Electron spin-phonon interaction symmetries and tunable spin relaxation in silicon and germanium

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Compared with direct-gap semiconductors, the valley degeneracy of silicon and germanium opens up new channels for spin relaxation that counteract the spin degeneracy of the inversion-symmetric system. Here the symmetries of the electron-phonon interaction for silicon and germanium are identified and the resulting spin lifetimes are calculated. Room-temperature spin lifetimes of electrons in silicon are found to be comparable to those in gallium arsenide, however, the spin lifetimes in silicon or germanium can be tuned by reducing the valley degeneracy through strain or quantum confinement. The tunable range is limited to slightly over an order of magnitude by intravalley processes.

PACS numbers: 71.70.Fk, 72.25.Dc, 72.25.Rb, 72.10.Di

I. INTRODUCTION

The favorable material properties of silicon have permitted it to dominate the microelectronics industry for over half a century, however a new genre of spintronic concepts into hybrid silicon device architectures. Polarized spins relax in semiconductors because the spin-orbit interaction entangles orbital and spin degrees of freedom, and thus ordinary scattering from defects or lattice vibrations leads to a loss of spin coherence. In materials without inversion asymmetry the entanglement of spin and orbit manifests as an effective momentum transfer, which allows the Elliott-Yafet spin relaxation. The spin coherence times in silicon are long at low temperature, and the spin-orbit interaction and lattice symmetry reduces spin relaxation rates relative to optically accessible (direct-gap) semiconductors. The silicon band structure, however, has multiple valleys that permits low-energy scattering of electrons by large momenta, which allows the Elliott-Yafet process to be more effective. Numerical calculations that include these effects have been successful at explaining the spin lifetime in silicon as a function of temperature. Tuning the spin lifetime in inversion-asymmetric semiconductors with a single direct gap have largely focused on the electric-field-induced Rashba spin-orbit interaction that shortens the spin lifetime, unaddressed is the potential for new methods of tuning the spin lifetime associated with the valley degeneracy of the semiconductor.

II. ELECTRON-PHONON SCATTERING

The intrinsic spin-relaxation time is determined by electron-phonon scattering. For one-phonon absorption (+) and emission (−) processes, the scattering probabil-
up to the first order in matrix elements in terms of the deformation potentials the
spin index, and \( R \) labels the spin state, and \( n_q \) is the phonon occupation number. To evaluate \( M^\pm_{\sigma',\sigma}(k',k) \) for various types of scattering processes in the material, we use a first-nearest-neighbor \( sp^3 \) tight-binding model (TBM) with on-site spin-orbit interaction to obtain the wave functions,

\[
\psi_{\sigma}(r) = \frac{1}{\sqrt{N}} \sum_{j,a,l,s} c_{al} e^{ik_{ja}(r-R_{ja})} \chi_s, \tag{2}
\]

where \( N \) is the number of unit cells, \( j \) labels unit cells, \( a \) labels the two basis atoms within a unit cell, \( l \) labels the atomic orbital bases, \( \chi \) is a two-component spinor, \( s \) is the spin index, and \( R_{ja} \) is the position vector of atoms. We choose the spin quantization axis to be aligned with the \( z \) axis and determine the coefficients \( c_{al} \) by maximizing the expectation value of the spin operator \( \langle S_z \rangle \).

In the spherical band approximation, we express the matrix elements in terms of the deformation potentials up to the first order in \( \delta q = (k'-k_f) - (k-k_f) \):

\[
M^\pm_{\sigma',\sigma}(k',k) \approx \frac{\hbar}{2V\omega} (D^2_{0,\sigma',\sigma} + D^2_{1,\sigma',\sigma}|\delta q|^2) (n_q + \frac{1}{2} \mp \frac{1}{2}) \tag{3}
\]

where \( \rho \) is the density, \( V \) is the crystal volume, \( \omega \) is the phonon frequency, and \( k_i \) and \( k_f \) are the wave numbers of the initial and final valley minima, respectively. For Si, there are six valleys on the \( \Delta \) axes, e.g., \( k_0 = (2\pi/a)(0.85,0,0) \), and for Ge, there are four valleys at the \( L \) points, e.g., \((\pi/a)(1,1,1)\). A spherical averaging around the valley minimum is carried out for evaluating \( D_1 \). We have assumed only the following types of matrix elements are nonzero, \( \langle \phi_{\alpha}(R) | \partial H/\partial R | \phi_{\beta}(R) \rangle \), \( \langle \phi_{\alpha'}(R') | (\partial H/\partial R) | \phi_{\beta}(R) \rangle \), and \( \langle \phi_{\alpha'}(R') | (\partial H/\partial R) | \phi_{\beta}(R) \rangle \), all have the same magnitude. Since the atomic potential is not explicitly known in the TBM, we can only determine the relative strengths of the processes. The overall magnitude is later determined by fixing the mobility to be 1450 cm\(^2\)/Vs in Si and 3800 cm\(^2\)/Vs in Ge. Calculated deformation potentials for different phonon processes are summarized in Table I. The relative strengths of different processes are consistent with the semimipirical values in the literature.

Various electron-phonon scattering rates are computed as follows. For the intravalley acoustic process, a linear phonon dispersion, \( \omega = c|q| \) is used and the scattering rate including both absorption and emission is

\[
\frac{1}{\tau_A} = \frac{\sqrt{2D Xm^{3/2}}}{\pi \rho \omega^2 c^3} k_B T \langle \sqrt{E} \rangle_T, \tag{4}
\]

where \( m = (m_L m_T)^{1/3} \) is the averaged effective mass, and \( c = 3/(1/c_L^2 + 2/c_T^2) \) is the averaged speed of sound. We use \( \rho = 2329 \text{ kg/m}^3 \), \( m_L = 0.9163 m_e \), \( m_T = 0.1905 m_e \), \( c_L = 8500 \text{ m/s} \), and \( c_T = 5900 \text{ m/s} \) for Si, and \( \rho = 5323 \text{ kg/m}^3 \), \( m_L = 1.59 m_e \), \( m_T = 0.0823 m_e \), \( c_L = 4900 \text{ m/s} \), and \( c_T = 3500 \text{ m/s} \) for Ge. A thermal averaging of the initial electron energy is carried out with the Boltzmann distribution, appropriate for non-degenerate systems,

\[
\langle g(E) \rangle_T = \frac{4}{3\sqrt{\pi T S/2}} \int_0^\infty g(E)E^{3/2}e^{-E/T} dE. \tag{5}
\]

In this regime the spin lifetime is independent of the carrier density; for degenerate carrier densities the spin life-
TABLE I. Deformation potentials. The unit for $D_{0}$’s is eV/Å, and for $D_{1}$’s is eV. For intravalley acoustic processes, $D_{1} = 3.1$ eV, $D_{A, \pi+} = 0.0016$ eV for Si, and $D_{A} = 3.8$ eV, $D_{A, \pi+} = 0.032$ eV for Ge. For spin-flip processes, the superscript $xy$ indicates that both the initial and final valleys are in the $x$-$y$ plane, and the superscript $z$ indicates that the initial and final valleys are separated along the $z$ direction. $T_{\omega\tau}$ is the effective phonon frequency in Kelvin. The deformation potentials listed here do not include the valley degeneracy of final states. The parentheses indicate that the $D_{1z}^{\pm}$ term is negative.

| Phonon | $T_{\omega\tau}$ (K) | $D_{0}$ | $D_{1}$ | $D_{1z}^{xy}$ | $D_{1z}^{\pi+}$ | $D_{1z}^{\sigma}$ |
|--------|----------------------|--------|--------|-------------|-------------|-------------|
| $\Gamma_{5}^{+}$ | 730 | 0 | 0.34 | 0 | 0.14 | 0 | 0.19 |
| $\Delta_{1}' + \Delta_{3}$ | 700 | 4.5 | (3.2) | 0 | 0.031 | 0 | 0.01 |
| $\Delta_{1}$ | 210 | 0 | 0.04 | 0 | 0.028 | 0 | 0.04 |
| $\Delta_{3}$ | 140 | 0 | 2.7 | 0 | 0.009 | 0 | 0.0015 |
| $\Sigma_{1} + \Sigma_{2}$ | 630 | 3.2 | (2.3) | 0.03 | 0.11 | 0.044 | 0.17 |
| $\Sigma_{1} + \Sigma_{3}$ | 500 | 3 | (1.1) | 0.018 | 0.075 | 0.026 | 0.097 |
| $\Sigma_{2} + \Sigma_{4}$ | 210 | 0.0083 | 2.2 | 0.0083 | 0.041 | 0.0059 | 0.058 |
| $\Gamma_{5}^{+}$ | 430 | 3.5 | 4.6 | 0 | 0 | 0 | 0 |

TABLE II. Selection rules with the inclusion of time-reversal symmetry with spin. For electron representations, $\Delta_{1}^{+}$ is $\Delta_{1}$ at $k_{0}$ transformed to a valley on a perpendicular axis to $k_{0}$, and $L_{1}^{+}$ is $L_{1}$ transformed from one $L$ valley to a different valley. The phonon representation $\Delta_{1}^{+}(2k_{0})$ becomes $\Delta_{6}^{+}(2k_{0} - (4\pi/a)(1, 0, 0))$ in the reduced Brillouin zone scheme used in Table I.

| Phonon | $T_{\omega\tau}$ (K) | $D_{0}$ | $D_{1}$ | $D_{1z}^{xy}$ | $D_{1z}^{\pi+}$ | $D_{1z}^{\sigma}$ |
|--------|----------------------|--------|--------|-------------|-------------|-------------|
| $\Gamma_{5}^{+}$ | 730 | 0 | 0.34 | 0 | 0.14 | 0 | 0.19 |
| $\Delta_{1}' + \Delta_{3}$ | 700 | 4.5 | (3.2) | 0 | 0.031 | 0 | 0.01 |
| $\Delta_{1}$ | 210 | 0 | 0.04 | 0 | 0.028 | 0 | 0.04 |
| $\Delta_{3}$ | 140 | 0 | 2.7 | 0 | 0.009 | 0 | 0.0015 |
| $\Sigma_{1} + \Sigma_{2}$ | 630 | 3.2 | (2.3) | 0.03 | 0.11 | 0.044 | 0.17 |
| $\Sigma_{1} + \Sigma_{3}$ | 500 | 3 | (1.1) | 0.018 | 0.075 | 0.026 | 0.097 |
| $\Sigma_{2} + \Sigma_{4}$ | 210 | 0.0083 | 2.2 | 0.0083 | 0.041 | 0.0059 | 0.058 |
| $\Gamma_{5}^{+}$ | 430 | 3.5 | 4.6 | 0 | 0 | 0 | 0 |

TABLE III. Selection rules with the inclusion of time-reversal symmetry with spin. The spin-flip part of $\Delta_{1}$ ($\Delta_{1}'$) in Table II in Si and of $\Gamma_{5}^{+}$ in Ge are also forbidden by time reversal.

| Phonon | $T_{\omega\tau}$ (K) | $D_{0}$ | $D_{1}$ | $D_{1z}^{xy}$ | $D_{1z}^{\pi+}$ | $D_{1z}^{\sigma}$ |
|--------|----------------------|--------|--------|-------------|-------------|-------------|
| $\Gamma_{5}^{+}$ | 730 | 0 | 0.34 | 0 | 0.14 | 0 | 0.19 |
| $\Delta_{1}' + \Delta_{3}$ | 700 | 4.5 | (3.2) | 0 | 0.031 | 0 | 0.01 |
| $\Delta_{1}$ | 210 | 0 | 0.04 | 0 | 0.028 | 0 | 0.04 |
| $\Delta_{3}$ | 140 | 0 | 2.7 | 0 | 0.009 | 0 | 0.0015 |
| $\Sigma_{1} + \Sigma_{2}$ | 630 | 3.2 | (2.3) | 0.03 | 0.11 | 0.044 | 0.17 |
| $\Sigma_{1} + \Sigma_{3}$ | 500 | 3 | (1.1) | 0.018 | 0.075 | 0.026 | 0.097 |
| $\Sigma_{2} + \Sigma_{4}$ | 210 | 0.0083 | 2.2 | 0.0083 | 0.041 | 0.0059 | 0.058 |
| $\Gamma_{5}^{+}$ | 430 | 3.5 | 4.6 | 0 | 0 | 0 | 0 |

III. DISCUSSION

Our results can be qualitatively understood from the selection rules, derived from symmetry, that apply to scattering processes between the valley minima, i.e., $D_{0}$’s. The selection rules without spin-orbit coupling were discussed by Lax and Hopfield and are listed in Table II. When electron spin is included, the irreducible representation at the conduction-band minima in Si (Ge) becomes $\Delta_{6}$ ($L_{1}^{+}$) instead of $\Delta_{1}$ ($L_{1}^{+}$). We analyzed the selection rules including time-reversal symmetry using the same subgroup technique developed in Refs. 26 and 28 and list the results in Table III. The allowed phonon representations at $q$ (right-hand side of the equations) are obtained from the characters at $k$ and $k'$ (the two representations on the left-hand side of the equations). Details of our calculations of the selection rules are pre-

![FIG. 3](https://example.com/fig3.png) (Color online) Spin-relaxation time at $T = 300$ K as a function of valley energy shift, $\Delta E_{0}$, shown by black solid lines. The energy shift is the energy offset of four (three) valleys relative to the remaining two (one) in Si (Ge). The symbols in panel (a) have the same meaning as in Fig. 1 and in panel (b) are the same as in Fig. 2.
In Si the spin-orbit interaction mixes spin up and down by about 1% in wave function and gives a spin-flip probability about 10^{-4}. It can be seen from Fig. 4 that the Σ phonons (also known as the f processes) dominate the mobility and the spin flip near room temperature. For mobility, Δ phonons (also known as the g processes) also contribute substantially, consistent with the selection rules of $Δ_2$ and $Σ_1$ in Table II. For spin flip, the $Σ_2$ and $Σ_3$ phonons become allowed with nonzero spin-orbit interaction in addition to $Σ_1$ (Table III). The intravalley optical ($Γ_{25}^+$) phonons and the Δ phonons remain forbidden for spin flip by time reversal and, therefore, are not as effective as the Σ phonons. Although the coupling strength for the low-energy Σ phonon is weaker, this is somewhat compensated by the temperature dependence of the phonon distribution and it ends up that all Σ phonons contribute approximately the same to spin flip near room temperature.

In Ge the spin-flip probability due to spin-orbit interaction is about one order of magnitude larger, but the number of possible phonon processes is reduced. So the spin-relaxation time is only about one order of magnitude smaller than in Si as shown in Fig. 2. For mobility, the intervalley $X_1$ and the intravalley optical ($Γ_{25}^+$) phonons are more important due to the selection rules in Table II. For spin flip, the high-energy ($X_3$) phonon is allowed with finite spin-orbit interaction, but the low-energy ($X_3$) phonon is still forbidden by time reversal. Although the coupling to $Γ_{25}$ phonons is as strong as the coupling to $X_1$ phonons, the spin-flip part is forbidden by time reversal and ineffective (Table III).

Now that the structure and symmetry of the spin-relaxation mechanisms has been clarified, the analysis of the effect of strain is straightforward. Strain (or quantum confinement) breaks valley degeneracy and can eliminate multivalley scattering processes. In Si, a [001] strain can change the lowest-energy valley degeneracy from six to two (located on the same axis). In Ge, a [111] strain can yield just a single nondegenerate valley at the conduction-band edge. We have performed a simple estimate that only takes into account the valley energy shift, $ΔE_0$, by modifying $±\hbar\omega_0 \rightarrow ±\hbar\omega_0 - ΔE_0$ and the initial electron distribution in each valley. As shown in Fig. 3 the spin lifetime averaged over all valleys can be lengthened substantially: 1% strain gives about 0.09 eV shift in Si, and 0.16 eV shift in Ge. Positive energy shift ($ΔE_0 > 0$) corresponds to the configuration that four valleys out of six are shifted to higher energy in the case of Si, and three out of four in the case of Ge. Negative shift reverses the ordering. For positive shifts, the intervalley Σ processes in Si or the X processes in Ge can be completely eliminated. This tuning is eventually limited by the intervalley Δ and the intravalley optical ($Γ_{25}^+$) processes in Si, and by the intravalley acoustic processes in Ge. For negative shifts, the elimination of the intervalley processes is only partial, so the tuning range is much smaller.

### IV. CONCLUSIONS

We have presented a thorough symmetry analysis of the electron spin-phonon interaction processes for silicon and germanium, finding a spin lifetime for nondegenerate carriers at room temperature comparable to those in III-V semiconductors when the scattering determining the carrier mobility is dominated by phonons. However, strain or quantum confinement can lift the valley degeneracy, which lengthens the spin lifetime substantially (over an order of magnitude at room temperature).

### ACKNOWLEDGEMENTS

This work was supported in part by an ONR MURI and an ARO MURI.

### Appendix A: Selection Rules

In this Appendix we show the calculations of the characters of the product representations for obtaining the selection rules in Tables II and III. Each electron-phonon scattering process involves three subgroups of the wave vectors, $k$, $k'$ and $q$. Instead of using the intersection group formed by the elements common to all three subgroups and creating the corresponding character tables, the selection rules are derived using the existing character tables of the subgroups at these wave vectors. The two multiplication rules, with and without time-reversal symmetry, will be presented. We choose to compute the characters of the phonon representations at $q$ from the products of the electron representations at $k$ and $k'$. Once the characters at $q$ are obtained, the decomposition into irreducible representations is done in the usual way using the subgroup of the wave vector $q$.

#### TABLE IV. Double group characters at $Δ = k_0(1,0,0)$.

| Class | $Δ_1$ | $Δ_2$ | $Δ_2'$ | $Δ_1'$ | $Δ_3$ | $Δ_5$ | $Δ_7$ |
|-------|-------|-------|--------|--------|-------|-------|-------|
| $(E)[0]$ | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| $(E)[0]$ | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| $(C_2[0], (C_2')[0])$ | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| $2(C_3[τ])$ | $λ$ | $−λ$ | $−λ$ | $λ$ | 0 | $\sqrt{2}λ$ | $−\sqrt{2}λ$ |
| $2(C_3'[τ])$ | $λ$ | $−λ$ | $−λ$ | $λ$ | 0 | $−\sqrt{2}λ$ | $\sqrt{2}λ$ |
| $2(iC_2[τ])$, $2(iC_2'[τ])$ | $λ$ | $−λ$ | $−λ$ | $λ$ | 0 | 0 | 0 |
| $2(iC_2[0], (iC_2')[0])$ | 1 | $−1$ | $−1$ | $1$ | 0 | 0 | 0 |

$λ = \exp(i\pi σ_4/4)$, $E$ is 2π rotation, $N_{Δ star}(Δ(C)) = 1$, $Δ_0 = Δ_1 \otimes D_{1/2}$, $Δ_7 = Δ_2 \otimes D_{1/2}$

We first carry out calculations without time-reversal symmetry. To obtain the product character at $q$ for each class $C$ using the characters at $k$ and at $k'$, the usual character multiplication rules are modified as follows.

$$χ_q^{iΔj}(C) = χ_kC(k)[χ_k(C)]^* \cdot N_{q star}k(C), \quad (A1)$$
where $i$ and $j$ are the irreducible representations, and $N_{q \text{ star } \mathbf{k}}(C)$ is the number of wave vectors that are unchanged by the class $C$, out of a set of non-equivalent $\mathbf{k}$ points. This set of non-equivalent $\mathbf{k}$ points is generated by the subgroup of $q$ and is called "$q$ star of $\mathbf{k}$." The product character is simply zero if $C$ is not a common class of all three subgroups.

### Table V. Double group characters at $L = (\pi/a)(1, 1, 1)$.

| Class | $L_1^\pm$ | $L_2^\pm$ | $L_3^\pm$ | $L_4^\pm$ | $L_5^\pm$ |
|-------|-----------|-----------|-----------|-----------|-----------|
| $(E|0)$ | 1 | 1 | 2 | 1 | 1 |
| $(E|0)$ | 1 | 1 | 2 | -1 | -1 |
| 3$(C_2|\tau)$ | 1 | -1 | 0 | $i$ | -$i$ |
| 3$(C_2|\tau)$ | 1 | -1 | 0 | -$i$ | $i$ |
| 2$(C_3|0)$ | 1 | 1 | -1 | -1 | 1 |
| 2$(C_3|0)$ | 1 | 1 | -1 | 1 | -1 |
| $(i|\tau)Z$ | $\pm \chi(Z)$ | $\pm \chi(Z)$ |

$Z$ can be any of the six classes shown above. $L_6^\pm = L_1^\pm \otimes D_{1/2} = L_2^\pm \otimes D_{1/2}$

### Table VI. Group characters at $\Gamma = (0, 0, 0)$.

| Class | $\Gamma_{x}^\pm$ | $\Gamma_{y}^\pm$ | $\Gamma_{z}^\pm$ | $\Gamma_{z}^\pm$ | $\Gamma_{x}^\pm$ |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $(E|0)$ | 1 | 1 | 2 | 3 | 3 |
| 3$(C_2|\tau)$ | 1 | -1 | 0 | 1 | -1 |
| 6$(C_4|\tau)$ | 1 | -1 | 0 | -1 | 1 |
| 8$(C_3|0)$ | 1 | 1 | -1 | 0 | 0 |
| $(i|\tau)$ | $\pm 1$ | $\pm 1$ | $\pm 2$ | $\pm 3$ | $\pm 3$ |
| 3$(iC_2^0|\tau)$ | $\pm 1$ | $\pm 1$ | $\mp 2$ | $\mp 1$ | $\mp 1$ |
| 6$(iC_4|0)$ | $\mp 1$ | $\mp 1$ | $\mp 1$ | $\pm 1$ | $\pm 1$ |
| 8$(iC_3|\tau)$ | $\mp 1$ | $\mp 1$ | $\pm 1$ | $\mp 1$ | $\mp 1$ |

### Table VII. Group characters at $\Sigma = (0, 1, 1, 0)$.

| Class | $\Sigma_1$ | $\Sigma_2$ | $\Sigma_3$ | $\Sigma_4$ | $N_{\Sigma \text{ star } \Delta}$ |
|-------|-----------|-----------|-----------|-----------|-----------------|
| $(E|0)$ | 1 | 1 | 1 | 1 | 2 |
| $(C_2|\tau)$ | $\lambda^2$ | $-\lambda^2$ | $-\lambda^2$ | $\lambda^2$ | 0 |
| $(iC_2^0|\tau)$ | $\lambda^2$ | $-\lambda^2$ | $-\lambda^2$ | $\lambda^2$ | 2 |
| $(iC_2^0|0)$ | 1 | -1 | 1 | -1 | 0 |

### Table VIII. Group characters at $X = (2\pi/a)(1, 0, 0)$.

| Class | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $N_{X \text{ star } L}$ |
|-------|-------|-------|-------|-------|-----------------|
| $(E|0)$ | 2 | 2 | 2 | 2 | 4 |
| $(C_2|0)$ | 2 | 2 | -2 | -2 | 0 |
| $(C_2|\tau), (C_2^*|\tau + t_{xy})$ | 0 | 0 | -2 | 2 | 2 |
| 2$(iC_2|0)$ | 2 | -2 | 0 | 0 | 2 |
| $(E|t_{xy})$ | -2 | -2 | -2 | -2 | 4 |
| $(C_2^*|t_{xy})$ | -2 | -2 | 2 | 2 | 0 |
| $(C_2|\tau + t_{xy}), (C_2^*|\tau)$ | 0 | 0 | -2 | -2 | 2 |
| 2$(iC_2^0|t_{xy})$ | -2 | 2 | 0 | 0 | 2 |

$t_{xy} = (a/2)(1, 1, 0)$

Time reversal can add additional constraints to the selection rules if there exists a group element that connects the time-reversed process ($-\mathbf{k} \rightarrow -\mathbf{k}$) to the original process ($\mathbf{k} \rightarrow \mathbf{k}'$). That is, we need an element $Q$ from the subgroup of $q$ that interchanges $\mathbf{k}$ and $-\mathbf{k}'$. To incorporate the time reversal symmetry, the character multiplication rule is modified to the symmetric or antisymmetric combination of the characters of the original process and the process connected via $Q$,

$$\chi_{q \text{ star } \mathbf{k}}(C) = \frac{1}{2} \left[ \chi_{q \text{ star } \mathbf{k}}(C) \pm \lambda^j_k(C^2) N_{q \text{ star } \mathbf{k}}(QC) \right]$$

where $C^2$ is the class of the square of elements in $C$ and $Q$ is the element that interchanges $\mathbf{k}$ and $-\mathbf{k}'$. The positive (symmetric) sign is used in the cases without spin and the negative (antisymmetric) sign is used with spin. Again, all the relevant characters for the product representations are listed in Tables [X][XII][XIII].
can be identified as the first entry in the column of QC when C is the identity class. For $\Delta$ phonons in Si and $\Gamma$ phonons in Ge, Q is simply the identity element. Upon closer examination, we also found that the spin-flip part of the $\Delta$ phonon process in Si and of the $\Gamma^{+}_{25}$ phonon process in Ge are forbidden because the final state is exactly the time reverse of the initial state (e.g., $|\alpha\rangle = |k\uparrow\rangle$ and $|\hat{T}\alpha\rangle = |−k\downarrow\rangle$),

$$\langle \hat{T}a|\hat{H}_{\text{ep}}|\alpha\rangle = \langle \hat{T}a|\hat{T}\hat{H}_{\text{ep}}\hat{T}^{-1}|\hat{T}^2\alpha\rangle , \quad (A3)$$

where $\hat{T}$ is the time-reversal operator, $\hat{T}^2 = −\hat{1}$ in the presence of half-integer spin, and $\hat{H}_{\text{ep}} = \hat{T}\hat{H}_{\text{ep}}\hat{T}^{-1}$ is the time-reversal invariant electron-phonon interaction Hamiltonian.

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TABLE IX. Characters of the product representations at $\Gamma$.

| $C$  | $QC$ | $N(QC)$ | $C^2$ | $\Delta_1$ | $\Delta_1 \otimes \Delta_1$ | $\Delta_1 \otimes \Delta_1$ | $\Delta_2$ | $\Delta_2$ |
|------|------|----------|-------|------------|----------------|----------------|------------|------------|
| $(E|0)$ | $(i|\tau)$ | 0 | $(E|0)$ | 1 | 6 | 3 | $(E|0)$ | 2 | 24 | 12 |
| $(C_2|0)$ | $(iC_2|\tau)$ | 4 | $(E|0)$ | 1 | 2 | 3 | $(E|0)$ | 2 | 24 | 12 |
| $(C_4|\tau)$ | $(iC_4|0)$ | 0 | $(C_2|0)$ | 1 | 2 | 1 | $(C_2|0)$, $(C_4|0)$ | 0 | 4 | 2 |
| $(C_2|\tau)$ | $(iC_2|0)$ | 2 | $(E|0)$ | 1 | 0 | 1 | $(E|0)$ | 2 | 0 | 6 |
| $(i|\tau)$ | $(E|0)$ | 6 | $(E|0)$ | 1 | 0 | 3 | $(E|0)$ | 2 | 0 | 6 |
| $(iC_2|\tau)$ | $(iC_2|0)$ | 2 | $(C_2|0)$ | 1 | 0 | 1 | $(C_2|0)$, $(C_2|0)$ | 0 | 0 | 0 |
| $(iC_2|0)$ | $(C_2|\tau)$ | 0 | $(E|0)$ | 1 | 2 | 1 | $(E|0)$ | 2 | 0 | 6 |

Only classes that have non-trivial characters are shown.

$\Delta_1 \otimes \Delta_1 = \Gamma_1^+ \oplus \Gamma_1^+ \oplus \Gamma_5^+$ and $\Delta_6 \otimes \Delta_6 = \Gamma_1^+ \oplus \Gamma_1^+ \oplus 2\Gamma_5^+ \oplus \Gamma_7^+$ without time-reversal symmetry

TABLE X. Characters of the product representations at $\Delta = 2k_0$.

| $C$  | $C^2$ | $\Delta_6$ | $\Delta_6 \otimes \Delta_6$ | $\Delta_6 \otimes \Delta_6$ |
|------|-------|------------|----------------|----------------|
| $(E|0)$ | $(E|0)$ | 1 | 1 | 1 | $(E|0)$ | 2 | 4 | 1 |
| $(C_2|0)$ | $(E|0)$ | 1 | 1 | 1 | $(E|0)$ | -2 | 0 | 1 |
| $(C_4|\tau)$ | $(E|0)$ | 1 | 1 | 1 | $(E|0)$ | 2 | 2 | 1 |
| $(iC_2|\tau)$ | $(E|0)$ | 1 | 1 | 1 | $(E|0)$ | -2 | 0 | 1 |
| $Q$ is the identity element. $\Delta_6 \otimes \Delta_6 = \Delta_1 \oplus \Delta_1^+ \oplus \Delta_5$ without time-reversal symmetry

TABLE XI. Characters of the product representations at $\Sigma = k_0(1,1,0)$.

| $C$  | $C^2$ | $\Delta_1 \otimes \Delta_1$ | $\Delta_1 \otimes \Delta_1$ |
|------|-------|----------------|----------------|
| $(E|0)$ | $(E|0)$ | 1 | 1 |
| $(C_2|0)$ | $(E|0)$ | 1 | 0 |
| $(iC_2|\tau)$ | $(iC_2|0)$ | 1 | 1 |
| $\Delta_1 \otimes \Delta_1 = \Sigma_4 \oplus \Delta_6 \otimes \Delta_6 = 2\Sigma_4 \oplus 2\Sigma_6 \oplus 2\Sigma_6 \oplus 2\Sigma_6$ without time-reversal symmetry

TABLE XII. Characters of the product representations at $\Gamma$.

| $C$  | $C^2$ | $L_1^+ \otimes L_1^+$ |
|------|-------|----------------|
| $(E|0)$ | $(E|0)$ | 1 | 4 |
| $(C_2|\tau)$ | $(E|0)$ | 1 | 2 |
| $(i|\tau)$ | $(E|0)$ | 1 | 4 |
| $(iC_2|\tau)$ | $(E|0)$ | 1 | 2 |

$Q$ is the identity element. Only classes that have non-trivial characters are shown.

$L_6^0 \otimes L_6^0 = \Gamma_1^+ \oplus \Gamma_5^+ \oplus \Gamma_7^+ \oplus 2\Gamma_{15}^+ \oplus 2\Gamma_{25}^+$ without time-reversal symmetry

TABLE XIII. Characters of the product representations at $X$.

| $C$  | $C^2$ | $L_1^+ \otimes L_1^+$ |
|------|-------|----------------|
| $(E|0)$ | $(C_2|0)$ | 0 | 1 |
| $(C_2|\tau)$ | $(C_2|0)$ | 4 | 0 |
| $(iC_2|\tau)$ | $(C_2|0)$ | 2 | 2 |

Four other non-trivial classes that have exactly the opposite characters are not shown.

$L_1^+ \otimes L_1^+ = X_1 \oplus X_3$ and $L_6^{0} \otimes L_6^{0} = 2X_1 \oplus 2X_2 \oplus 2X_3 \oplus 2X_4$ without time-reversal symmetry.