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Metal-insulator transition in PrRu$_4$P$_{12}$ and SmRu$_4$P$_{12}$ investigated by optical spectroscopy

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

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and around 30 meV for SmRu₄P₁₂. These peaks are due to optical excitations across the energy gap, and below we refer to them as the “gap excitation peaks.” The effective carrier density, calculated as $N_{\text{eff}}(\omega) = (2m_0/\pi e^2)\int_0^\infty \sigma(\omega')d\omega'$, 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 $\omega \approx 0.5$ 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 PrRu₄P₁₂. We have used the Lorentz oscillator to fit the gap excitation peak and the usual Drude function to fit the free-carrier component. To fit the background continuum, another Lorentz oscillator was placed at $\sim 100$ meV for all $T_s$. 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 PrRu₄P₁₂ and SmRu₄P₁₂. Also plotted in Fig. 3(b) is the $T$ dependence of the intensity of a superlattice spot of PrRu₄P₁₂ investigated by x-ray diffraction. 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 PrRu₄P₁₂ is indeed related to the CDW formation. The observed characteristics of the gap for PrRu₄P₁₂ are in sharp contrast to those for the Kondo semiconductors, such as Ce₃Bi₄Pt₃ and YbBi₁₂, where the gap width in $\sigma(\omega)$ is nearly unchanged with $T$.

For SmRu₄P₁₂, 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. In view of the prediction that the MIT in SmRu₄P₁₂ is related with an AFQ ordering, one possible origin for these results above $T_{\text{MI}}$ is the fluctuation of the quadrupole moments above $T_Q (\approx T_{\text{MI}})$: 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. In fact, it has been reported that $T_Q$ increases under magnetic field, which can be understood as resulting from a suppression of the fluctuations, similarly to the case of CeB₆. 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. 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 $T_{\text{MI}}$. Below show only four phonon peaks, similarly to other filled-plotted as a function of detailed phonon peaks using the Lorentz oscillator functions. The strongly suggests that the crystal structure of PrRu$_4$P$_{12}$ un-modes, the section intensity as a function of temperature. The superlattice diffrac-

FIG. 3. (Color online) (a) An example of the fitting for PrRu$_4$P$_{12}$, as discussed in the text. (b) The position of the gap excitation peak as a function of temperature. The superlattice diffraction intensity ($|F|^2$) of PrRu$_4$P$_{12}$ (open circles) is also shown (Ref. 5) for comparison.

skutterudite structure predicts eight infrared-active phonon modes, the $\sigma(\omega)$ spectra of PrRu$_4$P$_{12}$ and SmRu$_4$P$_{12}$ at 295 K show only four phonon peaks, similarly to other filled-skutterudite compounds. Below $T_{\text{MI}}$ for PrRu$_4$P$_{12}$, however, several additional peaks appear in $\sigma(\omega)$, as shown in Fig. 2(b) and plotted in Fig. 4(a). The total number of observed phonon peaks below $T_{\text{MI}}$ is larger than eight, which strongly suggests that the crystal structure of PrRu$_4$P$_{12}$ undergoes a symmetry lowering below $T_{\text{MI}}$. To evaluate the detailed $T$ dependence of the phonons, we have fitted the phonon peaks using the Lorentz oscillator functions. The peak energies and the linewidths obtained from the fitting are plotted as a function of $T$ in Fig. 4. The phonon peaks near 285 and 347 cm$^{-1}$ for PrRu$_4$P$_{12}$, which are already present above $T_{\text{MI}}$, show blueshifts of $\sim$3 cm$^{-1}$ and a narrowing of about 40% below $T_{\text{MI}}$. These two phonon modes involve the vibrations of $P$. This result and the observation of more than eight phonon peaks appear consistent with the slight displacement of $P$ atoms below $T_{\text{MI}}$ indicated by the super-lattice 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 $T_{\text{MI}}$, 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 $T_{\text{MI}}$, and the peaks show red shifts below $T_{\text{MI}}$ 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 $T_{\text{MI}}$ 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 $T_{\text{MI}}$.

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 $T_{\text{MI}}$. 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 $T_{\text{MI}}$, 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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To compare with the transport gap given by the resistivity, the gap magnitude in $\sigma(\omega)$ can be estimated by extrapolating the linearly varying portion of $\sigma(\omega)$ at lowest $T$ in Fig. 2(c) and 2(d). This gives $\sim 15$ meV for PrRu4P12 and $\sim 10$ meV for SmRu4P12, which are consistent with the transport gaps (see Refs. 1 and 2).

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