PHYSICAL REVIEW B **89**, 075131 (2014)

Emergence of reentrant metal-nonmetal transition in $Pr_{0.85}Ce_{0.15}Ru_4P_{12}$ and $Pr(Ru_{0.95}Rh_{0.05})_4P_{12}$

Kotaro Saito,[1,*] Claire Laulhé,[1,†] Takahiro Sato,[1] Lijie Hao,[1,‡] Jean-Michel Mignot,[2] and Kazuaki Iwasa[1]
[1]*Department of Physics, Tohoku University, Sendai, Miyagi 980-8571, Japan*
[2]*Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif-sur-Yvette, France*

(Received 8 October 2013; published 24 February 2014)

The metal-nonmetal transition in Ce- and Rh-substituted $PrRu_4P_{12}$ was investigated through magnetic susceptibility, x-ray superlattice reflection, and inelastic neutron scattering (INS) measurements. The saturation in the magnetic susceptibility at low temperatures suggests a singlet ground state for Pr sites in both compounds. This finding is in contrast to the staggered order of singlet and triplet ground states found in the ordered phase of $PrRu_4P_{12}$, which leads to a diverging susceptibility. The intensities of x-ray superlattice reflections of both compounds develop below 45 K and decrease rapidly below 10 K with a simultaneous decrease in electrical resistivity. INS experiments reveal that $4f$ electron states in both compounds change drastically from two distinct crystal field (CF) level schemes corresponding to an order parameter in the multipole ordered phase ($10\text{ K} < T < 45\text{ K}$) to a nearly uniform CF level scheme below 10 K. The uniform CF ground state at the Pr sites carries no degree of freedom relevant to the staggered ordering pattern and electronic gap formation. Therefore, the substituted systems exhibit a reentrant metallic state at the lowest temperature. These phenomena may originate from effective electron doping due to atomic substitution.

DOI: 10.1103/PhysRevB.89.075131 PACS number(s): 71.20.Eh, 71.27.+a, 71.30.+h, 78.70.Nx

I. INTRODUCTION

Phase transitions involving the ordering of charge or magnetic moments have been studied in various materials for many years. These two degrees of freedom can be described as an electric monopole and a magnetic dipole of electrons, respectively. Recently, higher-rank multipole order in rare earth compounds has been a focus of many investigations, such as electric quadrupole ordering in CeB_6, and magnetic octupole ordering in $Ce_{0.7}La_{0.3}B_6$ and NpO_2 [1–4]. These systems have cubic crystal structures with high local symmetry, which often results in degenerate crystal field (CF) ground states maintaining various multipole degrees of freedom.

Rare earth filled skutterudites RT_4X_{12} (R: rare earth; T: transition metal; X: pnictogen), which crystallize in the bcc structure with space group $Im\overline{3}$, often have characteristic ground states involving $4f$ electrons at the R site [5,6]. Some of these compounds are thought to potentially undergo multipole ordering. Among these compounds, $PrRu_4P_{12}$ shows a metal-nonmetal transition at $T_{MI} = 63$ K without a distinct anomaly in the magnetic susceptibility [7]. This transition is accompanied by a structural modulation characterized by conservation of the local Pr-site symmetry of the T_h point group and a change in translational symmetry to $Pm\overline{3}$ with wave vector $\mathbf{q} = (100)$, which corresponds to the nesting vector of the Fermi surface [8,9]. On the other hand, $LaRu_4P_{12}$ also shows nesting properties similar to $PrRu_4P_{12}$ but does not exhibit a metal-nonmetal transition. Thus, this metal-nonmetal transition is not of the conventional Peierls type and $4f$ electrons must play a crucial role [10,11]. Inelastic neutron scattering (INS) experiments in $PrRu_4P_{12}$ have revealed two CF level schemes with a strong temperature dependence [12]. The two Pr sites are labeled Pr1 and Pr2 in this paper. The Pr2 site shows a remarkable switching of the ground state from a Γ_1 CF singlet to $\Gamma_4^{(2)}$ CF triplet around 40 K. This phenomenon can be explained by an unconventional charge density wave (CDW) accompanied by antiferroic multipole ordering of the Pr $4f$ electrons. In this scenario, the modulation of the carrier density screens the $4f$ electron multipole moment as a consequence of hybridization between $4f$ and $2p$ electrons from P atoms surrounding each Pr ion [13,14]. However, the nature of this higher-rank multipole ordering is not yet clear from a microscopic point of view.

Similarly to $PrRu_4P_{12}$, Rh-substituted samples $Pr(Ru_{1-x}Rh_x)_4P_{12}$ with a few percent Rh concentration undergo a metal-nonmetal phase transition [15]. In Rh 3% and Rh 5% substituted samples, x-ray superlattice reflections appear below approximately 50 K as signatures of the CDW with multipole ordering [16]. However, the behaviors of pure and the Rh-substituted samples differ significantly at the lowest temperatures. Below 15 K, a strong reduction of the resistivity was reported for the Rh-substituted system $Pr(Ru_{1-x}Rh_x)_4P_{12}$ ($x = 0.03$–0.25) [15], as well as a significant decrease in the superlattice reflection intensity [16]. Interestingly enough, an abrupt decrease in resistivity is also observed at 7 K in the nonmetal phase of the Ce-substituted system $Pr_{1-x}Ce_xRu_4P_{12}$ ($x = 0.10$ and 0.15) [17]. The magnetic susceptibility of both Rh- and Ce-substituted compounds shows no divergence at low temperatures, suggesting that all Pr sites have a singlet ground state in both systems. In contrast, pure $PrRu_4P_{12}$ has a staggered order of triplet and singlet ground states [15,17]. A suppression or sudden decrease in resistivity indicates the destruction of multipole ordering and superlattice structures. The reentrant behavior in both compounds may be related to

---

[*] Present address: Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki, 305-0801, Japan; kotaro.saito@kek.jp

[†] Present address: Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette, France.

[‡] Present address: Neutron Scattering Laboratory, China Institute of Atomic Energy, Beijing 102413, People's Republic of China.

©2014 American Physical Society

the fluctuation of multipole moments or a weakness of the ordering to perturbations from the atomic substitution.

In this paper, we report the temperature-dependent properties of $4f$ electron states in $\mathrm{Pr(Ru_{0.95}Rh_{0.05})_4P_{12}}$ and $\mathrm{Pr_{0.85}Ce_{0.15}Ru_4P_{12}}$ obtained from magnetic susceptibility, INS, and x-ray superlattice diffraction experiments. In particular, we focus on the $4f$ electron states involved in the reentrant transition to a metallic phase at low temperature.

Note that, as discussed later, we found that the physical properties of the phase normally considered to be reentrant had some differences with the high-temperature metallic phase. In this sense, strictly speaking, the use of the term "reentrant" is a misnomer. However, we choose this term to convey the general idea that a metallic phase appears again at low temperatures.

II. EXPERIMENTS

Polycrystalline samples of $\mathrm{Pr(Ru_{0.95}Rh_{0.05})_4P_{12}}$ and $\mathrm{Pr_{0.85}Ce_{0.15}Ru_4P_{12}}$ were synthesized by a Sn-flux method at ambient pressure [18]. Here, we use the chemical composition of the starting materials to denote our samples. The crystal structures were confirmed to be that of filled skutterudite using powder x-ray diffraction measurements. Several weak impurity peaks were identified as $\mathrm{Ru_2P}$ and $\mathrm{Ru_3Sn_7}$. Contributions from these impurities in our experiments are considered to be negligible due to their low volume fraction as estimated from the intensity of the strongest diffraction peak for each impurity.

Inelastic neutron scattering experiments were carried out at two triple axis spectrometers: TOPAN installed at the 6G beam hole of the research reactor JRR-3, Japan Atomic Energy Agency, Tokai, Japan for the Rh 5% sample and 2T at the research reactor Orphée, Laboratoire Léon Brillouin, Saclay, France for the Ce 15% sample. Fixed final energies E_f were 13.5 and 14.7 meV with energy resolutions at the elastic positions of 1.5 and 1.1 meV, respectively. Helium closed-cycle refrigerators were used to cool down the samples. Samples were in the form of polycrystalline powder (∼3 g) wrapped in aluminum foil. Single crystal x-ray diffraction experiments were conducted at Tohoku University using a four-circle diffractometer equipped with a rotating-anode generator producing Mo $K\alpha$ radiation. The magnetic susceptibilities of single crystals of the Rh 5% and Ce 15% samples were measured from 300 to 2 K with a Quantum Design magnetic property measurement system (MPMS) magnetometer. The dimensions of the single crystals were about $2 \times 2 \times 2\ \mathrm{mm}^3$ for both x-ray and magnetic susceptibility experiments.

III. RESULTS

A. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility is shown in Fig. 1 for both substituted systems, and $\mathrm{PrRu_4P_{12}}$ for comparison. The Curie-type divergence at low temperatures in $\mathrm{PrRu_4P_{12}}$ originates from a triplet ground state at half of the Pr sites in the multipole ordered phase. In contrast, a Van Vleck-type plateau is observed for both substituted systems at low temperatures, indicating a singlet ground state for each Pr site over the corresponding temperature range. This observation qualitatively agrees with previous studies of both substituted systems [15,17]. The anomaly at 7 K observed for the Ce 15% sample may correspond to the hump in the susceptibility of a Ce 10% sample reported in Ref. [17]. Usually, this type of anomaly would be a sign of antiferromagnetic ordering. As shown later, powder neutron diffraction measurements do not support the idea and we will present that the hump can be explained by a rearrangement of the CF level scheme. Note that the actual concentrations of Rh and Ce in both systems may vary somewhat between the present paper and previous studies due to the different synthesis methods. For instance, an ambient-pressure flux method was used in the present study while a high-pressure method was used in Refs. [15,17]. However, the physical properties found in the present study are consistent with those found in the previous works.

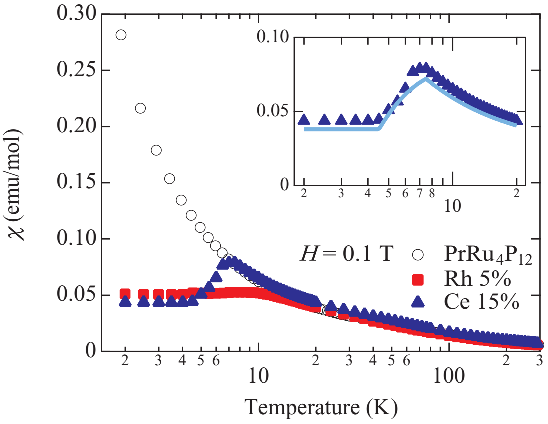

FIG. 1. (Color online) Temperature dependence of magnetic susceptibility. A polycrystalline sample of $\mathrm{PrRu_4P_{12}}$ and single crystals of substituted systems were used. The solid line in the inset refers to a calculation below 20 K using CF parameters obtained from INS experiments on a Ce 15% substituted sample. See text for details of the calculation.

B. X-ray diffraction

Figure 2 shows the temperature dependence of x-ray superlattice reflection intensities of pure, Rh 5%, and Ce 15% samples. Fundamental reflection intensities measured at 16 0 0

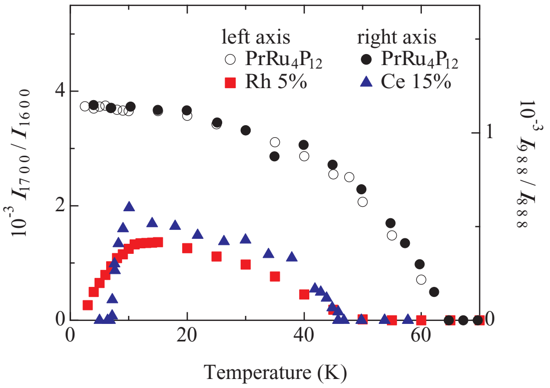

FIG. 2. (Color online) Temperature dependence of x-ray superlattice reflection intensities normalized with respect to the fundamental reflections. Error bars are within the size of the symbols for all data sets.

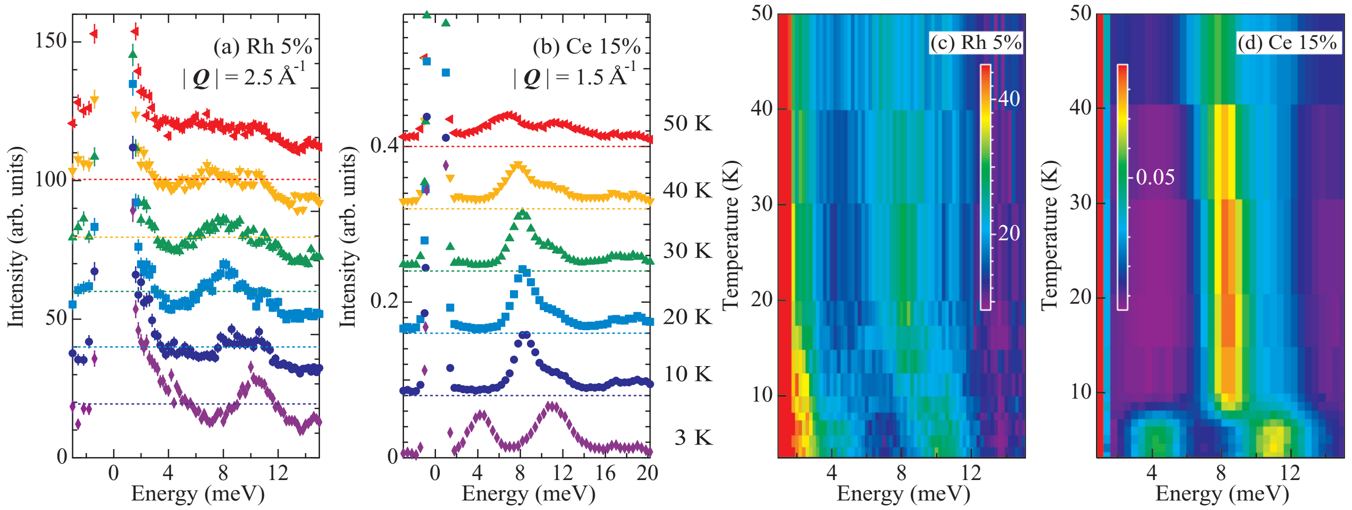

FIG. 3. (Color online) (a) and (b) Temperature dependence of selected INS spectra for Rh 5% and Ce 15%. Horizontal broken lines indicate an offset along the ordinate for each data set. Temperatures for both panels are shown on the right-hand side of (b). (c) and (d) Contour maps showing the temperature dependence of the spectra, which more clearly show the similarity between the two substituted systems at low temperatures.

or 8 8 8 were used to normalize the data. In $\mathrm{PrRu_4P_{12}}$, superlattice reflections at 17 0 0 and 9 8 8 corresponding to $\mathbf{q} = (100)$ appear below T_{MI}, and their intensities increase monotonically toward a finite value with decreasing temperature to 2 K. On the other hand, for the Rh- and Ce-substituted systems, superlattice reflection intensities develop below $T_{\mathrm{MI}} \sim 45$ K and then decrease below about 10 K for both substituted systems. Superlattice reflection intensities in $\mathrm{PrRu_4P_{12}}$ and its substituted systems appear simultaneously with an increase in electrical resistivity and reflect the development of the order parameter of multipole ordering and CDW. In this way, the reduction of the intensities below 10 K in the substituted systems, which coincides with a drop in resistivity, indicates a relaxation in atomic displacements due to the collapse of multipole ordering and the CDW state.

C. Neutron scattering

Some of the authors have previously reported INS experiments for $\mathrm{Pr(Ru_{1-\mathit{x}}Rh_{\mathit{x}})_4P_{12}}$ $(x = 0, 0.03, 0.15)$ [19]. However, the temperature range in these previous experiments was not low enough to investigate the "reentrant metallic phase" of Rh-substituted compounds, which is the main focus of this paper. Here, we show INS spectra of Rh 5% and Ce 15% samples from 3 to 50 K (Fig. 3). The two substituted systems show a similar temperature dependence of the spectra. Weak and broad humps at 6 and 11 meV are seen above $T_{\mathrm{MI}} \sim 45$ K for both compounds. In the nonmetallic phase with multipole ordering (15 K $< T <$ 45 K for Rh 5%, 9 K $< T <$ 45 K for Ce 15%), a temperature-dependent peak moving from 7 to 8 meV is observed as in $\mathrm{PrRu_4P_{12}}$, corresponding to the shift of the $\Gamma_4^{(1)}$ excited state relative to the Γ_1 ground state at the Pr1 site [12]. In the Rh-substituted system below 15 K [Figs. 3(a) and 3(c)], additional inelastic intensities appear at around 4 and 10 meV, while a characteristic temperature-dependent peak at 8 meV in the multipole ordered phase decreases its intensity. This decrease is in contrast with the enhancement in the corresponding peak in $\mathrm{PrRu_4P_{12}}$ with decreasing temperature. Similarly, for the Ce-substituted system below 10 K [Figs. 3(b) and 3(d)], two additional peaks at 4 and 11 meV develop and the temperature-dependent peak at 8 meV as an indication of the ordering diminishes simultaneously in an even clearer fashion than those in the Rh-substituted system. A contribution from phonon modes to the two peaks at low temperatures can be excluded since no similar peaks are observed in the spectrum of the isostructural compound $\mathrm{LaRu_4P_{12}}$. None of the peaks mentioned before show dispersive features and their intensities follow the Q dependence of the magnetic form factor of $\mathrm{Pr^{3+}}$. These facts support the idea that the peaks originate from CF excitations.

It should be noted that additional intensity exists around 2.4 meV as a tail of the elastic peak, only for the Rh-substituted system. This intensity was detected for several Rh-substituted samples in our previous cold neutron inelastic scattering experiments [19]. We concluded that the intensity could be assigned to a CF excitation peak for a Pr site. This spectral component is not involved in the multipole ordering because its intensity is enhanced when the order is suppressed with increasing Rh concentration. Furthermore, from Fig. 3 and our unpublished results obtained from cold neutron experiments, the temperature dependence of this intensity shows neither a clear anomaly at the transition temperature of the "reentrant metallic phase" nor that of the multipole ordering phase. This observation indicates that a part of the Pr sites affected by Rh substitution is not related to multipole ordering or the "reentrant metallic phase."

We also carried out neutron powder diffraction experiments on a Ce 15% sample to examine the possibility of antiferromagnetic ordering at 7 K. The diffraction patterns obtained at 3 and 10 K near the small fundamental Bragg peak of 110 are shown in Fig. 4. No extra peak is detected within the Brillouin zone below 7 K, where the magnetic susceptibility shows an anomaly. A somewhat uniform shift in the intensity patterns does not support the appearance of a magnetic reflection.

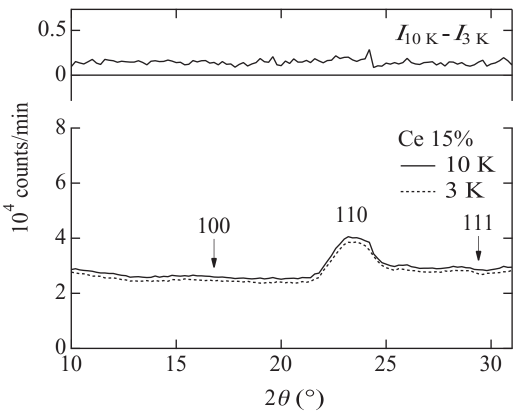

FIG. 4. Powder neutron diffraction for Ce 15%. Diffraction patterns in the Brillouin zone around 110 measured at 3 and 10 K (lower panel) and the difference in intensities between these temperatures (upper panel). No clear peak was detected.

IV. ANALYSIS

Judging from the INS and x-ray superlattice diffraction experiments, multipole ordering in Rh- and Ce-substituted systems occurs in an intermediate temperature range and then disappears below about 10 K for both systems. We label this lower-temperature phase the remetallized phase in the following discussion. The similarity in positions (4 and 11 meV) and intensity ratios of the two inelastic peaks in the remetallized phase for both substituted compounds suggests that they have similar $4f$ electron states. To determine these states in the remetallized phase, we have analyzed the INS spectra of Ce 15% using a CF model. We assume that the $T_{\rm h}$ symmetry, confirmed for Pr sites in the pure system, is conserved in the remetallized phase based on the fact that diffraction data give no evidence for symmetry lowering. The CF Hamiltonian used here is [20]

$$\mathscr{H}_{\rm CF} = W\left[x\frac{O_4}{60} + (1-|x|)\frac{O_6^c}{1260} + y\frac{O_6^t}{30}\right], \qquad (1)$$

where O_4, O_6^c, and O_6^t are linear combinations of Stevens' operator equivalents proposed by Lea *et al.* [21,22]. CF parameters W, x, and y are determined by a least-squares fitting procedure of transition probabilities between eigenstates for Eq. (1) to the experimental data. Diagonalization of Eq. (1) gives a set of CF eigenfunctions: a singlet Γ_1, a doublet Γ_{23}, and two triplets $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$.

Before presenting the fitting results, we describe our analysis in detail. According to the CF analysis of $\mathrm{PrRu_4P_{12}}$ in Ref. [12], a temperature-dependent inelastic peak in $\mathrm{PrRu_4P_{12}}$ moving between 7 and 9 meV below $T_{\rm MI}$ corresponds to the Γ_1-$\Gamma_4^{(1)}$ transition at Pr1. The remarkable feature of the CF level schemes in $\mathrm{PrRu_4P_{12}}$ is the switching of the ground state at Pr2 from Γ_1 above 40 K to $\Gamma_4^{(2)}$ below 40 K. As a result of this switching, another temperature-dependent peak of $\mathrm{PrRu_4P_{12}}$ moving between 11 and 14 meV can be attributed to the Γ_1-$\Gamma_4^{(1)}$ and/or $\Gamma_4^{(2)}$-$\Gamma_4^{(1)}$ transitions at Pr2. The CF analysis in Ref. [12] also shows that the variation of the intensity ratio of the aforementioned peaks is a signature of ground state switching. In the INS spectra of the Ce 15% system presented in Fig. 3(b), the peak moving between 7 and 8 meV can be assigned to the CF excitation Γ_1-$\Gamma_4^{(1)}$ at Pr1. In addition, the shoulderlike peak moving between 11 and 12 meV can be attributed to the combination of Γ_1-$\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$-$\Gamma_4^{(1)}$ transitions at Pr2 because the intensity ratio of the 7–8 meV peak to the 11–12 meV peak is close to that found in $\mathrm{PrRu_4P_{12}}$ around 40 K, where the ground state at Pr1 corresponds to Γ_1 and that for Pr2 is nearly degenerate Γ_1 and $\Gamma_4^{(2)}$. For this reason, we presume that the CF parameters for Pr1 and Pr2 are close to those for $\mathrm{PrRu_4P_{12}}$ at 40 K as listed in Ref. [12], which are then used as initial parameters in the following analysis.

We also introduce other assumptions to fit the INS spectra in the remetallized phase. In both substituted systems below approximately 10 K, two peaks located at 4 and 11 meV emerge suddenly, as seen in Fig. 3(c) and 3(d). This phenomenon indicates a drastic change in the CF level schemes of both Pr1 and Pr2. In our analysis for the Ce 15% sample, we assume that the Pr sites in the remetallized phase below 6 K possess completely different CF level schemes compared to those in the ordered state above 10 K. The broad and asymmetric shape of the two peaks at 4 and 11 meV clearly seen below 6 K indicates a distribution of inequivalent CF level schemes. From our x-ray results, showing the suppression of superlattice reflections in Fig. 2, the difference between Pr1 and Pr2 is expected to become very small and not detectable with a laboratory x-ray source. Very recently, one of the authors has confirmed that the superlattice reflections of the Ce 15% sample completely disappear in the remetallized phase by using synchrotron x rays [23]. This observation indicates that the long-range order of crystallographically inequivalent Pr sites no longer exists in the remetallized phase of the Ce 15% sample. The disappearance of the superlattice does not contradict a simple idea that the random distribution of Ce ion modifies a local environment of neighboring Pr sites and causes nonuniform distribution of CF levels of Pr ions, which gives rise to the broadening and asymmetry in the experimental spectra.

We adopt a facile treatment in which the broadening and asymmetry are approximated by two slightly broad peak components originating from two similar CF level schemes with the same Γ_1 ground state. These two schemes exist randomly in the system with the same probability and are labeled Pr3 and Pr4. Note that this model gives exactly the same result as the case for superlattice formation of Pr3 and Pr4, which is denied by synchrotron experiments.

Based on these considerations, we perform a least-squares fitting analysis of the INS spectra of the Ce 15% system by taking into account the CF excitations from the two virtual sites described above using inelastic spectra from 9.1 to 3 K. Lorentzian functions are used for inelastic peak profiles. In addition to the CF parameters in Eq. (1) for each Pr site, peak widths of the nonmetallic and remetallized phases are also fitted. Note that all fitted parameters are supposed to be temperature independent. Thus, differences in inelastic spectra within the temperature range are predominantly originated from changes in $4f$ electron states from the Pr1 and Pr2 pair into the Pr3 and Pr4 pair. This will be described in detail below. A normalized Gaussian function is used as a resolution function for the deconvolution of inelastic peaks. The ground

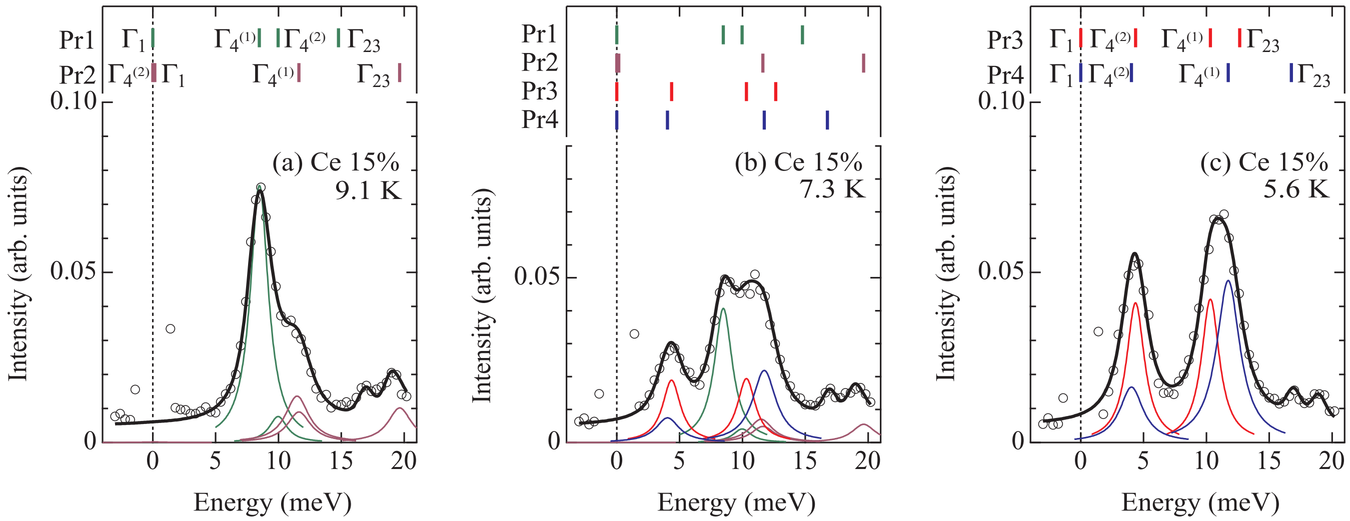

FIG. 5. (Color online) (a)–(c) INS spectra at selected temperatures and fitting curves for the Ce 15% sample. Black thick lines are total fitting curves. There are two spurious peaks above 16 meV. Green and purple curves represent inelastic peaks from Pr1 and Pr2 in the multipole ordered phase, respectively. Red and blue curves are those from Pr3 and Pr4 in the remetallized phase, respectively. Individual peaks are deconvolved with a resolution function. Bars in the upper part of the graphs indicate a CF level scheme for each Pr site.

state for all Pr sites is expected to be a nonmagnetic Γ_1 singlet from the Van Vleck-type plateau in the magnetic susceptibility below 5 K, as shown in Fig. 1. Spurious peaks seen between 16 and 20 meV, which are independent of temperature, are included in the fitting function as Lorentzian peaks with fixed parameters for all temperatures.

The results of the fits for the Ce 15% sample at different temperatures are shown in Fig. 5. First, we look into the fitting result at 9.1 K in the multipole ordered phase shown in Fig. 5(a). As noted previously, the spectrum is well reproduced by CF level schemes similar to $\mathrm{PrRu_4P_{12}}$ at 40 K: 8 meV corresponds to the excitation between Γ_1 and $\Gamma_4^{(1)}$ at Pr1, and 11 meV corresponds to the excitation between nearly degenerate $\Gamma_1/\Gamma_4^{(2)}$ states and $\Gamma_4^{(1)}$ at Pr2. The determined fitting parameters in the CF Hamiltonian Eq. (1) are listed in Table I. The temperature-dependent intensity superimposed on a temperature-independent spurious peak at 18 meV is attributed to the excitation from $\Gamma_4^{(2)}$ to Γ_{23} of Pr2. Next, we look into the fitting result at 5.6 K in the remetallized phase shown in Fig. 5(c). The spectrum was fitted by taking into account two similar CF level schemes of Pr3 and Pr4, both producing two peaks near 4 and 11 meV. Good agreement is obtained from the model using the CF parameters in Table I, in particular, for the asymmetric shape of the observed peak at 11 meV. The determined level schemes are shown in the upper part of Fig. 5(c). In the temperature range 6 K $< T <$ 9 K, the coexistence of four Pr sites causes the superposition of several peaks around 10 meV. Under this scenario, the data at 7.3 K shown in Fig. 5(b) can be interpreted as a combination of the spectra at 5.6 and 9 K. We succeeded in reproducing the spectrum at 7.3 K by assuming that the fraction of intensities associated with the Pr1 and Pr2 pair to that for the Pr3 and Pr4 pair varies linearly between 8.5 and 5.9 K. We checked a simpler model with only one Pr site with a single set of Lorentzian peaks at 4 and 11 meV at the lowest temperature. The fit quality for this case is less satisfactory than for a two-site model because the two Lorentzians result in excess intensities in the overlap region around 7 meV. In addition, the Pr3 and Pr4 peaks have finite widths. These observations imply that the CF level schemes are not uniform but rather randomly distributed in the samples. Thus, the remetallized phase is accompanied by a drastic rearrangement of the CF level schemes in the Ce-substituted system and can be regarded as a new electronic phase with inhomogeneity.

TABLE I. Crystal field parameters of the Ce 15% sample obtained by a least-squares fitting analysis between 9.1 and 3.15 K. Parameter sets for each phase are calculated separately.

	W (meV)	x	$\|y\|$
Pr1	0.172 ± 0.005	-0.485 ± 0.02	0.020 ± 0.002
Pr2	0.352 ± 0.005	0.527 ± 0.003	0.025 ± 0.011
Pr3	0.126 ± 0.002	-0.365 ± 0.03	0.186 ± 0.005
Pr4	0.142 ± 0.001	0.157 ± 0.04	0.185 ± 0.018

We also calculated the magnetic susceptibility using the determined CF level schemes, as shown by the solid line in the inset of Fig. 1. Between 4.5 and 7.5 K, we suppose that the volume ratio of the two phases changes linearly with temperature. Although there is a slight difference between the calculations and experimental results, the Curie-type curve above 7.5 K and the Van Vleck plateau below 4.5 K are quantitatively reproduced by the CF level schemes. In view of these results, our assumption of a drastic change in the 4f electron ground state explains reasonably well the temperature dependence of the magnetic susceptibility.

Note that we neglected the effect of Ce ions on both inelastic peaks and on the magnetic susceptibility due to the relatively small volume fraction. In fact, no significant CF signal from Ce ions is detected. According to a calculation, we expect the peak intensity for a transition between the Γ_7 and Γ_8 CF states of a Ce^{3+} ion in cubic symmetry to be 23% of the Γ_1-$\Gamma_4^{(1)}$ transition of Pr1, which is not easily resolved with the present data.

V. DISCUSSION

According to the present analysis of the $4f$ electronic states, a quasidegeneracy of the Γ_1 and $\Gamma_4^{(2)}$ ground states at the Pr2 sites arises in the Ce-substituted system in the lower-temperature range of the nonmetallic phase. This phenomenon indicates that the staggered multipole moments are suppressed and strong fluctuations of the f electron ground state exist in the Ce-substituted system. Such a large entropy state destabilizes the ordered CDW phase. In the multipole ordered phase of the Ce-substituted system, the superlattice distortion shown in Fig. 2 and the resistivity in Ref. [17] are reduced compared to those for $PrRu_4P_{12}$, and slightly broadened CF excitation spectra are observed. The suppression of lattice distortions indicates that a long-range ordered superlattice formation is disturbed by Ce impurities in the Pr bcc lattice. The order parameter then becomes correspondingly smaller, which is consistent with the highly degenerate ground state at the Pr2 sites as a consequence of the suppression of the temperature-dependent CF level shifts corresponding to the order parameter. The smaller resistivity suggests the existence of residual carriers or a midgap density of states in the band structure.

Figure 6 shows the temperature dependence of the peak widths obtained by individual fitting of the spectra from 50 to 9.1 K at each temperature. The intrinsic peak width of the CF excitation peak becomes narrow if the $4f$ electrons localize and becomes wide if they hybridize with conduction electrons. Although the degree of broadening due to the random field effect by Ce doping is unclear for the moment, the broader peak width of the Ce 15% sample than that of $PrRu_4P_{12}$ in the ordered phase still corresponds to the remanent carriers and suppression of the order parameter. Furthermore, an increase in the peak width of the Ce-substituted sample below 10 K supports the remetallization of the system. The combination of the suppression of the superlattice and the incomplete vanishing of the Fermi surface results in a decrease in the free energy gain from the CDW formation, which in turn will favor the recovery of the metallic phase below about 7 K.

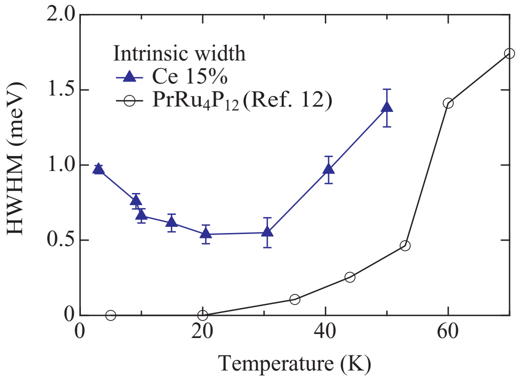

FIG. 6. (Color online) Temperature dependence of the intrinsic width of inelastic peaks for the Ce 15% sample obtained from individual fitting at each temperature. A data point at 3 K represents the width of the Pr3 and Pr4 pair fitted together with CF parameters in Table I. Values for $PrRu_4P_{12}$ are taken from Ref. [12].

Rh- and Ce-substituted systems exhibit similar physical properties in the remetallized phase, including a decrease in electrical resistivity in Refs. [15,17], a Van Vleck-type plateau in the magnetic susceptibility at low temperatures (Fig. 1), a decrease in superlattice reflection intensity (Fig. 2), and a rearrangement of the CF level schemes (Fig. 3). Thus, it is expected that Rh and Ce substitution have a common mechanism leading to these effects on the CDW state of $PrRu_4P_{12}$.

Rh substitution into the Ru site is considered to lead to electron doping into the conduction band due to an additional $4d$ electron per site. Ce ions substituted into Pr sites are usually expected to be trivalent, which means the $4f^1$ state is introduced as a local impurity within the multipole lattice of the $4f^2$ configuration. According to a x-ray absorption near edge structure (XANES) study on $CeRu_4P_{12}$, the valence of a Ce ion is close to 3+ [24]. However, the magnetization of $CeRu_4P_{12}$ saturates at $0.15\mu_B$/Ce, which is much less than that expected for the Ce^{3+} state, even in a cubic crystal field [25]. An NMR study of $CeRu_4P_{12}$ showed the existence of a Ce^{4+} component [26]. In addition, the lattice constants of RRu_4P_{12} are 8.0605, 8.0461, and 8.0543 Å for $R =$ La, Ce, and Pr, respectively [27]. $CeRu_4P_{12}$ has the smallest lattice constant among these compounds, consistent with a finite content of the Ce^{4+} state, while La and Pr are trivalent ions. Based on these reports, it is reasonable to assume that Ce substitution into the Pr site of $PrRu_4P_{12}$ results in electron doping into the conduction band.

Using these facts, the transition to the remetallized phase in both substituted systems may be associated with the electron doping effect of Rh and Ce substitutions. A quantitative study of the effects of carrier doping owing to atomic substitution is beyond the scope of this paper. However, we naturally expect that the roughly flat Fermi surface responsible for the metal-nonmetal transition at T_{MI} is sensitive to carrier doping. The near perfect nesting property of the Fermi surface discussed in Ref. [9] and the electron and hole concentrations as suggested by a Hall resistivity study in Ref. [28] might be modified by Rh or Ce substitution. Such a modification of the band state suppresses the order parameter of the nonmetallic phase, i.e., the magnitudes of the $4f$ multipole moments, atomic displacements, and the band gap. In fact, the x-ray superlattice reflection intensities decrease at the lowest temperatures in both substituted systems compared to $PrRu_4P_{12}$, as shown in Fig. 2. Changes in hybridization by carrier doping could be one reason for the rearrangement of CF level schemes in the remetallized phase. Theorists have pointed out that the p-f hybridization effect strongly modifies the CF level scheme, which cannot be accounted for solely through a point charge model [29]. In their study, two hybridization effects characterized by the number of f electrons (f^1 and f^3) are introduced as intermediate states, and considered as parameters that alter the CF level scheme of the Pr^{3+} ion. The f^1 intermediate process favors a $\Gamma_4^{(2)}$ triplet ground state, and the f^3 process favors a Γ_1 singlet ground state. As described before, the substitution of Ce and Rh would correspond to electron doping into the conduction band. In other words, the excess electrons in the conduction band increase the probability of the f^3 process via p-f hybridization. This process stabilizes the Γ_1 $4f$ CF state, in agreement with the present experimental result.

Although Rh- and Ce-substituted systems have similar effects at low temperatures, there are some differences with respect to remetallization. In particular, a crossover-type behavior for Rh 5% and a phase transition-type behavior for the Ce 15% system are observed in the superlattice reflection intensities. In a previous report by some of the authors, a thermal activation model was proposed for multipole ordering in Rh-substituted systems to explain a crossover-type behavior [19]. In that model, the CF ground states for the entire temperature range for all Pr sites are expected to be Γ_1 singlets due to the absence of a divergence behavior just above the remetallization temperature in the magnetic susceptibility. This model assumes that there is no quasiquartet ground state with degenerate Γ_1 and $\Gamma_4^{(2)}$ states. Apart from the ground state, the excited level schemes of Pr1 and Pr2 sites in the ordered phase are presumed to be different, resulting in an ordered state with a staggered arrangement of $4f$ states supported by thermal activation. This scenario would explain the relatively weak superlattice reflection intensity in the ordered phase and its consequent decrease at low temperatures. Due to the much broader INS spectra of the Rh-substituted system compared to the Ce-substituted system, it is difficult to determine the CF level schemes precisely in the Rh-substituted system. Therefore, we cannot determine the valid scenario for the crossover-type behavior: a staggered CF ground state as in the Ce-substituted system or the thermal activation scenario discussed previously [19]. However, the CDW state with multipole ordering is not the ground state in both substituted systems, and the suppression of the f-electron multipole degree of freedom is a common feature, which is essential for the remetallization.

A rigorously reentrant behavior of the metal-nonmetal transition was theoretically studied, and the phase diagram was calculated as a function of the effective splitting energy between the Γ_1 ground state and the $\Gamma_4^{(2)}$ excited state in the normal metallic state [30]. This study suggests that orbital fluctuations due to triplet occupation are inherent in the phase transition, and a reentrant behavior appears if the fluctuation is small with a large effective splitting between Γ_1 and $\Gamma_4^{(2)}$. In other words, the high- and low-temperature phases in that model possess the exactly same metallic state. A recent experiment by some of the authors has revealed that the crystal structure in the remetallized phase of the Ce 5% substituted system is identical to that for the metallic phase above T_{MI} [23]. However, the observed CF level schemes in these two phases are not identical, as shown in the spectra at 3 and 50 K of the Ce-substituted system in Fig. 3(b). Another metallic phase is induced in the ground state through the atomic substitution, so strictly speaking this phenomenon is not a reentrant transition. We expect that there are additional effects relevant for remetallization in the substituted systems. An open question is how this system reduces its entropy without an ordering of electronic states or lattice relaxation.

VI. CONCLUSION

We have investigated the electronic ground states in the low-temperature phases of Rh- and Ce-substituted $\mathrm{PrRu_4P_{12}}$. Both systems possess relaxed superstructures in the reentrant metallic phase below approximately 10 K, and have a nonmagnetic ground state at all Pr sites. At least for a Ce-substituted system, the CF level schemes in the low-temperature phases change drastically at the reentrant transition, and are different from those in the normal metallic phase above T_{MI}, suggesting the formation of a distinct electronic phase. Further studies are necessary to reveal the details of the electronic states in these systems. For example, one could take into account the hybridization term owing to the residual conduction electrons.

ACKNOWLEDGMENTS

The authors would like to thank C. Sekine for motivating us to proceed with the present study. H. Nakao, Y. Murakami, K. Tomiyasu, and M. Onodera are acknowledged for their support during this study. The experiment performed at JRR-3 was conducted by the Joint-use Research Program for Neutron Scattering, ISSP, The University of Tokyo. The machine time committee of Laboratoire Léon Brillouin is also acknowledged for offering us prior machine time on 2T to compensate for the severe damage to the Japanese Neutron Science Society by the Great East Japan Earthquake. This study was supported in part by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan through KAKENHI [Scientific Research on Priority Areas “Skutterudite” (15072206), Scientific Research on Innovative Areas “Heavy Electrons” (20102005)] and by Japan Society for the Promotion of Science (JSPS) through by KAKENHI [Scientific Research (S) (21224008), Scientific Research (A) (23244068), Challenging Exploratory Research (24654080), and JSPS Fellows (11J03397)]. K.S. was supported by a JSPS Research Fellowship. C.L. and L.H. were supported by JSPS Postdoctoral Fellowships for Foreign Researchers (P08728 and P04059, respectively).

---

[1] J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47-48**, 145 (1985).

[2] T. Tayama, T. Sakakibara, K. Tenya, H. Amitsuka, and S. Kunii, J. Phys. Soc. Jpn. **66**, 2268 (1997).

[3] D. Mannix, Y. Tanaka, D. Carbone, N. Bernhoeft, and S. Kunii, Phys. Rev. Lett. **95**, 117206 (2005).

[4] J. A. Paixão, C. Detlefs, M. J. Longfield, R. Caciuffo, P. Santini, N. Bernhoeft, J. Rebizant, and G. H. Lander, Phys. Rev. Lett. **89**, 187202 (2002).

[5] B. C. Sales, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier, Amsterdam, 2003), Vol. 33, p. 1.

[6] H. Sato, H. Sugawara, Y. Aoki, and H. Harima, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 2009), Vol. 18, p. 1.

[7] C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi, Phys. Rev. Lett. **79**, 3218 (1997).

[8] C. H. Lee, H. Matsuhata, H. Yamaguchi, C. Sekine, K. Kihou, T. Suzuki, T. Noro, and I. Shirotani, Phys. Rev. B **70**, 153105 (2004).

[9] H. Harima and K. Takegahara, Physica B **312-313**, 843 (2002).

[10] G. P. Meisner, Physica B+C **108**, 763 (1981).

[11] S. R. Saha, H. Sugawara, Y. Aoki, H. Sato, Y. Inada, H. Shishido, R. Settai, Y. Ōnuki, and H. Harima, Phys. Rev. B **71**, 132502 (2005).

[12] K. Iwasa, L. Hao, K. Kuwahara, M. Kohgi, S. R. Saha, H. Sugawara, Y. Aoki, H. Sato, T. Tayama, and T. Sakakibara, Phys. Rev. B **72**, 024414 (2005).

[13] T. Takimoto, J. Phys. Soc. Jpn. **75**, 034714 (2006).

[14] Y. Kuramoto, Prog. Theor. Phys. Suppl. **176**, 77 (2008).

[15] C. Sekine, N. Hoshi, I. Shirotani, K. Matsuhira, M. Wakeshima, and Y. Hinatsu, Physica B **378–380**, 211 (2006).

[16] C. Laulhé, K. Saito, K. Iwasa, H. Nakao, and Y. Murakami, J. Phys.: Conf. Ser. **200**, 012102 (2010).

[17] C. Sekine, M. Takusari, and T. Yagi, J. Phys. Soc. Jpn. **80**, SA024 (2011).

[18] W. Jeitschko and D. Braun, Acta Crystallogr., Sect. B **33**, 3401 (1977).

[19] K. Saito, C. Laulhé, K. Iwasa, and Y. Murakami, J. Phys.: Conf. Ser. **200**, 012170 (2010).

[20] K. Takegahara, H. Harima, and A. Yanase, J. Phys. Soc. Jpn. **70**, 1190 (2001); **70**, 3468 (2001); **71**, 372 (2002).

[21] K. W. H. Stevens, Proc. Phys. Soc. A **65**, 209 (1952).

[22] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[23] K. Iwasa *et al.* (unpublished).

[24] C. H. Lee, H. Oyanagi, C. Sekine, I. Shirotani, and M. Ishii, Phys. Rev. B **60**, 13253 (1999).

[25] I. Shirotani, T. Uchiumi, C. Sekine, M. Hori, S. Kimura, and N. Hamaya, J. Solid State Chem. **142**, 146 (1999).

[26] K. Fujiwara, K. Ishihara, K. Miyoshi, J. Takeuchi, C. Sekine, and I. Shirotani, Physica B **281-282**, 296 (2000).

[27] C. Sekine, H. Saito, T. Uchiumi, A. Sakai, and I. Shirotani, Solid State Commun. **106**, 441 (1998).

[28] H. Sato, H. Sugawara, D. Kikuchi, S. Sanada, K. Tanaka, H. Aoki, K. Kuwahara, Y. Aoki, and M. Kohgi, Physica B **378–380**, 46 (2006).

[29] J. Otsuki, H. Kusunose, and Y. Kuramoto, J. Phys. Soc. Jpn. **74**, 200 (2005).

[30] R. Shiina, J. Phys. Soc. Jpn. **78**, 104722 (2009).