Role of $d$ orbitals in the Rashba-type spin splitting for noble-metal surfaces

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We investigate the Rashba-type spin splitting in the Shockley surface states on Au(111) and Ag(111) surfaces, based on first-principles calculations. By turning on and off spin-orbit interaction (SOI) partly, we show that although the surface states are mainly of $p$-orbital character with only small $d$-orbital one, $d$-channel SOI determines the splitting and the spin direction while $p$-channel SOI has minor and negative effects. The small $d$-orbital character of the surface states, present even without SOI, varies linearly with the crystal momentum $k$, resulting in the linear $k$ dependence of the splitting, the Hallmark of the Rashba type. As a way to perturb the $d$-orbital character of the surface states, we discuss effects of electron and hole doping to the Au(111) surface.

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I. INTRODUCTION

Approximated to the second order in power of the inverse of the speed of light, $c$, the relativistic Dirac equation is reduced to the usual nonrelativistic Schrödinger equation for the two-component spinor wave function with the three relativistic correction terms: the mass-velocity term, the Darwin term, and the spin-orbit interaction (SOI) term. Among them, SOI induces many intriguing magnetic and electronic phenomena in condensed matter physics, such as the intrinsic spin Hall effect\cite{1} and the Rashba-Bychkov effect (simply, the Rashba effect) in two-dimensional (2D) semiconductor heterostructures\cite{2} and recently it is known as one of the main mechanisms of the generation of the robust metallic surface (or edge) states in topological insulators.\cite{3} These phenomena have been expected to open a new pathway to the spin-dependent electronics and the quantum computing, and thus SOI in condensed matters has been of great interest both theoretically and experimentally.\cite{4,5}

So far, exploration of SOI phenomena has been limited to materials with elements of high atomic numbers such as noble metals of Pt and Au, and $p$-orbital (semi-)metals like Sb, Tl, Pb, and Bi. Among them, Au has the atomic SOI strength, $(1/2)\xi_{5d}$, of 0.35 eV for the $5d$ level,\cite{6,7} attracting special interest due to the SOI-induced Rashba-type spin-splitting of the surface states in Au(111) surface first observed by angle-resolved photoemission spectroscopy.\cite{8} Such spin splitting was also observed in other clean (semi-)metallic surfaces\cite{9,10} and surface alloys\cite{11,12}, however, the splitting was unresolvably small in another noble-metal Ag surface\cite{13,14} although Ag has the atomic SOI strength, $(1/2)\xi_{4d}$, of 0.13 eV for the $4d$ level.\cite{15}

Previous theoretical studies pointed out that the dissimilarity in Au and Ag is attributed to their differences in the intrinsic atomic SOI strength\cite{16} and the degree of asymmetry of the wave function near the nucleus of surface atoms or, stated differently, the hybridization of different-parity orbitals in the surface-state wave functions.\cite{17} Compared with Ag, Au has a distinguishing feature that the energy-level separation between $5d$ and $6s$ orbitals is rather small\cite{18,19} which is related to the relativistic mass-velocity and Darwin terms.\cite{20} This proximity of $5d$- and $6s$-orbital energy levels in Au increases $d$-orbital character in the surface states\cite{18} which is found important for the splitting.\cite{21,22} However, the role of $d$ orbitals in the splitting is still unknown except that they make the surface states asymmetric.

In our present work, we investigate the origin of the Rashba-type splitting in the Shockley surface states on Au(111) and Ag(111) surfaces, focusing on the role of $d$ orbitals. By turning on and off parts of the SOI Hamiltonian, we find that the splitting originates from interaction between $d$ orbitals via $d$-channel SOI although the surface states are derived mainly from $p$ orbitals with only small $d$-orbital character, and the spin direction is also determined by the $d$-channel SOI. The linear dependence of the splitting on the wave vector, $k$, which is the Hallmark of the Rashba type, is found to be derived from $k$-linear dependence of $d_{xz}$ ($d_{yz}$)-orbital character of the surface states which exists even without SOI. These results show that the small $d$-orbital character of the noble-metal surface states determines the Rashba-type splitting while the large $p$-orbital one has weak and negative effects. As a way to modify the splitting by varying $d$-orbital character of the surface states, we consider electron and hole doping to the Au(111) surface.

II. CALCULATIONAL METHOD

Our present calculations are based on ab initio density-functional methods\cite{21,22} which employ a Troullier-Martins norm-conserving pseudopotential\cite{23} and the Perdew-Burke-Ernzerhof-type generalized-gradient approximation for the exchange-correlation potential.\cite{24} Wave functions are expanded with the localized pseudoatomic orbital bases.\cite{22} The SOI term is incorporated within a fully relativistic $j$-dependent pseudopotential\cite{22} and treated in the $l$-dependent fully-separable nonlocal form using additional Kleinman-Bylander projectors.\cite{25} In treating the SOI Hamiltonian, we consider non-self-consistently only the effect of
atomic core potentials with the $\vec{L} \cdot \vec{S}$ form, where $\vec{L}$ and $\vec{S}$ are the orbital and spin angular momentum operators, respectively. Although we can also include contribution of self-consistent part of potentials to SOI, our test calculations confirm that this contribution makes very little difference in the electronic band structures\textsuperscript{17} which is smaller than $10^{-4}$ eV. Thus, we do not include the contribution of the self-consistent part of the potentials to SOI in our following calculations.

For surface calculations, we model Au(111) and Ag(111) surfaces with supercell including a slab of 30 atomic layers and a vacuum region of about 20 Å thickness, and we take $36 \times 36 \times 1$ Monkhorst-Pack special-$k$-point meshes in the full Brillouin zone (BZ)\textsuperscript{26} to integrate the charge density. While Ag(111) exhibits no surface reconstruction, the Au(111) surface reportedly has a surface reconstruction of a $22 \times \sqrt{3}$ unit cell, the “herringbone reconstruction”\textsuperscript{29} Since this reconstruction has negligible effect on the electronic structures of the surface states,\textsuperscript{26} we safely take the clean-cut bulk atomic structures for Au(111) and Ag(111) surfaces.\textsuperscript{11}

### III. ELECTRONIC BAND STRUCTURES FOR Au(111) AND Ag(111) SURFACES

Figures 1(a) and (b) show our calculated band structures of Ag(111) and Au(111) surfaces, respectively. Compared with corresponding experimental values,\textsuperscript{14} the maximum binding energies of our surface bands are 60 meV larger for Ag(111) [Fig. 1(a)] and 100 meV smaller for Au(111) [Fig. 1(b)], consistent with previous all-electron calculations.\textsuperscript{15} The accuracy of the binding energy can be improved by careful description of decay of the wave functions into the vacuum\textsuperscript{22} but we already have good accuracy for the Rashba-type splitting. Our surface bands show $k_0 = 0.013$ Å\textsuperscript{-1} for the Rashba splitting in $k$ space, defined by the offset by which the extremum of the surface-state dispersion shifts from the crossing point $\bar{\Gamma}$ and $E_{\text{R}} = 2.8$ meV for the Rashba energy, defined by the energy difference between the crossing point and the maximum binding energy. When we fit our surface bands to an expression, $E_{\pm} = \frac{\hbar^2 k^2}{2m_e} \pm ak + E_0$, we obtain the electron effective mass $m^* = 0.26 m_e$, where $m_e$ is the electron bare mass, and the Rashba parameter $\alpha = 0.460$ eV Å\textsuperscript{-1}. These results are in good agreement with the reported experiments\textsuperscript{14,15} and theories.\textsuperscript{10,18,31} In addition, if we shift the surface bands to match the maximum binding energy with the experimental value, 487 meV for Au(111), the calculated Fermi wave vectors are 0.165 and 0.194 Å\textsuperscript{-1} for the inner and outer Fermi surfaces (FSs), respectively, which are also in good agreement with reported experimental and theoretical results.\textsuperscript{14,15}

These results show that our Kohn-Sham (KS) Hamiltonian, $H_{\text{KS}}(k) = H_0(k) + H_{\text{SO}}(k)$, which is the sum of the scalar relativistic part, $H_0(k)$, and the SOI term, $H_{\text{SO}}(k)$, describes the Rashba-type splitting in Au(111) surface accurately.

### IV. ORBITAL CONTRIBUTIONS TO THE RASHBA SPLITTING IN THE SURFACE STATES ON Au(111) SURFACE

In semiconductor devices, the relativistic response of electron spin to the electric field, $E\hat{n}$, yields the $k$-linear Rashba Hamiltonian $H_R = \alpha R (\hat{n} \times \vec{k}) \cdot \hat{\sigma}$, with the Pauli matrices $\hat{\sigma}$ and $\alpha_R = e\hbar^2 E/(4m^2_e c^2)$. These terms are derived from the microscopic SOI Hamiltonian

$$H_{\text{SO}} = \frac{\hbar}{4m_e^2 c^2} (\nabla V \times \vec{p}) \cdot \hat{\sigma} \tag{1}$$

and the nearly-free electron nature for 2D electron gases confined to surfaces or interfaces. While this model can explain the $k$-linear Rashba splitting, it cannot explain the correct size of splitting\textsuperscript{2,10} due to ignoring the effect of ion cores.\textsuperscript{2}
To find the origin of the Rashba-type splitting, we consider orbital-angular-momentum (l) decomposition of the SOI term, i.e., $H_{SO}(k) = H_{SO}^{l=1}(k) + H_{SO}^{l=2}(k)$, and calculate the band structures with either $H_{SO}^{l=1}(k)$ or $H_{SO}^{l=2}(k)$. This approach is possible because $H_{SO}(k)$ in our calculation is expressed as a sum of l-dependent Kleinman-Bylander-type projectors. Figures 1(c) and (d) show that when only the p-channel SOI, i.e., $H_{SO}^{l=1}(k)$, is switched on, the band splitting of the surface states is reduced greatly, but when only the d-channel SOI, i.e., $H_{SO}^{l=2}(k)$, is switched on, the splitting is even slightly larger than that for the full $H_{SO}$ case. While $n^2$ in both cases are very close to the full $H_{SO}$ case, the Rashba parameter is $\alpha_p = 0.118$ eVÅ in the former case and $\alpha_d = 0.564$ eVÅ in the latter case, giving the following relation.

$$\alpha_{\text{full}} \approx -\alpha_p + \alpha_d .$$

This shows that the Rashba-type splitting in Au(111) surface originates from the d-channel SOI while the p-channel SOI slightly reduces the splitting.

In the above, we examined l decomposition of the SOI Hamiltonian. Now we consider orbital decomposition of the surface states on Au(111) surface, i.e., $\psi_{nk} = \psi_{nk,s} + \psi_{nk,p} + \psi_{nk,d}$, where $\psi_{nk}$ is the wave function of the nth surface band for the wave vector k and $\psi_{nk,s}$, $\psi_{nk,p}$, and $\psi_{nk,d}$ are s-, p- and d-orbital parts of the state, respectively. With this decomposition, we calculate the expectation values $\langle \psi_{nk,i} \mid H_{SO}(k) \mid \psi_{nk,j} \rangle$ of the full $H_{SO}$ for $i, j = s, p, d$ to analyze orbital contributions to the Rashba-type splitting. We find that the d-d SOI energy, i.e., $\langle \psi_{nk,d} \mid H_{SO}(k) \mid \psi_{nk,d} \rangle$, has opposite signs for the two bands, contributing most substantially to the band splitting. Then, the p-d SOI energy, i.e., $\langle \psi_{nk,p} \mid H_{SO}(k) \mid \psi_{nk,d} \rangle$, contributes to the splitting by about 10% of the d-d one. In contrast, the p-p and s-p SOI energies contribute weakly and negatively to the band splitting, i.e., they reduce the splitting slightly, and the s-s and s-d ones are almost zero. These results again show that the d-orbital character of the surface states determines the Rashba-type splitting in Au(111) surface although the surface states are mainly of p-orbital one.

To verify this picture for the difference in the Rashba-type splitting in Au(111) and Ag(111) surfaces, we calculate the band structures without SOI and estimate d-orbital characters in their surface states similarly to the previous works. As shown in Figs. 2(a) and (b), the Ag(111) surface states have negligible d-orbital part, but the Au(111) surface states have relatively significant d-orbital one. This difference, due to the smaller energy separation between Au 5d and 6s levels than that between Ag 4d and 5s levels, confirms the importance of d orbitals in the Rashba-type splitting.

As a double check, we consider shift of the bulk d-band energies, that is, we modify the KS Hamiltonian matrix by adding $\delta E_d$ to its diagonal elements for d orbitals after self-consistency, and then calculate the band structure. As shown in Table I, with no shift ($\delta E_d = 0$), the Au(111) surface bands are split by $\Delta_{k_x} = 135$ meV at the inner Fermi wave vector, and the Rashba splitting in k space is $k_0 = 0.013$ Å$^{-1}$, as mentioned above, and the Ag(111) surface bands have almost zero energy splitting (3 meV).

For Au(111), when $\delta E_d = -0.5$ eV, the energy splitting $\Delta_{k_y}$ decreases to 92 meV and $k_0$ decreases to 0.009 Å$^{-1}$ and when $\delta E_d = 1.0$ eV, $\Delta_{k_y}$ increases to 191 meV and $k_0$ increases to 0.019 Å$^{-1}$. For Ag(111), when $\delta E_d = 5.0$ eV,
the higher-energy surface state while it decreases in the lower-energy surface state. We note that 0.1 meV makes the shifted d-band energy in Ag close to the unshifted d-band energy in Au, but the splitting in Ag(111) is still smaller than that in Au(111) due to the difference in the intrinsic atomic SOI strength.

TABLE I. Dependence of the Rashba splitting on the bulk states significantly. We note that characters in the surface states but it does not mix the bulk states along the \( k_x \) axis, when the \( z \) axis is the positive direction normal to the top surface. As shown in Fig. 2(c), \( d_{xz} \)-orbital character increases from zero, as \( k \) increases along the \( k_x \) axis, while \( s_+ \), \( p_z \), and \( d_{z^2} \)-orbital characters decrease slowly. Considering the symmetry, surface states along different \( k \) direction, i.e., along the \( k_y \) axis, have \( d_{xz} \) orbital significantly instead of \( d_{yz} \). When we use \( \psi_{k,d_{xz}}^{(0)} \) and \( \psi_{k,d_{z^2}}^{(0)} \) for \( d_{xz} \)- and \( d_{z^2} \)-orbital parts of a surface state \( \psi_{k,d}^{(0)} \) (not including spin) without SOI, respectively, we obtain that the SOI-induced energy splitting \( \Delta_k \) of the two surface bands is given by

\[
\Delta_k \approx 2 \left| \left< \psi_k^{(0)} \right| H_{\text{SO}}^{(1)}(k) \left| \psi_k^{(0)} \right> \right| \approx 2 \left| \left< \psi_{k,d_{xz}}^{(0)} \right| H_{\text{SO}}^{(1)}(k) \left| \psi_{k,d_{xz}}^{(0)} \right> + \left< \psi_{k,d_{z^2}}^{(0)} \right| H_{\text{SO}}^{(1)}(k) \left| \psi_{k,d_{z^2}}^{(0)} \right> \right| \propto \left| \psi_{k,d_{xz}}^{(0)} \right| \left| \psi_{k,d_{z^2}}^{(0)} \right| \left| k \right|,
\]

where \( H_{\text{SO}}^{(1)}(k) \) is SOI between up- and down-spin states.

Thus, the linearly \( k \)-dependent \( \psi_k^{(0)} \) makes the Rashba-type splitting \( \Delta_k \) proportional to \( \left| k \right| \). As SOI splits the two surface bands, the \( d_{xz} \)-orbital character increases in the higher-energy surface state while it decreases in the lower-energy one [Fig. 2(d)]. SOI redistributes \( d \)-orbital characters in the surface states but it does not mix the surface states with bulk states significantly. We note that even without SOI, the \( d_{xz} \) and \( d_{z^2} \) orbitals in the surface states along the \( k_x \) axis form a nonzero \( y \) component of the orbital angular momentum, which may be related to a recent study of the Rashba splitting.

V. SPIN AND ORBITAL ANGULAR MOMENTUM OF Au(111) SURFACE STATES

Another important feature of the Rashba-type splitting is the helical spin structure. To find the role of \( d \) orbitals in the spin structure, we calculate expectation values of the spin angular momentum (SAM) operator. In addition, motivated by a recent work on the topological insulator we also calculate the orbital angular momentum (OAM) by projecting the surface-state wave functions onto a set of localized functions defined in a sphere centered at the top-surface Au atom and then evaluating expectation values of OAM operators around the atom using the projected wave functions. In our results, SAM is mainly from \( p_z \)-orbital while OAM is mainly from \( d \) orbitals. When viewed from the vacuum side toward the top surface, SAM is clockwise at the inner FS and counter-clockwise at the

\[\begin{array}{|c|c|c|}
\hline
\text{Parameter} & \delta E_d \text{(eV)} & \Delta_{k_0} \text{(meV)} & k_0 \text{ (Å}^{-1}) \\
\hline
\text{Au}(111) & -0.5 & 92 & 0.009 \\
 & 0.0 & 135 & 0.013 \\
 & 0.5 & 172 & 0.016 \\
 & 1.0 & 191 & 0.019 \\
\hline
\text{Ag}(111) & 0.0 & 3 & 0.000 \\
 & 2.0 & 18 & 0.003 \\
 & 4.0 & 39 & 0.006 \\
 & 5.0 & 48 & 0.006 \\
\hline
\end{array}\]

FIG. 3. (Color online) SAM and OAM of Au(111) surface states at the Fermi energy. (a) SAM and (b) OAM with the full SOI. (c) SAM with only \( p \)-channel SOI, \( H_{\text{SO}}^{(1)} \). (d) SAM with only \( d \)-channel SOI, \( H_{\text{SO}}^{(2)} \). Black arrows represent SAM, and blue and red arrows do OAMs from \( p \) and \( d \) orbitals, respectively. For clarity, OAM from \( p \) orbital is doubled.
outer FS [Fig. 3(a)], which is consistent with the reported experiments\cite{37} and calculations\cite{38} When viewed from the same side, OAM from $d$ orbitals is clockwise at both FSs while OAM from $p_z$ orbital is counter-clockwise at the inner FS and clockwise at the outer FS [Fig. 3(b)]. Total OAM is clockwise at both FSs and has smaller magnitude than SAM. These features for OAM are also in good agreement with the recent experimental and theoretical reports\cite{36} but are different from the $p$-orbital-based Bi$_2$Se$_3$ topological insulator where OAM has opposite directions for the two surface bands and has larger amplitude than SAM\cite{36}.

We also study the roles of $p$- and $d$-channel SOIs in determining the spin direction. As shown in Figs. 3(c) and (d), our result shows that when only the $p$-channel SOI, i.e., $H_{SO}^{p}(k)$, is switched on, the spin direction is opposite to the full $H_{SO}$ case given in Fig. 3(a), but when only the $d$-channel SOI, i.e., $H_{SO}^{d}(k)$, is switched on, the spin direction is the same with the full $H_{SO}$ case. This result shows again that the $d$-channel SOI is indeed decisive in the Rashba-type splitting while the $p$-channel SOI has minor and opposite effects.

VI. ELECTRONIC PERTURBATIONS TO Au(111) SURFACE

As a way to change the Rashba-type splitting in the noble-metal surface, we consider electron and hole doping, similarly to Xe and Na adsorption experiments.\cite{35} We performed self-consistent calculations with different numbers of electrons. In the undoped case, the surface-state wave function is asymmetric at the surface Au atom, with greater amplitude in the vacuum side than in the bulk side [Fig. 4(a)]. Compared with this, electron (hole) doping makes the wave function less (more) asymmetric [Fig. 4(a)], resulting from decrease (increase) of the $d_{z^2}$ orbital character in the wave function due to change in the degree of the inversion symmetry breaking, affected by change of the potential near the surface. As shown in Eq. (6), the Rashba splitting $\Delta_k$ in noble-metal surfaces depends on the size of $d_{z^2}$ orbital in the surface-state wave functions. Thus, change in the $d$-orbital characters changes the energy splitting. For Au (111) surface, we obtain 40 meV decrease for 0.5 electron doping per surface Au atom, and 10 meV increase for 0.5 hole doping [Fig. 4(b)]. These changes are $\sim$100 times the Rashba effect in semiconductor devices at electric fields corresponding to the doping concentrations.

VII. CONCLUSION

In conclusion, we investigated the Rashba-type splitting in the Shockley surface states on Au(111) and Ag(111) surfaces, based on first-principles calculations including SOI. We showed that although the surface states have predominantly $p$-orbital character and only small $d$-orbital one, interaction between $d$-orbital parts via the $d$-channel SOI produces the Rashba-type splitting. The small $d_{z^2}$ ($d_{x^2-y^2}$)-orbital part of the surface states, present even without SOI, depends linearly on $k$ so that the atomic SOI results in the linearly $k$-dependent Rashba-type splitting. The $d$-channel SOI determines the helical spin structure of the surface states although the spins are mainly from $p$ orbitals. The $p$-channel SOI has minor and opposite effects in Au(111) surface. Thus, the role of $d$ orbitals in Au(111) surface has some similarity to graphene where small $3d$ orbitals contribute dominantly to the SOI-induced energy gap\cite{40} but shows difference from $p$-orbital-based Bi$_2$Se$_3$-type topological insulators.\cite{36} As a way of varying the splitting size in Au(111) surface, we discussed effects of electron and hole doping.

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FIG. 4. (Color online) Effects of doping on the Rashba-type splitting on Au(111) surface. (a) Squared amplitudes of surface-state wave functions at the same $k_F$, the Fermi wave vector of the inner FS in the undoped case, in 0.5 electron-doped, undoped, and 0.5 hole-doped cases, shown from left to right panels. The color scale is in units of per Å$^3$. The surface Au atom is marked with a dot at the center of each panel. (b) Band splitting $\Delta_{k_F}$ vs doping. All splittings are taken at the same $k_F$ as in (a).
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where $m_*$ is an electron mass, $V(r)$ is a potential, and $R(r)$ is the radial part of the atomic orbital.
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33. Examining the coefficients of pseudoatomic orbitals in the surface-state wave functions, we find that the negative contribution from the $p$-channel SOI with respect to the $d$-channel SOI in Eq. (2) results from the opposite relation of the relative phases in the on-site hybridizations between $p_x$ ($p_y$) and $p_z$ orbitals and between $d_{xz}$ ($d_{yz}$) and $d_{z^2}$ orbitals. Thus, for a deeper understanding of the negative sign in Eq. (2), one needs to find the mechanism that determines the phases of different orbital parts in the wave functions before SOI is included in the Hamiltonian. It is beyond the scope of our present study.
34. In Fig. 2, the norm, $|\psi_{n\vec{k},\mu}|$, of an orbital character, $\mu$, of a state, $\psi_{n\vec{k}}$, is defined as
   \[ |\psi_{n\vec{k},\mu}| = \left| \frac{1}{\sqrt{\sum _\alpha \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \phi^*_\alpha \phi_\alpha (\vec{r} - \vec{r}_s) \psi_{n\vec{k}}(\vec{r})}} \right|^2. \]
for $\mu = s$, $p_x$, $p_y$, $d_{xz}$, $d_{yz}$, etc. Here $n$ is the band index, $\vec{k}$ is the wavevector, $\operatorname{Re}[\cdot]$ denotes the real part of a complex number, asterisks denote complex conjugates, $\vec{r}_s$ is the position of the $s$th atom in the supercell, $\phi_\alpha(\vec{r})$ is the pseudoatomic orbital of the orbital character, $\mu$, of the $s$th atom, and $c_{n\vec{k},\alpha\mu}$ is the expansion coefficient of $\psi_{n\vec{k}}(\vec{r})$ using the pseudoatomic orbitals, i.e.,
   \[ \psi_{n\vec{k}}(\vec{r}) = \sum _{\alpha\mu} c_{n\vec{k},\alpha\mu} \phi_\alpha (\vec{r} - \vec{r}_s - \vec{R}), \]
where $\vec{R}$ is the in-plane lattice vector of the Au or Ag (111) surface. With this definition, the norm of the orbital character of a state satisfies $\sum _\mu |\psi_{n\vec{k},\mu}|^2 = 1$, where the sum is over all orbital characters. In Figs. 2(a) and (b), the norm, $|\psi_{n\vec{k},all\,d}|$, of all $d$-orbital characters, is defined as
   \[ |\psi_{n\vec{k},all\,d}| = \sqrt{\sum _\mu |\psi_{n\vec{k},\mu}|^2}, \]
where the sum is over five $d$-orbital characters.
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