, site diagonal and site off-diagonal contributions, respectively. The solid lines show fitting functions for the total contributions (see in the text).

By comparing the calculated value of K_Γ with the fitting function as shown in Fig. 4, we obtain the extrapolated values: $K_\Gamma(\infty) = 23.28 e^2 \text{\AA}^4$ (trigonal) and $K_\Gamma(\infty) = 2.51 e^2 \text{\AA}^4$ (tetragonal), together with the decay length: $\xi_\Gamma = 3.77$ (trigonal) and $\xi_\Gamma = 3.56 \text{\AA}$ (tetragonal). We find that K_Γ for the trigonal mode is about 10 times larger than that for the tetragonal mode as shown in Fig. 4, where the site diagonal contribution for the trigonal mode is almost the same as that for the tetragonal mode, while the site off-diagonal contribution for the trigonal mode is much larger than that for the tetragonal mode. The result is consistent with the experimental result, where the softening of C_{44} is considerably larger than that of $(C_{11} - C_{12})/2$,¹⁾ if the coupling constants g_Γ for the both modes, which have not been determined so far, are of the same order of magnitude.

Remarkably, the widely extended vacancy states on the region $R = 5 \sim 20 \text{\AA}$ contribute to about 90 % of the absolute value of K_Γ as shown in Fig. 4, although they contribute to only 20 % of the local DOS as shown in Fig. 3. In fact, the decay length ξ_Γ for the Curie constant K_Γ is about twice larger than the decay length ξ for the local DOS (see also the inset of Fig. 3). We note that the effective quadrupole moments estimated by $(K_\Gamma)^{1/2}$ are $4.82 e\text{\AA}^2$ (trigonal) and $1.58 e\text{\AA}^2$ (tetragonal), which are considerably larger than molecular quadrupole moments of the order of $0.1 e\text{\AA}^2$.²⁶⁾

3.3 Multipole susceptibility

It is expected that the widely extended vacancy states also yield the extreme enhancement of the other multipole susceptibilities. Then, we also calculate the electric dipole and octupole susceptibilities by using the same method as the quadrupole susceptibilities. The Curie constants K_Γ for the corresponding multipole suscepti-

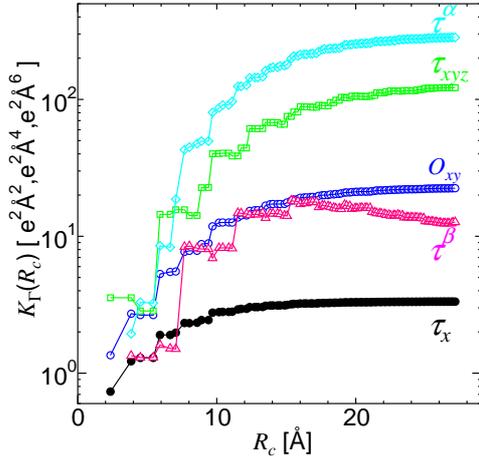


Fig. 5. The Curie constants K_Γ for various multipole susceptibilities as functions of R_c . The closed circles (\bullet), open circles (\circ), squares (\square), diamonds (\diamond) and triangles (\triangle) represent the K_Γ for the dipole τ_x , quadrupole O_{xy} , octupole τ_{xyz} , τ^α and τ^β susceptibilities, respectively.

bilities are obtained by replacing $\phi_\Gamma(\mathbf{r})$ in eq. (10) with

$$\phi_\Gamma(\mathbf{r}) \equiv \begin{cases} x & \text{for } \tau_x \\ y & \text{for } \tau_y \\ z & \text{for } \tau_z \end{cases}$$

for the electric dipole and

$$\phi_\Gamma(\mathbf{r}) \equiv \begin{cases} xyz & \text{for } \tau_{xyz} \\ x(3x^2 - r^2)/\sqrt{3} & \text{for } \tau_x^\alpha \\ y(3y^2 - r^2)/\sqrt{3} & \text{for } \tau_y^\alpha \\ z(3z^2 - r^2)/\sqrt{3} & \text{for } \tau_z^\alpha \\ x(y^2 - z^2) & \text{for } \tau_x^\beta \\ y(z^2 - x^2) & \text{for } \tau_y^\beta \\ z(x^2 - y^2) & \text{for } \tau_z^\beta \end{cases}$$

for the electric octupole.

Fig. 5 shows K_Γ for several multipole susceptibilities as functions of R_c . It is found that K_Γ for one order higher multipole susceptibilities show about 10 times larger enhancement. In the octupole susceptibilities, the site diagonal contributions for τ_{xyz} , τ^α , τ^β are the same order of $10 e^2 \text{\AA}^6$ (not shown), while the site off-diagonal contribution for τ^α is much larger than that for the other mode resulting in the extreme enhancement of τ^α . We note that K_Γ for τ^β decreases with increasing R_c because its site off-diagonal contribution is negative.

4. Summary and Discussion

In summary, we have investigated the electronic state around a single vacancy in infinite Si crystal on the basis of the Green's function approach. It has been found that the T_2 triplet vacancy states within the band gap are widely extended up to 20 \AA and are responsible for the extreme enhancement of the Curie constant of the quadrupole susceptibilities resulting in the elastic softening at low temperature. The Curie constant for the trigonal mode (O_{yz} , O_{zx} , O_{xy}) is considerably larger than that for the tetragonal mode (O_2^0 , O_2^2). These results are consistent with the low temperature elastic softening ob-

served in the ultrasonic experiments.¹⁾ We have also calculated the other multipole susceptibilities and found that the remarkable enhancement of the Curie constant for the octupole susceptibilities especially in τ^α mode; which is expected to be observed in future experiments.

In the present study, we have assumed that the T_d -point symmetry remaining the orbital degeneracy is preserved in a single vacancy in infinite Si crystal. Even in this case, a lattice relaxation with keeping the symmetry might take place; which results in a modification of the tight-binding parameters around the vacancy. To discuss this effect, we need a first-principle calculation with keeping the symmetry. A recent molecular dynamics simulation combined with a first-principle calculation revealed that such a high symmetric vacancy state is realized at a finite temperature.¹⁵⁾ The explicit calculation of the quadrupole susceptibility including the effect of the lattice relaxation is an important future problem. In addition, the explicit estimation of the quadrupole-strain coupling g_Γ is also important to determine the absolute value of the elastic softening.

At a finite vacancy concentration, the effect of the inter-vacancy interaction is considered to be also important. In fact, the ultrasonic experiments revealed that there exists the antiferro-type inter-vacancy interaction of order of 2 K.¹⁾ On the basis of the Green's function approach employed in the present study, we can discuss the effect of the inter-vacancy interaction by introducing the spatially separated two vacancies in infinite Si crystal. Such a calculation is under the way.

The effects of the Coulomb interaction and the coupling between electrons and Jahn-Teller phonons, which have not been considered in the present study, are crucial to determine the many-body groundstate in a Si vacancy and have been intensively discussed from the cluster model calculations.^{20,21)} Actually, the non-magnetic groundstate in V^0 with 3-fold orbital degeneracy has been obtained due to the effect of nonadiabatic couplings between electrons and Jahn-Teller phonons,^{20,21)} in contrast to the present study where the spin degeneracy is unresolved as an artifact of the noninteracting calculation. In addition, the effect of the spin-orbit interaction neglected in this study is also crucial for the magnetic groundstates of V^+ and V^- which are expected to be realized in the B-doped¹⁹⁾ and P-doped Si, respectively. On the basis of the Green's functions for a Si vacancy obtained by the present study, we can discuss the many-body effect by including the selfenergy corrections due to the Coulomb interaction and the electron-phonon coupling. The detailed results of the selfenergy corrections in the presence of the spin-orbit interaction will be reported in a subsequent paper.

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- 25) Substituting an empirical exponential function

$$e^2 \sum_j \sum_{\alpha\beta} \phi_{\Gamma}(\mathbf{r}_i) \phi_{\Gamma}(\mathbf{r}_j) A_{i\alpha j\beta}^{T_2} A_{j\beta i\alpha}^{T_2} \propto e^{-|\mathbf{r}_i|/\xi_{\Gamma}},$$
 into eq.(14) and replacing the i -summation with the \mathbf{r}_i -integral up to $|\mathbf{r}_i| = R_c$, we can obtain the fitting function of $K_{\Gamma}(R_c)$.
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