The filled-skutterudite compounds \(RTr_4P_{12}\) (\(R = \) rare earth, \(Tr = Fe, Ru, Os; \) and \(Pn=\text{pnictogen})\) have attracted much attention for exhibiting novel physical properties, i.e., metal-insulator (M-I) transition unconventional superconductivity semiconducting behavior magnetic ordering and their prospect in thermoelectric applications. Particularly interesting are the \(Pr\)-based skutterudites in which quadrupolar interactions are believed to play an important role for the anomalous properties \(PrRu_4P_{12}\) shows an exotic M-I transition at \(T_{MI} \approx 60\ K\) with a non-magnetic origin, as suggested by no anomaly in the magnetic susceptibility \(\chi\) and no essential effect of the magnetic field on the specific-heat anomaly up to 12 T. Although several studies have been carried out, the mechanism of the M-I transition remains one of the most mysterious puzzles in the skutterudites.

From the band-structure calculation, Harima has suggested that the M-I transition could be triggered by the nearly perfect nesting of the main Fermi surface (FS) with \(q = (1,0,0)\); the shape of the main FS is nearly cubic and its volume is one-half of the body-centered cubic (bcc) Brillouin zone (BZ). Actually, both the electron and the x-ray diffraction experiments have revealed a doubling of the unit-cell volume across \(T_{MI}\); it is suggested that the structure changes from bcc \((Im3)\) to simple cubic \((Pm3)\), caused by the different shift of Ru and P ions around two adjacent Pr ions, i.e., between the corner and body-centered Pr ion sites in bcc structure. However, the predicted distortion of P-ion to obtain an insulating band structure is much larger than that experimentally determined by the x-ray diffraction. If the 4\(f\) electrons in \(PrRu_4P_{12}\) are localized, as indicated by the Curie-Weiss behavior of \(\chi\) or only weakly hybridize with conduction electrons, then the electronic structure is expected to be basically the same as the reference material \(LaRu_4P_{12}\), which shows a superconducting transition at \(T_C \approx 7\ K\) without a 4\(f\) electron. In that case, \(LaRu_4P_{12}\) is also expected to have the same nesting instability, however no M-I transition has been reported. Thus, it is essentially important to clarify the FS of both compounds experimentally to understand the origin of the M-I transition in \(PrRu_4P_{12}\). However, the high transition temperature of \(T_{MI} \approx 60\ K\) prevents the observation of dHvA oscillations in the metallic state of \(PrRu_4P_{12}\). As an alternative way, the experimental determination of FS in \(LaRu_4P_{12}\) should be useful to understand the origin of the M-I transition in \(PrRu_4P_{12}\), if it is carefully compared with the computed FSs of the two compounds based on the band-structure calculation.

We have succeeded in growing high-quality single crystals of \(LaRu_4P_{12}\) and in observing the dHvA effect, the preliminary result of which has been briefly reported in Ref. 20. In this paper, we report the detailed experimental results on the dHvA effect and magnetoresistance along with the band-structure calculation in \(LaRu_4P_{12}\), followed by a discussion on the possible origin of the M-I transition in \(PrRu_4P_{12}\).

Single crystals of \(LaRu_4P_{12}\) were grown by the tin-flux method which is basically the same as described in Ref. 7. The raw materials were 4N (99.99\% pure) -La, -Ru, 6N-P, and 5N-Sn. The residual resistivity ratio \((RRR)\) of the present sample is about 700, indicating the high sample quality. The dHvA experiments were performed in a top loading \(^3\)He cryostat down to 0.4 K with a 15 T superconducting (SC) magnet and a top loading dilution refrigerator cooled down to \(\sim 30\ M\) with a 17 T SC magnet. The dHvA signals were detected by means of the conventional field modulation method with a low frequency \((f \sim 10\ Hz)\). The magnetoresistance was measured by the dc four-probe method using a top loading \(^3\)He cryostat equipped with a 16 T SC magnet.

Figure 1 shows (a) a typical recorder trace of the dHvA oscillations and (b) the corresponding fast Fourier trans-
formation (FFT) spectra in LaRu$_4$P$_{12}$ at 31 mK for the magnetic field ($H$) along the $\langle111\rangle$ direction. The dHvA signals have been observed just above the superconducting upper critical field $H_{C2} \sim 36.5$ kOe, indicating also the high quality of the sample. Figure 2(a) shows the angular dependences of dHvA frequencies both in the (010) plane and the ($\overline{1}00$) plane. The calculated dHvA frequencies are shown in Fig. 2(b), the description of which is given later. In the experiment, six fundamental dHvA branches labeled $\alpha$, $\beta$, $\omega$, $\delta$, $\varepsilon$, and $\mu$ have been observed. The largest frequency branch $\alpha$ is observed over the whole field angles both in the (010) plane and ($\overline{1}00$) plane, although it is not perfectly continuous. The $\beta$, $\omega$, and $\mu$ branches are observed in the limited angular range around $[111]$ direction. The $\delta$ branch is observed in a narrow angular range centered at the [001] direction. The $\varepsilon$ branch is observed in a wider angular range in the (010) plane except near [100].

We have measured the transverse magnetoresistance (TMR), $\Delta \rho/\rho = [\rho(H) - \rho(0)]/\rho(0)$, in LaRu$_4$P$_{12}$ to confirm the existence of open orbit on the FS. Figure 3 shows the field dependence of TMR for the field along the [100] and [101] directions and the inset shows the angular dependences of TMR under the constant fields of 7 T and 14 T in the (010) plane. As was also observed in LaFe$_4$P$_{12}$, the angular dependence of TMR in LaRu$_4$P$_{12}$ is highly anisotropic, suggesting the existence of an open orbit. Actually, as shown later, we have observed the multiply connected (48th-band) hole FS in LaRu$_4$P$_{12}$, which is similar to that of LaFe$_4$P$_{12}$. LaRu$_4$P$_{12}$ is an uncompensated metal with a different carrier concentration of electrons and holes, since it has one molecule per unit cell. If TMR increases with the field, then an open orbit exists for the direction perpendicular to both the current and field. In the present experiment for $H \parallel [100]$, TMR increases with $H^{1.1}$, suggesting the existence of an open orbit.

In order to assign the origin of dHvA branches, the band-structure calculation has been performed by using the full potential linearized augmented-plane-wave (FLAPW) method with the local-density approximation (LDA). We used the room-temperature lattice constant $a = 8.0608 \AA$ and the fractional coordinates of P at the 24g site as $x = 0$, $y = 0.3594$, and $z = 0.1434$ for the calculation. The details of the calculation are essentially
the same as in Ref. 13. Figures 4 and 5 show the calculated energy band structure and the FS in LaRu$_4$P$_{12}$, respectively. The FS is composed of the 46th, 47th and 48th band hole sheets. The main difference with the FS of PrRu$_4$P$_{12}$ is the existence of the 46th and 47th small hole sheets in LaRu$_4$P$_{12}$, while PrRu$_4$P$_{12}$ has only a multiply connected 49th band hole-FS sheet with one band counted for two localized 4f electrons. The 46th and 47th bands form nearly spherical sheets centered at the Γ point, which stretch slightly along the ⟨111⟩ and ⟨100⟩ directions, respectively. The 48th band gives a multiply connected hole-FS sheet centered at the Γ point. Its shape is roughly a round cube whose volume is nearly one half of the BZ size and has a good nesting vector $\mathbf{q}$ = (1,0,0) as expected also in the 49th-band FS of PrRu$_4$P$_{12}$.

The calculated dHvA frequencies, shown in Fig. 2(b), reasonably reproduce the angular dependence of the observed dHvA branches $\alpha$, $\beta$, $\delta$, $\varepsilon$, and $\mu$ except $\omega$. The $\alpha'$ branch is found to originate from the electronlike orbits in the 48th band FS. The other dHvA branches predicted in the band-structure calculation have not been observed in the present experiments, and the probable origin of this discrepancy is discussed later. We have also estimated the cyclotron effective mass $m^*_c$ from the temperature dependence of the dHvA amplitude. The comparison of dHvA frequencies and $m^*_c$ between the experiment and calculation is given in Table I. The effective mass in the experiment is enhanced roughly twice compared with the calculated one, which is consistent with the enhancement of the Sommerfeld coefficient ($\gamma$) between the experiment and the theory. Such a large mass enhancement in the La compound is also found in LaFe$_4$P$_{12}$. The large mass enhancement in LaRu$_4$P$_{12}$ should be ascribed to the electron-phonon interaction, taking into account the rather high value of the superconducting transition temperature $T_C$. Following the McMillan formula with the value of Coulomb pseudopotential $\mu'$ = 0.13, the Debye temperature $\Theta_D$ = 405 K, and $T_C$ = 7.3 K, the electron-phonon coupling constant is estimated to be 0.65 in LaRu$_4$P$_{12}$, which is considered as a moderate-coupling superconductor. The value of $\gamma$ = 44.4 mJ/mol K$^2$ and the jump of specific heat at $T_C$ yield the ratio $\Delta C/\gamma T_C \approx 1.58$, which is larger than 1.43 of weak-coupling BCS theory.

The most probable reason why some of the theoretical branches are not observed in the present experiment, particularly for the large dHvA orbits, is a strong reduction of the dHvA signals due to their large curvature factors $A''$ ($A'' = |\partial^2 A/\partial k^2|$), where $A$ is the extremal cross-sectional area of the FS and $k_H$ is the wave-vector component along the field direction. The rapid change of $A$ as a function of $k_H$, i.e., the large value of $A''$, diminishes the dHvA amplitude for that extremal area. For the field angle $\theta$ = 30 degrees: $A'' = 0.14$ for the $\alpha$ branch whereas $A'' = 22$ for the $\psi$ branch in the calculation [see Fig. 2(b)]. However, that is not the case for $\tau$ and $\eta$ branches, which originate from 49th- and 46th-band FSs, i.e., for $H[111]$, $A'' = 0.18$ for the $\tau$ branch and $A'' = 0.61$ for the $\eta$ branch. The experimental limitations, i.e., insufficient temperatures and magnetic fields, could not be the origin of no observation of the $\tau$ and the $\eta$ branches, since the $\mu$ branch with almost the same curvature factor ($A'' = 0.4$) and the larger effective mass (see Table I) than those of the $\tau$ and $\eta$ branches (the calculated effective masses for $H[111]$ are 0.34$m_0$ for the $\tau$ branch and 0.23$m_0$ for the $\eta$ branch) has been clearly observed. Therefore, dHvA signals should be observed if the $\tau$ and $\eta$ branches really exist. The disagreement between the experiment and calculation concerning the $\tau$ and $\eta$ branches may be ascribed to the small difference of the lattice parameter and/or the effect beyond the LDA treatment. Note that the band structure calculation shows the absence of FSs responsible for the $\tau$ and $\eta$ branches in
PrRu$_4$P$_{12}$, though the difference of lattice parameter between LaRu$_4$P$_{12}$ (8.0608 Å) and PrRu$_4$P$_{12}$ (8.0424 Å) is quite small (~0.2%).\cite{12} Thermal expansion measurement suggests that the lattice constant decreases about 1.2% at low temperatures (≤20 K) in LaRu$_4$P$_{12}$.\cite{12} The band-structure calculation using the low-temperature lattice parameters will be clarified in future work.

From the present dHvA experiment and the band-structure calculation, we have confirmed that the shape of the main FS of LaRu$_4$P$_{12}$ is like a distorted cube [see Fig. 5(a)] and its volume is nearly one-half of the first FS of LaRu$_4$P$_{12}$ structure calculation, we have confirmed that the shape of the main FS of LaRu$_4$P$_{12}$ structure calculation using the low-temperature lattice parameters will be clarified in future work.

Table I: Comparison of the dHvA frequency $F$ and cyclotron effective mass $m^*_c$ between the experiment and the band structure calculation in LaRu$_4$P$_{12}$.

| Field direction | Branch | Experiment | Theory |
|-----------------|--------|------------|--------|
| $H[100]$       | $\alpha$ | $5.81$ | $2.9$ | $5.73$ | $1.87$ |
|                 | $\delta$ | $0.51$ | $3.9$ | $0.47$ | $2.34$ |
| $H[110]$       | $\alpha'$ | $6.40$ | - | $6.65$ | $4.73$ |
|                 | $\epsilon$ | $0.50$ | $2.6$ | $0.61$ | $1.40$ |
| $H[111]$       | $\alpha$ | $7.70$ | $9.0$ | $7.50$ | $4.73$ |
|                 | $\beta$ | $2.89$ | $11.8$ | $3.05$ | $3.8$ |
|                 | $\omega$ | $0.99$ | $3.0$ | - | - |
|                 | $\mu$ | $0.19$ | $3.2$ | $0.17$ | $1.32$ |

The obtained topology of the main FS in LaRu$_4$P$_{12}$ is similar to that by band calculation in PrRu$_4$P$_{12}$.

Then such a M-I transition should be expected also in LaRu$_4$P$_{12}$, however none has been reported yet; at least the resistivity and specific heat measurements show no M-I transition above $T_C$.\cite{12} One can infer that the presence of two small spherical $\tau$ and $\eta$ band FSs predicted by the band calculation, which are absent in PrRu$_4$P$_{12}$, might suppress M-I transition in LaRu$_4$P$_{12}$. However, the absence of $\tau$ and $\eta$ branches in the present experiment rules out such a scenario with large reliability as mentioned above. In PrRu$_4$P$_{12}$, the change of crystalline structure\cite{12,13} and the marked increase of resistivity below $T_{MI}$ (Ref. 2) are explained by the nesting model, suggesting the disappearance of the entire FS below $T_{MI}$, based on the band-structure calculations with the localized 4$f$ electrons.\cite{15,16} Note that in PrFe$_4$P$_{12}$, which shows an antiferro-quadrupolar transition below 6.5 K, where only the main part of the FS disappears, the metallic state prevails and heavy fermion behavior appears\cite{16,15}. The inelastic neutron scattering (INS) experiment in PrRu$_4$P$_{12}$ shows sharp crystal electric field (CEF) excitation peaks below $T_{MI}$ that gradually broaden across and above $T_{MI}$, suggesting that the 4$f$ electrons are basically localized, though their hybridization with the conduction electrons ($c-f$ hybridization) increases to some extent across and above $T_{MI}$. Considering all these facts, naturally, the present experiment suggests an essential 4$f$ electron contribution, which is the main difference between the two compounds, for the M-I transition. The $c-f$ hybridization might cooperate with the FS-nesting condition in causing the M-I transition in PrRu$_4$P$_{12}$, which explains the absence of the M-I transition in LaRu$_4$P$_{12}$ with no 4$f$ electron contribution.

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