Low temperature phase of YbPd investigated by Raman scattering

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Abstract. The possibility of the structural change in YbPd has been investigated by Raman scattering in the temperature range from 4 K to 300 K. One peak was clearly observed around 91 cm⁻¹ below 132 K. This is a clear evidence of a structural change at the transition temperature 132 K from the CsCl structure. The polarization dependence of the 91 cm⁻¹ peak shows that the cubic and tetragonal symmetries are ruled out for the crystal structure at 4 K.

1. Introduction

YbPd is an intermediate valence compound and four transitions at 0.5, 1.9, 105, and 125 K have been reported from the measurements of specific heat, thermal expansion, resistivity, and magnetic susceptibility [1]. The transition at 1.9 K is a magnetic order [2]. The magnetic ordered state has attracted attention, since it is realized accompanying valence fluctuation of magnetic ions. The valence of Yb is reported as 2.8+ by X-ray absorption spectrum of Yb L₃ edge [1] and as 2.75+ by photoemission spectrum, eliminating surface contribution [3]. At low temperatures, neutron scattering [4] and Mössbauer [2] measurements have shown that a half of Yb are Yb³⁺ and have magnetic moment.

Since the Yb state in the intermediate valence compound is affected by a change of its surroundings, the transitions at 105 K and 125 K should be elucidated. The thermal expansion coefficient shows volume expansion around 105 K and 125 K with decreasing temperature. Reflecting the expansion, the transition temperature decreases under pressures, and the transition at 105 K vanishes at 1.5 GPa [5]. Although the expansion suggests decrease of Yb valence, the valence did not show any change at these transitions [1]. Therefore, it is reasonable to consider that the anomalous thermal expansion is originated by successive structural transitions from the room temperature CsCl structure. However, any structural distortion has not been detected by neutron scattering [4] and Mössbauer measurement of¹⁷⁰Yb [2] which has a quadrupole moment in its excited nuclear state. These results suggest that structural distortion is, if any, quite small despite relatively high transition temperature. Such a small distortion would indicate that the transitions are not caused by structural instability.
Figure 1. Temperature dependence of $(x,x)$ Raman spectra.

Figure 2. Polarization dependence of Raman spectra on (100) surface at 4 K.

The transitions at 105 K and 125 K are still unclear. It is important whether or not the structure changes at the transitions, even for the magnetic ordered state below 1.9 K. Raman scattering measurement is one of the most sensitive tools to investigate changes of structure and symmetry. This paper reports the Raman scattering results of YbPd at low temperatures.

2. Experimental

The single crystal of YbPd was grown by a self-flux method under Ar atmosphere. Detailed method has been reported elsewhere. The crystal has a cubic shape with (100) surfaces. The transition temperatures at 105 K and 125 K became 110 K and 132 K, respectively, in this crystal. The reason for the increase of the transition temperatures is unknown. But the single crystal exhibits sharper transitions than the previous polycrystal sample does. The energy dispersive X-ray spectroscopy confirms that composition of the present single crystal is more stoichiometric. Thus, the quality of the single crystal is good.

Raman scattering spectra were measured using a triple-monochromator (JASCO NR-1800) with a liquid-N$_2$ cooled CCD detector (Princeton Instruments Inc. LN/CCD-1100PB). Excitation light was 514.5nm line of an Ar$^+$ laser and its power was 10 mW before a sample surface. For the measurements at low temperatures, a cryostat cooled by a GM cryocooler (SHI SRDK-205) was used.

We use the conventional description of Raman scattering geometry, such as $(x,y)$. $(x,y)$ means that polarization of the excitation light along $x$ is irradiated on the sample, and that polarization of scattered light along $y$ is measured. The propagation directions of light, $z$ or $\bar{z}$, are omitted, because the back-scattering geometry was used for all measurements.

3. Result and discussion

Evaluation of structural distortion using Raman scattering method is very simple in this case. YbPd has the CsCl structure at room temperature. Since the CsCl structure has no Raman active mode, if we observe any peak of phonon at low temperatures, we can conclude the
structural distortion. Figure 1 shows temperature dependence of Raman spectra for (x,x) geometry. As expected, there is no peak above 132 K, while at 4 K, two peaks are clearly observed at 60 cm$^{-1}$ and 91 cm$^{-1}$. In this energy region, possible elementary excitations are phonon or crystal field excitations of Yb$^{3+}$. The crystal field excitations have been reported at 38 cm$^{-1}$ and 99 cm$^{-1}$ by neutron inelastic scattering measurement[4]. These energies are different from ones observed by present study. Moreover, the polarization dependence of the 91 cm$^{-1}$ peak does not consist with polarization dependence expected for the crystal field excitations. Therefore, the observed peaks are phonon excitations. This result is a clear evidence of structural distortion from the CsCl structure. Since the peak at 90 cm$^{-1}$ was observed at least up to 120 K as shown in Fig. 1, the structural change occurs at the transition of 132 K. The peak at 60 cm$^{-1}$ appears at the lowest temperature. This appearance suggests the additional distortion occurs at a lower temperature.

Figure 2 shows polarization dependence of Raman spectra at 4 K. We focus on the 90 cm$^{-1}$ peak. This mode shows strong intensity whenever the polarization directions of the incident and scattered lights are parallel. This is the characteristic of the fully-symmetric representation $\Gamma_1$ among the irreducible representations. On the other hand, this mode was observed weakly in (x,y) spectra, while it was not observed in (x + y, x - y) spectra. From these results, we can write the Raman tensor $R$ in the two dimensional space on the (100) surface as,

$$R = \begin{pmatrix} a & c \\ c & b \end{pmatrix}.$$  \hspace{1cm} (1)

The intensity of the peak is described by $a^2$ for (x,x), $b^2$ for (y,y), $c^2$ for (x,y), and $(a-b)^2/4$ for (x + y, x - y). From the experimental results, we obtain $a = b$ and $c \neq 0$. From the form of the tensor $R$, the cubic symmetry is ruled out, since the tensor of $\Gamma_1$ is proportional to the unit matrix in all cubic symmetries, including $m\bar{3}$. In addition, the four-fold axis normal to the (100) surface is lost, since the four-fold axis exists, $c$ is exactly zero for $\Gamma_1$. The fact that the peak was not observed in the (x + y, x - y) spectra means that the tensor R becomes diagonal when principal axes are taken along the [110] directions. Therefore, principal axes on the surface become the [110] directions from the [100] ones. Since the four-fold axes do not lie along the [110] directions, all four-fold axes have vanished at 4 K. Consequently, the crystal symmetry is neither cubic nor tetragonal at 4 K. The possible symmetries are orthorhombic, rhombohedral, or their subgroups. Figure 3 summarizes the possible symmetries on the (100) surface at 4 K. Since the three-fold axes along [111] don’t lie on the (100) surface, we can not discuss their existence from the present study.

**Figure 3.** Symmetries on the (100) surface: a) at room temperature, b) at 4 K.
4. Conclusion
We have measured Raman spectra of YbPd single crystal in the temperature range from 4 K to 300 K. At 4 K, two peaks were clearly observed at 60 cm$^{-1}$ and 91 cm$^{-1}$, while no peak was found at 300 K. These peaks are clear evidence of structural distortion from the CsCl structure in YbPd. Since the peak at 90 cm$^{-1}$ has been observed up to 120 K, the structural distortion occurs at the 132 K transition. From the detailed measurements of polarization dependence on the (100) surface at 4 K, it is found that all four-fold axes vanish at low temperatures. Therefore, the crystal symmetry at 4 K is neither cubic nor tetragonal.

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