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Electronic structures of the filled-skutterudite compounds \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\), which undergo a metal-insulator transition (MIT) at \(T_{\text{MI}}=60\text{ K}\) and 16 K, respectively, have been studied by means of optical spectroscopy. Their optical conductivity spectra have clearly revealed an energy gap of \(\sim 10\text{ meV}\) below \(T_{\text{MI}}\). The detailed temperature and energy dependencies of the energy gap are shown, which give much more information about the gap compared with that from the electrical resistivity experiment. For \(\text{PrRu}_4\text{P}_{12}\), in addition, optical phonon peaks in the spectra show anomalies upon the MIT, including broadening and shifts at \(T_{\text{MI}}\) and an appearance of new peaks below \(T_{\text{MI}}\). These results are discussed in terms of density waves or orbital ordering previously predicted for these compounds.

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Metal-insulator transition in \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\) investigated by optical spectroscopy

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Ternary compounds \(\text{RM}_4\text{X}_{12}\) (\(\text{R}=\text{rare earth elements}; \text{M} =\text{Fe, Ru, Os}; \text{X} =\text{P, As, Sb}\)) with the filled-skutterudite structure (space group \(\text{Im}\bar{3}\)) exhibit a wide variety of physical properties. Among them, \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\) are known to undergo a metal-insulator transition (MIT) at \(T_{\text{MI}}\sim 60\text{ K}\) (Ref. 1) and 16 K, respectively. For \(\text{PrRu}_4\text{P}_{12}\), the magnetic susceptibility shows no anomaly at \(T_{\text{MI}}\) and the valence of \(\text{Pr}\) is 3+ and independent of temperature.3 Thus, the MIT in \(\text{PrRu}_4\text{P}_{12}\) is driven neither by a magnetic transition nor by a valence transition. Recently, evidence for superlattice formation below \(T_{\text{MI}}\) has been found by electron and x-ray diffraction experiments.4–6 Also, the band calculation study points out that the Fermi surfaces of \(\text{Ru}_4\text{P}_{12}\) should have a strong tendency for nesting in spite of the isotropic crystal structure.7 In fact, the band calculation for \(\text{PrRu}_4\text{P}_{12}\) assuming the displacement of P ions predicts an energy gap at the Fermi level \(E_{\text{F}}\).8 From these results, the MIT in \(\text{PrRu}_4\text{P}_{12}\) has been considered to result from a charge-density wave (CDW) transition caused by Fermi surface nesting.4–7 In contrast, for \(\text{SmRu}_4\text{P}_{12}\), the magnetic susceptibility clearly shows an anomaly near \(T_{\text{MI}}\). Moreover, recent works have revealed that the MIT involves two successive transitions at \(\sim 14\text{ K}\) and \(\sim 16\text{ K}\).10,11 The two transitions and their magnetic-field dependencies appear qualitatively very similar to those of \(\text{CeB}_6\), which shows an antiferroquadrupolar (AFQ) ordering at the higher transition temperature \(T_{\text{Q}}\) and an antiferromagnetic ordering at the lower one.12 Therefore, it has been suggested that the MIT in \(\text{SmRu}_4\text{P}_{12}\) should be related to an orbital ordering.

In spite of much discussion about the nature of MIT in \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\), however, microscopic characteristics of the energy gap had been largely unknown, since the electrical resistivity was the only experiment that had clearly detected the energy gap. In this work, therefore, we have probed the microscopic electronic structures associated with the gap formation in \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\).13 The optical technique is a powerful means for studying the electronic structures near \(E_{\text{F}}\) and has been applied to several skutterudite compounds including \(\text{RFe}_4\text{P}_{12}\),14 \(\text{CeRu}_4\text{Sb}_{12}\), and \(\text{YbFe}_4\text{Sb}_{12}\).15 \(\text{CeOs}_4\text{Sb}_{12}\).16 We have clearly observed the energy gap formation in \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\). In addition, anomalies of optical phonon peaks are observed around \(T_{\text{MI}}\). We will discuss the microscopic mechanism for the gap formation in these compounds, based on the detailed \(T\) and energy dependences of the gap in the present data.

The polycrystalline samples were used of \(\text{PrRu}_4\text{P}_{12}\) (Ref. 1) and \(\text{SmRu}_4\text{P}_{12}\) (Ref. 2) had sizes of \(\sim 3\times 3\times 1\text{ mm}^3\), and their surfaces were mechanically polished. Temperature-dependent reflectivity spectra \([R(\omega)]\) were measured under near-normal incidence, using a Fourier-transform interferometer and thermal sources at photon energies between 8 meV and 2 eV. A gold or silver film deposited \textit{in situ} onto the sample surface was used as a reference of reflectivity.17 Between 2 and 30 eV at room temperature, a grating spectrometer and synchrotron radiation source were used at the beamline BL7B of UVSOR, Institute for Molecular Science. The optical conductivity \(\sigma(\omega)\) was obtained from Kramers-Kronig transformation applied to the measured \(R(\omega)\). A Hagen-Rubens or a constant extrapolation was used below 8 meV, and a \(\omega^{-4}\) extrapolation above 30 eV.18

Figure 1 shows the temperature \((T)\) dependence of \(R(\omega)\) for \(\text{PrRu}_4\text{P}_{12}\) and \(\text{SmRu}_4\text{P}_{12}\). The insets show \(R(\omega)\) up to 30 eV. Between 295 K and 80 K, both compounds show typically metallic \(R(\omega)\), with a plasma edge at \(\sim 0.4\text{ eV}\). The peaks above 0.4 eV are due to interband transitions. Below 80 K, in contrast, \(R(\omega)\) decreases rapidly with decreasing \(T\), indicating strong variations of the electronic structures near \(E_{\text{F}}\). In addition, sharp phonon peaks appear below 50 meV. The corresponding \(\sigma(\omega)\) spectra are shown in Fig. 2. For both compounds, \(\sigma(\omega)\) at 295 and 80 K are characterized by a Drude-type component due to free carriers, rising toward zero photon energy. Below 80 K, however, \(\sigma(\omega)\) at the low-energy region is suppressed, and an energy gap is progressively formed with decreasing \(T\). Associated with the gap formation, a broad peak grows around 60 meV for \(\text{PrRu}_4\text{P}_{12}\)
and around 30 meV for SmRu$_4$P$_{12}$. These peaks are due to optical excitations across the energy gap, and below we refer to them as the "gap excitation peaks."$^{19}$ The effective carrier density, calculated as $N_{\text{eff}}(\omega) = (2m/\pi e^2)\int_0^{\omega} \sigma(\omega') d\omega'$,$^{18}$ is plotted in the insets of Figs. 2(a) and 2(b). They show that the optical sum rule is satisfied within a range of $\omega \sim 0.5$ eV. This shows that the MIT is accompanied with the variation of electronic structures over $\sim 0.5$ eV from $E_F$, which is much larger than the gap magnitude.

In order to estimate the $T$ dependence of the energy gap, we identify the position of the gap excitation peak as the characteristic energy for the gap formation. To evaluate the peak position accurately, we have carried out spectral fittings, an example of which is shown in Fig. 3(a) for PrRu$_4$P$_{12}$. We have used the Lorentz oscillator to fit the gap excitation peak and the usual Drude function to fit the free-carrier component.$^{18}$ To fit the background continuum, another Lorentz oscillator was placed at $\sim 100$ meV for all $T$s.$^{20}$ The phonon peaks were also fitted as described later and were subtracted out. Figure 3(b) shows the $T$ dependence of the peak position obtained by the fitting. It is clear that the peak energy increases with cooling for both PrRu$_4$P$_{12}$ and SmRu$_4$P$_{12}$. Also plotted in Fig. 3(b) is the $T$ dependence of the intensity of a superlattice spot of PrRu$_4$P$_{12}$ investigated by x-ray diffraction.$^5$ The $T$ evolution of the gap excitation peak closely follows that of the superlattice diffraction, hence the lattice deformation due to CDW. This result strongly suggests that the observed gap in PrRu$_4$P$_{12}$ is indeed related to the CDW formation. The observed characteristics of the gap for PrRu$_4$P$_{12}$ are in sharp contrast to those for the Kondo semiconductors, such as Ce$_3$Bi$_4$Pt$_{13}$ and YbB$_{12}$,$^{22}$ where the gap width in $\sigma(\omega)$ is nearly unchanged with $T$.$^{21,22}$

For SmRu$_4$P$_{12}$, it is noteworthy that a decrease of $\sigma(\omega)$ is already seen at 20 K (below $\sim 15$ meV), although a clear gap develops only below 16 K. The decrease of $\sigma(\omega)$ above $T_{\text{MI}}$ probably indicates a precursor to the MIT, i.e., the density of states near $E_F$ starts decreasing already above $T_{\text{MI}}$. This is consistent with the result that the resistivity increases gradually with cooling below $\sim 50$ K, before rapidly rising below $T_{\text{MI}} = 16$ K.$^2$ In view of the prediction that the MIT in SmRu$_4$P$_{12}$ is related with an AFQ ordering,$^{10,11}$ one possible origin for these results above $T_{\text{MI}}$ is the fluctuation of the quadrupole moments above $T_Q$ ($= T_{\text{MI}}$): Although the long-range AFQ ordering can exist only below $T_Q$, short-range ordering may exist even above $T_Q$ with a strong fluctuation of quadrupole moments.$^{23}$ In fact, it has been reported that $T_Q$ increases under magnetic field,$^{10,11}$ which can be understood as resulting from a suppression of the fluctuations, similarly to the case of CeB$_6$.$^{23}$ Such strong fluctuation of the quadrupole moments may have reduced the density of states and $\sigma(\omega)$ above $T_{\text{MI}}$. For example, for a perovskite oxide which forms an energy gap due to charge ordering, both a decrease in $\sigma(\omega)$ and an increase of resistivity with cooling have been observed above the ordering temperature.$^{24}$ A fluctuation of charge order has been proposed as a possible origin for this case.

Although the factor group analysis for the filled-
dergoes a symmetry lowering below $T_{MI}$. Below 285 and 347 cm$^{-1}$ for PrRu$_4$P$_{12}$, which are already present above $T_{MI}$, we have plotted the peak energies and the linewidths obtained from the fitting are detailed in Fig. 2. The position of the gap excitation peak as a function of temperature. The superlattice diffraction data. Namely, displacement of $P$ atoms may change the strength of bonding, leading to the peak shifts, and the associated symmetry lowering may result in more than eight phonon peaks. The observed narrowing is likely to result from the rapid decrease of free carriers below $T_{MI}$, since it should reduce the phonon damping due to carrier-phonon interaction. Clearly, the present results regarding the phonons are consistent with a CDW formation. It is noteworthy that the phonon peak characteristics of PrRu$_4$P$_{12}$ are qualitatively similar to those of 1T-TaS$_2$, which is a typical CDW compound. Namely, the infrared spectra of 1T-TaS$_2$ also show many additional phonon peaks, peak shifts, and peak narrowing below the CDW transition temperature.

The results of similar fitting for the phonons of SmRu$_4$P$_{12}$ are shown in Figs. 4(d)–4(f). In contrast to PrRu$_4$P$_{12}$, no additional phonon peaks appear below $T_{MI}$, and the peaks show red shifts below $T_{MI}$ with almost no changes in the linewidth. The shifts are much smaller than those observed for PrRu$_4$P$_{12}$. Although a Fermi surface nesting is also predicted for SmRu$_4$P$_{12}$, the present result shows that the modulation in the charge density below $T_{MI}$ is much weaker than that in PrRu$_4$P$_{12}$. This is consistent with the previous results that the ordering in SmRu$_4$P$_{12}$ should be of orbital or magnetic origin. In any case, the variations of the optical phonon peaks in $\sigma(\omega)$ upon the MIT are very different between PrRu$_4$P$_{12}$ and SmRu$_4$P$_{12}$. Remarkably, the elastic constants of these compounds, which are closely related to the acoustic phonons, have also shown very different variations around $T_{MI}$.

In conclusion, we have measured $\sigma(\omega)$ spectra of PrRu$_4$P$_{12}$ and SmRu$_4$P$_{12}$ to study the evolution of electronic structures upon the MIT. Their $\sigma(\omega)$ spectra have clearly shown the formation of an energy gap below $T_{MI}$. For PrRu$_4$P$_{12}$, the $T$ evolution of the energy gap and the phonon peaks in $\sigma(\omega)$ are consistent with those associated with a CDW transition involving a symmetry lowering and a slight displacement of $P$ atoms. For SmRu$_4$P$_{12}$, no clear sign of a density wave was observed in the evolution of $\sigma(\omega)$. The data suggest a decrease in the density of states even above $T_{MI}$, which was discussed in terms of short-range orbital ordering preceding the MIT. The present results strongly suggest that the origin of the MIT is different between these compounds, similarly to the prediction by other experiments.

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