Structural modulation and multipolar ordering in the metal-nonmetal compounds Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$

C Laulhé, K Saito, K Iwasa, H Nakao, Y Murakami
Department of Physics, Tohoku University, Aramaki-aza-Aoba 6-3, Aoba-ku, Sendai 980-8578, JAPAN
E-mail: laulhe@m.tains.tohoku.ac.jp

Abstract. We present a X-ray diffraction study of Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ ($x = 0$, 0.05), which exhibit a metal-nonmetal transition at about 50-60 K. Superlattice reflections which are related to [Ru,Rh] and P atom displacements could be observed below the transition temperature. In PrRu$_4$P$_{12}$, these displacements are found to increase gradually as the temperature decreases, in agreement with previous studies. In Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$, the [Ru$_{0.95}$Rh$_{0.05}$] and P atom displacements first increase with decreasing temperature below 50 K, but nearly cancel at lowest temperatures. We discuss this unexpected structural behavior by considering the Pr 4$f$ electron states in the Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ compounds.

1. Introduction
The filled skutterudites RT$_4$X$_{12}$ (R = rare earth; T = Fe, Ru, Os; X = P, As, Sb) exhibit a wide range of physical properties involving f electrons. Among them, PrRu$_4$P$_{12}$ undergoes a metal-nonmetal transition [1] accompanied by a structural modulation [2] at $T_{\text{MI}} \approx 63$ K. Since the modulation vector $\vec{q} = (1\ 0\ 0)$ corresponds to a nesting condition of the Fermi surface [3], this transition was first interpreted as a conventional charge density wave (CDW) formation, due to electron-phonon coupling. However, neutron scattering experiments gave evidence for a staggered pattern of two Pr-sites below $T_{\text{MI}}$, with inequivalent and temperature-dependent 4$f$-electron crystal field levels [4, 5]. A characteristic feature of the temperature dependence is the switching of the singlet ground state into a triplet ground state for one of the two Pr-sites, at 40K [4]. On the theoretical side, it has been proposed that this drastic evolution of the crystal field levels would be the consequence of antiferro-ordering of the Pr 4$f$-electron hexadecapoles, due to a strong hybridization between the Pr 4$f$ states and the P p states that form the conduction band [6]. In this multipole-ordered state, the electronic potential has the new periodicity $\vec{q} = (1\ 0\ 0)$, which could favor gap opening and the CDW formation. The exact description on how electron-phonon coupling and p–f hybridization effects would cooperate to give rise to the metal-nonmetal transition in PrRu$_4$P$_{12}$ still remains an open question.

In the Rh-substituted compounds Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$, the supplementary valence electron brought by Rh-atoms ($Z_{\text{Ru}} = 44$, $Z_{\text{Rh}} = 45$) is expected to increase the Fermi level energy with respect to PrRu$_4$P$_{12}$, and thus to reduce the Fermi surface nesting properties at $\vec{q} = (1\ 0\ 0)$. Accordingly, resistivity measurements showed that the metal-nonmetal transition, though it survives in the Rh-doped samples, is gradually suppressed with increasing Rh-content [7]. The aim of the present work is to determine the influence of Rh-doping on the order parameter.
of the transition. We approached this problem experimentally by studying the temperature dependence of structural modulations in Pr(Ru_{0.95}Rh_{0.05})_4P_{12}, using X-ray diffraction. The PrRu_4P_{12} compound is also considered for reference purposes.

2. Experimental methods

Single crystals of PrRu_4P_{12} and Pr(Ru_{0.95}Rh_{0.05})_4P_{12} were prepared by the Sn flux method. The indicated Rh-concentration corresponds to the target composition, which may differ from the actual composition after chemical reaction. The resistance was measured on a selected single crystal for both these compounds, in the temperature range 10 - 120 K. The standard DC four point probe method was used on a Quantum Design PPMS apparatus. The diffracted intensities were collected from the same two crystals, on a 4-circle diffractometer equipped with a Molybdenum rotating-anode generator. For the latter experiments, the crystals temperature was controlled between 3 and 70 K by a He-gas closed-cycle refrigerator. The sample temperature could be estimated with an accuracy of less than 1 K.

3. Description of the structural modulation in Pr(Ru_{1-x}Rh_x)_4P_{12}

In Pr(Ru_{0.95}Rh_{0.05})_4P_{12} like in PrRu_4P_{12}, superlattice reflections appear at low temperatures, at the reciprocal lattice points \( \bar{Q} = (h, k, l) \) with \( h + k + l = \text{odd} \). These mark the loss of the body-centered structure characteristic of the \( \text{Im\bar{3}} \) high temperature phase, due to a modulation of [Ru,Rh] and P atom positions with propagation vector \( \vec{q} = (1, 0, 0) \) [2]. As an example, the figure 1 shows the \( \theta/2\theta \) scan profiles of the (17 0 0) superlattice reflection in the two studied samples, at 3, 15, and 65 K.

![Figure 1. \( \theta/2\theta \) scan profile of the (17 0 0) reflection.](image)

The temperature-dependence of the (17 0 0) integrated intensity is detailed in figure 2 for PrRu_4P_{12} and Pr(Ru_{0.95}Rh_{0.05})_4P_{12}. It can first be observed that the superlattice reflection appears at a lower temperature in Pr(Ru_{0.95}Rh_{0.05})_4P_{12} (50.5 K) than in PrRu_4P_{12} (64.6 K). For both samples, these temperatures just correspond to the point at which resistance deviates from the line extrapolated from the data in the high-temperature range. Below the transition
temperature, the (17 0 0) reflection appears to be less intense in the 5% Rh-doped sample, denoting a change in the structural distortions with respect to PrRu$_4$P$_{12}$. As the most surprising result, the (17 0 0) integrated intensity shows quite different temperature evolution in the two studied samples. In PrRu$_4$P$_{12}$, it increases with decreasing temperature and finally saturates at the lowest temperatures, as reported earlier [8]. In Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$, it increases when the temperature decreases from 50 K down to 15 K, but then suddenly drops at around 10 K. Concerning the latter observation, an experimental artifact due to sample rotation can be readily excluded since the 2θ, θ, and χ angles were refined at each temperature. No additional superlattice reflection could be observed below the 10 K temperature, so that the crystal structure seems to be reentrant against the temperature variation.

In order to describe the rapid evolution of structural distortions so evidenced for Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ in the temperature range [3 - 15 K], we analyzed the integrated intensities of about 35 reflections at 3 and 14.5 K. We considered reciprocal lattice points that all lie in a small region around the (16 0 0) point, to ensure minimal absorption effects. The function $(S \times |F|^2)/(1+\lambda \times |F|^2)$ was fitted to the experimentally determined intensities, where $S$ is a scale factor and $F$ the structure factor. The parameter $\lambda$ stands to take into account the extinction effects. The structure factor was calculated from the structural model that describes the low temperature phase of PrRu$_4$P$_{12}$. In the space group $Pm\bar{3}$, the fractional coordinates of atoms were thus taken as: Pr1 (0, 0, 0), Pr2 (0.5, 0.5, 0.5), [Ru$_{1-x}$Rh$_x$] (0.25 + δ, 0.25 + δ, 0.25 + δ), P1 (0, 0.3576 + δ$_u$, 0.1444 + δ$_v$), and P2 (0, 0.8576 − δ$_u$, 0.6444 − δ$_v$) [2, 8]. In this model, the structural distortions should be read as non-zero values of the δ, δ$_u$, and δ$_v$ parameters. Note that choosing this model, we implicitly assume that the atomic positions are the same in the high temperature phases of Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ and PrRu$_4$P$_{12}$. We expect the latter to be a reasonable hypothesis, since the covalent radii of Ru and Rh atoms are identical, and the Rh-concentration remains small. During the fitting procedure, S, λ, δ, δ$_u$, and δ$_v$ were taken as free parameters. All the Debye-Waller factors were fixed to a single, arbitrary value, similarly to what is done in Ref. [8] for the diffraction analysis of PrRu$_4$P$_{12}$. In the latter case, such a procedure proved to yield values of the Ru and P displacements that are fairly similar to those obtained by a proper analysis [2]. Good quality fits of the experimental integrated intensities could be obtained at 3 and 14.5 K, as shown on figure 3. Hence, the Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ crystal can be described with the same structural model as PrRu$_4$P$_{12}$. The refined values for [Ru$_{0.95}$Rh$_{0.05}$] and P displacement parameters are: (3 K) δ = 0.0002, δ$_u$ = 0.0000, and δ$_v$ = 0.0002, (14.5 K) δ = 0.0004, δ$_u$ = −0.0001, and δ$_v$ = 0.0003, the uncertainty being of 0.0001. Given the structural model used and within the accuracy of our fits, it is found that the transition metal atom displacements and the two components of the P displacement vary in the same proportions when the temperature changes from 14.5 to 3 K. Moreover, the ratio between the transition metal atom and P displacements is identical in

![Figure 3. Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$: integrated intensities of the measured superlattice reflections.](image-url)
Pr$_4$(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ and in PrRu$_4$P$_{12}$ [8]. These observations would indicate that the structural distortions in the Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ system involve coupled [Ru,Rh] and P atom displacements. For Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$, maximal intensity of the superlattice reflections is observed at 14.5 K (see figure 2). Hence, the displacement parameters at this temperature correspond to the maximal displacement amplitudes of [Ru$_{0.95}$Rh$_{0.05}$] and P atoms. These are found twice smaller than in PrRu$_4$P$_{12}$ [8]. As the temperature decreases further down to 3 K, the atom displacement amplitudes in Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ get divided by two.

4. Concluding discussion

By means of X-ray diffraction, we studied the structural distortions that accompany the metal-nonmetal transition in Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ and PrRu$_4$P$_{12}$. Below the transition temperature, the [Ru$_{0.95}$Rh$_{0.05}$] and P atom displacements observed in the 5% Rh-doped sample are very similar to those observed in PrRu$_4$P$_{12}$, though their amplitude is lower. As the temperature decreases, the displacement values in Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ once increase but surprisingly drop below about 10 K, which is not observed for PrRu$_4$P$_{12}$. In order to explain the latter difference, the combination of $f$ electron, lattice distortion, and Fermi surface nesting contributions that exist in the Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$ system should be taken into account. Considering $f$ electrons, two Pr-sites can be distinguished in PrRu$_4$P$_{12}$: at lowest temperatures, one has a singlet ground state for $f$ electrons, while the other has a triplet ground state [4]. In Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ samples obtained from the same synthesis as for the present study, magnetic susceptibility measurements and inelastic neutron scattering experiments have shown that at least two inequivalent crystal field level schemes exist among Pr sites, but all have the same singlet ground state [9]. In this case, multipole ordering likely takes place in the temperature range [10 - 50 K] owing to the thermal occupation of inequivalent excited crystal field levels, but disappears at low temperature due to an uniform ground state dominantly occupied. Recalling the reduction of the [Ru$_{0.95}$Rh$_{0.05}$] and P displacements in Pr(Ru$_{0.95}$Rh$_{0.05}$)$_4$P$_{12}$ below 10 K, we infer that the structural modulations and multipole ordering cannot exist separately in Pr(Ru$_{1-x}$Rh$_x$)$_4$P$_{12}$.

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