Linear dichroism in angle-resolved core-level photoemission spectra reflecting 4f ground-state symmetry of strongly correlated cubic Pr compounds

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We report experimentally observed linear dichroism in angle-resolved core-level photoemission spectra of PrIr2Zn20 and PrB6 in cubic symmetry. The different anisotropic 4f charge distributions between the compounds due to the crystalline-electric-field splitting are responsible for the difference in the linear dichroism, which has been verified by spectral simulations with the full multiplet theory for a single-site Pr3+ ion in cubic symmetry. The observed linear dichroism and polarization-dependent spectra in two different photoelectron directions for PrIr2Zn20 are reproduced by theoretical analysis for the Γ5 ground state, whereas those of the Pr 3d and 4d core levels indicate the Γ5 ground state for PrB6.

I. INTRODUCTION

Rare-earth-based strongly correlated electron systems show various interesting phenomena such as competition between magnetism and unconventional superconductivity, charge and/or multipole ordering, and the formation of a narrow (∼meV) gap at low temperatures. In these systems, the total angular momentum J of the 4f electrons is the good quantum number due to the stronger Coulomb interactions between the 4f electrons and their spin-orbital coupling than the crystalline electric field (CEF). Therefore, the observable is not the orbital degrees of freedom but the quadrupoles which are described as second-order tensors of J. When the dipole magnetic moments are quenched but the quadrupoles remain active under CEF, this is possible in non-Kramers ions with an integer number of J under cubic symmetry, the quadrupoles often play an important role in forming exotic electronic ground states such as the antiferroquadrupolar (AFQ) state with a staggered quadrupolar component and a non-Fermi liquid (NFL) state attributed to the two-channel (quadrupole) Kondo effect. Furthermore, the feasibility of superconductivity mediated by quadrupolar fluctuations in the Pr-based superconductor PrOs4Sb12 with Tc = 1.5 K has been pointed out by neutron scattering and NQR measurements. A well-known example of a 4f2 cubic system is PrPb3 which undergoes an AFQ transition at TQ = 0.4 K. Here reported cubic PrIr2Zn20 undergoes an AFQ ordering at TQ = 0.11 K and a superconducting transition at Tc = 0.05 K. Below 10 K, the increase in magnetic susceptibility for this compound tends to saturate, which implies the van Vleck susceptibility with nonmagnetic CEF ground states of the Γ3 doublet. On the other hand, PrB6 with a cubic crystal structure show the incommensurate antiferromagnetic transition at 7 K and a commensurate antiferromagnetic ordering at 4.2 K. These phenomena suggest the Γ5 ground state for PrB6. However, direct or microscopic verifications of the proposed 4f ground-state symmetry are still lacking for these compounds. In this letter, we show spectroscopic signs for the Γ3 symmetry of the Pr3+ sites in the ground state of PrIr2Zn20 and for the Γ5 ground state of PrB6 on the basis of linear dichroism in angle-resolved core-level photoemission from the Pr sites.

Generally, it is difficult to experimentally determine the 4f ground-state symmetry. Inelastic neutron scattering is useful for detecting the CEF splittings, but other excitations such as phonon excitations often hamper the observation of magnetic 4f-4f excitations. In addition, the symmetry itself cannot be directly probed by unpolarized neutrons. Linear dichroism (LD) in 3d-to-4f soft X-ray absorption spectroscopy (XAS) for single crystals is powerful owing to the dipole selection rules, as reported for tetragonal Ce compounds. On the other hand, the selection rules work also in the photoemission process. Furthermore, by virtue of the angle-resolved measurements with the acceptance angle of ± several degrees, there is another measurement parameter as the photoelectron direction relative to the single-crystalline axis in addition to the excitation light polarization. Indeed, by using LD in 3d core-level hard X-ray photoemission (HAXPES) spectra, the Yb3+ 4f ground state has been determined for cubic YbB12. LD in the core-level
HAXPES for cubic Pr compounds is also expected to be observed, as discussed below.

The Pr ions are encapsulated in the highly symmetric Frank-Kasper cages formed by 16 zinc atoms in PrIr$_2$Zn$_{20}$, where the actual local point-group symmetry is $T_d^{20}$. For PrB$_6$, on the other hand, the Pr ions are in the $O_h$ symmetry$^{20}$. Because of the even number of $4f$ electrons, the CEF electronic states are free from the Kramers theorem. The ninefold degenerated ground-state multiplets with $J = 4$ ($L = 5, S = 1$) in the $4f^2$ configurations determined by the Hund’s rules is lifted by the CEF Hamiltonian for the $T_d$ or $O_h$ symmetry,

$$H_{CEF} = B_{40}(O_{40} + 5O_{44}) + B_{60}(O_{60} - 21O_{64}),$$

where $O_{mn}$ and $B_{mn}$ denote the Stevens operator and the CEF parameter, respectively$^{21}$. Then the ninefold $J = 4$ states split generally into one singlet, one doublet, and two triplets as

$$|\Gamma_1\rangle = \sqrt{5/24}|+4\rangle + \sqrt{7/12}|0\rangle + \sqrt{5/24}|-4\rangle, \quad |\Gamma_3\rangle = \begin{cases} \sqrt{7/24}|+4\rangle - \sqrt{5/12}|0\rangle + \sqrt{7/24}|-4\rangle, \\
\sqrt{1/2}|+2\rangle + \sqrt{1/2}|-2\rangle \end{cases},$$

$$|\Gamma_4\rangle = \begin{cases} \sqrt{1/8}|\pm 3\rangle + \sqrt{7/8}|\mp 1\rangle, \\
\sqrt{1/2}|+4\rangle - \sqrt{1/2}|-4\rangle \end{cases},$$

$$|\Gamma_5\rangle = \begin{cases} \sqrt{7/8}|\pm 3\rangle - \sqrt{1/8}|\mp 1\rangle, \\
\sqrt{1/2}|+2\rangle - \sqrt{1/2}|-2\rangle \end{cases},$$

where the integers in the kets denote $J_z$. It is known that the $\Gamma_4$ states are ruled out from the candidates of the ground state because there is no solution of $B_{40}$ and $B_{60}$ to set them as the lowest state$^{22}$. Since their $4f$ charge distributions deviate from spherical symmetry owing to the CEF splitting even in the cubic symmetry, as shown in Fig. 1, it is natural to expect the observation of LD in core-level photoemission spectra, we optimized the photon flux so as to set comparable photoelectron count rates between the s- and p-polarization configurations. Single crystals of PrIr$_2$Zn$_{20}$ synthesized by the melt-growth method$^{11,24}$ were fractured along the (110) plane in situ, where the base pressure was $1 \times 10^{-7}$ Pa. The experimental geometry was controlled using our developed two-axis manipulator$^{25}$ where the photoelectron detection along the [100] direction was set by polar rotation of 45° from the normal direction parallel to the [110] direction, and the [111] direction was set by polar rotation by ~35° after azimuthal rotation. A single crystal of PrB$_6$ synthesized by the floating zone method was fractured along the (100) plane in situ. The sample and surface qualities were examined on the basis of the absence of O and C 1s core-level spectral weights.

We have observed LD in HAXPES$^{22,24}$ at BL19LXU of SRing-\textsuperscript{\textregistered} using a MBS A1-HE hemispherical photoelectron spectrometer. A Si(111) double-crystal monochromator selected linearly polarized 7.9 keV radiation within the horizontal plane, which was further monochromatized using a Si(620) channel-cut crystal. To switch the linear polarization of the excitation light from the horizontal to vertical directions, two single-crystalline (100) diamonds were used as a phase retarder placed downstream of the channel-cut crystal. The $P_L$ (degree of linear polarization) of the polarization-switched X-ray after the phase retarder was estimated as ~0.89, corresponding to the vertically linear polarization component of 93.8%. Since the detection direction of photoelectrons was set in the horizontal plane with an angle to incident photons of 60°, the experimental configuration at the vertically (horizontally) polarized light excitation corresponds to the s-polarization (p-polarization). To precisely detect LD in the Pr 3d core-level photoemission spectra, we optimized the photon flux so as to set comparable photoelectron count rates between the s- and p-polarization configurations. Single crystals of PrIr$_2$Zn$_{20}$ synthesized by the melt-growth method$^{11,24}$ were fractured along the (110) plane in situ, where the base pressure was $1 \times 10^{-7}$ Pa. The experimental geometry was controlled using our developed two-axis manipulator$^{25}$ where the photoelectron detection along the [100] direction was set by polar rotation of 45° from the normal direction parallel to the [110] direction, and the [111] direction was set by polar rotation by ~35° after azimuthal rotation. A single crystal of PrB$_6$ synthesized by the floating zone method was fractured along the (100) plane in situ. The sample and surface qualities were examined on the basis of the absence of O and C 1s core-level spectral weights.

II. EXPERIMENTAL

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caused by possible impurities or surface oxidization. The energy resolution was set to 500 meV. The measuring temperature is 5 K (10 K) for PrIr$_2$Zn$_{20}$ (PrB$_6$), which is sufficiently lower than the excited states.\(^\text{32}\)

III. RESULTS AND DISCUSSIONS

![Graph](image)

FIG. 2. Core-level HAXPES raw spectra in the p-polarization configurations. The inset shows polarization-dependent Pr 3$d_{5/2}$ core-level HAXPES raw spectra (solid lines) of PrIr$_2$Zn$_{20}$ in the [100] direction and optimized Shirley-type backgrounds (see text), which we have subtracted from the raw spectra (dashed lines).

The polarization-dependent Pr$^{3+}$ 3$d_{5/2}$ HAXPES spectra in the [100] direction of PrIr$_2$Zn$_{20}$ are shown in Fig. 2. Caused by the relatively low density of the Pr ions as <5% determined by the composition, the intrinsic Pr 3$d_{5/2}$ signals are much weaker than the background contributed by the photoelectrons from the other orbitals in the other elements. A broad peak at a binding energy of \(\sim 934\) eV, shoulder centered at 939 eV and another shoulder structure ranging from 925 to 930 eV exist in the spectra. The former peak and the shoulder at 939 eV are ascribed to the Pr$^{3+}$ states (\(3d^54f^2\) final states) with the atomic-like multiplets structure, and the shoulder structure at 925 – 930 eV comes from the \(3d^54f^3\) final states with hybridization between the \(4f\) and conduction electrons. The so-called Shirley-type backgrounds are also displayed in Fig. 2. We have optimized the backgrounds as follows: After the normalization of the background-subtracted spectra by Pr$^{3+}$ 3$d_{5/2}$ spectral weight in the \(931 – 940\) eV region except for the \(3d^54f^3\) final states region, the intensities in the high binding energy region of 941 – 942 eV become equivalent between the s- and p-polarization configurations. The reference binding energy on the higher side for subtracting the background has been set to 940.8 eV corresponding to the local minimum of the raw spectral weight. As a result, there are finite spectral weights at \(\sim 940\) eV in the background-subtracted spectra. However, they should be intrinsic due to the overlap of the tails of the lifetime-broadened Pr$^{3+}$ 3$d_{5/2}$ main peaks and a plasmonic energy-loss structure at the higher binding energy.

![Graph](image)

FIG. 3. (a) Geometry for the polarization-dependent HAXPES measurements in the [100] direction for PrIr$_2$Zn$_{20}$. (b) same as (a) but for the photoelectron in the [111] direction. (c) Polarization-dependent Pr 3$d_{5/2}$ core-level HAXPES spectra and LD of PrIr$_2$Zn$_{20}$ compared with the simulated ones for the \(\Gamma_3\) and \(\Gamma_1\) states in the [100] direction. The experimental LD is displayed in the energy region of the normalization (931 – 940 eV). Simulated LD assuming the \(\Gamma_5\) state is also shown in the lower panel. The Shirley-type background has been subtracted from the raw spectra (Fig. 2). (d) Same as (c) but data in the [111] direction.

Figure 3 shows comparisons of the polarization-dependent background-subtracted Pr$^{3+}$ 3$d_{5/2}$ HAXPES spectra of PrIr$_2$Zn$_{20}$ and their LD (defined as the difference in the spectral weight between the s- and p-polarization configurations) with the photoelectron directions of [100] and [111] with the simulated ones for the \(\Gamma_3\) and \(\Gamma_1\) states. For the experimental spectra and the simulated spectra for the \(\Gamma_3\) state, the LDs are found
to be finite but subtle. As shown in Fig. 3(c), the sign of the experimental LD at \( \sim 934 \) eV is positive, whereas that in the 935–938 eV region is negative along the [100] direction. These tendencies are consistent with the simulated LDs for the \( \Gamma_3 \) and \( \Gamma_1 \) states although the LD for the \( \Gamma_1 \) state is much stronger at \( \sim 934 \) eV than the experimentally observed LD. For the data in the [100] direction in Fig. 3(d), the LD in the 932–940 eV region in the experiment is strongly suppressed compared with that in the [100] direction, being consistent with, at least not contradictory to, the simulation for the \( \Gamma_3 \) state. If the 4\( f \) ground state of PrIr\(_2\)Zn\(_20\) were in the \( \Gamma_1 \) symmetry, a finite LD beyond the statistics would be seen with the negative sign at \( \sim 934 \) eV. The sign and amount of LD for the \( \Gamma_5 \) state are completely inconsistent with our experimental results in both directions. Therefore, we can conclude that our experimental results support the \( \Gamma_3 \) ground-state symmetry for PrIr\(_2\)Zn\(_20\). The relatively smaller LDs in the [111] direction than in the [100] direction in both experiments and simulations originate from the larger number of the equivalent direction (e.g. [100], [010] and [001]) in the cubic unit cell (8 for [111] and 6 for [100]), where the simulated LD in the [110] direction (not shown here) is much smaller than that in the [100] and [111] directions. (Note that the LD cancels out for really angle-integrated spectra over 4\( \pi \) steradian.)

Figure 4 shows the polarization-dependent background-subtracted Pr\(^{3+}\) 3d\(_{5/2}\) and 4\( d \) core-level HAXPES spectra and LDs of cubic PrB\(_6\) in the [100] direction. In the case of PrB\(_6\), the broad peak and the shoulder structures are seen in the Pr\(^{3+}\) 3d\(_{5/2}\) spectra. On the other hand, there are multiplets ranging from 114 to 127 eV and a shoulder structure ranging from 106 to 114 eV in the Pr\(^{3+}\) 4\( d \) spectra. The former multiplets are ascribed to the Pr\(^{3+}\) states \((|4f^6/4f^2\rangle \text{ final states)}\), and the latter shoulder structure comes from the \(|4f^6/4f^3\rangle \text{ final states with hybridization between the 4}\( f \) and conduction electrons. These features are qualitatively consistent with the previous reported ones. The 3d\(_{5/2}\) main peak is broader for PrB\(_6\) than for PrIr\(_2\)Zn\(_{20}\) in Fig. 3(c), of which the origin is unclear at present.

The simulated polarization-dependent Pr\(^{3+}\) 3d\(_{5/2}\) (4\( d \)) HAXPES spectra for the \( \Gamma_5 \) state and LDs for the \( \Gamma_1 \), \( \Gamma_3 \), and \( \Gamma_5 \) states are also shown in Fig. 4. For obtaining the simulated Pr\(^{3+}\) 4\( d \) spectra, the 4\( d \)-4\( f \) Slater integrals (4\( d \) spin-orbit coupling) are reduced to 80% (100%) to best reproduce the experimental Pr\(^{3+}\) 4\( d \) core-level photoemission spectra with respect to the multiple splittings. To reproduce the spectra, the Lorentzian width of 3.0 eV (full width of half maximum), which is larger than the value for PrIr\(_2\)Zn\(_{20}\) of 1.8 eV show in Fig. 3(c), has been employed for PrB\(_6\). The peak at 934 eV is slightly stronger in the p-polarization configuration than in the s-polarization one for both experimental and simulated spectra while the sign of LD is flipped in the binding energies of 120–125 eV. As shown in Figs. 4(b) and 4(c), the observed LDs are qualitatively reproduced by the simulations for the \( \Gamma_5 \) state although LDs are somehow smaller in the experiment for which an origin is unclear. Furthermore, the LD signs for the \( \Gamma_3 \) and \( \Gamma_1 \) states are completely opposite to those of the experimental data in all binding energy region. Thus, our results undoubtedly indicate the \( \Gamma_5 \) ground-state symmetry for PrB\(_6\), being consistent with the previous report. Note that the Pr 4\( d \) spectral weight has not unfortunately been detected for PrIr\(_2\)Zn\(_{20}\) since it has been buried in the background from the other sites by the HAXPES at \( h\nu = 7.9 \) keV.
IV. SUMMARY

In summary, we have performed the polarization-dependent core-level HAXPES of the Pr\textsuperscript{3+} sites in cubic PrIr\textsubscript{2}Zn\textsubscript{20} and PrB\textsubscript{6}. Our results support the so far predicted their ground-state symmetry, showing the potential of LD in the core-level HAXPES for probing the partially-filled strongly correlated orbital symmetry of the Pr compounds in cubic symmetry, as established for the Yb systems\textsuperscript{18,28}.

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