Raman scattering investigation of filled skutterudite $PrRu_4P_{12}$

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Abstract

Raman scattering spectra of the single crystalline $PrRu_4P_{12}$ have been measured in the temperature region between 1.5 K and 300 K. Below T_{MI}, new peaks appear at phonon region and these peaks are assigned as the Raman-active phonons with $Pm\bar{3}$ symmetry. While, the broad spectra in the lower energy region than 200cm^{-1} become sharp below T_{MI} and the detailed polarization measurements conclude that these are the crystal field excitations(CF) due to two-different Pr sites. Furthermore, temperature dependence of the CF energy levels for Pr2 has been clarified.

Key words: Skutterudite compounds, Raman scattering, CF excitation
PACS: 78:30.-j; 63:20.Dj; 71:27+a

Filled skutterudite of $PrRu_4P_{12}$ undergoes a metal-insulator(M-I) transition at $T_{MI} \simeq 60$ K[1], where the structural transition also occurs. In spite of several investigations of resistivity[1], electron diffraction[2], and band calculation[3], the mechanism of the M-I transition is still unclear. For Raman scattering[4], we have reported that the possible symmetry of the low temperature phase is $Pm\bar{3}$, judging from the number of the observed phonons. Furthermore, the phonon energy and line width also change at around 35K, where the resistivity shows inflection[1], and other additonal peaks below 200cm^{-1} have been assigned as the CF excitations. In this report, we have measured detailed Raman scattering spectra of the CF excitations in $PrRu_4P_{12}$.

The crystal symmetry is $Im\bar{3}$ for the metal phase $T > T_{MI}$. Raman-active phonons in this symmetry are $\Gamma_R = 2A_g + 2E_g + 4T_g$, where A_g, E_g, and T_g denote the irreducible representations. These phonons correspond to the vibrations of pnicogen atoms. The symmetry of the phonons is determined by the following polarization geometries: A_g phonons appear for the (x,x) geometry, E_g in (x,x) and (x+y,x-y), and T_g in (x,y). In the notation of (α,β), α and β are the polarization directions of incident and scattered light, respectively. In this study, x and y correspond to the crystal axes of [1,0,0] and [0,1,0], respectively. The experimental details of the present experiments have already been reported in the previous report[4].

Figure 1 shows the representative temperature dependence of the E_g spectra of $PrRu_4P_{12}$. The observed spectra can be mainly divided into two energy region; the energy region above and below 200cm^{-1}. For the higher energy region than 200cm^{-1}, two E_g peaks, marked by solid arrows, are Raman-active phonons in the high temperature phase ($Im\bar{3}$). Below T_{MI}, two additional phonon peaks (dotted arrows) appear. Since they satisfy the polarization dependence of the E_g symmetry, they are assigned as the Raman-active phonons in the $Pm\bar{3}$. The observation of new phonons is the experimental evidence of the structural phase transition at T_{MI}.

For the lower energy region than 200cm^{-1}, several peaks, marked by triangles, are very broad for $T > T_{MI}$ and becomes sharp for $T < T_{MI}$ as shown in Fig.1. Figure 2 shows the polarization dependence of the lower energy region spectra at 5K. We have assigned the

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peaks as the CF excitations in the previous report, because of the poor polarization dependence and the good energy agreement with the CF excitation energy reported by Iwasa et al[5].

The site symmetries of Pr at corner (Pr1) and body-center (Pr2) become inequivalent below $T_{\rm MI}$. The reported CF energy schemes are depicted in Fig. 2(b). The observed peaks corresponds to the transition between the CF levels and the corresponding transition, marked by A-D, are shown by solid and dotted arrows for Pr1 and Pr2, respectively. The polarization selection rule for the CF excitations are obtained as follows. For Pr1, only one excitation named A peak from Γ_1 to $\Gamma_4^{(1)}$ has been clearly observed and its symmetry is T_g. For Pr2, three clear peaks have been observed and are named as B, C, and D peaks. The B peak transition of $\Gamma_4^{(2)}$-Γ_1 is T_g, the C peak $\Gamma_4^{(2)}$-$\Gamma_4^{(1)}$ A_g+E_g+T_g, and the D peak Γ_1-Γ_{23} E_g. These observed peaks satisfy above polarization selection rule, in spite of the small amount of oblique intensity due to misalignment of crystal axes setting. Therefore, this polarization dependence supports that the A-D peaks are the excitation due to the CF of Pr.

Temperature dependence of the energies of the A-D peaks are shown in Fig.3. Below 30K, the energy of all peaks is almost temperature independent, but, above 30K, the energy of the A, B, and C peaks decreases and their line width becomes broad. For the Pr2 site, the energy interval between the B and C peaks is almost constant even above 30K and the energy of the D peak does not depend on temperature. These results suggest that the levels of Γ_1, $\Gamma_4^{(1)}$, and Γ_{23} decreases simultaneously without any change of their energy intervals. Finally, the ground state of $\Gamma_4^{(2)}$ is mixed with Γ_1 at about 45K for Pr2. Thus, the ground symmetry is not well defined for T >45K. We note here the resistivity shows anomalous inflection[1] at about 45K. The relationship between the CF and resistivity is not understood at this stage.

This work was supported by a Grant-in-Aid for Scientific Research Priority Area "Skutterudite" (No. 15072205) and for COE Research (No. 13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. The low temperature experiments is supported by N-BARD of Hiroshima University.

References

[1] C. Sekine *et al*, Phys. Rev. Lett. **79** (1997) 3218.

[2] C. H. Lee *et al*, J. Phys.: Condens. Matter **13** (2001) L45.

[3] H. Harima *et al*, Acta Polon. Phys. B **34** (2003) 1189.

[4] N. Ogita *et al*, Physica B **359-361** (2005) 847.

[5] K. Iwasa *et al*, Physica B **359-361** (2005) 833.

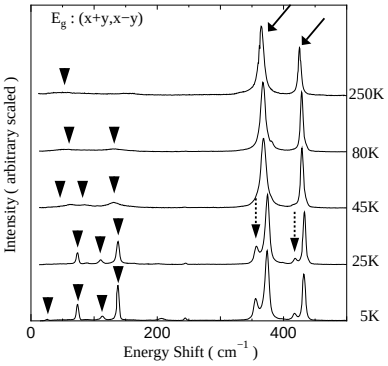

Fig. 1. Representative temperature dependence of E_g spectra of $PrRu_4P_{12}$. The solid arrows denote the Raman-active Eg phonons in the high temperature phase(Im$\bar{3}$), and dotted arrows are phonons observed below $T_{\rm MI}$. The triangles are CF excitations at the low energy region.

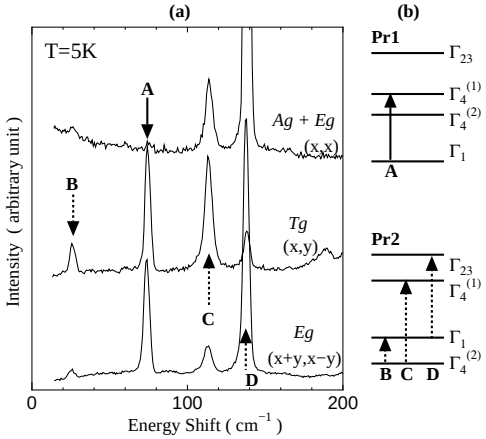

Fig. 2. (a)Polarization dependence of the CF transition and (b) CF levels of Pr1 and Pr2 reported by Iwasa[5].

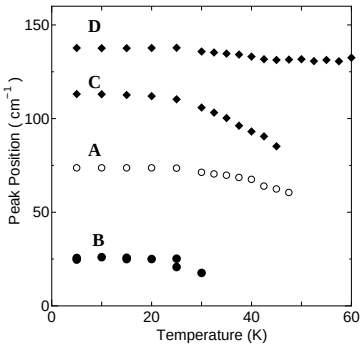

Fig. 3. Temperature dependence of the CF energies. A, B, C and D transitions are shown in Fig. 2 (b).