# Eigenstate analysis of the crystal electric field at low-symmetry sites: Application for an orthogonal site in the tetragonal crystal Ce<sub>2</sub>Pd<sub>2</sub>Pb

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We have established an analyzing method to determine eigenstates of 4f electrons under the crystal electric field (CEF) at low-symmetry sites. This analysis requires macroscopic physical properties only, namely the saturation moments along several symmetrical directions of the crystal in addition to the magnetic susceptibility and specific heat, instead of the spectrum of the inelastic neutron scattering frequently used for such a complicated circumstance. As a successful case, the eigenstates of a CEF Hamiltonian under an orthogonal point group  $C_{2v}$ are determined for the  $J = \frac{5}{2}$  state of the cerium ion in a tetragonal compound Ce<sub>2</sub>Pd<sub>2</sub>Pb. During the analysis, an angular momentum operator along the arbitrary direction is deduced from the space rotation operator. A matrix representation of the projection operator that transforms the basis of wave functions from  $|J_z\rangle$  to  $|J_x\rangle$  or  $|J_y\rangle$  is also shown for  $J = \frac{5}{2}$ . This analysis reveals the anisotropic moments within highly symmetrical structures, and will contribute to understanding anisotropic field responses in rare-earth compounds.

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# I. INTRODUCTION

Quantum spin states in f-electron magnets have attracted much attention in recent years [1–8]. These magnets are characterized by strongly anisotropic moments and low degenerated pseudospin states. They are results of the spin-orbit coupling in the f electron and crystal electric field (CEF) in crystals, which are counterparts of d-electron magnets. That is, the orbital degree of the freedom remains as the total angular momentum in f electrons, while it is quenched by the strong CEF in d electrons. As a result, f-electron magnets yield strongly anisotropic moments under the CEF. The strong magnetic anisotropy in f-electron magnets has the potential to induce not only quantitatively different responses of the magnetic field but also qualitatively different phases and/or quantum states depending on the direction of the field [3,8,9].

The anisotropy of the local moment in f-electron magnets is attributed to the property of the eigenstate under a CEF Hamiltonian [10,11]. This Hamiltonian determines fundamental properties of the magnetic moment, not only the magnetic anisotropy but also the degeneracy of the ground state and the orbital anisotropy of the wave function that yield the exchange interaction. Therefore, the determination of the eigenstates is important to understand the peculiar properties of f-electron magnets. In principle, the CEF Hamiltonian can be determined from the charge distribution around the f electrons; however, it is quite sensitive to the effective charge, position, and symmetry of surrounding ions. For instance, a tetragonal compound Ce<sub>2</sub>Pd<sub>2</sub>Pb discussed

in this paper has a strongly anisotropic moment while its isostructural compound  $Ce_2Pt_2Pb$  has a mostly isotropic moment in the tetragonal plane although Pt and Pd are expected to have the same core charge [12]. Therefore, experimental results should be used to accurately determine the eigenstates. For this purpose, the magnetic susceptibility along several crystallographic directions is conventionally used. The CEF eigenstates have been experimentally determined not only for cubic structures but also for low-symmetry structures such as hexagonal, tetragonal, and trigonal ones [13–16].

The analysis of the CEF eigenstate using magnetic susceptibility is known to have a limitation about the site symmetry of rare-earth ions. This limitation restricts that the point-group symmetry of the rare-earth site must be the same as that of the crystal; in other words, the rare-earth element should locate on the highest symmetrical site in the crystal. Otherwise, the anisotropy of the local symmetry of the rare-earth site is averaged by the crystal symmetry. Although several macroscopic approaches can extract partial characters of the eigenstates [3,17,18], microscopic measurements such as inelastic neutron scattering have been required to determine the CEF eigenstates in such a complicated circumstance thus far [19–22].

In this paper, we report an analyzing method to determine CEF eigenstates under the complicated circumstance; namely, the CEF Hamiltonian has a lower point-group symmetry than that of the crystal. This analysis requires macroscopic physical properties only, namely the susceptibility, specific heat, and low-temperature magnetization along several crystallographic directions. The key point of this analysis is the magnetization analysis using the total angular momentum operator along arbitrary directions. As a successful case, we present an an-

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FIG. 1. Crystal structure of  $Ce_2Pd_2Pb$ . (a) Perspective view around the unit cell shown by the solid cuboid. (b) Cerium plane in panel (a). Small arrows show several crystallographic directions in the Miller indices. Large arrows indexed as x, y, and z axes represent two different local coordinates on the cerium atom. The solid and broken outlined atoms have different local coordinates, while both the atoms belong to the same crystallographic site. Filled ellipse and the symbol m indicate the twofold rotational axis and mirror plane, respectively.

alyzed result of a cerium compound Ce<sub>2</sub>Pd<sub>2</sub>Pb, together with its growth method and several physical properties of singlecrystalline samples.

Ce<sub>2</sub>Pd<sub>2</sub>Pb crystallizes in the Mo<sub>2</sub>FeB<sub>2</sub>-type structure (space group No. 127, *P4/mbm*; see Fig. 1) [23,24]. In this structure, cerium atoms form in a special arrangement, the socalled Shastry-Sutherland lattice (SSL), known to be a typical case of geometrical frustration. This structure is a tetragonal one, but the cerium site (4*h*) belongs to an orthogonal local point group  $C_{2v}$ . Therefore, seemingly two types of cerium sites, as shown by the solid and broken outlines in Fig. 1(b), can be found in the structure; however, they locate on the same crystallographic site but only have different local coordinates. From several investigations using polycrystalline samples, it is found that this compound has a rather localized 4*f* electron and undergoes an antiferromagnetic transition approximately at 6 K [23,25].

### **II. EXPERIMENTAL METHOD**

Single-crystalline samples of Ce<sub>2</sub>Pd<sub>2</sub>Pb and La<sub>2</sub>Pd<sub>2</sub>Pb were grown using the Bridgman technique. The starting materials of Ce<sub>2</sub>Pd<sub>2</sub>Pb are stoichiometric amounts of pure metals, Ce (3N), Pd (4N), and Pb (6N). They are sealed into a crucible made of tungsten metal using electric-beam welding. The crucible is once heated up to 1600 °C and then rapidly cooled down to 1000 °C at 20 °C/minute. This process intends to prevent the formation of other compounds. Then, it is slowly cooled down to 800 °C at 0.7 °C/hour. The resultant ingot has a single phase of Ce<sub>2</sub>Pd<sub>2</sub>Pb, but some domains are there. We picked up small samples from the ingot and checked domains using a Laue diffraction measurement. To obtain single-crystalline samples, a polisher was used to remove minor domains and to prepare oriented surfaces. La<sub>2</sub>Pd<sub>2</sub>Pb was grown by a similar method. The samples of Ce<sub>2</sub>Pd<sub>2</sub>Pb have a metallic conductivity and their residual resistivity at 1.5 K is approximately 12  $\mu\Omega$  cm. The electrical resistivity was measured using a conventional dc four-wire method. The specific heat was measured using a commercial calorimeter



FIG. 2. Temperature dependence of the magnetic susceptibility. (a) M/H along three symmetrical directions of the tetragonal crystal. The arrow indicates the antiferromagnetic transition temperature  $T_{\rm N}$ . The legend for the markers is represented in panel (b). (b) The reciprocal susceptibility of the same data in panel (a). Solid curves are calculated reciprocal susceptibility from the CEF wave functions.

(PPMS; Quantum Design, Inc.) and a handmade calorimeter for temperature ranges from 1.8 K to 300 K and from 0.1 K to 10 K, respectively. For the magnetization and the magnetic susceptibility measurements, we used a commercial magnetometer (MPMS; Quantum Design, Inc.) in the field range <7 T. For the higher field range >7 T, the magnetization was obtained from a handmade magnetometer calibrated against the magnetization obtained from the MPMS.

#### **III. RESULTS**

Figure 2 shows the magnetic susceptibility M/H along three symmetrical directions of tetragonal crystals, the  $\langle 100 \rangle$ , (110), and (001) directions. A clear kink at approximately 6 K in Fig. 2(a) is attributed to an antiferromagnetic transition. The effective moment is estimated from a linear fit for the reciprocal susceptibility as shown in Fig. 2(b) above 200 K. We obtained 2.57(3)  $\mu_{\rm B}/{\rm Ce}$  [2.60(3)  $\mu_{\rm B}/{\rm Ce}$ ] for the  $\langle 100 \rangle$ and (110) ((001)) directions. These values are close to the 2.54  $\mu_B$ /Ce expected for a free Ce<sup>3+</sup> ion. The susceptibility along (100) is identical to that along (110) within the experimental uncertainty. On the other hand, the susceptibility along the (001) direction is different from that perpendicular to the direction. It is a general consequence of the tetragonal symmetry that the susceptibility is isotropic within the tetragonal plane. In Ce<sub>2</sub>Pd<sub>2</sub>Pb, the point-group symmetry of the cerium site is  $C_{2v}$ . The orthogonal local symmetry  $C_{2v}$  of the CEF splits the sixfold eigenstates of the total angular momentum  $J = \frac{5}{2}$  of Ce<sup>3+</sup> ion into three doublets. This symmetry yields an orthogonal local anisotropy in the susceptibility; however, it becomes a tetragonal one in the whole crystal because the susceptibilities of the two orthorhombic cerium sites are averaged in the unit cell. Therefore, the tetragonal anisotropy in the susceptibility is attributed to the sum of the two types of orthogonal cerium sites.

To obtain the eigenenergy of the CEF Hamiltonian, we measured the specific heat of Ce<sub>2</sub>Pd<sub>2</sub>Pb ( $C_{Ce}$ ) and that of nonmagnetic analog La<sub>2</sub>Pd<sub>2</sub>Pb ( $C_{La}$ ). Here,  $C_{La}$  exhibits a



FIG. 3. (a) Temperature dependence of the specific heat of  $Ce_2Pd_2Pb$  and  $La_2Pd_2Pb$ . Inset shows the specific heat (left axis) and the electrical resistivity (right axis) of  $La_2Pd_2Pb$  at low temperatures. (b) Magnetic contribution of the specific heat  $C_{mag}$  of  $Ce_2Pd_2Pb$  in the logarithmic temperature scale. The solid curve shows the magnetic entropy indexed on the right axis. Calculated specific heat  $C_{CEF}$  for the CEF energies also shown as a dotted curve.

peak anomaly accompanying zero electrical resistivity at approximately 0.3 K as shown in the inset of Fig. 3(a). These anomalies indicate a superconducting transition in La<sub>2</sub>Pd<sub>2</sub>Pb. As shown in the main panel of Fig. 3(a), Ce<sub>2</sub>Pd<sub>2</sub>Pb has a larger specific heat than that of La<sub>2</sub>Pd<sub>2</sub>Pb within the whole measured temperatures because of the contribution of the 4felectron. Assuming that the other contribution than that of the 4f electron is the same within both compounds, we obtain the contribution of the 4f electron as  $C_{\text{mag}} = C_{\text{Ce}} - C_{\text{La}}$  as shown in Fig. 3(b). Below 10 K, two sharp peaks are found in  $C_{\text{mag}}$ . The peak at  $T_{\rm N} = 5.6$  K is attributed to an antiferromagnetic transition as seen in the susceptibility [see Fig. 2(a)]. Another small peak at 3.5 K is probably due to a change in the magnetic structure. The magnetic entropy  $S_{mag}$  is obtained from an integration of  $C_{\text{mag}}/T$  as shown in the right axis of Fig. 3(b).  $S_{\text{mag}}$  saturates to  $R \ln 2$  up to 30 K, where R is the gas constant. The value  $R \ln 2$  indicates the degree of freedom of the ground state doublet, the so-called Kramers doublet, and excited



FIG. 4. Magnetization along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 001 \rangle$  directions at (a) 1.8 K and (b) 7 K. Broken lines are linear fits above 7 T. Solid curves are the numerically calculated magnetization using the parameters listed in Table II.

states are negligibly occupied <30 K. Since the Kramers doublet has the time-reversal symmetry, the long-range orders arise from the magnetic degree of freedom. Note that the Kondo effect seems to contribute very weakly in Ce<sub>2</sub>Pd<sub>2</sub>Pb because the Kondo coherence peak is not found on  $C_{mag}$ .

Above 30 K,  $S_{\text{mag}}$  increases again and seems to approach  $R \ln 6$  at higher temperatures, which is associated with the broad hump of  $C_{\text{mag}}$  at approximately 80 K. This behavior is attributed to the thermal excitation between the CEF eigenstates. To estimate the excitation energies, we fit  $C_{\text{mag}}(T)$  above 30 K using a Schottky-type formula for the specific heat under the CEF energy splitting ( $C_{\text{CEF}}$ ):

$$C_{\text{CEF}} = \frac{N_{\text{A}}k_{\text{B}}\beta^2}{Z^2} \sum_{i,j} \frac{(E_i - E_j)^2}{2} e^{-\beta(E_i + E_j)},$$
 (1)

where  $\beta = (k_{\rm B}T)^{-1}$  and  $Z = \sum_{i} e^{-\beta E_{i}}$  are the inverse temperature and a partition function, respectively. We use *i* and *j* (*i*, *j* = 0, 1, 2) for the indication of the eigenenergy hereafter. The resultant curve almost reproduces the experiment as shown in Fig. 3(b). Obtained energy gaps are  $\Delta E_{1}/k_{\rm B} = 133$  K and  $\Delta E_{2}/k_{\rm B} = 426$  K for the first- and the second-excited states from the ground state, respectively. Here,  $\Delta E_{i} = E_{i} - E_{0}$ . The energy  $E_{i}$  corresponds to the *i*th eigenenergy of the CEF Hamiltonian, Eq. (2).

Figure 4 shows the magnetization curve along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 001 \rangle$  directions. The magnetization curves along the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions show successive steps. These steps indicate phase transitions between the long-range ordered states. Since we focus on the CEF eigenstates in the Ce<sub>2</sub>Pd<sub>2</sub>Pb in the present paper, these phase transitions will be discussed elsewhere. The magnetization curves along both the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions saturate above 7 T. The saturation moment is anisotropic even in the tetragonal plane, indicating that the orthogonal symmetry of the cerium site remains within the tetragonal crystal. This anisotropy is an important difference between the magnetization and susceptibility. The saturation moment and paramagnetic contribution are evalu-

ated from a linear fit >7 T as 1.32(2)  $\mu_{\rm B}$  [0.93(2)  $\mu_{\rm B}$ ] and 2.5 × 10<sup>-3</sup>  $\mu_{\rm B}/T$  (3.4 × 10<sup>-3</sup>  $\mu_{\rm B}/T$ ) per Ce atom along the (100) ((110)) direction, respectively. The magnetization along the (001) direction shows no saturation up to 18 T.

# **IV. DISCUSSION**

In  $Ce_2Pd_2Pb$ , the Ce site (4*h*) belongs to an orthogonal point group  $C_{2v}$  that has the twofold rotational axis and two orthogonalized mirror planes. As shown in Fig. 1(b), four Ce atoms exist in the primitive cell of Ce<sub>2</sub>Pd<sub>2</sub>Pb. The twofold rotational axes of two of the four Ce atoms, outlined by the red solid circle, are oriented in the [110] direction, and those of the others, outlined by the blue broken circle, are oriented in the  $[\bar{1}10]$  direction. The two mirror planes lie within and perpendicular to the *ab* plane, respectively, and both the planes contain the twofold rotational axis. These orthogonal Ce sites are connected with the *b*-glide operation and therefore they maintain the tetragonal space group P4/mbm of the crystal structure. In the case of  $C_{2v}$ , it is convenient to select a quantized axis from a twofold axis or a direction perpendicular to each mirror plane. This is because the direction perpendicular to mirror planes is identical to the twofold axis for the axial vector, or pseudovector, such as angular momentum. In this paper, we define the twofold rotational axis as the x axis and the [001] direction as the z axis. As a result, the direction perpendicular to the remaining mirror plane is defined as the y axis. These local axes are depicted in Fig. 1(b). Hereafter, we choose the quantized direction of the angular momentum as the z axis (crystallographic [001]direction) unless otherwise noted.

For the point group  $C_{2v}$ , the CEF Hamiltonian for  $J = \frac{5}{2}$  is described as follows:

$$\hat{\mathcal{H}}_{\text{CEF}} = B_2^0 \hat{O}_2^0 + B_2^2 \hat{O}_2^2 + B_4^0 \hat{O}_4^0 + B_4^2 \hat{O}_4^2 + B_4^4 \hat{O}_4^4.$$
(2)

Here,  $\hat{O}_n^m$  and  $B_n^m$  are the Stevens operators and their coefficients [10,11]. Note that all of the coefficients  $B_n^m$  are the real numbers in  $C_{2v}$ . Five arbitrary coefficients in the Hamiltonian Eq. (2) reflect degrees of freedom for eigenenergies and coefficients in the eigenstates, respectively. The CEF wave function of the *i*th eigenenergy is obtained as an eigenstate of  $\hat{\mathcal{H}}_{CEF}$  as follows:

$$|\psi_i^{\pm z}\rangle = \alpha_i \left|\pm\frac{5}{2}\right\rangle + \beta_i \left|\pm\frac{1}{2}\right\rangle + \gamma_i \left|\mp\frac{3}{2}\right\rangle. \tag{3}$$

Here,  $\alpha_i$ ,  $\beta_i$ , and  $\gamma_i$  are real numbers. The upper index  $\pm z$  means a pseudospin doublet quantized along the *z* axis. Each eigenstate is doubly degenerated because of the time-reversal symmetry. Therefore, the plus (minus) sign can be mapped to the up (down) state of a pseudospin  $s_p = \frac{1}{2}$ . Nine coefficients in  $\psi_i$  have only three degrees of freedom because of the orthonormal and normalization conditions. The remaining two degrees of freedom in Eq. (2) are attributed to the eigenenergies.

When the magnetic field is applied, the single-ion Hamiltonian is obtained as the sum of the CEF and Zeeman energy:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{CEF}} + (g_J \hat{\boldsymbol{J}}) \cdot (\mu_{\text{B}} \boldsymbol{H})$$
$$= \hat{\mathcal{H}}_{\text{CEF}} + \mu_{\text{B}} H g_J \hat{J}_d.$$
(4)

Here,  $g_J = 6/7$  is the Landé *g* factor,  $\hat{J}$  is the total angular momentum operator, and  $\hat{J}_d$  is a component of  $\hat{J}$  along the magnetic field *H*. If the energy scale of the field is sufficiently smaller than the excitation energy of CEF, we can treat the Zeeman energy  $\mu_B H g_J \hat{J}_d$  as a perturbation for CEF. Neglecting the thermal population, we can calculate the magnitude of the local moment along arbitrary directions using  $\alpha_0$ ,  $\beta_0$ , and  $\gamma_0$ . Along the symmetrical axis, namely, local *x*, *y*, or *z* axes, the local moment of the ground state is described as follows:

$$M_0^x = g_J \left| \sqrt{5}\alpha_0 \gamma_0 + 2\sqrt{2}\beta_0 \gamma_0 + \frac{3}{2}\beta_0^2 \right|,$$
 (5)

$$M_0^{\gamma} = g_J \left| \sqrt{5} \alpha_0 \gamma_0 - 2\sqrt{2} \beta_0 \gamma_0 + \frac{3}{2} \beta_0^2 \right|, \tag{6}$$

$$M_0^z = g_J \left| \frac{5}{2} \alpha_0^2 + \frac{1}{2} \beta_0^2 - \frac{3}{2} \gamma_0^2 \right|.$$
 (7)

These local moments correspond to the saturation moment at sufficiently low temperatures. Since the direction of the local coordinate depends on the local site, we must take account of the contributions from two types of orthogonalized Ce sites in the unit cell to obtain the macroscopic magnetization and susceptibility. As a result, the saturation moment per cerium atom along crystallographic axes is described as follows:

$$M^{(100)} = \sqrt{\frac{(M^x)^2 + (M^y)^2}{2}},$$
(8)

$$M^{(110)} = \frac{M^x + M^y}{2},$$
 (9)

$$M^{\langle 001\rangle} = M^z. \tag{10}$$

Note that an total angular momentum operator along an arbitrary direction is used to obtain  $M^{(100)}$ . In this crystal structure,  $M^{(100)}$  and  $M^{(110)}$  are anisotropic even in the tetragonal plane. They become the same value in the most isotropic case,  $M^x = M^y$ .

As seen here, the orthogonal anisotropy of the CEF eigenstate remains in the magnetization even in the tetragonal plane. Therefore, we can determine the eigenstate of the ground state  $|\psi_0^{\pm z}\rangle$  from the saturation moment obtained from the low-temperature magnetization. Substituting the experimental results,  $M^{(100)} = 1.32(2) \ \mu_{\rm B}/{\rm Ce}$  and  $M^{(110)} =$ 0.93(2)  $\mu_{\rm B}/{\rm Ce}$ , into Eqs. (8) and (9), we can obtain the local moments as  $M^x = 0.00(3) \mu_B$  and  $M^y = 1.87(3) \mu_B$ , or their swap. These values indicate that the local moment has a strong anisotropy in the tetragonal plane. Then, regarding  $M^x$  and  $M^{y}$  as  $M_{0}^{x}$  and  $M_{0}^{y}$ , we can obtain candidates of the ground state as the parameter sets ( $\alpha_0$ ,  $\beta_0$ ,  $\gamma_0$ ) satisfying Eqs. (5) and (6) from scanning the parameters within the normalization condition,  $(\alpha_0)^2 + (\beta_0)^2 + (\gamma_0)^2 = 1$ . This scan can be performed as sampling on the unit sphere in the parameter space. As a result, we can find only four possible candidates for the ground state. The two of the four candidates can be represented as one expression:

$$|\psi_0^{\pm z}\rangle = 0.41 \left|\pm\frac{5}{2}\right\rangle - 0.50p \left|\pm\frac{1}{2}\right\rangle + 0.76 \left|\mp\frac{3}{2}\right\rangle,$$
 (11)

where the parameter  $p = \pm 1$  represents a degree of freedom that swaps x and y axes. Detailed coefficients are listed in

TABLE I. The eigenstates and eigenenergies of the CEF;  $p = \pm 1$  is the sign parameter that swaps the local x and y axes.

$ \psi_i^{\pm z} angle$	$\alpha_i$	$\beta_i/p$	$\gamma_i$	$\Delta E_i$ (K)
$ert \psi_{0}^{\pm z}  angle ert \psi_{1}^{\pm z}  angle ert \psi_{1}^{\pm z}  angle ert \psi_{2}^{\pm z}  angle$	+0.411(27)	-0.501(16)	+0.762(15)	0
	+0.781(20)	-0.238(35)	-0.578(12)	133(3)
	+0.471(32)	+0.832(10)	+0.293(24)	426(12)

Table I. The sign of *p* cannot be determined from macroscopic measurements because of the *b*-glide operation in P4/mbm. The other two candidates,  $|\phi_0^{\pm z}\rangle = 0.13|\pm \frac{5}{2}\rangle 0.90p|\pm \frac{1}{2}\rangle - 0.42|\mp \frac{3}{2}\rangle$ , are also found from the same restriction; however, they are not appropriate because these ground states and their excited states cannot reproduce  $\chi(T)$ and  $M^{\langle 001 \rangle}(H)$ .

Once the ground state is determined, the coefficients of excited states  $|\psi_i^{\pm z}\rangle$  can be determined from only one coefficient because of the orthonormal and normalization conditions. Since the eigenenergies of  $|\psi_i^{\pm z}\rangle$  have been estimated from the specific heat measurement as  $\Delta E_1/k_{\rm B} = 133$  K and  $\Delta E_2/k_{\rm B} = 426$  K, we can determine the excited eigenstates from a curve fit for the magnetic susceptibility with one arbitrary coefficient only. The temperature dependence of the susceptibility along each local direction is calculated using the following formula:

$$\chi^{d}(T) = \beta \mu_{\rm B}^{2} g_{J}^{2} \sum_{i} \frac{e^{-\beta E_{i}}}{Z} \langle \psi_{i}^{\pm d} | \hat{J}_{d} | \psi_{i}^{\pm d} \rangle^{2} + 2 \mu_{\rm B}^{2} g_{J}^{2} \sum_{i} \frac{e^{-\beta E_{i}}}{Z} \sum_{j(\neq i)} \frac{\langle \psi_{j}^{\pm d} | \hat{J}_{d} | \psi_{i}^{\pm d} \rangle^{2}}{E_{j} - E_{i}}.$$
 (12)

Here,  $\beta = (k_{\rm B}T)^{-1}$  and  $|\psi_j^{\pm d}\rangle$  is a wave function diagonalized for  $\hat{J}_d$  in degenerated eigenstates of Eq. (2). The susceptibility along a crystallographic direction  $\langle hkl \rangle$  is obtained from that of the local coordinate as follows:

$$\chi^{\langle 100\rangle} = \chi^{\langle 110\rangle} = \frac{\chi^x + \chi^y}{2}, \qquad (13)$$

$$\chi^{\langle 001\rangle} = \chi^z. \tag{14}$$

Based on the susceptibility of 4f electrons, the following formula is used to fit the experimental susceptibility along the crystallographic  $\langle hkl \rangle$  direction:

$$\left(\frac{M^{\langle hkl\rangle}(T)}{H}\right) = \frac{\chi^{\langle hkl\rangle}(T)}{1 - \lambda^{\langle hkl\rangle}\chi^{\langle hkl\rangle}(T)} + \chi_0.$$
(15)

The molecular field  $\lambda^{\langle hkl \rangle}$  is obtained as  $\lambda^{\langle 100 \rangle} = \lambda^{\langle 110 \rangle} = -3.9(5)$  Ce-mol/emu and  $\lambda^{\langle 001 \rangle} = -1.6(5)$  Ce-mol/emu. Magnetic contributions from other than 4*f* electrons, e.g., the closed-shell diamagnetism and Pauli paramagnetism, are obtained as  $\chi_0 = -1.1(6) \times 10^{-5}$  emu/Ce-mol. The calculated susceptibility is shown in Fig. 2(b) as solid curves. The curves show good agreement with experimental results. The resultant wave functions of the first- and second-excited states are listed in Table I.

Magnetization curves of the isolated moments that have no exchange interaction between them can be obtained from

TABLE II. The coefficients of the CEF Hamiltonian Eq. (2).  $p = \pm 1$  is the sign parameter that swaps the local *x* and *y* axes.

$B_2^0$ (K)	$B_2^2/p$ (K)	$B_{4}^{0}$ (K)	$B_4^2/p$ (K)	$B_{4}^{4}$ (K)
-4.91(15)	34.6(2.7)	0.64(13)	1.15(12)	-0.041(16)

numerically diagonalizing Eq. (4). Note that although we have not directly diagonalized the CEF Hamiltonian Eq. (2), the coefficients of the Stevens operators can be obtained from the eigenenergy and eigenstates as described in the Appendix. The determined coefficients are listed in Table II. Since two types of orthogonalized Ce sites exist in the unit cell, the operator  $\hat{J}_d$  depends on the local sites. To calculate the magnetization curve along the  $\langle 110 \rangle$  direction, we adopt  $\hat{J}_{\pi/4}$  and  $\hat{J}_{-\pi/4}$  for the half of the Ce ions and others, respectively. The total magnetization is obtained as a sum of them. Similarly,  $\hat{J}_x$  and  $\hat{J}_y$  are adopted for the magnetization curve along the (100) direction. Calculated magnetizations are shown in Fig. 4 as solid curves. At 1.8 K, the calculated curves reproduce only the saturated region,  $\mu_0 H > 7$  T, along the  $\langle 100 \rangle$  and (110) directions. This is because Ce<sub>2</sub>Pd<sub>2</sub>Pb is an antiferromagnetically ordered state at the temperature. Therefore, the calculated curves that ignore an exchange interaction between moments cannot reproduce the actual magnetization. On the other hand, the calculated curves for  $T = 7 \text{ K} (> T_{\text{N}})$  almost reproduce experimental results along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and (001) directions. A small deviation between the calculated and experimental magnetizations can be attributed to the exchange interaction between Ce moments. These results indicate that the determined parameters are significantly close to the actual values.

Our analysis reveals a strong magnetic anisotropy of the CEF ground state in Ce<sub>2</sub>Pd<sub>2</sub>Pb. This anisotropy can be regarded as an anisotropic g factor for the pseudospin  $s_p = 1/2$ defined as  $g_i^d = 2M_i^d$ . From the coefficients in Table I, the g factor along the *x*, *y*, and *z* axes are calculated as  $g_0^x = 0.00(5)$ ,  $g_0^y = 3.69(5)$ , and  $g_0^z = 0.55(14)$ , respectively, when p = +1 is chosen in Eq. (11). Reparably, the sign change of p swaps the value of  $g_0^x$  and  $g_0^y$ . This anisotropy suggests a rather axial-type moment along the local y axis, and is similar to that of Yb<sub>2</sub>Pt<sub>2</sub>Pb. In Yb<sub>2</sub>Pt<sub>2</sub>Pb,  $g_0^x = 0.00$ ,  $g_0^y = 7.09$ , and  $g_0^z = 0.18$  are obtained from a calculation by a point charge model [26]. This compound exhibits fascinating partial order and spinon dispersion under the field along the (110)direction [3,5]. In this situation, one of two orthogonalized Yb moments and the other are influenced by a large Zeeman splitting  $g_0^{y} \mu_B H$  and a nearly zero splitting  $g_0^{x} \mu_B H$ , respectively. Therefore, the characteristic anisotropy of the g factor is expected to be a key component of the fascinating properties. The similarities of the crystal structure and the magnetic anisotropy between Ce<sub>2</sub>Pd<sub>2</sub>Pb and Yb<sub>2</sub>Pt<sub>2</sub>Pb motivate us to investigate the magnetic ground state in Ce<sub>2</sub>Pd<sub>2</sub>Pb.

One might wonder how such a strong anisotropy can be derived from rather moderate coefficients in Eq. (11). It can be understood by the following basis transformation. Until here, we have chosen the local z axis as the quantized direction. It determines the implicitly defined basis set of the wave function as  $|J_z\rangle$ ; e.g.,  $|\pm \frac{5}{2}\rangle$  means the eigenstate of

 $J_z = \pm \frac{5}{2}$ . As is well known, the basis set can be transformed using projection operators. In this case, the quantized direction can be changed using a projection operator  $\sum_{J_d} |J_d\rangle \langle J_d|$ (d = x, y, z). The projection operator can be represented as a tensor or a matrix, but its representation depends on the basis set. An explicit representation of the matrix is written in the Appendix. If p = +1 is chosen, the ground state quantized along the y axis, namely the direction of the largest g factor,  $|\psi_0^{\pm y}\rangle = (|\psi_0^{+z}\rangle \pm i |\psi_0^{-z}\rangle)/\sqrt{2}$ , is written using the basis set  $|J_v\rangle$  as follows:

$$\left|\psi_{0}^{\pm y}\right\rangle = 0.925 \left|\pm\frac{5}{2}\right\rangle_{y} + 0.343 \left|\pm\frac{1}{2}\right\rangle_{y} - 0.165 \left|\mp\frac{3}{2}\right\rangle_{y}.$$
 (16)

On the other hand, if p = -1 is chosen, the ground state quantized along the *x* axis  $|\psi_0^{\pm x}\rangle = (|\psi_0^{+z}\rangle \pm |\psi_0^{-z}\rangle)/\sqrt{2}$  can be written using the basis  $|J_x\rangle$  as follows:

$$|\psi_0^{\pm x}\rangle = 0.925 \left|\pm\frac{5}{2}\right|_x - 0.343 \left|\pm\frac{1}{2}\right|_x - 0.165 \left|\mp\frac{3}{2}\right|_x.$$
(17)

Here,  $|J_y\rangle_y (|J_x\rangle_x)$  is the eigenstate of the total angular momentum along the y axis (x axis). These representations indicate that the large g factor along the y axis (x axis) of the ground state with p = +1 (-1) is dominantly attributed to the  $J_y (J_x)$ =  $\frac{5}{2}$  component.

Finally, we summarize the analyzing method proposed in this paper. This method allows us to analyze the CEF eigenstate under a lower point-group symmetry than that of the whole crystal, e.g., an orthogonal site within a tetragonal crystal. The sequence of the analysis is summarized as follows:

(1) First, the saturation moments of the CEF ground state along several symmetrical directions of the crystal are obtained from the magnetization at sufficiently low temperature and high magnetic field.

(2) Then, the candidates of the ground state are estimated so that they satisfy the obtained saturation moments within the experimental uncertainty.

(3) If possible or necessary, the CEF eigenenergies are obtained from the specific heat. Independent estimation of eigenenergies reduces the uncertainty of the curve fit at the next step.

(4) Finally, the candidates of the ground state are narrowed down from the curve fit for the magnetic susceptibility using the restriction obtained above.

Resultant eigenstates have some degree of freedom that reflects the multiplicity of the local site, but probably it is removed by an analysis based on the point charge model.

## V. CONCLUSION

We have explained an analyzing method to determine CEF eigenstates at a complicated circumstance that the magnetic site has a lower point-group symmetry than that of the whole crystal. This method has the advantage of relying on macroscopic data only, namely the magnetic susceptibility, specific heat, and the saturation moment along several symmetrical directions, while the other analyses thus far for this circumstance require inelastic neutron scattering. Using this analysis, we have revealed an axial-type magnetic anisotropy in the CEF ground state in Ce<sub>2</sub>Pd<sub>2</sub>Pb. We also present

an angular momentum along arbitrary directions and the matrix representation of the projection operator that transforms the quantized direction of the total angular momentum. The presented method utilizes the anisotropy of the saturation moment that reflects the local site symmetry. Since the saturation moment is generally anisotropic even in the directions along which the susceptibility is isotropic, this method has the potential to become a general one for the complicated circumstance.

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#### APPENDIX

# 1. Commutation between the total angular momentum and space rotation operators

We note some of the relations similar to the commutation relation frequently used with the space rotation operator. Note that we assume that the spin and orbital momentums are strongly coupled by the spin-orbital coupling and therefore the total angular momentum is the conserved quantity. Here, we use a normalized total angular momentum; namely, their operators commute as follows:

$$[\hat{J}_i, \hat{J}_j] = i\varepsilon_{ijk}\hat{J}_k,\tag{A1}$$

where  $\varepsilon_{ijk}$  is the Levi-Civita symbol. The following are deduced for the rotation along the *x* axis:

$$\hat{J}_x e^{i\theta \hat{J}_x} = e^{i\theta \hat{J}_x} \hat{J}_x, \tag{A2}$$

$$\hat{J}_{y}e^{i\theta\hat{J}_{x}} = e^{i\theta\hat{J}_{x}}(\hat{J}_{y}\cos\theta + \hat{J}_{z}\sin\theta), \tag{A3}$$

$$\hat{J}_z e^{i\theta \hat{J}_x} = e^{i\theta \hat{J}_x} (-\hat{J}_y \sin \theta + \hat{J}_z \cos \theta), \tag{A4}$$

$$\hat{J}_{+}e^{i\theta\hat{J}_{x}} = e^{i\theta\hat{J}_{x}} \left( \hat{J}_{+}\cos^{2}\frac{\theta}{2} + \hat{J}_{-}\sin^{2}\frac{\theta}{2} + i\hat{J}_{z}\sin\theta \right), \quad (A5)$$

$$\hat{J}_{-}e^{i\theta\hat{J}_{x}} = e^{i\theta\hat{J}_{x}} \left( \hat{J}_{+}\sin^{2}\frac{\theta}{2} + \hat{J}_{-}\cos^{2}\frac{\theta}{2} - i\hat{J}_{z}\sin\theta \right).$$
(A6)

For the rotation along the y axis,

$$\hat{J}_x e^{i\theta \hat{J}_y} = e^{i\theta \hat{J}_y} (-\hat{J}_z \sin \theta + \hat{J}_x \cos \theta), \tag{A7}$$

$$\hat{J}_{y}e^{i\theta\hat{J}_{y}} = e^{i\theta\hat{J}_{y}}\hat{J}_{y}, \qquad (A8)$$

$$\hat{J}_z e^{i\theta \hat{J}_y} = e^{i\theta \hat{J}_y} (\hat{J}_z \cos \theta + \hat{J}_x \sin \theta), \tag{A9}$$

$$\hat{J}_{+}e^{i\theta\hat{J}_{y}} = e^{i\theta\hat{J}_{y}} \left( \hat{J}_{+}\cos^{2}\frac{\theta}{2} - \hat{J}_{-}\sin^{2}\frac{\theta}{2} - \hat{J}_{z}\sin\theta \right), \quad (A10)$$
$$\hat{J}_{-}e^{i\theta\hat{J}_{y}} = e^{i\theta\hat{J}_{y}} \left( -\hat{J}_{+}\sin^{2}\frac{\theta}{2} + \hat{J}_{-}\cos^{2}\frac{\theta}{2} - \hat{J}_{z}\sin\theta \right). \quad (A11)$$

 $= \left( \begin{array}{c} y_{+} \sin y_{-} \cos y_{-} \sin y_$ 

For the rotation along the z axis,

$$\hat{J}_x e^{i\theta J_z} = e^{i\theta J_z} (\hat{J}_x \cos \theta + \hat{J}_y \sin \theta)$$

$$=e^{i\theta\hat{f}_z}\left(\frac{e^{-i\theta}\hat{f}_+ + e^{i\theta}\hat{f}_-}{2}\right),\tag{A12}$$

$$\hat{J}_{y}e^{i\theta\hat{J}_{z}} = e^{i\theta\hat{J}_{z}} \left(-\hat{J}_{x}\sin\theta + \hat{J}_{y}\cos\theta\right)$$

$$= e^{i\theta J_z} \left( \frac{2i}{2i} \right),$$
(A13)  
$$\hat{J}_z e^{i\theta \hat{J}_z} = e^{i\theta \hat{J}_z} \hat{J}_z,$$
(A14)

$$\hat{J}_{+}e^{i\theta\hat{J}_{z}} = e^{i\theta\hat{J}_{z}}e^{-i\theta}\hat{J}_{+}, \qquad (A15)$$

$$\hat{J}_{-}e^{i\theta\hat{J}_{z}} = e^{i\theta\hat{J}_{z}}e^{+i\theta}\hat{J}_{-}.$$
(A16)

### 2. Total angular momentum operator along arbitrary directions

Operators along an arbitrary direction can be deduced using the space rotational operator  $\hat{R}(\theta) = e^{-i\theta \cdot \hat{J}}$ , where  $\theta$  and  $\hat{J}$ are a rotation vector and the total angular momentum operator, respectively. The component of  $\hat{J}$  along an arbitrary direction  $\hat{J}_{\theta,\phi}$  can be deduced as follows:

$$\hat{J}_{\theta,\phi} = \hat{R}_z^{\dagger}(-\phi)\hat{R}_y^{\dagger}(\frac{\pi}{2}-\theta)\hat{J}_x\hat{R}_y(\frac{\pi}{2}-\theta)\hat{R}_z(-\phi)$$
  
=  $\hat{J}_x\sin\theta\cos\phi + \hat{J}_y\sin\theta\cos\phi + \hat{J}_z\cos\theta$ ,

where  $\hat{R}_z(\phi) = e^{-i\phi \hat{J}_z}$  and  $\hat{R}_y(\frac{\pi}{2} - \theta) = e^{-i(\frac{\pi}{2} - \theta)\hat{J}_y}$  are defined as the space rotation operator along the *z* and *y* axes, respectively. Here,  $\theta$  ( $\phi$ ) is defined as the angles from the *z* axis to *xy* plane (from the *x* axis to *y* axis). In the Kramers doublet, the saturation moment  $M^{\theta,\phi}$  along the direction is obtained from the first perturbation of  $\hat{J}_{\theta,\phi}$  as follows:

$$M^{\theta,\phi} = \sqrt{(M^x)^2 \sin^2 \theta \cos^2 \phi + (M^y)^2 \sin^2 \theta \sin^2 \phi + (M^z)^2 \cos^2 \theta},$$
(A17)

where  $M^x$ ,  $M^y$ , and  $M^z$  are the saturation moment along the *x*, *y*, and *z* directions, respectively.

On the other hand, a local zero-field susceptibility  $\chi = \lim_{H \to 0} \frac{M}{H}$  along the  $(\theta, \phi)$  direction can be calculated using the first- and second-perturbation terms as follows:

$$\chi^{\theta,\phi} = \chi^x \sin^2 \theta \cos^2 \phi + \chi^y \sin^2 \theta \sin^2 \phi + \chi^z \cos^2 \theta,$$
(A18)

where  $\chi^x$ ,  $\chi^y$ , and  $\chi^z$  are the local susceptibilities along the *x*, *y*, and *z* axes, respectively. Note that Eq. (A18) is valid not only for the CEF ground states but also in high temperatures influenced by the excitations between the CEF eigenstates.

# 3. Relation between the eigenstate, eigenenergy, and coefficients of the Stevens operators in the configuration of $J = \frac{5}{2}$ and $C_{2v}$ , $D_2$ , or $D_{2h}$

The coefficients of the Stevens operator are obtained from the following procedures. Here, we define a matrix representation of  $\hat{\mathcal{H}}_{CEF}$  for the basis set  $|J_z\rangle$  as  $\mathcal{H}_{CEF}^{|J_z\rangle}$ , while that for the basis set  $|\psi_i^{\pm z}\rangle$  as  $\mathcal{H}_{CEF}^{|\psi_i^{\pm z}\rangle}$ . These matrices satisfy the following eigendecomposition:

$$\mathcal{H}_{\text{CEF}}^{|J_z\rangle} = \mathbf{Q}_{J_z, \psi_i^{\pm}} \mathcal{H}_{\text{CEF}}^{|\psi_i^{\pm z}\rangle} \mathbf{Q}_{J_z, \psi_i^{\pm}}^{\dagger}.$$
 (A19)

Here,  $\mathbf{Q}_{J_z,\psi_i^{\pm z}}^{\dagger} = \mathbf{Q}_{\psi_i^{\pm},J_z}$  is a unitary matrix that transforms the basis set from  $|J_z\rangle$  to  $|\psi_i^{\pm}\rangle$ . We can define  $\mathcal{H}_{CEF}^{|\psi_i^{\pm}\rangle}$  and  $\mathbf{Q}_{J_z,\psi_i^{\pm z}}$  as the following matrices:

$$\mathcal{H}_{CEF}^{|\psi_i^{\pm z}\rangle} = \begin{pmatrix} E_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & E_0 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_0 \end{pmatrix}, \quad (A20)$$
$$\mathbf{Q}_{J_z, \psi_i^{\pm z}} = \begin{pmatrix} \alpha_2 & 0 & \alpha_1 & 0 & \alpha_0 & 0 \\ 0 & \gamma_2 & 0 & \gamma_1 & 0 & \gamma_0 \\ \beta_2 & 0 & \beta_1 & 0 & \beta_0 & 0 \\ 0 & \beta_2 & 0 & \beta_1 & 0 & \beta_0 \\ \gamma_2 & 0 & \gamma_1 & 0 & \gamma_0 & 0 \\ 0 & \alpha_2 & 0 & \alpha_1 & 0 & \alpha_0 \end{pmatrix}. \quad (A21)$$

Here, the basis set  $|\psi_i^{\pm}\rangle$  is defined as the basis vector  $(|\psi_2^{+}\rangle, |\psi_2^{-}\rangle, |\psi_1^{+}\rangle, \dots, |\psi_0^{-}\rangle)$ , and the basis set  $|J_z\rangle$  is defined as the basis vector  $(|J_z = +\frac{5}{2}\rangle, |+\frac{3}{2}\rangle, \dots, |-\frac{5}{2}\rangle)$ . Using the above matrices, we can obtain a matrix representation of  $\hat{\mathcal{H}}_{CEF}$  for the basis set  $|J_z\rangle$  as follows:

$$\mathcal{H}_{CEF}^{|J_{z}\rangle} = \begin{pmatrix} E_{\alpha,\alpha} & 0 & E_{\alpha,\beta} & 0 & E_{\alpha,\gamma} & 0\\ 0 & E_{\gamma,\gamma} & 0 & E_{\gamma,\beta} & 0 & E_{\gamma,\alpha} \\ E_{\beta,\alpha} & 0 & E_{\beta,\beta} & 0 & E_{\beta,\gamma} & 0\\ 0 & E_{\beta,\gamma} & 0 & E_{\beta,\beta} & 0 & E_{\beta,\alpha} \\ E_{\gamma,\alpha} & 0 & E_{\gamma,\beta} & 0 & E_{\gamma,\gamma} & 0\\ 0 & E_{\alpha,\gamma} & 0 & E_{\alpha,\beta} & 0 & E_{\alpha,\alpha} \end{pmatrix}.$$
(A22)

The explicit representation of the matrix elements is listed as follows:

$$E_{\alpha,\alpha} = E_0 \alpha_0^2 + E_1 \alpha_1^2 + E_2 \alpha_2^2,$$
 (A23)

$$E_{\beta,\beta} = E_0 \beta_0^2 + E_1 \beta_1^2 + E_2 \beta_2^2, \qquad (A24)$$

$$E_{\gamma,\gamma} = E_0 \gamma_0^2 + E_1 \gamma_1^2 + E_2 \gamma_2^2, \qquad (A25)$$

$$E_{\alpha,\beta} = E_{\beta,\alpha} = E_0 \alpha_0 \beta_0 + E_1 \alpha_1 \beta_1 + E_2 \alpha_2 \beta_2, \qquad (A26)$$

$$E_{\beta,\gamma} = E_{\gamma,\beta} = E_0 \beta_0 \gamma_0 + E_1 \beta_1 \gamma_1 + E_2 \beta_2 \gamma_2, \qquad (A27)$$

$$E_{\gamma,\alpha} = E_{\alpha,\gamma} = E_0 \gamma_0 \alpha_0 + E_1 \gamma_1 \alpha_1 + E_2 \gamma_2 \alpha_2.$$
 (A28)

Comparing the matrix  $\mathcal{H}_{CEF}^{|J_z\rangle}$  with a matrix representation of Eq. (2), one obtains the following relations:

$$B_2^0 = \frac{2E_{\alpha,\alpha} - E_{\beta,\beta}}{28},\tag{A29}$$

$$B_4^0 = \frac{4E_{\alpha,\alpha} + 5E_{\beta,\beta}}{840},$$
 (A30)

$$B_2^2 = \frac{5E_{\alpha,\beta} + 3\sqrt{5}E_{\beta,\gamma}}{14\sqrt{10}},$$
 (A31)

$$B_4^2 = \frac{3E_{\alpha,\beta} - \sqrt{5}E_{\beta,\gamma}}{42\sqrt{10}},$$
 (A32)

$$B_4^4 = \frac{E_{\gamma,\alpha}}{12\sqrt{5}}.$$
 (A33)

Using these relations, we can obtain the coefficient of the Stevens operator from the eigenstates and eigenenergy.

# 4. Matrix representation of the projection operator $\sum_{J_d} |J_d\rangle \langle J_d|$ (d = x, y, z) for $J = \frac{5}{2}$

In quantum mechanics, an expectation value is obtained from a operator and wave function. For instance, an expectation value  $\langle J_x \rangle$  is obtained from an operator  $\hat{J}_x$  and a bra-ket notation:

$$\langle J_x \rangle = \langle \psi | \hat{J}_x | \psi \rangle \,. \tag{A34}$$

The bra and ket are usually regarded as a row and column vector on an implicitly defined basis set. Defining the basis set makes it possible to write an operator as a matrix. If we do not use the implicitly defined basis set, the basis set should be defined using a projection operator. Since a projection operator is the identity operator, we can insert it anywhere in the bracket representation. To obtain a matrix representation for the basis set  $|J_z\rangle$ , namely  $(|J_z = +\frac{5}{2}\rangle, |+\frac{3}{2}\rangle, \ldots, |-\frac{5}{2}\rangle)$ , the projection operator  $\sum_{J_z} |J_z\rangle \langle J_z|$  is inserted as follows:

$$\begin{aligned} \langle J_x \rangle &= \langle \psi | \sum_{J'_z} |J'_z \rangle \, \langle J'_z | \, \hat{J}_x \sum_{J_z} |J_z \rangle \, \langle J_z | \psi \rangle \\ &= \sum_{J_z, J'_z} \langle \psi | J'_z \rangle \, \langle J'_z | \hat{J}_x | J_z \rangle \, \langle J_z | \psi \rangle \,. \end{aligned} \tag{A35}$$

This representation offers a matrix  $\mathbf{J}_x^{|J_z\rangle}$  that has elements  $\langle J_x' | \hat{J}_x | J_z \rangle$  as follows:

$$\mathbf{J}_{x}^{|J_{z}\rangle} = \begin{pmatrix} 0 & \frac{\sqrt{5}}{2} & 0 & 0 & 0 & 0\\ \frac{\sqrt{5}}{2} & 0 & \sqrt{2} & 0 & 0 & 0\\ 0 & \sqrt{2} & 0 & \frac{3}{2} & 0 & 0\\ 0 & 0 & \frac{3}{2} & 0 & \sqrt{2} & 0\\ 0 & 0 & 0 & \sqrt{2} & 0 & \frac{\sqrt{5}}{2}\\ 0 & 0 & 0 & 0 & \frac{\sqrt{5}}{2} & 0 \end{pmatrix}.$$
(A36)

Other components in Eq. (A35),  $\langle \psi | J'_z \rangle$  and  $\langle J_z | \psi \rangle$ , represent the bra- and ket-vector for the basis set  $|J_z\rangle$ , respectively. Therefore, a matrix representation of  $\hat{J}_x$  for the basis set  $|J_z\rangle$  is obtained:

$$\hat{J}_x = \mathbf{J}_x^{|J_z\rangle}.\tag{A37}$$

On the other hand, if we insert the projection operator  $\sum_{J_x} |J_x\rangle \langle J_x|$ , the following representation is obtained:

$$\langle J_x \rangle = \langle \psi | \sum_{J'_x} | J'_x \rangle \langle J'_x | \hat{J}_x \sum_{J_x} | J_x \rangle \langle J_x | \psi \rangle$$

$$= \sum_{J_x, J'_x} \langle \psi | J'_x \rangle \langle J'_x | \hat{J}_x | J_x \rangle \langle J_x | \psi \rangle .$$
(A38)

The elements  $\langle \psi | J'_x \rangle$  and  $\langle J_x | \psi \rangle$  represent the bra- and ket-vector for the basis set  $|J_x \rangle$ , namely  $(|J_x = +\frac{5}{2}\rangle, |+\frac{3}{2}\rangle, \dots, |-\frac{5}{2}\rangle)$ , respectively. Therefore, this representation should offer the following diagonal matrix  $\mathbf{J}_x^{|J_x|}$ 

that has elements  $\langle J'_x | \hat{J}_x | J_x \rangle$ :

$$\mathbf{J}_{x}^{|J_{x}\rangle} = \begin{pmatrix} +\frac{5}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & +\frac{3}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & +\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{3}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{5}{2} \end{pmatrix}.$$
(A39)

Then if we insert projection operators  $\sum_{J_x} |J_x\rangle \langle J_x|$  and  $\sum_{J_z} |J_z\rangle \langle J_z|$  sequentially, the following is obtained:

$$\langle J_x \rangle = \langle \psi | \sum_{J'_z} |J'_z \rangle \langle J'_z | \sum_{J'_x} |J'_x \rangle$$

$$\times \langle J'_x | \hat{J}_x \sum_{J_x} |J_x \rangle \langle J_x | \sum_{J_z} |J_z \rangle \langle J_z | \psi \rangle$$

$$= \sum_{J_x, J'_x, J_z, J'_z} \langle \psi | J'_z \rangle \langle J'_z | J'_x \rangle \langle J'_x | \hat{J}_x | J_x \rangle \langle J_x | J_z \rangle \langle J_z | \psi \rangle .$$
(A40)

Here,  $\langle J'_x | \hat{J}_x | J_x \rangle$  are the elements of the matrix in Eq. (A39), while  $\langle \psi | J'_z \rangle$  and  $\langle J_z | \psi \rangle$  represent the elements of the bra- and ket-vector for the basis set  $| J_z \rangle$ , respectively. Therefore,  $\langle J'_z | J'_x \rangle$  and  $\langle J_x | J_z \rangle$  represent elements of basis transform matrices  $\mathbf{Q}_{J_z,J_x}$  and  $\mathbf{Q}_{J_x,J_z}$ , respectively. Note that  $\mathbf{Q}_{J_x,J_z} =$  $\mathbf{Q}_{J_z,J_x}^{\dagger}$  because they are a unitary matrix. Using these matrices, the following matrix representation of Eq. (A40) for the basis set  $| J_z \rangle$  is obtained:

$$\hat{J}_x = \mathbf{Q}_{J_z, J_x} \mathbf{J}_x^{|J_x\rangle} \mathbf{Q}_{J_z, J_y}^{\dagger}.$$
 (A41)

Comparing Eqs. (A37) and (A41), we obtain the following:

$$\mathbf{J}_{x}^{|J_{z}\rangle} = \mathbf{Q}_{J_{z},J_{x}}\mathbf{J}_{x}^{|J_{x}\rangle}\mathbf{Q}_{J_{z},J_{x}}^{\dagger}.$$
 (A42)

Since the matrix  $\mathbf{J}_{x}^{|J_{x}\rangle}$  is a diagonal matrix, this equation corresponds to the eigendecomposition of the matrix  $\mathbf{J}_{x}^{|J_{z}\rangle}$ . Therefore, from the eigenvectors of  $\mathbf{J}_{x}^{|J_{z}\rangle}$ ,  $\mathbf{Q}_{J_{z},J_{x}}$  that transforms the basis set from  $|J_{x}\rangle$  to  $|J_{z}\rangle$  is obtained as follows:

 $\mathbf{Q}_{J_z,J_x}$ 

$$= \frac{e^{-i\pi/4}}{4\sqrt{2}} \begin{pmatrix} +1 & -\sqrt{5}i & -\sqrt{10} & +\sqrt{10}i & +\sqrt{5} & -i \\ +\sqrt{5} & -3i & -\sqrt{2} & -\sqrt{2}i & -3 & +\sqrt{5}i \\ +\sqrt{10} & -\sqrt{2}i & +2 & -2i & +\sqrt{2} & -\sqrt{10}i \\ +\sqrt{10} & +\sqrt{2}i & +2 & +2i & +\sqrt{2} & +\sqrt{10}i \\ +\sqrt{5} & +3i & -\sqrt{2} & +\sqrt{2}i & -3 & -\sqrt{5}i \\ +1 & +\sqrt{5}i & -\sqrt{10} & -\sqrt{10}i & +\sqrt{5} & +i \end{pmatrix}$$
(A43)

Here, the phase factors of the eigenvectors are determined so that following relations are satisfied:

$$\mathbf{Q}_{J_x,J_y} = \mathbf{Q}_{J_y,J_z} = \mathbf{Q}_{J_z,J_x},\tag{A44}$$

$$\mathbf{Q}_{J_{y},J_{x}} = \mathbf{Q}_{J_{z},J_{y}} = \mathbf{Q}_{J_{x},J_{z}}.$$
 (A45)

The argument thus far holds in general for  $J = \frac{5}{2}$ . In the remainder of this section, we will derive relations applicable to the orthogonal symmetries,  $C_{2v}$ ,  $D_2$ , and  $D_{2d}$ . For the eigenstates of the Hamiltonian Eq. (2), described in Eq. (3), the Kramers doublet quantized along the x axis  $|\psi_i^{\pm x}\rangle =$ 

 $(|\psi_i^{+z}\rangle \pm |\psi_i^{-z}\rangle)/\sqrt{2}$  is written for the basis set  $|J_z\rangle$  as follows:

$$|\psi_i^{\pm x}\rangle = \frac{1}{\sqrt{2}} \left( \alpha_i \left| + \frac{5}{2} \right\rangle \pm \gamma_i \left| + \frac{3}{2} \right\rangle + \beta_i \left| + \frac{1}{2} \right\rangle$$
  
 
$$\pm \beta_i \left| -\frac{1}{2} \right\rangle + \gamma_i \left| -\frac{3}{2} \right\rangle \pm \alpha_i \left| -\frac{5}{2} \right\rangle \right).$$
 (A46)

Using  $\mathbf{Q}_{J_x,J_z}$ , we can transform the basis set  $|J_z\rangle$  of Eq. (A46) into the basis set  $|J_x\rangle$  as follows:

$$\left|\psi_{i}^{\pm x}\right\rangle = \alpha_{i}^{x}\left|\pm\frac{5}{2}\right\rangle_{x} + \beta_{i}^{x}\left|\pm\frac{1}{2}\right\rangle_{x} + \gamma_{i}^{x}\left|\pm\frac{3}{2}\right\rangle_{x}.$$
 (A47)

Here, the ket-vector  $|J_x\rangle_x$  represents the eigenstate of  $\hat{J}_x$  that has the eigenvalue  $J_x$ . The coefficients  $\alpha_i^x$ ,  $\beta_i^x$ , and  $\gamma_i^x$  are obtained from Eq. (3) and  $\mathbf{Q}_{J_xJ_z}$  as follows:

$$\alpha_i^x = \frac{\alpha_i + \sqrt{10}\beta_i + \sqrt{5}\gamma_i}{4},\tag{A48}$$

$$\beta_i^x = \frac{-\sqrt{10}\alpha_i + 2\beta_i - \sqrt{2}\gamma_i}{4}, \qquad (A49)$$

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$$\gamma_i^x = \frac{\sqrt{5}\alpha_i + \sqrt{2}\beta_i - 3\gamma_i}{4}.$$
 (A50)

Similarly, the eigenstates quantized along the y axis,  $|\psi^{\pm x}\rangle = (|\psi^{+z}\rangle \pm i |\psi^{-z}\rangle)/\sqrt{2}$ , can be written by the basis set of  $|J_y\rangle$  as follows:

$$\left|\psi_{i}^{\pm y}\right\rangle = \alpha_{i}^{y}\left|\pm\frac{5}{2}\right\rangle_{y} + \beta_{i}^{y}\left|\pm\frac{1}{2}\right\rangle_{y} + \gamma_{i}^{y}\left|\pm\frac{3}{2}\right\rangle_{y}.$$
 (A51)

Here, the ket-vector  $|J_y\rangle_y$  represents the eigenstate of  $\hat{J}_y$  that has the eigenvalue  $J_y$ . The coefficients  $\alpha_i^y$ ,  $\beta_i^y$ , and  $\gamma_i^y$  are obtained from Eq. (3) and  $\mathbf{Q}_{J_y,J_z}$  as follows:

$$\alpha_i^y = \frac{\alpha_i - \sqrt{10}\beta_i + \sqrt{5}\gamma_i}{4},\tag{A52}$$

$$\beta_i^y = \frac{\sqrt{10}\alpha_i + 2\beta_i + \sqrt{2}\gamma_i}{4},\tag{A53}$$

$$\gamma_i^y = \frac{\sqrt{5}\alpha_i - \sqrt{2}\beta_i - 3\gamma_i}{4}.$$
 (A54)

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