Valence-lattice interaction on YbPd

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Abstract. An intermediate valence compound YbPd undergoes successive structural transitions at 105 K and 125 K. The recent inelastic X-ray scattering measurement have revealed softening of longitudinal acoustic (LA) mode around X point, \(q = (0, 0, 0.5)\). We have attempted to reproduce this softening from first-principles calculations. The calculated results with fixed valence Yb do not show any anomaly in the LA mode around X. To include valence change in the lattice vibrations, the nearest-neighbor valence-lattice interaction has been added. The interaction reduces the energy of the LA mode around X as observed by the experiment. This soft mode leads to the structure below 105 K. On the other hand, the lowest energy is found at the slightly different wavevector, \(q = (0.1, 0.1, 0.5)\). This wavevector corresponds to the superlattice reflection observed by the experiment in the intermediate incommensurate phase between 105 K and 125 K. Therefore, the successive structural transitions of YbPd can be correctly reproduced by including this valence-lattice interaction.

1. Introduction

YbPd is an intermediate valence compound. The averaged valence of Yb is about +2.81. YbPd shows four transitions at 0.5, 1.9, 105, and 125 K, while LuPd does not show any transition1. One of the noticeable features of YbPd is that this compound undergoes successive structural transitions at 105 K and 125 K. Lattice distortions through these two transitions have been studied by Raman scattering2 and ultrasonic3, 4 measurements, and by pressure dependence of these transition temperatures5, 6, 7, 8, 9. Recently, the X-ray diffraction experiments have revealed the structures of the low-temperature phases10, 11. In phase I above 125 K, YbPd has the CsCl structure. In phase II between 105 K and 125 K, it is an incommensurate structure with the superlattice reflection at \(q_{\delta} = (\delta, \delta, 0.5)\), where \(\delta \sim 0.07\). In phase III below 105 K, it is the tetragonal structure with the superlattice reflection at X point, \(q_X = (0, 0, 0.5)\). These structural transitions are considered to be caused by the valence fluctuation of Yb. Therefore, it is expected that the phase III is the charge ordered phase. However, the averaged value of the Yb valence changes by quite small values around these transition temperatures1. This result has been confirmed by resonant X-ray diffraction analysis in the phase III, where the valences at two Yb cites are +3.0 and +2.611. The valence of a half of Yb still takes intermediate value
below 105 K. This fact will be important to think of anomalous behaviors of the transition at 0.5 K[1, 8, 9, 12].

Phonon dispersion curve of YbPd has been measured by inelastic X-ray scattering (IXS)[13]. It has elucidated that the responsible mode to the structural transitions is one of the longitudinal acoustic (LA) modes around X. The measurements show clear softening around X for the LA branch, while the transverse acoustic (TA) branches do not show any anomaly. This result is consistent with the structure in the phase III. The displacement of Pd in the phase III agrees with the LA mode displacement at X. This suggests that the soft LA mode is the origin of the structural transitions. If we take into account for the valence interaction of Yb, it is natural conclusion that the ordered structure has the NaCl-type arrangement of two kinds of Yb valences. This arrangement gives the superlattice reflection at R point, $q = (0.5, 0.5, 0.5)$. Therefore, the soft mode at X and the resultant phase III structure strongly suggests that the interaction between lattice and Yb valence are important.

To investigate an effect of such valence-lattice interaction (VLI) in YbPd, we have performed first-principles calculations of phonon dispersion curve in the local density approximation (LDA). Since it is difficult to treat correctly the local nature of Yb valences in LDA, the Yb valence has been fixed in the LDA calculations. After those calculations, the effect of the valence change on the lattice vibrations is added to the LDA result as the VLI term. Thus, the phonon dispersion curves including VLI are obtained, and the effect of VLI is discussed.

2. Calculation method
The phonon dispersion curves have been obtained by using ABINIT package[14, 15, 16], which can calculate electronic states based on the density functional theory[17, 18] with the plane-wave basis set. We have used LDA potential parameterized by Perdew and Wang[19] for the exchange-correlation energy and the norm-conserved pseudo-potentials[20] generated by fhi98PP[21]. The cut-off energy of plane-wave basis is 24 Ha, where 1 Ha = 27.21 eV. The integration in the reciprocal space is performed on the $8 \times 8 \times 8$ Monkhost-Pack grid[22]. Since YbPd is a metal, cold smearing method[23] is used for occupation number broadening with the smearing temperature, 0.04 Ha. To calculate phonon dispersion curves, the density functional perturbation theory[24] is used to calculate dynamical matrices. The inter-atomic force constants (IFC’s) are obtained from the dynamical matrices by the Fourier transform on the $4 \times 4 \times 4$ simple grid. The phonon dispersion curves are calculated using the IFC’s.

In this paper, the 4f-electrons of Yb is included in the core state, and is not used in the cycle of self-consistent loop of electronic state calculations. The f-orbital renormalized in our calculations is 5f-orbital. The 5f-orbital is almost empty, because of its high energy. This means that orbital freedom of f-electrons is not considered, and that 4f-electron distribution is sphere. The number of f-electrons is fixed, and it determines the valence of Yb. If 13 f-electrons are in the core state, the number of valence electrons is 3. The Yb atom using this Yb pseudo-potential is called Yb$^{3+}$ in this paper. The Yb$^{2+}$ pseudo-potential has 14 f-electrons in the core state. To obtain reasonable results, the semi-core states must be included in the calculation. Two electrons of 5s-orbital and six electrons of 5p-orbital are treated as valence electrons in the case of Yb. Therefore, the Yb pseudo-potentials are created for 5s, 5p, 5d, and 5f orbital, and Yb$^{3+}$ and Yb$^{2+}$ have 11 and 10 valence electrons, respectively. The Pd pseudo-potential is made for 5s, 5p, and 4d orbital, and Pd has 10 valence electrons.

3. Results and discussion
The calculations have been performed for the cubic CsCl type structure in the phase I. Its space group is Pm3m, the atomic positions of Yb and Pd are $(0, 0, 0)$ and $(0.5, 0.5, 0.5)$, respectively. At first, the lattice constant was optimized by the ground state calculations for Yb$^{2+}$Pd and Yb$^{3+}$Pd. It is 3.393 Å and 3.372 Å for Yb$^{2+}$Pd and Yb$^{3+}$Pd, respectively. Using these lattice
constants, the phonon dispersion curves were calculated. These results will be called as LDA results, as contrasted with the result including VLI. The calculated phonon dispersion curves are shown in Fig. 1. Both of Yb$^{2+}$Pd and Yb$^{3+}$Pd do not show softening behavior in the LA mode around X. As expected, the freedom of Yb valence change is important to reduce the LA mode energy around X. On the other hand, weak anomalous softening is found around $q = (0.35, 0.35, 0.35)$ and around $q_{RX} = (0.15, 0.15, 0.50)$, as shown in Fig. 1 by arrows. These anomalies are also found in the calculated phonon dispersion of LuPd (not shown here) at slightly different wavevectors. These anomalies will relate to their electronic band structure. As shown later, the anomaly at $q_{RX}$ plays important role in the presence of the incommensurate phase II, and is called as $q_{RX}$ anomaly.

An interaction between atomic displacement and Yb valence change will be considered. A large effect of valence change $\delta \rho_i$ of an Yb atom $i$ will be treated as the change of Hartree term, $A \delta \rho_i / d_{ji}$, where $d_{ji}$ is a distance to an atom $j$ and $A$ is a constant. For simplicity, only the nearest-neighbor interactions are considered. Then, an atom $j$ is one of the 8 Pd atoms surrounding the Yb atom $i$. The distance $d_{ji}$ is expanded by atomic displacement $u_i$ up to its first-order term. Therefore, the change of the Hartree term, $H_{VLI}$, can be written as,

$$H_{VLI} = \sum_{i \in \text{Yb}} \sum_{j \in \text{n.n. Pd}} A \delta \rho_i \cdot u_j \cdot e_{ji},$$

where $e_{ji}$ is the unit vector from the atom $i$ to the atom $j$. It is important fact that the summation of $j$ is taken only for the nearest-neighbor Pd atoms. The term proportional to the Yb displacement $u_i$ vanishes after the summation of $j$. Therefore, the VLI is acted between Yb valence change $\delta \rho_{Yb}$ and Pd displacement $u_{Pd}$. Finally, applying Fourier transformation of $\delta \rho_i$ and $u_j$, we obtain,

$$H_{VLI} = \int d^3 q \, \delta \rho_{Yb}(q)^* \, C(q) \cdot u_{Pd}(q),$$

Fig. 1. The phonon dispersion curves of Yb$^{3+}$Pd (solid line) and Yb$^{2+}$Pd (dashed line) obtained from the first-principles calculations with the Yb valence fixed. There is no anomaly in the LA mode along $\Delta$ line, while weak anomalies are seen in both curves as shown by arrows.
where \( C(q) \) is the vector coefficient which depends on wavevector \( q \), that is,

\[
C(q) = \begin{pmatrix}
K \sin \pi q_x a & \cos \pi q_y a & \cos \pi q_z a \\
K \cos \pi q_x a & \sin \pi q_y a & \cos \pi q_z a \\
K \cos \pi q_x a & \cos \pi q_y a & \sin \pi q_z a
\end{pmatrix},
\]

where \( K \) is a constant proportional to \( A \). To use this term to calculate lattice dynamics, we need to know dynamics of valence fluctuation. As the term \( H_{VLI} \) is a perturbation term for \( \delta \rho_{Yb}(q) \), its reaction can be written approximately as linear response to the potential change \( \delta V(q) = \partial H_{VLI}/\partial \delta \rho_{Yb}(q) \).

\[
\delta \rho_{Yb}(q) = -\chi \delta V(q) = -\chi C(q) \cdot u_{Pd}(q),
\]

where we ignore \( q \)-dependence and frequency-dependence of charge susceptibility \( \chi \). In this definition, \( \chi \) is positive, because negative potential \( V \) increases the charge \( \rho \). The \( q \)- and \( \omega \)-dependencies of \( \chi \) will be important, and some evidences of its effect might be observed in the IXS spectra[13] as the broadened peak of the LA mode and as the broad low-energy background.

To substitute Eq. (4) in Eq. (2), we get the final form of \( H_{VLI} \).

\[
H_{VLI} = -\int d^3q \chi |C(q) \cdot u_{Pd}(q)|^2.
\]

This term takes the same form as that of dynamical matrices. Therefore, adding the term to the dynamical matrices obtained from LDA calculations, we can draw phonon dispersion curves with the valence fluctuation effect. This model will be called as LDA+VLI, and has only one parameter, \( \chi |K|^2 \). Here, \( |K|^2 \) is fixed and \( \chi \) is varied. As expected, the energy of the LA mode at \( X \) decreases with increasing \( \chi \). We define \( \chi_0 \) as the \( \chi \) value when the LA mode energy becomes 0.

Figure 2 shows the phonon dispersion curve calculated by LDA+VLI with \( \chi = 0.90\chi_0 \) and with IFC’s of Yb\(^{2+}\)Pd. It is seen that the LA mode energy around \( X \) is much reduced, while the TA modes are almost independent of VLI. The experimental data by IXS measurement[13] at room temperature are also plotted in Fig. 2. The agreement between our model and experimental data is quite well, except for the LA modes around \( q = (0.25, 0, 0) \). The experimental data changes rather sharp in \( q \). This discrepancy will be originated from long-range VLI or \( q \)- and \( \omega \)-dependences of \( \chi \).

It is a noticeable result of our model that the modes at a slightly different wavevector from \( X \) get lower energy. At lower temperatures, the energy at \( X \) becomes lower than that at \( q_5 \). Then, the structure changes to that in the phase III. Thus, this LDA+VLI model can reproduce successive structural transitions. The presence of the phase II needs the collaboration of VLI and electron-lattice interaction in LDA. Since the \( q_{RX} \) anomaly is also present for Yb\(^{3+}\)Pd, the incommensurate phase is also derived with VLI and IFC’s of Yb\(^{3+}\)Pd. Therefore, the conclusions are independent of valence of the Yb pseudo-potential, though \( \delta \) of \( q_5 \) and transition temperatures depends on it.
Figure 2. The phonon dispersion curve including the term $H_{VLI}$ with $\chi = 0.90\chi_0$ and with IFC’s for Yb$^{3+}$Pd. The filled and open circles are experimental data of IXS[13] for longitudinal modes and transverse modes, respectively. The LA mode energy around X is much reduced by $H_{VLI}$. However, the energy minimum is taken at (0.1, 0.1, 0.5) by the effect of the anomaly in Yb$^{3+}$Pd at (0.15, 0.15, 0.50).

The VLI depends on displacements of Pd, not those of Yb. The VLI reduces energies of Pd vibrations. Optical modes are less affected, since most of these modes are vibrations of Yb atoms. The VLI is the function of inner products $C \cdot u$. As $C$ is parallel to $q$ along the directions with high symmetry, e.g. $\Delta$, $\Lambda$, and $\Sigma$ lines, the VLI cannot change transverse mode energies, while it decreases the energies of the longitudinal modes. $q$-dependence of VLI is estimated by $|C(q)|^2$. From Eq. (3), $|C(q)|^2$ takes the maximum value, $|K|^2$, at X, and the minimum value, 0, at M, R, and $\Gamma$. It is an important result that $C(0) = 0$. The averaged valence change $\delta \rho(0)$ is proportional to $C(0)$ from Eq. (4). Therefore, the result that $C(0) = 0$ leads to the conclusion that the structural transition shows no change in the averaged valence value through the VLI considered in this paper. This conclusion is consistent with the experimental result that the change of Yb valence is much smaller than that expected[1].

Another important result is that $|C(q)|^2$ takes the maximum at X. Therefore, at low temperatures with large $\chi$, the structure derived from the LA mode at X will appear, as discussed above. In the LA mode at X, only Pd moves parallel to the wavevector $q_X = (0, 0, 0.5)$. Then, the unit cell becomes tetragonal with doubled lattice parameter along $c$ axis. Yb atoms locate on $(0, 0, 0)$ and $(0, 0, 0.5)$, and Pd atoms locate on $(0.5, 0.5, z)$ with $z \sim 0.25$. The parameter $z$ corresponds to the displacement of the LA mode at X. This structure is consistent with the experimental result in the phase III[11, 13].

4. Conclusion
We have performed the first-principles calculations of phonon dispersion curves on YbPd with Yb valence fixed in LDA level, and have attempted to include valence fluctuation freedom by adding the VLI term $H_{VLI}$ to the dynamical matrices obtained from LDA calculations. The LDA result shows no anomaly around X point, but weak anomaly at $q_{RX}$. The VLI term reduces dramatically the energy of the LA mode around X. Since the effect of the VLI term
takes maximum at X, the VL1 term leads to the structure in the low-temperature phase III. However, the phonon energy becomes 0 at a slightly different point, $(0.1, 0.1, 0.5)$, before the energy at X becomes 0, because of the effect of $q_{RX}$ anomaly. This wavevector corresponds to the structure in the intermediate phase II. Therefore, our model can reproduce successive structural transitions correctly.

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