57Fe Mössbauer Spectroscopic Study of PrFe$_4$P$_{12}$

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Abstract

We have investigated the local electronic state of PrFe$_4$P$_{12}$ at an Fe site using $^{57}$Fe Mössbauer spectroscopy. All the $^{57}$Fe Mössbauer spectra of PrFe$_4$P$_{12}$ are a pure quadrupole pattern. The magnitude of the nuclear quadrupole splitting does not, however, show any temperature dependence at the phase transition reported by the x-ray diffraction experiment at low temperature. The present result suggests that the local symmetry around Fe atoms in PrFe$_4$P$_{12}$ does not change beyond the experimental error of the $^{57}$Fe Mössbauer spectroscopy.

Key words: PrFe$_4$P$_{12}$; $^{57}$Fe Mössbauer spectroscopy; nuclear quadrupole splitting

PrFe$_4$P$_{12}$ is one of the interesting materials in filled Skutterdite compounds. The jumps can be observed at $T_A = 6.5$ K in its specific heat measurement.[1] The temperature dependence of the magnetic susceptibility measurements has the peak like an antiferromagnetic order. However, no magnetic reflection can be observed below $T_A$ in the powder neutron diffraction experiments.[2]

Recently, the superlattice reflection can be observed in the x-ray diffraction experiment at low temperature.[4] This result suggests that the iron atoms displace little a bit from the location at room temperature. The neutron scattering experiments under the applied magnetic field suggest that the phase transition at $T_A$ is caused by the quadrupole order.[5] Although many experiments have been done, the order parameter of the phase transition at $T_A$ has not determined yet in PrFe$_4$P$_{12}$. We have applied the $^{57}$Fe Mössbauer spectroscopy to the investigation of the local electronic state in PrFe$_4$P$_{12}$.

The single crystal sample was prepared with Sn-flux method.[3] The sample is crushed into powder in air for the transmission $^{57}$Fe Mössbauer measurements. The used γ-ray source is $^{57}$Co in Rh. The Doppler velocity is calibrated using the spectrum of α-Fe at room temperature. The zero isomer shift was defined as that of α-Fe at room temperature.

All the spectra obtained in the present work are pure paramagnetic doublets due to the nuclear quadrupole splitting. This result suggests that the PrFe$_4$P$_{12}$ is nonmagnetic within the experimental error of the $^{57}$Fe Mössbauer spectroscopy.

The values of the isomer shift and nuclear quadrupole splitting are +0.05 and 0.40 mm s$^{-1}$, respectively, at room temperature. The isomer shift value indicates that the 3d electrons of Fe atoms are well hybridized with the other atoms. These values obtained at room temperature are almost equal to those of the other filled-Skutterdite compounds, LaFe$_4$P$_{12}$ and EuFe$_4$P$_{12}$. [7,8] These facts indicate that the local electronic state of Fe in PrFe$_4$P$_{12}$ is quite similar to those of LaFe$_4$P$_{12}$.
Figure 1. $^{57}$Fe Mössbauer spectra of PrFe$_4$P$_{12}$ at 298 and 5 K.

Figure 2. Temperature dependence of the nuclear quadrupole splitting in PrFe$_4$P$_{12}$ below 40 K.

and EuFe$_4$P$_{12}$.

Figure 2 shows the temperature dependence of the nuclear quadrupole splitting (QS) in the low temperature region of PrFe$_4$P$_{12}$. The magnitude of QS has shown no changes around $T_A$, although PrFe$_4$P$_{12}$ occurs the phase transition at $T_A$. The QS value is correlated with the local symmetry around the probe atoms. In $^{57}$Fe Mössbauer spectroscopy, the QS value is sensitive when the valence states of Fe is trivalent. According to the isomer shift value at room temperature, the valence state of Fe in PrFe$_4$P$_{12}$ almost occupies the trivalent state. The QS value is caused by the local symmetry.

The temperature dependence of the QS value suggests that the local symmetry around Fe atoms does not change at $T_A$ beyond the experimental error, although the recent x-ray diffraction experiment suggest that the Fe atoms are displaced at $T_A$ together with P atoms that locates the nearest neighbor sites, or the displacement of Fe atoms are too small to detect the $^{57}$Fe Mössbauer spectroscopy. In the Pr-based skutterdite compound, PrRu$_4$P$_{12}$, the P atoms are displaced at the transition temperature due to the metal-insulator transition.[6] We think that the temperature dependence of the QS value shows the displacement of Fe atoms with P atoms.

To summarize, the present work suggests that the transition at $T_A$ is not a magnetic transition. The local electronic state at room temperature in an Fe site is almost the same as that of LaFe$_4$P$_{12}$ and EuFe$_4$P$_{12}$. The change of the local symmetry cannot be observed at $T_A$.

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References