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Metal-insulator transition in $PrRu_4P_{12}$ and $SmRu_4P_{12}$ investigated by optical spectroscopy

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Electronic structures of the filled-skutterudite compounds $PrRu_4P_{12}$ and $SmRu_4P_{12}$, 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 ~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 $PrRu_4P_{12}$, 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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Ternary compounds RM_4X_{12} (R=rare earth elements; M=Fe, Ru, Os; X=P, As, Sb) with the filled-skutterudite structure (space group $Im\bar{3}$) exhibit a wide variety of physical properties. Among them, $PrRu_4P_{12}$ and $SmRu_4P_{12}$ are known to undergo a metal-insulator transition (MIT) at $T_{MI}\sim 60$ K (Ref. 1) and 16 K,[2] respectively. For $PrRu_4P_{12}$, the magnetic susceptibility shows no anomaly at T_{MI},[1] and the valence of Pr is 3+ and independent of temperature.[3] Thus, the MIT in $PrRu_4P_{12}$ is driven neither by a magnetic transition nor by a valence transition. Recently, evidence for superlattice formation below T_{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 RRu_4P_{12} should have a strong tendency for nesting in spite of the isotropic crystal structure.[7] In fact, the band calculation for $PrRu_4P_{12}$ assuming the displacement of P ions predicts an energy gap at the Fermi level (E_F).[8] From these results, the MIT in $PrRu_4P_{12}$ has been considered to result from a charge-density wave (CDW) transition caused by Fermi surface nesting.[4,7–9] In contrast, for $SmRu_4P_{12}$, the magnetic susceptibility clearly shows an anomaly near T_{MI}.[2] Moreover, recent works have revealed that the MIT involves two successive transitions at ~14 K and ~16 K.[10,11] The two transitions and their magnetic-field dependencies appear qualitatively very similar to those of CeB_6, which shows an antiferroquadrupolar (AFQ) ordering at the higher transition temperature T_Q and an antiferromagnetic ordering at the lower one.[12] Therefore, it has been suggested that the MIT in $SmRu_4P_{12}$ should be related to an orbital ordering.

In spite of much discussion about the nature of MIT in $PrRu_4P_{12}$ and $SmRu_4P_{12}$, 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 $PrRu_4P_{12}$ and $SmRu_4P_{12}$.[13] The optical technique is a powerful means for studying the electronic structures near E_F and has been applied to several skutterudite compounds including RFe_4P_{12},[14] $CeRu_4Sb_{12}$ and $YbFe_4Sb_{12}$,[15] and $CeOs_4Sb_{12}$.[16] We have clearly observed the energy gap formation in $PrRu_4P_{12}$ and $SmRu_4P_{12}$. In addition, anomalies of optical phonon peaks are observed around T_{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 that were used of $PrRu_4P_{12}$ (Ref. 1) and $SmRu_4P_{12}$ (Ref. 2) had sizes of $\sim 3\times 3\times 1$ 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 *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 $R(\omega)$.[18] A Hagen-Rubens or a constant extrapolation was used below 8 meV, and a ω^{-4} extrapolation above 30 eV.[18]

Figure 1 shows the temperature (T) dependence of $R(\omega)$ for $PrRu_4P_{12}$ and $SmRu_4P_{12}$. 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 ~0.4 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_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 $PrRu_4P_{12}$

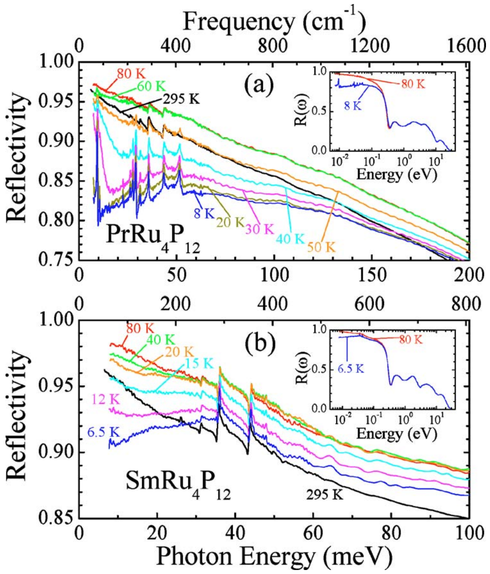

FIG. 1. (Color online) Optical reflectivity spectra $[R(\omega)]$ of $PrRu_4P_{12}$ (a) and $SmRu_4P_{12}$ (b) at different temperatures. Each inset shows $R(\omega)$ in a wider range of photon energies.

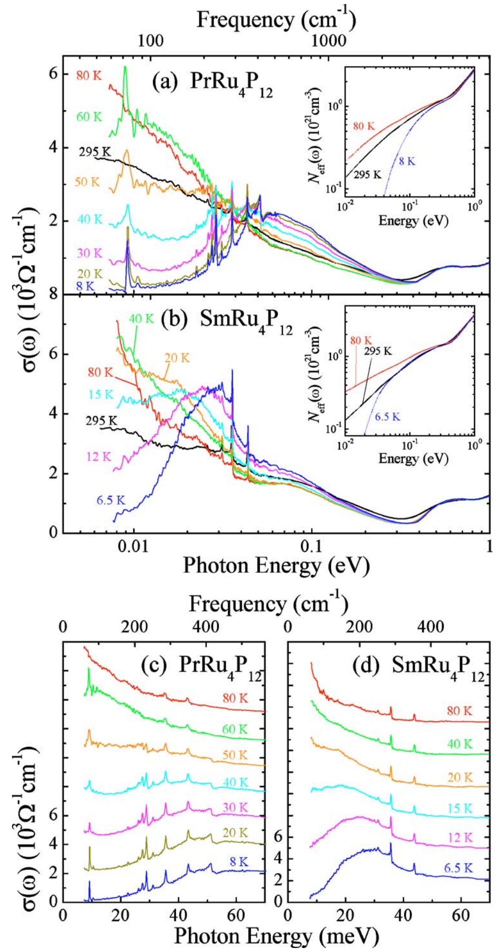

FIG. 2. (Color online) Optical conductivity spectra $\sigma(\omega)$ of (a) $PrRu_4P_{12}$ and (b) $SmRu_4P_{12}$ at different temperatures. Each inset shows the integrated spectral weight $N_{\text{eff}}(\omega)$ (see text). The low-energy portion of the spectra in (a) and (b) are shown in (c) and (d), respectively. For clarity, each spectra are offset by $2\times10^3\ \Omega^{-1}\,\text{cm}^{-1}$ for (c) and $3\times10^3\ \Omega^{-1}\,\text{cm}^{-1}$ for (d).

and around 30 meV for $SmRu_4P_{12}$. 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 $N_{\text{eff}}(\omega)=(2m_0/\pi e^2)\int_0^\omega \sigma(\omega')d\omega'$,[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 ~ 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 $PrRu_4P_{12}$. 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 ~ 100 meV for all Ts.[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 $PrRu_4P_{12}$ and $SmRu_4P_{12}$. Also plotted in Fig. 3(b) is the T dependence of the intensity of a superlattice spot of $PrRu_4P_{12}$ 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 $PrRu_4P_{12}$ is indeed related to the CDW formation. The observed characteristics of the gap for $PrRu_4P_{12}$ are in sharp contrast to those for the Kondo semiconductors, such as $Ce_3Bi_4Pt_3$[21] and YbB_{12},[22] where the gap width in $\sigma(\omega)$ is nearly unchanged with T.[21,22]

For $SmRu_4P_{12}$, it is noteworthy that a decrease of $\sigma(\omega)$ is already seen at 20 K (below ~ 15 meV), although a clear gap develops only below 16 K. The decrease of $\sigma(\omega)$ above T_{MI} probably indicates a precursor to the MIT, i.e., the density of states near E_F starts decreasing already above T_{MI}. This is consistent with the result that the resistivity increases gradually with cooling below ~ 50 K, before rapidly rising below $T_{\text{MI}}=16$ K.[2] In view of the prediction that the MIT in $SmRu_4P_{12}$ is related with an AFQ ordering,[10,11] one possible origin for these results above T_{MI} is the fluctuation of the quadrupole moments above T_Q ($\simeq T_{\text{MI}}$): 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_{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-

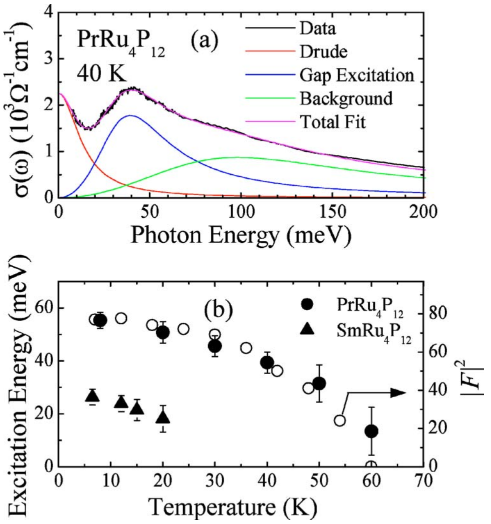

FIG. 3. (Color online) (a) An example of the fitting for $PrRu_4P_{12}$, as discussed in the text. (b) The position of the gap excitation peak as a function of temperature. The superlattice diffraction intensity ($|F|^2$) of $PrRu_4P_{12}$ (open circles) is also shown (Ref. 5) for comparison.

skutterudite structure predicts eight infrared-active phonon modes, the $\sigma(\omega)$ spectra of $PrRu_4P_{12}$ and $SmRu_4P_{12}$ at 295 K show only four phonon peaks, similarly to other filled-skutterudite compounds.[14–16] Below T_{MI} for $PrRu_4P_{12}$, 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_{MI} is larger than eight, which strongly suggests that the crystal structure of $PrRu_4P_{12}$ undergoes a symmetry lowering below T_{MI}. To evaluate the detailed T dependence of the phonons, we have fitted the phonon peaks using the Lorentz oscillator functions.[25] The peak energies and the linewidths obtained from the fitting are plotted as a function of T in Fig. 4.[26] The phonon peaks near 285 and 347 cm^{-1} for $PrRu_4P_{12}$, which are already present above T_{MI}, show blueshifts of $\sim$3 cm^{-1} and a narrowing of about 40% below T_{MI}. These two phonon modes involve the vibrations of P.[14] This result and the observation of more than eight phonon peaks appear consistent with the slight displacement of P atoms below T_{MI} indicated by the superlattice diffraction data.[4–6] 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 $PrRu_4P_{12}$ are qualitatively similar to those of 1T-TaS_2,[27] 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.

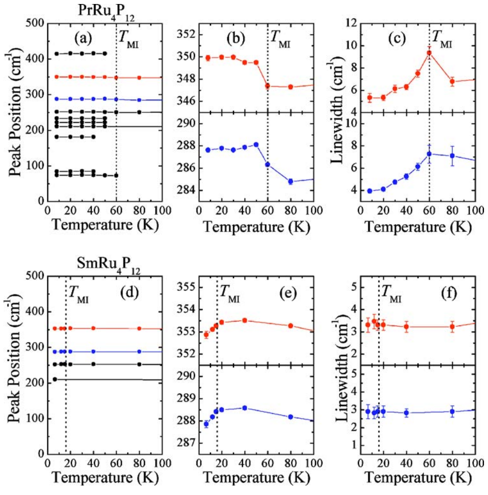

FIG. 4. (Color online) The peak frequencies and the linewidths of phonon peaks in $\sigma(\omega)$ as a function of temperature for $PrRu_4P_{12}$ (a)–(c) and $SmRu_4P_{12}$ (d)–(f).

The results of similar fitting for the phonons of $SmRu_4P_{12}$ are shown in Figs. 4(d)–4(f). In contrast to $PrRu_4P_{12}$, 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 $PrRu_4P_{12}$. Although a Fermi surface nesting is also predicted for $SmRu_4P_{12}$, the present result shows that the modulation in the charge density below T_{MI} is much weaker than that in $PrRu_4P_{12}$. This is consistent with the previous results that the ordering in $SmRu_4P_{12}$ should be of orbital or magnetic origin.[10,11] In any case, the variations of the optical phonon peaks in $\sigma(\omega)$ upon the MIT are very different between $PrRu_4P_{12}$ and $SmRu_4P_{12}$. Remarkably, the elastic constants of these compounds, which are closely related to the acoustic phonons, have also shown very different variations around T_{MI}.[28]

In conclusion, we have measured $\sigma(\omega)$ spectra of $PrRu_4P_{12}$ and $SmRu_4P_{12}$ 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 $PrRu_4P_{12}$, 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 $SmRu_4P_{12}$, 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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