

Odd-frequency Cooper pairs in two-band superconductors and their magnetic responseYasuhiro Asano^{1,2,3} and Akihiro Sasaki¹¹*Department of Applied Physics, Hokkaido University, Sapporo 060-8628, Japan*²*Center of Topological Science and Technology, Hokkaido University, Sapporo 060-8628, Japan*³*Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia*

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We discuss the appearance of odd-frequency Cooper pairs in two-band superconductors by solving the Gor'kov equation analytically. We introduce the equal-time s -wave pair potentials as realized in MgB_2 and iron pnictides. Although the order parameter symmetry is conventional, the band degree of freedom enriches the symmetry variety of pairing correlations. The hybridization and the asymmetry between the two conduction bands induce odd-frequency pairs as a subdominant pairing correlation in the uniform ground state. To study the magnetic response of odd-frequency Cooper pairs, we analyze the Meissner kernel represented by the Gor'kov Green function. In contrast to the even-frequency pairs linked to the pair potential, the induced odd-frequency Cooper pairs indicate a paramagnetic property. We also discuss the relation between the amplitude of the odd-frequency pairing correlation and the stability of superconducting states in terms of the self-consistent equation for the pair potential.

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I. INTRODUCTION

The electronic structure at the Fermi level governs such characteristics of superconductivity as effective dimensionality, anisotropy in electromagnetic properties, and the symmetry of the superconducting order parameter. Many of the superconductors discovered so far have multibands at the Fermi level. These indicate unique characteristics such as a high-critical transition temperature in iron pnictides [1], unconventional superconductivity in heavy fermionic compounds [2–4], unusual vortex states [5] in MgB_2 [6,7], and topologically nontrivial superconducting states in Cu-doped Bi_2Se_3 [8,9]. A microscopic understanding of the pairing mechanism would make it possible to explain these features.

At the superconducting transition temperature T_c , a superconductor chooses three discrete symmetry options for Cooper pairing: frequency symmetry, spin configuration, and momentum parity. In each case, there are two possibilities: pairing can be either symmetric or antisymmetric with respect to the interchange of the corresponding arguments, namely the times, spins, or coordinates of the two electrons forming a Cooper pair. Black-Schaffer and Balatsky [10] have shown that the multiband superconducting order parameter has an extra alternative symmetry option that originates from the band degree of freedom, namely even-band-parity and odd-band-parity. The Fermi-Dirac statistics of electrons require the constraint that the pairing functions must be antisymmetric under the permutation of the two electrons. As a consequence, Cooper pairs can be classified into eight symmetry classes as shown in Table I. The classification of Cooper pairs in single-band superconductors corresponds to the top four classes in Table I. Conventional superconductors and d -wave high- T_c superconductors belong to the ESEE class. Spin-triplet p -wave superconductors such as Sr_2RuO_4 and UPt_3 belong to the ETOE class. It is known that the spatial inhomogeneity of the pair potential in the ETOE (ESEE) superconductors generates Cooper pairs that belong to the OTEE (OSOE) class [11–13]. Actually odd-frequency Cooper pairs [14] appear at a surface of unconventional superconductors as a

subdominant pairing correlation [11–13]. The possibilities of odd-frequency superconductivity have also been discussed theoretically [15–21]. Recent theoretical papers studied the mechanisms of odd-frequency superconductivity in multiband superconductors [22,23]. The bottom four symmetry classes have been pointed out by the authors of Ref. [10]. Indeed, they show that the hybridization between the two conduction bands generates Cooper pairs belonging to the OSEO class. The appearance of odd-frequency pairs in a uniform ground state may be a surprising conclusion when we pay attention to a unique property of them.

Although diamagnetism is the most fundamental property of all superconductors, a number of theoretical studies have suggested that odd-frequency Cooper pairs have a *paramagnetic* property [13,24–27]. A μSR experiment [28] has caught a clear sign of paramagnetic Cooper pairs very recently. In addition, a recent experimental finding of a zero-bias anomaly in a ferromagnet/superconductor proximity structure [29], which is also closely related to the paramagnetic property, has suggested the existence of odd-frequency pairs [30–32]. The paramagnetic Cooper pairs attract magnetic fields [33,34], which implies the thermodynamic instability of odd-frequency pairing states. (See also Appendix A for details.) Actually, in single-band superconductors, odd-frequency pairs always appear as a spatially localizing subdominant pairing correlation. Thus the instability of an odd-frequency pair does not affect the transition temperature if the superconductor is sufficiently large. However, we have never encountered the type of magnetic response exhibited by induced odd-frequency pairs in multiband superconductors. If they are paramagnetic, the superconducting condensate might be unstable due to the presence of odd-frequency pairs. We address these issues in the present paper.

In this paper, we will show the existence of odd-frequency pairs in a two-band superconductor with the spin-orbit interactions or the band asymmetry. Within the theoretical model that we consider in this paper, odd-frequency Cooper pairs always exhibit a paramagnetic property irrespective of their generation mechanism. Since odd-frequency pairs appear

TABLE I. Eight symmetry classes of Cooper pairs in the presence of the band degree of freedom.

	Frequency	Spin	Momentum parity	Band parity
ESEE	Even	Singlet	Even	Even
ETOE	Even	Triplet	Odd	Even
OSOE	Odd	Singlet	Odd	Even
OTEE	Odd	Triplet	Even	Even
ESOO	Even	Singlet	Odd	Odd
ETEO	Even	Triplet	Even	Odd
OSEO	Odd	Singlet	Even	Odd
OTOO	Odd	Triplet	Odd	Odd

as a subdominant pairing correlation in a uniform ground state, their paramagnetic instability suppresses the transition temperature. We also find that the band hybridization generates even-frequency Cooper pairs whose symmetry is different from that of the order parameter. We conclude that the rich symmetry variety of the induced pairing correlations in the bulk state is a key feature of multiband superconductors.

This paper is organized as follows. In Sec. II, we present a theoretical model describing two-band superconductors. The anomalous Green functions of the Gor'kov equation are calculated, and the magnetic property of odd-frequency pairs is discussed for the intra- and interband pairing order parameter in Secs. III and IV, respectively. The conclusion is provided in Sec. V.

II. TWO-BAND MODEL

The Hamiltonian of two-band electronic states is

$$\begin{aligned}
H_N = & \sum_{\alpha=\uparrow,\downarrow} \sum_{\lambda=1,2} \int d\mathbf{r} \psi_{\lambda,\alpha}^\dagger(\mathbf{r}) \xi_\lambda(\mathbf{r}) \psi_{\lambda,\alpha}(\mathbf{r}) \\
& + \sum_{\alpha} \int d\mathbf{r} \{ \psi_{1,\alpha}^\dagger(\mathbf{r}) V_0(\mathbf{r}) \psi_{2,\alpha}(\mathbf{r}) \\
& + \psi_{2,\alpha}^\dagger(\mathbf{r}) V_0^*(\mathbf{r}) \psi_{1,\alpha}(\mathbf{r}) \}
\end{aligned}$$

$$H_{\text{BCS}}(\mathbf{k}) = \frac{1}{2} \begin{bmatrix} \xi_1 & 0 & V_0 + V_3 & V_1 - iV_2 & 0 & \Delta_1 & 0 & \Delta_{12} \\ 0 & \xi_1 & V_1 + iV_2 & V_0 - V_3 & -\Delta_1 & 0 & s_{\text{spin}} \Delta_{12} & 0 \\ V_0^* + V_3 & V_1 - iV_2 & \xi_2 & 0 & 0 & -s_{\text{spin}} \Delta_{12} & 0 & \Delta_2 \\ V_1 + iV_2 & V_0^* - V_3 & 0 & \xi_2 & -\Delta_{12} & 0 & -\Delta_2 & 0 \\ 0 & -\Delta_1^* & 0 & -\Delta_{12}^* & -\xi_1 & 0 & -V_0^* + V_3 & V_1 + iV_2 \\ \Delta_1^* & 0 & -s_{\text{spin}} \Delta_{12}^* & 0 & 0 & -\xi_1 & V_1 - iV_2 & -V_0^* - V_3 \\ 0 & s_{\text{spin}} \Delta_{12}^* & 0 & -\Delta_2^* & -V_0 + V_3 & V_1 + iV_2 & -\xi_2 & 0 \\ \Delta_{12}^* & 0 & \Delta_2^* & 0 & V_1 - iV_2 & -V_0 - V_3 & 0 & -\xi_2 \end{bmatrix}, \quad (6)$$

where $\xi_{\lambda,\mathbf{k}} = \frac{k^2}{2m_\lambda} - \mu_\lambda$, $V_1(\mathbf{k}) = -L_2 k_3 + L_3 k_2$, $V_2(\mathbf{k}) = -L_3 k_1 + L_1 k_3$, and $V_3(\mathbf{k}) = -L_1 k_2 + L_2 k_1$. We note that $V_j(\mathbf{k})$ for $j = 1-3$ are odd-momentum-parity functions satisfying $V_j(\mathbf{k}) = -V_j(-\mathbf{k})$. In this paper, we assume that the hybridization potentials are much smaller than the Fermi energy in the two conduction bands. The basic property of the

$$\begin{aligned}
& + \sum_{\alpha,\beta} \int d\mathbf{r} \{ \psi_{1,\alpha}^\dagger(\mathbf{r}) (i\mathbf{L} \times \nabla) \cdot \boldsymbol{\sigma}_{\alpha,\beta} \psi_{2,\beta}(\mathbf{r}) \\
& + \psi_{2,\alpha}^\dagger(\mathbf{r}) (i\mathbf{L} \times \nabla) \cdot \boldsymbol{\sigma}_{\alpha,\beta} \psi_{1,\beta}(\mathbf{r}) \}, \quad (1)
\end{aligned}$$

where $\xi_\lambda(\mathbf{r}) = -\frac{\nabla^2}{2m_\lambda} - \mu_\lambda$, $\hat{\sigma}_j$ for $j = 1-3$ are the Pauli matrices in spin space, and $\psi_{\lambda,\alpha}^\dagger(\mathbf{r})$ ($\psi_{\lambda,\alpha}(\mathbf{r})$) is the creation (annihilation) operator of an electron in band λ (1 or 2) with spin α (\uparrow or \downarrow) and at a location \mathbf{r} . The hybridization potential expressed by V_0 is independent of electron spin. We also consider the hybridization caused by the spin-orbit interaction represented by \mathbf{L} .

Throughout this paper, we assume the equal-time s -wave pair potential (i.e., even-frequency even-momentum-parity class) described by

$$\Delta_{\lambda\nu;\alpha\beta} = g_{\lambda,\nu} \sum_{\mathbf{k}} \langle \psi_{\lambda,\alpha}(\mathbf{k}) \psi_{\nu,\beta}(-\mathbf{k}) \rangle = -\Delta_{\nu\lambda;\beta\alpha}, \quad (2)$$

where $g_{\lambda,\nu} = g_{\nu,\lambda}$ represents the attractive interaction and $\langle \dots \rangle$ represents the quantum and thermal average. The last equation is derived from the Fermi-Dirac statistics of electrons. In this paper, we confine ourselves to the pair potentials consisting of two electrons with opposite spin. We define the spin-singlet intraband pair potential by

$$\Delta_\lambda \equiv \Delta_{\lambda\lambda;\uparrow\downarrow} = -\Delta_{\lambda\lambda;\downarrow\uparrow}, \quad (3)$$

which belongs to the ESEE class in Table I. Such intraband pair potentials have been considered in previous literature [35–37]. There are two types of pair potentials for the interband order parameters. The pair potential is defined by

$$\Delta_{12} \equiv \Delta_{12;\uparrow\downarrow} = -\Delta_{21;\downarrow\uparrow}, \quad (4)$$

$$= -s_{\text{spin}} \Delta_{21;\uparrow\downarrow} = s_{\text{spin}} \Delta_{12;\downarrow\uparrow}, \quad (5)$$

where s_{spin} is 1 for spin-triplet symmetry belonging to the ETEO class and -1 for spin-singlet symmetry belonging to the ESEE class.

The BCS Hamiltonian in momentum space is represented by

superconducting states are determined by the band structures and the effective attractive interaction in the absence of hybridization. We will discuss the effects of weak hybridizations on superconducting states. In what follows, we calculate the Green functions by solving the Gor'kov equation for Eq. (6). To obtain the analytical expression of the Green function, we

reduce the 8×8 particle-hole space in Eq. (6) to two 4×4 particle-hole spaces, \mathcal{N}_1 and \mathcal{N}_2 , by selecting one hybridization potential among V_j for $j = 0-3$. For practical calculations, we often consider a simple two-band model described by

$$m_1 = m_2 = m, \quad \mu_{1(2)} = \mu_F + (-)\delta\mu, \quad (7)$$

with $\delta\mu \ll \mu_F$.

III. INTRABAND PAIRING ORDER

We first consider a two-band superconductor with equal-time spin-singlet s -wave intraband pair potentials (ESEE). In Eq. (6), we set $\Delta_{12} = 0$.

A. Spin-independent hybridization

When spin-flip hybridization is absent (i.e., $V_1 = V_2 = 0$), Eq. (6) can be block diagonalized. The reduced Hamiltonian is represented by

$$\check{H}_1(\mathbf{k}) = \begin{bmatrix} \xi_1 & W & s\Delta_1 & 0 \\ W^* & \xi_2 & 0 & s\Delta_2 \\ s\Delta_1^* & 0 & -\xi_1 & -W^* \\ 0 & s\Delta_2^* & -W & -\xi_2 \end{bmatrix}, \quad (8)$$

$$W = V_0 + sV_3(\mathbf{k}). \quad (9)$$

In \mathcal{N}_1 , the spin of an electron is \uparrow and that of a hole is \downarrow . While in the other particle-hole space \mathcal{N}_2 , the spin of an electron (a hole) is \downarrow (\uparrow). We set the sign factor s as $s = 1$ in \mathcal{N}_1 and -1 in \mathcal{N}_2 .

The Green function is defined by

$$[i\omega_n \check{I} - \check{H}(\mathbf{k})] \check{G}(\mathbf{k}, i\omega_n) = \check{I}, \quad (10)$$

$$\check{G}(\mathbf{k}, i\omega_n) = \begin{bmatrix} \hat{G} & \hat{F} \\ \hat{F} & \hat{G} \end{bmatrix}_{(\mathbf{k}, i\omega_n)}. \quad (11)$$

At $V_3 = 0$, the anomalous Green function is calculated as

$$\begin{aligned} \hat{F}_1(\mathbf{k}, i\omega_n) = & \frac{s}{2Z_1} [\{ (-X_1 + v_2^2)\Delta_+ + (K + iv_1v_2)\Delta_- \} \hat{\rho}_0 \\ & + \{ v_1(\xi_+\Delta_+ - \xi_-\Delta_-) - iv_2(\xi_+\Delta_- - \xi_-\Delta_+) \} \hat{\rho}_1 \\ & + \omega_n(v_1\Delta_- - iv_2\Delta_+) \hat{\rho}_2 \\ & + \{ (-X_1 + v_1^2)\Delta_- + (K - iv_1v_2)\Delta_+ \} \hat{\rho}_3], \end{aligned} \quad (12)$$

with

$$Z_1 = X_1^2 - Y_1, \quad (13)$$

$$X_1 = \frac{1}{2} [\omega_n^2 + \xi_+^2 + \xi_-^2 + |\Delta_+|^2 + |\Delta_-|^2 + |V_0|^2], \quad (14)$$

$$Y_1 = K^2 + |V_0|^2 \xi_+^2 + v_1^2 |\Delta_-|^2 + v_2^2 |\Delta_+|^2 - i2v_1v_2D_-, \quad (15)$$

where we have defined

$$\xi_{\pm} = \frac{\xi_{1,\mathbf{k}} + \xi_{2,\mathbf{k}}}{2}, \quad \xi_{\pm} = \frac{\xi_{1,\mathbf{k}} - \xi_{2,\mathbf{k}}}{2}, \quad (16)$$

$$\Delta_+ = \frac{\Delta_1 + \Delta_2}{2}, \quad \Delta_- = \frac{\Delta_1 - \Delta_2}{2}, \quad (17)$$

$$K = \xi_+\xi_- + D_+, \quad D_{\pm} = \frac{\Delta_+\Delta_-^* \pm \Delta_+^*\Delta_-}{2}, \quad (18)$$

$$V_0 = v_1 + iv_2. \quad (19)$$

Here $\hat{\rho}_j$ for $j = 1-3$ are Pauli matrices in the two-band space. The normal Green function is shown in Eq. (B1) in Appendix B. The relation

$$\hat{F}_1(\mathbf{k}, i\omega_n) = \hat{F}_1^*(\mathbf{k}, i\omega_n) \quad (20)$$

holds due to the symmetry of the Gor'kov equation for reduced Hamiltonian in Eq. (8). The components of the anomalous Green function in Eq. (12) are represented by

$$\hat{F}_1^{\mathcal{N}_1} = \begin{bmatrix} \mathcal{F}_{11,\uparrow\downarrow} & \mathcal{F}_{12,\uparrow\downarrow} \\ \mathcal{F}_{21,\uparrow\downarrow} & \mathcal{F}_{22,\uparrow\downarrow} \end{bmatrix}, \quad \hat{F}_1^{\mathcal{N}_2} = \begin{bmatrix} \mathcal{F}_{11,\downarrow\uparrow} & \mathcal{F}_{12,\downarrow\uparrow} \\ \mathcal{F}_{21,\downarrow\uparrow} & \mathcal{F}_{22,\downarrow\uparrow} \end{bmatrix},$$

in \mathcal{N}_1 and \mathcal{N}_2 , respectively. The Fermi-Dirac statistics of electrons requires

$$\mathcal{F}_{\lambda\lambda';\sigma\sigma'}(\mathbf{k}, i\omega_n) = -\mathcal{F}_{\lambda'\lambda;\sigma'\sigma}(-\mathbf{k}, -i\omega_n). \quad (21)$$

The intraband components are represented as

$$\begin{aligned} \mathcal{F}_{11,\uparrow\downarrow}(\mathbf{k}, i\omega_n) &= -\mathcal{F}_{11,\downarrow\uparrow}(\mathbf{k}, i\omega_n) \\ &= \frac{1}{2Z_1} [-(X_1 - K)(\Delta_+ + \Delta_-) + v_2^2\Delta_+ + v_1^2\Delta_- \\ &\quad - iv_1v_2(\Delta_+ - \Delta_-)], \end{aligned} \quad (22)$$

$$\begin{aligned} \mathcal{F}_{22,\uparrow\downarrow}(\mathbf{k}, i\omega_n) &= -\mathcal{F}_{22,\downarrow\uparrow}(\mathbf{k}, i\omega_n) \\ &= \frac{1}{2Z_1} [-(X_1 + K)(\Delta_+ - \Delta_-) + v_2^2\Delta_+ - v_1^2\Delta_- \\ &\quad + iv_1v_2(\Delta_+ + \Delta_-)]. \end{aligned} \quad (23)$$

These components are linked to the pair potential belonging to the ESEE class. The hybridization generates two types of interband pairing correlations. The interband components result in

$$\mathcal{F}_{12,\uparrow\downarrow}(\mathbf{k}, i\omega_n) = -\mathcal{F}_{12,\downarrow\uparrow}(\mathbf{k}, i\omega_n) = P_{1e} - P_{1o}, \quad (24)$$

$$\mathcal{F}_{21,\uparrow\downarrow}(\mathbf{k}, i\omega_n) = -\mathcal{F}_{21,\downarrow\uparrow}(\mathbf{k}, i\omega_n) = P_{1e} + P_{1o}, \quad (25)$$

$$P_{1e} = \frac{v_1(\xi_+\Delta_+ - \xi_-\Delta_-) - iv_2(\xi_+\Delta_- - \xi_-\Delta_+)}{2Z_1}, \quad (26)$$

$$P_{1o} = \frac{1}{2Z_1} [i\omega_n(v_1\Delta_- - iv_2\Delta_+)]. \quad (27)$$

We find that the component

$$F_{12,\uparrow\downarrow} - F_{12,\downarrow\uparrow} + F_{21,\uparrow\downarrow} - F_{21,\downarrow\uparrow} = 4P_{1e} \quad (28)$$

TABLE II. The symmetry classification of Cooper pairs with the equal-time spin-singlet even-momentum-parity intraband (even-band-parity) pair potential.

	Frequency	Spin	Momentum parity	Band parity	Magnetic response
Pair potential	Even	Singlet	Even	Even (intra)	Diamagnetic
Induced by V_0	Even	Singlet	Even	Even (inter)	Diamagnetic
	Odd	Singlet	Even	Odd	Paramagnetic
Induced by V_1, V_2, V_3	Even	Triplet	Odd	Even (inter)	Diamagnetic
	Odd	Triplet	Odd	Odd	Paramagnetic

belongs to the ESEE class, and

$$F_{12,\uparrow\downarrow} - F_{12,\downarrow\uparrow} - F_{21,\uparrow\downarrow} + F_{21,\downarrow\uparrow} = -4P_{1o} \quad (29)$$

has the odd-frequency spin-singlet odd-band parity symmetry (OSEO). The symmetry classification results are summarized in Table II. In Ref. [10], the authors assume that V_0 is a real potential. In such a case, the odd-frequency pairing correlation appears only for $\Delta_- \neq 0$ because $v_2 = 0$. In the normal state, it is possible to eliminate the phase of the hybridization potential. Namely the phase factor $e^{i\phi}$ in

$$\sum_{\alpha} \int d\mathbf{r} [\psi_{1\alpha}^{\dagger}(\mathbf{r}) |V_0| e^{i\phi} \psi_{2\alpha}(\mathbf{r}) + \text{H.c.}] \quad (30)$$

is eliminated by choosing $\psi_{1\alpha} \rightarrow \psi_{1\alpha} e^{i\phi/2}$ and $\psi_{2\alpha} \rightarrow \psi_{2\alpha} e^{-i\phi/2}$. The phase ϕ does not affect the physics in the normal state. When we consider more than one superconducting order parameter, however, such a gauge transformation affects the relative phase difference between the order parameters. This is why we keep the phase degree of freedom of the hybridization potential. Actually, the phase also plays an important role in the gap equations as discussed later.

The magnetic property of Cooper pairs can be discussed using the relationship between the electric current and the vector potential $\mathbf{j} = -\frac{ne^2}{mc} Q\mathbf{A}$. Within the linear response regime [38,39], the dimensionless pair density Q for a uniform magnetic field is calculated to be

$$Q = \frac{1}{2} T \sum_{\omega_n} \int d\xi \text{Tr} \{ \hat{G} \hat{G} + \hat{F} \hat{F} - \hat{G}_N \hat{G}_N \}_{(\xi, i\omega_n)} \quad (31)$$

for the simple two-band model in Eq. (7), where \hat{G}_N is the Green function in the normal state, and Tr means the summation over band degree of freedom. When we decompose the anomalous Green functions into

$$\hat{F} = \sum_{\nu=0}^3 f_{\nu} \hat{\nu}_{\nu}, \quad \hat{F} = \sum_{\nu=0}^3 \underline{f}_{\nu} \hat{\nu}_{\nu}, \quad (32)$$

the contribution of the ν th component of the anomalous Green function to the pair density becomes

$$Q_f(\nu) = T \sum_{\omega_n} \int d\xi f_{\nu} \underline{f}_{\nu}. \quad (33)$$

The component of f_{ν} is diamagnetic as usual for $Q_f(\nu) > 0$. On the other hand, f_{ν} is paramagnetic for $Q_f(\nu) < 0$. As shown in Eq. (12) and the relation in Eq. (20), $Q_f(2)$ is negative. Therefore the odd-frequency pairing correlation is paramagnetic. It is easy to confirm that all the even-frequency

pairing correlations are diamagnetic. The pair density for the simple model in Eq. (7) is represented as

$$Q = T \sum_{\omega_n} \int d\xi \left[\frac{X_1 - \omega_n^2}{2Z_1} - \omega_n^2 \frac{Y_1}{Z_1^2} \right]. \quad (34)$$

The total magnetic response of all the components must be diamagnetic to realize stable superconducting states (i.e., $Q > 0$). Generally speaking, the pair density Q has a more complicated expression than Eq. (34) in the presence of the band asymmetry. Details are shown in Appendix C. It is possible to discuss the type of magnetic response in general cases by checking if f_j contributes positively or negatively to $I_{\mathcal{F}}$ in Eq. (C7). We note that the expression of the response function in Eq. (C8) can be applied to highly asymmetric two-band superconductors.

The self-consistent equations for the intraband pair potentials are represented by

$$\Delta_1 = g_1 T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_k \frac{1}{2Z_1} [(X_1 - |V_0|^2/2 - K)\Delta_1 + \{(v_1^2 - v_2^2)/2 + i v_1 v_2\} \Delta_2], \quad (35)$$

$$\Delta_2 = g_2 T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_k \frac{1}{2Z_1} [(X_1 - |V_0|^2/2 + K)\Delta_2 + \{(v_1^2 - v_2^2)/2 - i v_1 v_2\} \Delta_1], \quad (36)$$

where g_{λ} is the pairing interaction at the λ th band. When we assume $g_1 > g_2$ in the simple model in Eq. (7), for instance, the transition temperature T_{c_1} for Δ_1 is larger than the transition temperature T_{c_2} for Δ_2 in the absence of hybridization. Equation (36) indicates that hybridization induces Δ_2 even for $T_{c_2} < T < T_{c_1}$. The relative phase between the two pair potentials is determined by the phase of the hybridization potential. For $V_0 = v_1$ and $v_2 = 0$, the sign of Δ_2 should be the same as that of Δ_1 , which leads to the decrease of Δ_- . As a result, the amplitude of the odd-frequency component in Eq. (12) decreases. On the other hand for $V_0 = i v_2$ and $v_1 = 0$, the sign of Δ_2 should be opposite that of Δ_1 . Therefore Δ_+ decreases, which results in the suppression of the odd-frequency component. The self-consistent equation minimizes the odd-frequency pairing correlations and maximizes the condensation energy automatically. In more general cases for $v_1 \neq 0$ and $v_2 \neq 0$, there is a relative phase difference between the two pair potentials.

B. Hybridization due to spin-orbit interaction without spin flipping

Next we consider a situation where $V_0 = 0$ and $V_3(\mathbf{k}) \neq 0$. The spin-orbit interaction hybridizes the two conduction bands. The Hamiltonian is represented by Eq. (8) with $V_0 = 0$. Here we assume that $V_3(\mathbf{k})$ is a real value for simplicity. The Green functions are represented by Eqs. (12) and (B1) with $v_1 \rightarrow sV_3(\mathbf{k})$ and $v_2 = 0$. The symmetry of the intraband pairing correlations remain unchanged from the ESEE class. The interband pairing correlations are calculated as

$$\mathcal{F}_{12,\uparrow\downarrow}(\mathbf{k}, i\omega_n) = \mathcal{F}_{12,\downarrow\uparrow}(\mathbf{k}, i\omega_n) = P_{2e} - P_{2o}, \quad (37)$$

$$\mathcal{F}_{21,\uparrow\downarrow}(\mathbf{k}, i\omega_n) = \mathcal{F}_{21,\downarrow\uparrow}(\mathbf{k}, i\omega_n) = P_{2e} + P_{2o}, \quad (38)$$

$$P_{2e} = \frac{1}{2Z_1}[V_3(\xi_+\Delta_+ - \xi_-\Delta_-)], \quad (39)$$

$$P_{2o} = \frac{1}{2Z_1}[i\omega_n V_3\Delta_-]. \quad (40)$$

We find that

$$\mathcal{F}_{12,\uparrow\downarrow} + \mathcal{F}_{12,\downarrow\uparrow} + \mathcal{F}_{21,\uparrow\downarrow} + \mathcal{F}_{21,\downarrow\uparrow} = 4P_{2e} \quad (41)$$

belongs to the ETOE class, and

$$\mathcal{F}_{12,\uparrow\downarrow} + \mathcal{F}_{12,\downarrow\uparrow} - \mathcal{F}_{21,\uparrow\downarrow} - \mathcal{F}_{21,\downarrow\uparrow} = -4P_{2o} \quad (42)$$

belongs to the OTOO class because V_3 is an odd-momentum-parity function. The hybridization caused by the spin-orbit interaction generates two types of spin-triplet Cooper pairs as summarized in the bottom two columns of Table II. We also conclude that the odd-frequency pairs generated by the hybridization are paramagnetic in the sense that $Q_f(2) < 0$ in Eq. (33).

C. Hybridization due to spin-orbit interaction with spin flipping

In the end of this section, we consider a situation where $V_0 = V_3 = 0$, $V_1(\mathbf{k}) \neq 0$ and $V_2(\mathbf{k}) \neq 0$. The spin-orbit interaction hybridizes the two conduction bands with opposite spin. The reduced Hamiltonian is represented by

$$H_2(\mathbf{k}) = \begin{bmatrix} \xi_1 & U^* & s\Delta_1 & 0 \\ U & \xi_2 & 0 & -s\Delta_2 \\ s\Delta_1^* & 0 & -\xi_1 & U^* \\ 0 & -s\Delta_2^* & U & -\xi_2 \end{bmatrix}, \quad (43)$$

$$U = V_1(\mathbf{k}) + isV_2(\mathbf{k}). \quad (44)$$

In the first particle-hole space (\mathcal{N}_1), the spin of an electron (a hole) in band “1” is \uparrow (\downarrow), and the spin of an electron (a hole) in band “2” is \downarrow (\uparrow). In the second particle-hole space (\mathcal{N}_2), the spin of a quasiparticle is opposite to those in \mathcal{N}_1 . The sign factor s is 1 and -1 in \mathcal{N}_1 and \mathcal{N}_2 , respectively. The phase of hybridization potential does not affect the physics, because it can be eliminated by a gauge transformation for each spin degree of freedom. In Eq. (43), therefore, we assume that V_1 and V_2 are real potential. The anomalous Green function results in

$$\begin{aligned} \hat{\mathcal{F}}_2(\mathbf{k}, i\omega_n) &= \frac{s}{2Z_2}[-X_2\Delta_- + K\Delta_+ + |V|^2\Delta_-]\hat{\rho}_0 \\ &+ \{i\omega_n V_1\Delta_- + (\xi_+\Delta_+ - \xi_-\Delta_-)isV_2\}\hat{\rho}_1 \end{aligned}$$

$$\begin{aligned} &+ \{i\omega_n sV_2\Delta_- - (\xi_+\Delta_+ - \xi_-\Delta_-)iV_1\}\hat{\rho}_2 \\ &+ \{-X_2\Delta_+ + K\Delta_-\}\hat{\rho}_3, \end{aligned} \quad (45)$$

with $Z_2 = X_2^2 - Y_2$ and

$$X_2 = \frac{1}{2}[\omega_n^2 + \xi_+^2 + \xi_-^2 + |\Delta_+|^2 + |\Delta_-|^2 + |V|^2], \quad (46)$$

$$Y_2 = K^2 + |V|^2(\xi_+^2 + |\Delta_-|^2), \quad (47)$$

where K and D_{\pm} are defined in Eq. (18) and $|V|^2 = V_1^2 + V_2^2$. The normal Green function is presented in Eq. (B3) in Appendix B. The first term of the f_1 component and that of the f_2 component in Eq. (45) represent the odd-frequency pairing correlations. By using the relation $\hat{\mathcal{F}}_2(\mathbf{k}, i\omega_n) = \hat{\mathcal{F}}_2^*(-\mathbf{k}, i\omega_n)|_{v_2 \rightarrow -v_2}$, we can confirm that the odd-frequency pairing correlations are paramagnetic. In the simple model in Eq. (7), the expression of the pair density in Eq. (34) is valid by applying Eqs. (46) and (47). The elements of Green function in Eq. (45) correspond to

$$\hat{\mathcal{F}}_2^{\mathcal{N}_1} = \begin{bmatrix} \mathcal{F}_{11,\uparrow\downarrow} & \mathcal{F}_{12,\uparrow\uparrow} \\ \mathcal{F}_{21,\downarrow\downarrow} & \mathcal{F}_{22,\downarrow\uparrow} \end{bmatrix}, \quad \hat{\mathcal{F}}_2^{\mathcal{N}_2} = \begin{bmatrix} \mathcal{F}_{11,\downarrow\uparrow} & \mathcal{F}_{12,\downarrow\downarrow} \\ \mathcal{F}_{21,\uparrow\uparrow} & \mathcal{F}_{22,\uparrow\downarrow} \end{bmatrix}$$

in \mathcal{N}_1 and \mathcal{N}_2 , respectively. To analyze the pairing symmetry, we rewrite the results of equal-spin pairing correlations into

$$\mathcal{F}_{12,\uparrow\uparrow} + \mathcal{F}_{21,\uparrow\uparrow} = \frac{-(V_1 - iV_2)}{Z_2}(\xi_+\Delta_+ - \xi_-\Delta_-), \quad (48)$$

$$\mathcal{F}_{12,\downarrow\downarrow} + \mathcal{F}_{21,\downarrow\downarrow} = \frac{(V_1 + iV_2)}{Z_2}(\xi_+\Delta_+ - \xi_-\Delta_-), \quad (49)$$

$$\mathcal{F}_{12,\uparrow\uparrow} - \mathcal{F}_{21,\uparrow\uparrow} = \frac{1}{Z_2}i\omega_n\Delta_-(V_1 - iV_2), \quad (50)$$

$$\mathcal{F}_{12,\downarrow\downarrow} - \mathcal{F}_{21,\downarrow\downarrow} = \frac{-1}{Z_2}i\omega_n\Delta_-(V_1 + iV_2). \quad (51)$$

The correlations in Eqs. (48) and (49) belong to the even-frequency spin-triplet odd-momentum-parity even-band-parity (ETOE) class because V_1 and V_2 are odd-momentum-parity functions. The correlations in Eqs. (50) and (51) belong to the odd-frequency spin-triplet odd-momentum-parity odd-band-parity (OTOO) class. The hybridization between the two bands generates these pairing correlations. The symmetry classification is shown in Table II. The spin-singlet pairing correlations that belong to the ESEE class are linked to the pair potentials. The self-consistent equation for the pair potentials are represented by

$$\begin{aligned} \Delta_1 &= g_1 T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \\ &\times \frac{1}{2Z_2} [(X_2 - |V|^2/2 - K)\Delta_1 + |V|^2\Delta_2/2], \end{aligned} \quad (52)$$

$$\begin{aligned} \Delta_2 &= g_2 T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \\ &\times \frac{1}{2Z_2} [(X_2 - |V|^2/2 + K)\Delta_2 + |V|^2\Delta_1/2]. \end{aligned} \quad (53)$$

These coupled equations allow us to understand the role of the odd-frequency pairing correlation. When the two conduction bands are identical to each other (i.e., $\xi_- = 0$ and $g_1 = g_2$),

$\Delta_1 = \Delta_2$ is expected in the self-consistent equations. As a result, the odd-frequency pairing correlation vanishes because $\Delta_- = 0$ as shown in Eq. (45). In such a case, we obtain the equation that determines the transition temperature T_{c_0} at $g_1 = g_2$,

$$1 = 2\pi N_0 g_1 T \sum_{\omega_n > 0}^{N_{c_0}} \frac{1}{\omega_n}, \quad (54)$$

where N_0 is the density of states at the Fermi level in each band per spin, $N_{c_0} = \omega_c / (2\pi T_{c_0})$, and ω_c is the cutoff energy. The equation is identical to the equation for determining the transition temperature in a single-band superconductor. Therefore the hybridization does not affect transition temperature when $\Delta_1 = \Delta_2$ is expected in superconducting states. On the other hand for $g_1 \gg g_2$, $\Delta_1 \gg \Delta_2$ is expected in superconducting states. By neglecting Δ_2 in Eq. (52), we find that

$$1 = 2\pi N_0 g_1 T \sum_{\omega_n > 0}^{N_c} \left[\frac{1}{\omega_n} - \frac{|V|^2/2}{\omega_n(\omega_n^2 + |V|^2)} \right] \quad (55)$$

determines the transition temperature T_c with $N_c = \omega_c / (2\pi T_c)$. Because of the second term in Eq. (55), $N_c > N_{c_0}$ is necessary for Eq. (55) to have a solution. The condition is identical to $T_c < T_{c_0}$. In this way, we conclude that the hybridization reduces the transition temperature when $\Delta_1 \neq \Delta_2$ is expected in superconducting states. In such states, the induced odd-frequency pairs are unstable because of their paramagnetic instability. The expression of the pair density in Eq. (34) with Eq. (7) is also valid for this case when we replace X_1 and Y_1 by corresponding values Eqs. (46) and (47). A stable superconducting state is possible as long as Q is positive. If we could control the fraction of odd-frequency pairs in real materials, it would be possible to detect them from the variation of T_c .

IV. INTERBAND PAIRING ORDER

In this section, we consider the superconducting order parameter that derived from the attractive interaction between two electrons in different conduction bands. The total Hamiltonian is given by Eq. (6) with $\Delta_1 = 0$ and $\Delta_2 = 0$. Even if we focus on equal-time s -wave pair potential, the band degree of freedom makes both the spin-triplet and the spin-singlet pair potentials possible. Here we assume that the attractive interaction acts on two electrons with different spins in different conduction bands. Actually the interband spin-triplet order parameters [9] have been discussed in Cu-doped Bi_2Se_3 .

A. Spin-singlet pairing order

We first consider the situation where the hybridization preserves spin by setting $V_1 = V_2 = 0$. The Hamiltonian is described by

$$\tilde{H}_3(\mathbf{k}) = \begin{bmatrix} \xi_1 & W & 0 & s\Delta \\ W^* & \xi_2 & s\Delta & 0 \\ 0 & s\Delta^* & -\xi_1 & -W^* \\ s\Delta^* & 0 & -W & -\xi_2 \end{bmatrix}, \quad (56)$$

$$W = V_0 + sV_3(\mathbf{k}) \quad (57)$$

for the spin-singlet pair potential [i.e., $s_{\text{spin}} = -1$ in Eq. (6)]. Hereafter we remove “12” from the subscript of the interband pair potential for simplicity. In the particle-hole space \mathcal{N}_1 , the spin of an electron is \uparrow in the two conduction bands, whereas that of a hole is \downarrow . The spin direction is opposite in \mathcal{N}_2 . At $V_3 = 0$, the anomalous Green function is calculated as

$$\hat{\mathcal{F}}_3(\mathbf{k}, i\omega_n) = \frac{s\Delta}{2Z_3} [(v_1\xi_+ - iv_2\xi_-)\hat{\rho}_0 + (-X_3 + \xi_-^2)\hat{\rho}_1 - \omega_n\xi_- \hat{\rho}_2 + (-v_1\xi_- + iv_2\xi_+)\hat{\rho}_3], \quad (58)$$

with $Z_3 = X_3^2 - Y_3$ and

$$X_3 = \frac{1}{2}[\omega_n^2 + \xi_+^2 + \xi_-^2 + |V_0|^2 + |\Delta|^2], \quad (59)$$

$$Y_3 = \xi_+^2\xi_-^2 + \xi_+^2|V_0|^2 + \xi_-^2|\Delta|^2. \quad (60)$$

The normal part is given in Eq. (B5) in Appendix B. The phase of the hybridization potential does not play any role in this case. Actually, Z_3 depends only on $|V_0|$ as shown in Eqs. (59) and (60). The elements of the anomalous Green function in Eq. (58) correspond to

$$\hat{\mathcal{F}}_3^{\mathcal{N}_1} = \begin{bmatrix} \mathcal{F}_{11,\uparrow\downarrow} & \mathcal{F}_{12,\uparrow\downarrow} \\ \mathcal{F}_{21,\uparrow\downarrow} & \mathcal{F}_{22,\uparrow\downarrow} \end{bmatrix}, \quad \hat{\mathcal{F}}_3^{\mathcal{N}_2} = \begin{bmatrix} \mathcal{F}_{11,\downarrow\uparrow} & \mathcal{F}_{12,\downarrow\uparrow} \\ \mathcal{F}_{21,\downarrow\uparrow} & \mathcal{F}_{22,\downarrow\uparrow} \end{bmatrix}, \quad (61)$$

in \mathcal{N}_1 and \mathcal{N}_2 , respectively.

The intraband pairing correlations become

$$\mathcal{F}_{11,\uparrow\downarrow} - \mathcal{F}_{11,\downarrow\uparrow} = \frac{\Delta}{Z_3}(\xi_+ - \xi_-)V_0, \quad (62)$$

$$\mathcal{F}_{22,\uparrow\downarrow} - \mathcal{F}_{22,\downarrow\uparrow} = \frac{\Delta}{Z_3}(\xi_+ + \xi_-)V_0^*. \quad (63)$$

They are generated by the hybridization and belong to the ESEE class. The band asymmetry generates the interband pairing correlation

$$\mathcal{F}_{12,\uparrow\downarrow} - \mathcal{F}_{12,\downarrow\uparrow} - \mathcal{F}_{21,\uparrow\downarrow} + \mathcal{F}_{21,\downarrow\uparrow} = \frac{2\Delta}{Z_3}i\omega_n\xi_-, \quad (64)$$

which belongs to the OSEO class. The odd-frequency pairing correlation is paramagnetic because $\underline{\mathcal{F}}(\mathbf{k}, i\omega_n) = \mathcal{F}^*(\mathbf{k}, i\omega_n)$. The pair potential is linked to the pairing correlation

$$\mathcal{F}_{12,\uparrow\downarrow} - \mathcal{F}_{12,\downarrow\uparrow} + \mathcal{F}_{21,\uparrow\downarrow} - \mathcal{F}_{21,\downarrow\uparrow} = \frac{2\Delta}{Z_3}(-X_3 + \xi_-^2). \quad (65)$$

The self-consistent equation becomes

$$1 = gT \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \frac{X_3 - \xi_-^2}{2Z_3}. \quad (66)$$

When we consider spin-orbit hybridization V_3 at $V_0 = 0$, the Green functions are given by Eqs. (B5) and (58) with $v_1 \rightarrow sV_3$ and $v_2 \rightarrow 0$. The intraband pairing correlations are

$$\mathcal{F}_{11,\uparrow\downarrow} + \mathcal{F}_{11,\downarrow\uparrow} = \frac{\Delta}{Z_3}(\xi_+ - \xi_-)V_3, \quad (67)$$

$$\mathcal{F}_{22,\uparrow\downarrow} + \mathcal{F}_{22,\downarrow\uparrow} = \frac{\Delta}{Z_3}(\xi_+ + \xi_-)V_3. \quad (68)$$

The hybridization V_3 generates pairing correlations that belong to the ETOE class. The results of the symmetry classification are summarized in Table III.

TABLE III. The symmetry classification of Cooper pairs with an equal-time spin-singlet s -wave even-band-parity (interband) pair potential.

	Frequency	Spin	Momentum parity	Band parity	Magnetic response
Pair potential	Even	Singlet	Even	Even (inter)	Diamagnetic
Induced by V_0	Even	Singlet	Even	Even (intra)	Diamagnetic
Induced by V_1, V_2, V_3	Even	Triplet	Odd	Even (intra)	Diamagnetic
Induced by ξ_-	Odd	Singlet	Even	Odd	Paramagnetic

Next we consider effects of spin-flip hybridization on the pairing correlations. At $V_0 = V_3 = 0$, the Hamiltonian can be reduced to

$$\check{H}_4(\mathbf{k}) = \begin{bmatrix} \xi_1 & U^* & 0 & s\Delta \\ U & \xi_2 & -s\Delta & 0 \\ 0 & -s\Delta^* & -\xi_1 & U \\ s\Delta^* & 0 & U^* & -\xi_2 \end{bmatrix}, \quad (69)$$

$$U = V_1(\mathbf{k}) + isV_2(\mathbf{k}). \quad (70)$$

In the first particle-hole space (\mathcal{N}_1), the spin of a quasiparticle in band “1” is \uparrow and that in band “2” is \downarrow for both an electron and a hole. In the second particle-hole space (\mathcal{N}_2), the spins of a quasiparticle are opposite of those in \mathcal{N}_1 . The Green function is calculated as follows:

$$\hat{\mathcal{F}}_4(\mathbf{k}, i\omega_n) = \frac{s\Delta}{2Z_4} [(V_1\xi_- + isV_2\xi_+)\hat{\rho}_0 + i\omega_n\xi_- \hat{\rho}_1 - i(X_4 - \xi_-^2)\hat{\rho}_2 - (V_1\xi_+ + isV_2\xi_-)\hat{\rho}_3], \quad (71)$$

with $Z_4 = X_4^2 - Y_4$, $|V|^2 \equiv V_1^2 + V_2^2$ and

$$X_4 = \frac{1}{2}[\omega_n^2 + \xi_+^2 + \xi_-^2 + |V|^2 + |\Delta|^2], \quad (72)$$

$$Y_4 = \xi_+^2\xi_-^2 + \xi_+^2|V|^2 + \xi_-^2|\Delta|^2. \quad (73)$$

The normal part is shown in Eq. (B7) in Appendix B. The elements of the anomalous Green function in Eq. (71) are represented by

$$\hat{\mathcal{F}}_4^{\mathcal{N}_1} = \begin{bmatrix} \mathcal{F}_{11,\uparrow\uparrow} & \mathcal{F}_{12,\uparrow\downarrow} \\ \mathcal{F}_{21,\downarrow\uparrow} & \mathcal{F}_{22,\downarrow\downarrow} \end{bmatrix}, \quad \hat{\mathcal{F}}_4^{\mathcal{N}_2} = \begin{bmatrix} \mathcal{F}_{11,\downarrow\downarrow} & \mathcal{F}_{12,\downarrow\uparrow} \\ \mathcal{F}_{21,\uparrow\downarrow} & \mathcal{F}_{22,\uparrow\uparrow} \end{bmatrix}$$

in \mathcal{N}_1 and \mathcal{N}_2 , respectively. It is easy to confirm that the hybridizations V_1 and V_2 generate the equal-spin intraband pairing correlations

$$F_{11,\uparrow\uparrow} = \frac{\Delta}{2Z_4}(\xi_+ - \xi_-)(-V_1 + iV_2), \quad (74)$$

$$F_{11,\downarrow\downarrow} = \frac{\Delta}{2Z_4}(\xi_+ - \xi_-)(V_1 + iV_2), \quad (75)$$

$$F_{22,\uparrow\uparrow} = \frac{\Delta}{2Z_4}(\xi_+ + \xi_-)(-V_1 + iV_2), \quad (76)$$

$$F_{22,\downarrow\downarrow} = \frac{\Delta}{2Z_4}(\xi_+ + \xi_-)(V_1 + iV_2). \quad (77)$$

They belong to the ETOE class. The band asymmetry generates the pairing correlation

$$F_{12,\uparrow\downarrow} - F_{12,\downarrow\uparrow} - F_{21,\uparrow\downarrow} + F_{21,\downarrow\uparrow} = \frac{2\Delta}{Z_4}i\omega_n\xi_-, \quad (78)$$

which belongs to the OSEO class. Since $\mathcal{F}_4(\mathbf{k}, i\omega_n) = -\mathcal{F}_4^*(-\mathbf{k}, i\omega_n)$, the odd-frequency pairing correlation is paramagnetic. The results of the symmetry classification are shown in Table III. The self-consistent equation is described by Eq. (66) with $X_3 \rightarrow X_4$ and $Z_3 \rightarrow Z_4$.

B. Spin-triplet pairing order

Finally we consider the spin-triplet odd-band-parity pair potential. When the hybridization preserves spin (i.e., $V_1 = V_2 = 0$), the reduced Hamiltonian is given by

$$\check{H}_5(\mathbf{k}) = \begin{bmatrix} \xi_1 & W & 0 & \Delta \\ W^* & \xi_2 & -\Delta & 0 \\ 0 & -\Delta^* & -\xi_1 & -W^* \\ \Delta^* & 0 & -W & -\xi_2 \end{bmatrix}, \quad (79)$$

with $W = V_0 + sV_3(\mathbf{k})$. At $V_3 = 0$, the Green function for $V_0 \neq 0$ becomes

$$\hat{\mathcal{F}}_5(\mathbf{k}, i\omega_n) = \frac{\Delta}{2Z_5} [\omega_n v_2 \hat{\rho}_0 + i\omega_n \xi_- \hat{\rho}_1 - i(X_5 - |V_0|^2 - \xi_-^2)\hat{\rho}_2 - i\omega_n v_1 \hat{\rho}_3], \quad (80)$$

with $Z_5 = X_5^2 - Y_5$ and

$$X_5 = \frac{1}{2}[\omega_n^2 + \xi_+^2 + \xi_-^2 + |V_0|^2 + |\Delta|^2], \quad (81)$$

$$Y_5 = (\xi_+^2 + |\Delta|^2)(\xi_-^2 + |V_0|^2). \quad (82)$$

The elements of the anomalous Green function in Eq. (80) correspond to Eq. (61). In this case, both the hybridization and the band asymmetry generate the odd-frequency pairing correlations. The hybridization induces the correlations

$$\mathcal{F}_{11,\uparrow\downarrow} + \mathcal{F}_{11,\downarrow\uparrow} = -\frac{\Delta}{Z_5}i\omega_n V_0, \quad (83)$$

$$\mathcal{F}_{22,\uparrow\downarrow} + \mathcal{F}_{22,\downarrow\uparrow} = \frac{\Delta}{Z_5}i\omega_n V_0^*. \quad (84)$$

The band asymmetry induces

$$\mathcal{F}_{12,\uparrow\downarrow} + \mathcal{F}_{12,\downarrow\uparrow} + \mathcal{F}_{21,\uparrow\downarrow} + \mathcal{F}_{21,\downarrow\uparrow} = \frac{2\Delta}{Z_5}i\omega_n \xi_-. \quad (85)$$

All of them belong to the OTEE class. Since $\mathcal{F}_5(\mathbf{k}, i\omega_n) = -\mathcal{F}_5^*(\mathbf{k}, i\omega_n)$, all of the odd-frequency pairing correlations are paramagnetic.

TABLE IV. The symmetry classification of Cooper pairs with an equal-time spin-triplet s -wave odd-band-parity pair potential.

	Frequency	Spin	Momentum parity	Band parity	Magnetic response
Pair potential	Even	Triplet	Even	Odd	Diamagnetic
Induced by V_0	Odd	Triplet	Even	Even (intra)	Paramagnetic
Induced by ξ_-	Odd	Triplet	Even	Even (inter)	Paramagnetic
Induced by V_1, V_2, V_3	Even	Triplet	Odd	Even (intra)	Diamagnetic

The Green function for $V_0 = 0$ and $V_3 \neq 0$ are presented in Eqs. (B9) and (80) with $v_1 \rightarrow sV_3$ and $v_2 \rightarrow 0$. The spin-orbit hybridization generates the correlations

$$\mathcal{F}_{11,\uparrow\downarrow} - \mathcal{F}_{11,\downarrow\uparrow} = -\frac{\Delta}{Z_5} i\omega_n V_3, \quad (86)$$

$$\mathcal{F}_{22,\uparrow\downarrow} - \mathcal{F}_{22,\downarrow\uparrow} = \frac{\Delta}{Z_5} i\omega_n V_3. \quad (87)$$

They belong to the OSOE class.

Finally we discuss the effects of spin-flip hybridization V_1 and V_2 on the pairing correlations. The Hamiltonian is given by Eq. (69) with $s\Delta \rightarrow \Delta$. The Green function is presented in Eqs. (B7) and (71) with $s\Delta \rightarrow \Delta$. The spin-flip hybridization generates the pairing correlations that belong to the ETOE class. The correlations $F_{11,\uparrow\uparrow}$ and $F_{22,\downarrow\downarrow}$ are equal to Eqs. (74) and (77), respectively. The remaining components $F_{11,\downarrow\downarrow}$ and $F_{22,\uparrow\uparrow}$ change their signs from Eqs. (75) and (76), respectively. The band asymmetry induces

$$F_{12,\uparrow\downarrow} + F_{12,\downarrow\uparrow} + F_{21,\uparrow\downarrow} + F_{21,\downarrow\uparrow} = \frac{2\Delta}{Z_4} i\omega_n \xi_-, \quad (88)$$

which belongs to the OTEE class and has a paramagnetic property because of $\mathcal{F}_4(\mathbf{k}, i\omega_n) = -\mathcal{F}_4^*(-\mathbf{k}, i\omega_n)$. The symmetry classification results for the spin-triplet order parameter are summarized in Table IV. The spin-orbit hybridization generates the equal-spin pairing correlation.

V. CONCLUSION

We have studied the magnetic response of the odd-frequency pairing correlations appearing in two-band superconductors by using analytical expressions of the anomalous Green function for the Gor'kov equation. We confine ourselves to the equal-time s -wave pair potential and introduce two types of hybridization potentials between the two conduction bands. One is a spin-independent hybridization potential. The other is a spin-dependent hybridization potential derived from the spin-orbit interaction. The hybridization potentials and the asymmetry in the two conduction bands generate the odd-frequency pairing correlations. We conclude that odd-frequency pairs always exhibit a paramagnetic response to external magnetic fields irrespective of their generation process. By analyzing the self-consistent equation for the order parameter, we found that the odd-frequency pairing correlations reduce the superconducting transition temperature because of their paramagnetic instability. The hybridization potential also generates even-frequency Cooper pairs, which belong to a different symmetry class from that of the pair potential. The appearance of the subdominant pairing correlation can be understood as a deformation of the ground state by

the hybridization and/or the band asymmetry [13]. Thus rich symmetry variety of Cooper pairs in a uniform ground state is an essential feature of two-band superconductors.

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APPENDIX A: PARAMAGNETIC PROPERTY OF ODD-FREQUENCY COOPER PAIRS

The superconducting state is described well by a phenomenological many-body wave function

$$\Psi(\mathbf{r}) = \sqrt{n_s} e^{i\varphi(\mathbf{r})}, \quad (A1)$$

where n_s is the uniform pair density and φ is the macroscopic phase. The phase coherence is an essential property of superconductivity, which is described by $\nabla\varphi = 0$ in the uniform ground state. The current density is defined by

$$\mathbf{j} = \frac{e\hbar}{2mi} (\Psi^* \nabla \Psi - \nabla \Psi^* \Psi) - \frac{e^2 |\Psi|^2}{mc} \mathbf{A}, \quad (A2)$$

under an external magnetic field $\mathbf{H} = \nabla \times \mathbf{A}$. By applying the rigid phase coherence $\nabla\varphi \approx 0$, we obtain the so-called London equation,

$$\mathbf{j} = -\frac{n_s e^2}{mc} \mathbf{A}. \quad (A3)$$

By substituting Eq. (A3) into the Maxwell equation $\nabla \times \mathbf{H} = (4\pi/c)\mathbf{j}$, we obtain

$$\nabla^2 \mathbf{A} - \frac{1}{\lambda_L^2} \mathbf{A} = 0, \quad (A4)$$

where $\lambda_L = (4\pi n_s e^2 / mc^2)^{-2}$ is the London penetration length. Equation (A4) indicates the exponential decay of a magnetic field into a superconductor. Thus all superconductors are diamagnetic. The negative sign on the right-hand side of Eq. (A3) is essential in this argument. Indeed, the charge square e^2 , the electron mass m , the speed of light c , and the pair density n_s are all positive values. The superconducting condensate decreases its free energy by keeping the rigid phase coherence, which results in the diamagnetism of a superconductor. Equation (A1) means nothing other than

the wave function of Cooper pairs which belong to the equal-time (even-frequency) spin-singlet s -wave class. Thus even-frequency Cooper pairs in a uniform superconductor are diamagnetic.

In a microscopic theory, the electric current is connected with the vector potential by a response function K as shown in Appendix C. The Cooper pairs are described by the anomalous Green function instead of the many-body wave function in Eq. (A1). In an inhomogeneous superconductor, odd-frequency Cooper pairs are generated by the spatial gradient of pair potential. For instance, odd-frequency pairs appear at a surface of spin-singlet d -wave or spin-triplet p -wave superconductor as a subdominant pairing correlation. Reference [33] demonstrated a paramagnetic response of odd-frequency pairs to an external magnetic field at surfaces of such unconventional superconductors. At the London equation in Eq. (A3), the paramagnetic property is represented by *negative* pair density $n_s < 0$, which immediately results in the penetration of magnetic field into a superconductor in Eq. (A4). The paramagnetic Cooper pairs attract a magnetic field and break the phase coherence. As a consequence, the existence of odd-frequency pairs increases the free energy as demonstrated in Ref. [34]. Therefore odd-frequency pairs are thermodynamically unstable. In single-band superconductors, the odd-frequency pairs always appear locally due to their instability.

To our knowledge, the odd-frequency pairing correlations derived from the Bogoliubov-de Gennes Hamiltonian are always paramagnetic and thermodynamically unstable. Thus the presence of uniform odd-frequency pairs in two-band superconductors is a surprising conclusion. To realize stable and diamagnetic two-band superconducting states, the total pair density (corresponding to Q in the text) must be positive.

Finally, a relation to Majorana physics [40,41] may be worth mentioning. We have shown that Majorana fermions in a topologically nontrivial superconducting nanowire always accompany odd-frequency pairs [42]. To our knowledge, subgap quasiparticles in single-band superconductors look like odd-frequency Cooper pairs.

APPENDIX B: NORMAL GREEN FUNCTION

The normal Green functions are summarized in this appendix. The results for H_1 are given by

$$\begin{aligned} \hat{G}_1(\mathbf{k}, i\omega_n) = & \frac{1}{2Z_1} [\{A_1 + |V_0|^2 \xi_+ + \xi_- K\} \hat{\rho}_0 \\ & - \{(B_1 - |\Delta_-|^2) v_1 + i D_- v_2\} \hat{\rho}_1 \\ & + \{(B_1 - |\Delta_+|^2) v_2 + i D_- v_1\} \hat{\rho}_2 \\ & + \{-X_1 \xi_- + (i\omega_n + \xi_+) K\} \hat{\rho}_3], \end{aligned} \quad (\text{B1})$$

$$A_1 = -(i\omega_n + \xi_+) X_1, \quad B_1 = X_1 - (i\omega_n + \xi_+) \xi_+, \quad (\text{B2})$$

at $V_3 = 0$. The two normal Green functions satisfy the relations $\hat{G}_1(\mathbf{k}, i\omega_n) = -\hat{G}_1^*(\mathbf{k}, i\omega_n)$.

The normal Green function for H_2 is given by

$$\begin{aligned} \hat{G}_2(\mathbf{k}, i\omega_n) = & \frac{1}{2Z_2} [\{A_2 + |V|^2 \xi_+ + \xi_- K\} \hat{\rho}_0 \\ & - \{(B_2 - |\Delta_-|^2) V_1 + i D_- s V_2\} \hat{\rho}_1 \\ & - \{(B_2 - |\Delta_-|^2) s V_2 - i D_- V_1\} \hat{\rho}_2 \\ & + \{-X_2 \xi_- + (i\omega_n + \xi_+) K\} \hat{\rho}_3], \end{aligned} \quad (\text{B3})$$

$$A_2 = -(i\omega_n + \xi_+) X_2, \quad B_2 = X_2 - (i\omega_n + \xi_+) \xi_+ \quad (\text{B4})$$

and satisfies the relation $\hat{G}_2(\mathbf{k}, i\omega_n) = -\hat{G}_2^*(-\mathbf{k}, i\omega_n)|_{V_2 \rightarrow -V_2}$. For H_3 , the normal Green function at $V_3 = 0$ is given by

$$\begin{aligned} \hat{G}_3(\mathbf{k}, i\omega_n) = & \frac{1}{2Z_3} [\{A_3 + \xi_+ (\xi_-^2 + |V_0|^2)\} \hat{\rho}_0 \\ & + B_3 v_1 \hat{\rho}_1 - B_3 v_2 \hat{\rho}_2 + (B_3 - |\Delta|^2) \xi_- \hat{\rho}_3], \end{aligned} \quad (\text{B5})$$

$$A_3 = -(i\omega_n + \xi_+) X_3, \quad B_3 = X_3 - (i\omega_n + \xi_+) \xi_+. \quad (\text{B6})$$

The two normal Green functions are related by $\hat{G}_3(\mathbf{k}, i\omega_n) = -\hat{G}_3^*(\mathbf{k}, i\omega_n)$.

One normal Green function for H_4 is calculated as

$$\begin{aligned} \hat{G}_4(\mathbf{k}, i\omega_n) = & \frac{1}{2Z_4} [\{A_4 + \xi_+ (\xi_-^2 + |V|^2)\} \hat{\rho}_0 \\ & - B_4 V_1 \hat{\rho}_1 - B_4 s V_2 \hat{\rho}_2 - (B_4 - |\Delta|^2) \xi_- \hat{\rho}_3], \end{aligned} \quad (\text{B7})$$

$$A_4 = -(i\omega_n + \xi_+) X_4, \quad B_4 = X_4 - (i\omega_n + \xi_+) \xi_+. \quad (\text{B8})$$

The other normal Green function can be obtained by using $\hat{G}_4(\mathbf{k}, i\omega_n) = -\hat{G}_4^*(-\mathbf{k}, i\omega_n)$.

For H_5 , the normal Green function at $V_3 = 0$ is represented by

$$\begin{aligned} \hat{G}_5(\mathbf{k}, i\omega_n) = & \frac{1}{2Z_5} [\{A_5 + \xi_+ (\xi_-^2 + |V_0|^2)\} \hat{\rho}_0 \\ & - (B_5 - |\Delta|^2) (v_1 \hat{\rho}_1 - v_2 \hat{\rho}_2 + \xi_- \hat{\rho}_3)], \end{aligned} \quad (\text{B9})$$

$$A_5 = -(i\omega_n + \xi_+) X_5, \quad B_5 = X_5 - (i\omega_n + \xi_+) \xi_+. \quad (\text{B10})$$

The two normal Green functions satisfy $\hat{G}_5(\mathbf{k}, i\omega_n) = -\hat{G}_5^*(\mathbf{k}, i\omega_n)$.

APPENDIX C: PAIR DENSITY

In this paper, we consider a two-band superconductor in type II. The relation

$$j_\mu(x) = - \int dx' K_{\mu\nu}(x, x') A_\nu(x'), \quad (\text{C1})$$

with $x = (\mathbf{r}, t)$ connects the electric current and the vector potential. Within the linear response to vector potential [38,39], the electric current is described by

$$j_\mu(\mathbf{q}, \omega_l) = -K_{\mu\nu}(\mathbf{q}, \omega_l) A_\nu(\mathbf{q}, \omega_l), \quad (\text{C2})$$

$$\begin{aligned}
K_{\mu\nu}(\mathbf{q}, \omega_l) &= \frac{e^2}{c} \left[\sum_{\lambda=1,2} \sum_{\alpha=\uparrow,\downarrow} \frac{n_{\lambda,\alpha}}{m_\lambda} \delta_{\mu\nu} \right. \\
&+ T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \sum_{\alpha,\alpha'} \sum_{\lambda,\lambda'} \frac{(\mathbf{k} + \mathbf{q}/2)_\mu}{m_\lambda} \frac{(\mathbf{k} + \mathbf{q}/2)_\nu}{m_{\lambda'}} \\
&\times \left\{ \mathcal{G}_{\lambda\alpha,\lambda'\alpha'}(\mathbf{k} + \mathbf{q}, \omega_n + \omega_l) \mathcal{G}_{\lambda'\alpha',\lambda\alpha}(\mathbf{k}, \omega_n) \right. \\
&\left. \left. + \mathcal{F}_{\lambda\alpha,\lambda'\alpha'}(\mathbf{k} + \mathbf{q}, \omega_n + \omega_l) \mathcal{F}_{\lambda'\alpha',\lambda\alpha}(\mathbf{k}, \omega_n) \right\} \right] \\
&\quad (C3)
\end{aligned}$$

for a two-band superconductor, where $n_{\lambda,\alpha}$ is the electron density with spin α in the band λ , and ω_l is a bosonic Matsubara frequency. In the static limit $\omega_l \rightarrow 0$ and the uniform magnetic field $\mathbf{q} \rightarrow 0$, the diagonal element describes the Meissner effect. In such a case, the Meissner kernel becomes

$$\begin{aligned}
K &\equiv K_{\mu\mu}(0,0) \\
&= \frac{e^2}{c} \left[\sum_{\lambda=1,2} \sum_{\alpha=\uparrow,\downarrow} \frac{n_{\lambda,\alpha}}{m_\lambda} + T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \sum_{\alpha,\alpha'} \sum_{\lambda,\lambda'} \frac{k}{m_\lambda} \frac{k}{m_{\lambda'}} \frac{1}{d} \right. \\
&\times \left\{ \mathcal{G}_{\lambda\alpha,\lambda'\alpha'}(\mathbf{k}, \omega_n) \mathcal{G}_{\lambda'\alpha',\lambda\alpha}(\mathbf{k}, \omega_n) \right. \\
&\left. \left. + \mathcal{F}_{\lambda\alpha,\lambda'\alpha'}(\mathbf{k}, \omega_n) \mathcal{F}_{\lambda'\alpha',\lambda\alpha}(\mathbf{k}, \omega_n) \right\} \right], \\
&\quad (C4)
\end{aligned}$$

where d is the dimensionality of a superconductor. When we decompose the Green function into

$$\mathcal{G}_{\lambda,\lambda'} = \sum_{j=0}^3 g_j \hat{\rho}_j, \quad \mathcal{F}_{\lambda,\lambda'} = \sum_{j=0}^3 f_j \hat{\rho}_j \quad (C5)$$

in two-band space, we obtain

$$I_{\mathcal{F}} \equiv \sum_{\lambda,\lambda'} \frac{1}{m_\lambda} \frac{1}{m_{\lambda'}} \mathcal{F}_{\lambda\alpha,\lambda'\alpha'}(\mathbf{k}, \omega_n) \mathcal{F}_{\lambda'\alpha',\lambda\alpha}(\mathbf{k}, \omega_n), \quad (C6)$$

$$\begin{aligned}
&= \left[\frac{1}{m_1^2} + \frac{1}{m_2^2} \right] (f_0 \underline{f}_0 + f_3 \underline{f}_3) + \frac{2}{m_1 m_2} (f_1 \underline{f}_1 + f_2 \underline{f}_2) \\
&+ \left[\left(\frac{1}{m_1} \right)^2 - \left(\frac{1}{m_2} \right)^2 \right] (f_0 \underline{f}_3 + f_3 \underline{f}_0), \\
&\quad (C7)
\end{aligned}$$

where we omit spin indices α and α' . The kernel becomes

$$K = \frac{e^2}{c} \left[\sum_{\lambda=1,2} \sum_{\alpha=\uparrow,\downarrow} \frac{n_{\lambda,\alpha}}{m_\lambda} + T \sum_{\omega_n} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \sum_{\alpha,\alpha'} \frac{k^2}{d} \{I_{\mathcal{G}} + I_{\mathcal{F}}\} \right]. \quad (C8)$$

Equation (C8) can be applied to highly asymmetric two-band superconductors.

For a simple model in Eq. (7), we obtain

$$K = \frac{n_e e^2}{mc} \left[1 + \frac{1}{4} T \sum_{\omega_n} \int d\xi \text{Tr} \{ \mathcal{G} \mathcal{G} + \mathcal{F} \mathcal{F} \} \right] \quad (C9)$$

at $m_1 = m_2 = m$, where $\xi = k^2/2m - \mu_F$, $n_e = 4n_0$ with n_0 being the electron density for each band per spin, and Tr represents summation over spin and band degree of freedom. We have used $N_0 v_F^2/d = n_0/m$, with N_0 being the density of states at the Fermi level in each band per spin. Since the relation

$$\frac{1}{4} \frac{1}{V_{\text{vol}}} \sum_{\mathbf{k}} \left[T \sum_{\omega_n} \frac{v_F^2}{d} \text{Tr} \{ \mathcal{G}_N \mathcal{G}_N \} \right] = -\frac{n_0}{m} \quad (C10)$$

holds for the Green function in the normal state \mathcal{G}_N [38], the Meissner kernel becomes

$$K = \frac{n_e e^2}{mc} Q, \quad (C11)$$

$$Q = \frac{1}{4} T \sum_{\omega_n} \int d\xi \text{Tr} \{ \mathcal{G} \mathcal{G} + \mathcal{F} \mathcal{F} - \mathcal{G}_N \mathcal{G}_N \}, \quad (C12)$$

where Q corresponds to the dimensionless pair density. In the simple model (7), we obtain $Q = 1$ at the zero temperature.

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