Electronic Structure of the Novel Filled Skutterudite $PrPt_4Ge_{12}$ Superconductor

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We have performed soft x-ray photoemission spectroscopy (SXPES) and resonant photoemission spectroscopy (RPES) of the filled skutterudite superconductor $PrPt_4Ge_{12}$ in order to study the electronic structure of valence band and the character of Pr $4f$. SXPES of $PrPt_4Ge_{12}$ measured with 1200 eV photon energy, where spectral contribution of Pr $4f$ is negligible, was found nearly identical with that of $LaPt_4Ge_{12}$, indicating similarity of Pt-Ge derived electronic states of the two compounds. Good correspondence with band calculations allows us to ascribe the dominant Ge $4p$ character of the density of states at the Fermi level (E_F). Pr $3d \rightarrow 4f$ RPES shows that, although Pr $4f$ electrons in $PrPt_4Ge_{12}$ are not as strongly hybridized with conduction electrons near E_F as in $PrFe_4P_{12}$, there are finite Pr $4f$ contribution to the states near E_F in $PrPt_4Ge_{12}$. These PES results give the information of fundamental electronic structure for understanding the physical properties of the novel filled skutterudite superconductor $PrPt_4Ge_{12}$.

KEYWORDS: $PrPt_4Ge_{12}$, filled skutterudite, superconductor, soft x-ray photoemission spectroscopy, Pr $3d \rightarrow 4f$ resonant photoemission, electronic structure

1. Introduction

The filled skutterudite compounds MT_4X_{12} (M as rare-earth or alkaline-earth metals, T as a transition metal and X as usually a pnicogen) have attracted much attention because of the variety of the physical properties that depend on the combination of M, T and X.[1,2] Recently, several new filled skutterudite compounds with a Pt-Ge framework have been successfully synthesized one after another,[3–6] constituting a new family of the filled skutterudite compounds.

$PrPt_4Ge_{12}$ is one of the Pt-Ge based filled skutterudite compounds with Pr atoms and exhibits superconductivity below the superconducting transition temperature T_c of 7.9 K,[4] unexpectedly high among the filled skutterudite superconductors containing Pr $4f$ electrons. A slightly smaller T_c of $PrPt_4Ge_{12}$ than that of $LaPt_4Ge_{12}$, non $4f$ counterpart of $PrPt_4Ge_{12}$, in spite of a smaller lattice constant of $PrPt_4Ge_{12}$ than that of $LaPt_4Ge_{12}$ is opposite to the simple expectation for T_c vs a lattice constant, implying need for other parameters for determining the superconductivity. The specific heat jump at T_c and superconducting gap values of $PrPt_4Ge_{12}$ are larger than those of $LaPt_4Ge_{12}$ which are close to the mean field BCS values, indicating strong-coupling superconductivity of $PrPt_4Ge_{12}$. More recently, the electronic specific heat and muon-spin rotation (μSR) measurements down to very low temperatures suggested the presence of pointlike nodes in the superconducting energy gap.7) On the other hand, NMR studies of $LaPt_4Ge_{12}$, its non $4f$ counterpart, suggested a conventional BCS-type superconductivity from nuclear spin-lattice relaxation rates $1/T_1$ of ^{195}Pt and ^{139}La under magnetic fields,8) though very recent NQR studies of $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$ reporting a marked difference of temperature dependence of $1/T_1$ of ^{73}Ge at a zero field could not conclude the highly anisotropic superconducting gap of $PrPt_4Ge_{12}$ nor the difference of superconducting gap structure between the two compounds.9) Some of these results seem to indicate the importance of 4 f electrons for the novel superconductivity in $PrPt_4Ge_{12}$.

In general, the Pr $4f$ electrons are thought to be more localized and less hybridized with conduction electrons than Ce $4f$ electrons due to their larger binding energies. This supports the fully localized treatment of Pr $4f$ in the band structure calculations of $PrPt_4Ge_{12}$.4) However in the case of the filled skutterudites, the large coordination number of 12 may fully compensate relatively weak hybridization, leading to strong effective hybridization.2) Indeed Kondo-like behaviors in the transport properties were observed for $PrFe_4P_{12}$.10) A strong $4f$-derived photoemission spectral intensity at the Fermi level (E_F) observed for $PrFe_4P_{12}$ was discussed in terms of the strong hybridization between the Pr $4f$ and the conduction electrons in the ground state, although the experimental non $4f$ valence band similar to calculated one indicated that the localized $4f$ model is a good starting point even for this compounds.11) Therefore direct observation of the electronic structure of $PrPt_4Ge_{12}$ is valuable in understanding the character of Pr $4f$ electrons as well as the valence band electronic structure, as a first step toward understanding the superconductivity in $PrPt_4Ge_{12}$.

In this study, we employed soft x-ray photoemission spectroscopy (SXPES) and resonant photoemission spectroscopy (RPES) in order to study the valence band and character of Pr $4f$ electrons of $PrPt_4Ge_{12}$. Soft x-ray valence band PES of $PrPt_4Ge_{12}$ and $LaPt_4Ge_{12}$ measured with the photon energy at 1200 eV show nearly identical spectra, which indicates the electronic structure derived from the Pt-Ge framework for both materials are almost the same. The RPES of $PrPt_4Ge_{12}$ and comparison with those of other filled skutterudite compounds with Pr atoms shows that, although Pr $4f$ electrons in $PrPt_4Ge_{12}$ are not as strongly hybridized with conduction electrons as in $PrFe_4P_{12}$, there are finite Pr $4f$ contribution to the states near E_F in $PrPt_4Ge_{12}$.

2. Experimental

Polycrystalline samples of $\mathrm{PrPt_4Ge_{12}}$ and $\mathrm{LaPt_4Ge_{12}}$ were prepared by a conventional arc-melting method using a nonconsumable tungsten electrode in atmosphere of high-purity argon (99.999%). The casted samples were repeatedly melted on a water-cooled copper hearth for homogeneity. No contamination from the electrode and the copper hearth was detected and the weight loss by the process was negligible. Then, the arc-melted samples were annealed at 1073 K for 24 h under a vacuum of 1×10^{-7} Torr. It was confirmed that they consisted of a single phase of $\mathrm{PrPt_4Ge_{12}}$ or $\mathrm{LaPt_4Ge_{12}}$ by analyses using an X-ray diffractometer. T_c's of $\mathrm{PrPt_4Ge_{12}}$ and $\mathrm{LaPt_4Ge_{12}}$ samples determined from magnetic susceptibility measurements were 7.9 and 8.2 K, respectively.

SXPES, RPES and soft x-ray absorption spectroscopy (XAS) were carried out at BL2C, KEK-PF, measured at 20 K and under an ultrahigh vacuum of better than 1×10^{-10} Torr. PES measurements were done with a SES2000 analyzer with total energy resolutions setting to 200-300 meV depending on the photon energies. XAS measurements with a total electron yield mode were also performed for the same samples. Clean sample surfaces for PES and XAS measurements were obtained with in-situ fracturing of samples at 20 K.

3. Results and Discussion

Figure 1 shows the valence band photoemission spectrum of $\mathrm{PrPt_4Ge_{12}}$ taken with 1200 eV photon energy, together with that of $\mathrm{LaPt_4Ge_{12}}$. The spectra are normalized to the intensity of the highest peak at 4.0 eV. The spectrum of $\mathrm{PrPt_4Ge_{12}}$ (bottom) is characterized with a prominent peak at 4.0 eV with a shoulder structure around 5.5 eV. It also has weak structures at 0.8, 2.1, 7.2 and 8.8 eV, as indicated with thick bars. These spectral features are also found in the spectrum of $\mathrm{LaPt_4Ge_{12}}$ (middle). A superposition of the two spectra (top) shows that the spectrum of $\mathrm{PrPt_4Ge_{12}}$ is nearly identical to that of $\mathrm{LaPt_4Ge_{12}}$, in spite of the difference in the M atoms. Since the expected photoelectron intensity of Pr $4f$ taking into account the ionization cross section12) and numbers of electrons in the unit cell is much smaller than those of Pt $5d$ and of Ge $4s$ and $4p$ for 1200 eV photon energy (Pr $4f$: Pt $5d$: Ge $4s$: Ge $4p$ = 1 : 66.7 : 3.1 : 1.7), the contribution of spectral intensity from Pr $4f$ electrons is negligible. Thus nearly identical spectral shape of the two compounds is mostly due to the similarity of their identical electronic structures derived from the Pt-Ge framework. Moreover, the PES spectrum of $\mathrm{SrPt_4Ge_{12}}$ also shows a very similar spectral shape,13) indicating that the electronic structure derived from the Pt-Ge framework is independent of M atoms in the filled skutterudite compounds in the first approximation.

For the spectrum of $\mathrm{PrPt_4Ge_{12}}$, we found that the whole spectral shape is similar to the total density of states calculated with fully localized treatment for Pr $4f$ (see Fig. 4 in Ref. 4). According to the calculations, the low-lying bands between 6 and 12 eV are predominantly bonding Ge $4s$ states. The majority of Pt $5d$ states is located between 2.5 and 5.5 eV binding energy and hybridizes strongly with the Ge 4p orbitals. The states at E_{F} are mainly (about 80%) due to Ge 4p bands. Good agreement of the experimental spectral shape with calculations allow us to make following assignments: the prominent structure around 5 eV is Pt 5d derived states hybridized with Ge 4p states. The structures of the higher binding energy side than the prominent structure is Ge 4s bands. Therefore, the structures near E_{F}, responsible for the superconductivity, are mainly Ge 4p bands.

While the PES studies of valence band spectra that mainly reflect electronic states derived from the Pt-Ge framework implied small influence of Pr 4f electrons to the valence band, RPES across the Pr 3d → 4f threshold, which measures the Pr 4f partial density of states, may provide more direct information on the character of Pr 4f. Photon energies used for RPES are indicated with arrows (A-H) on the Pr 3d → 4f XAS shown in Fig. 2(a). Note that the spectral shape of the XAS spectrum reflects a predominant $\mathrm{Pr}^{3+}(4f^2)$ character in the initial state.[14] The spectrum A in Fig. 2(b) is taken at photon energy A in Fig. 2(a), well bellow the onset of the Pr 3d → 4f absorption and thus represents an off-resonance spectrum. It shows a prominent peak at 4.0 eV and a shoulder around 5.5 eV, similar to the spectrum obtained with 1200 eV discussed above. The spectral shape at photon energy B is similar to that at A. As photon energy is further increased, intensity at 4.5 eV starts to increase at C, becomes maximum at E, and decreases for higher photon energy till G. The intensity variation around 4.5 eV binding energy of RPES spectra follows that of XAS spectrum [diamonds in Fig. 2(b)], indicating its Pr 3d → 4f resonant enhancement. The peak at 4.5 eV in the on-resonance spectrum (E) can be attributed to Pr $4f^1$ final states. It is noted that the peak has a shoulder structure around a 3.5 eV binding energy. This is not an atomiclike multiplet structure of Pr $4f^1$ in the final state, since the spin-orbit split Pr $4f^1$ final state consists basically of the j = 5/2 components, where the intensity of the j = 7/2 component is only 10 % of that of the j = 5/2 component and the binding energy of the small j = 7/2 component is higher than that of the large j = 5/2 component.[15] In compounds of Pr with transition metals, such a non-symmetric (or even a splitting) 4f spectra have been observed and attributed to hybridization of 4f states with transition metal d states in the final state.[16] A peak with a shoulder structure observed in $\mathrm{PrPt_4Ge_{12}}$ indicates an importance of the hybridization of Pr 4f states with Pt 5d states in the final state.

As for the binding energy region below 3 eV, we find another enhanced structure around the absorption maximum (D and E), as indicated with thick bars, whose binding energy shifts with photon energy. The binding energy shift (0.5 eV) of the peak between D and E is smaller than the difference (1.2 eV) of the photon energy. This may indicate that the transition from resonant Raman behavior to Auger-like regime occurs between D and E.[17] Similar behavior has been observed for $\mathrm{PrOs_4Sb_{12}}$, and the possibility that it shows intermediate states dependence was discussed.[18] In on-resonance spectra of Pr metal and Pr transition metal compounds,[15)] small enhancements near E_{F} was ascribed to an f-d decay of the intermediated states of the RPES process competing with the f-f decay. It should be noticed, however, that it can be also generated by the appearance of an additional $4f^{\mathrm{n}}$ final state from admixture of the $4f^{\mathrm{n}+1}$ configuration to the ground state.

It may be interesting to compare the RPES results with those of other filled skutterudite compounds with Pr in order to look at the hybridization between Pr $4f$ and conduction electrons in the ground state. In the heavy fermion filled skutterudite $\mathrm{PrFe_4P_{12}}$, a predominant peak close to E_{F} in the on-resonant spectrum was observed and attributed to originate from the strong hybridization between the Pr $4f$ and the conduction electrons. Absence of a predominant peak at E_{F} in the on resonance spectrum (E) of $\mathrm{PrPt_4Ge_{12}}$ is similar to $\mathrm{PrRu_4P_{12}}$, $\mathrm{PrRu_4Sb_{12}}$ and $\mathrm{PrOs_4Sb_{12}}$, but is different from that of $\mathrm{PrFe_4P_{12}}$, implying that the Pr $4f$ electrons in $\mathrm{PrPt_4Ge_{12}}$ are not as strongly hybridized with conduction electrons (or, itinerant) as those in $\mathrm{PrFe_4P_{12}}$.[11,18)] It is noted that the origin of the strong mass enhancement in $\mathrm{PrOs_4Sb_{12}}$ has been considered different from that in $\mathrm{PrFe_4P_{12}}$.[19)] In comparison with RPES of $\mathrm{PrOs_4Sb_{12}}$, the resonance behaviors of two compounds are rather similar as mentioned above.[18)] For $\mathrm{PrOs_4Sb_{12}}$, an Auger-like peak near E_{F} and correspondingly high intensity at E_{F} were observed for photon energies slightly below the one giving the highest intensity in the XAS spectrum. By comparing with RPES spectra of the presumably localized $4f$ system $\mathrm{Pr_4Sb_3}$, larger hybridization between Pr $4f$ and conduction electrons in $\mathrm{PrOs_4Sb_{12}}$ than that in $\mathrm{Pr_4Sb_3}$ was suggested.[18)] For $\mathrm{PrPt_4Ge_{12}}$, we find that the intensity at E_{F} also exhibits a small but finite enhancement near the Pr $3d \rightarrow 4f$ edge [open circles in Fig. 2(a)] that leads to comparable intensity at E_{F} to that of the f^1 final-state peak at 4.5 eV binding energy for D. The similarity in RPES results implies a similarity in electronic states between the two compound. If the observed enhancement is attributed to the admixture of the $4f^{\mathrm{n}+1}$ configuration to the ground state, present results indicate that, although Pr $4f$ electrons of $\mathrm{PrPt_4Ge_{12}}$ have a more localized-like character than $\mathrm{PrFe_4P_{12}}$, there can be some hybridization of Pr $4f$ with the conduction electrons which make a finite Pr $4f$ contribution for the states near E_{F} in $\mathrm{PrPt_4Ge_{12}}$. This might play some roles for the superconductivity in $\mathrm{PrPt_4Ge_{12}}$ with interesting behavior.[20)]

4. Summary

We have performed valence band SXPES of $\mathrm{PrPt_4Ge_{12}}$ and $\mathrm{LaPt_4Ge_{12}}$ and Pr $3d \rightarrow 4f$ RPES of $\mathrm{PrPt_4Ge_{12}}$. The SXPES study supports the expectation of the dominate Ge $4p$ character of the density of states at E_{F}. The very similar valence band spectral shape of $\mathrm{PrPt_4Ge_{12}}$, $\mathrm{LaPt_4Ge_{12}}$ and $\mathrm{SrPt_4Ge_{12}}$,[13)] indicates that the Pt-Ge derived electronic structure is universal. The PRES study of the new filled skutterudite superconductor $\mathrm{PrPt_4Ge_{12}}$ indicates that, although Pr $4f$ electrons in $\mathrm{PrPt_4Ge_{12}}$ are not as strongly hybridized with conduction electrons as in $\mathrm{PrFe_4P_{12}}$, there are finite Pr $4f$ contribution to the states near E_{F}

in $PrPt_4Ge_{12}$. The present SXPES results provide key electronic features in understanding the novel superconducting filled skutterudite $PrPt_4Ge_{12}$.

5. Acknowledgements

Acknowledgements: We thank Prof. K. Okada for valuable discussion. This work was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Heavy Electron" (No. 20102003) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. PES measurement were performed under the project 0852-003 and 09G545 at the Institute of Materials Structure Science in KEK. R. Y. acknowledges the financial support from Research Fellowship of the Japan Society for the Promotion of Science.

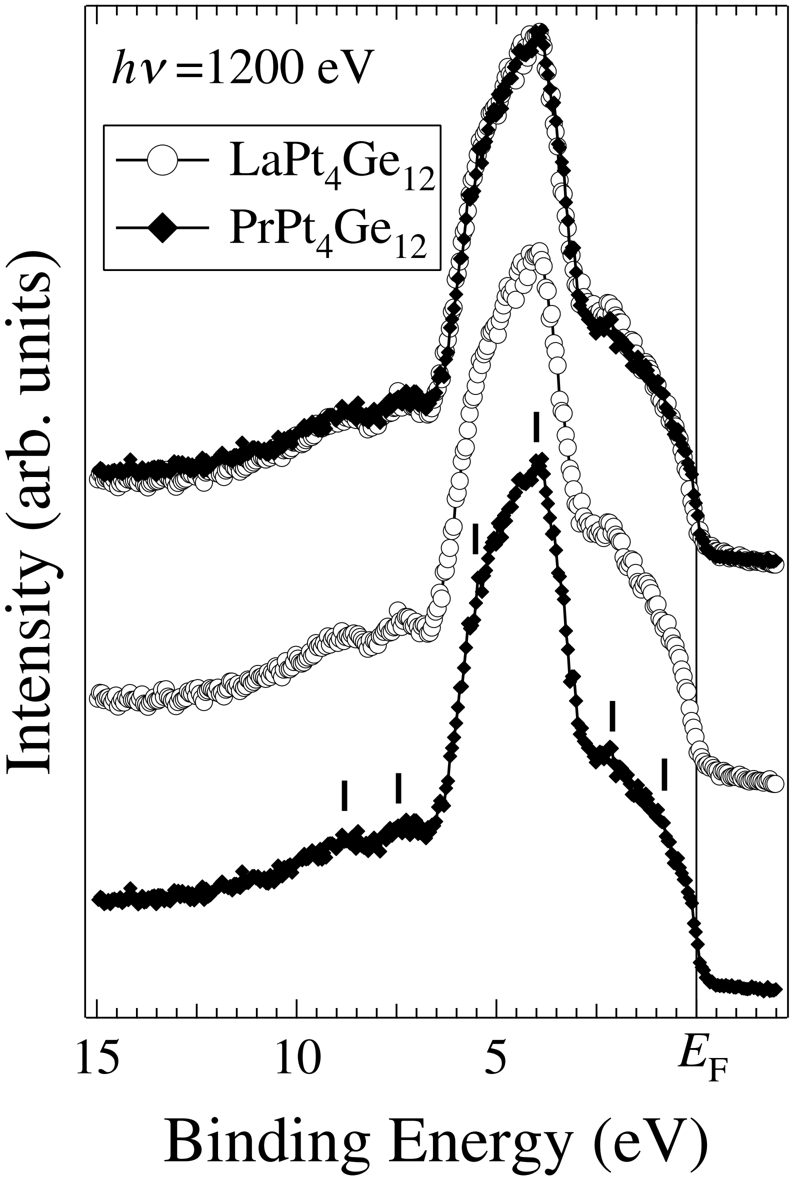

Fig. 1. Soft x-ray photoemission spectra of $PrPt_4Ge_{12}$ (bottom) and $LaPt_4Ge_{12}$ (middle) measured at 20 K and with a photon energy of 1200 eV. Note that nearly identical spectral shape of the two spectra (top).

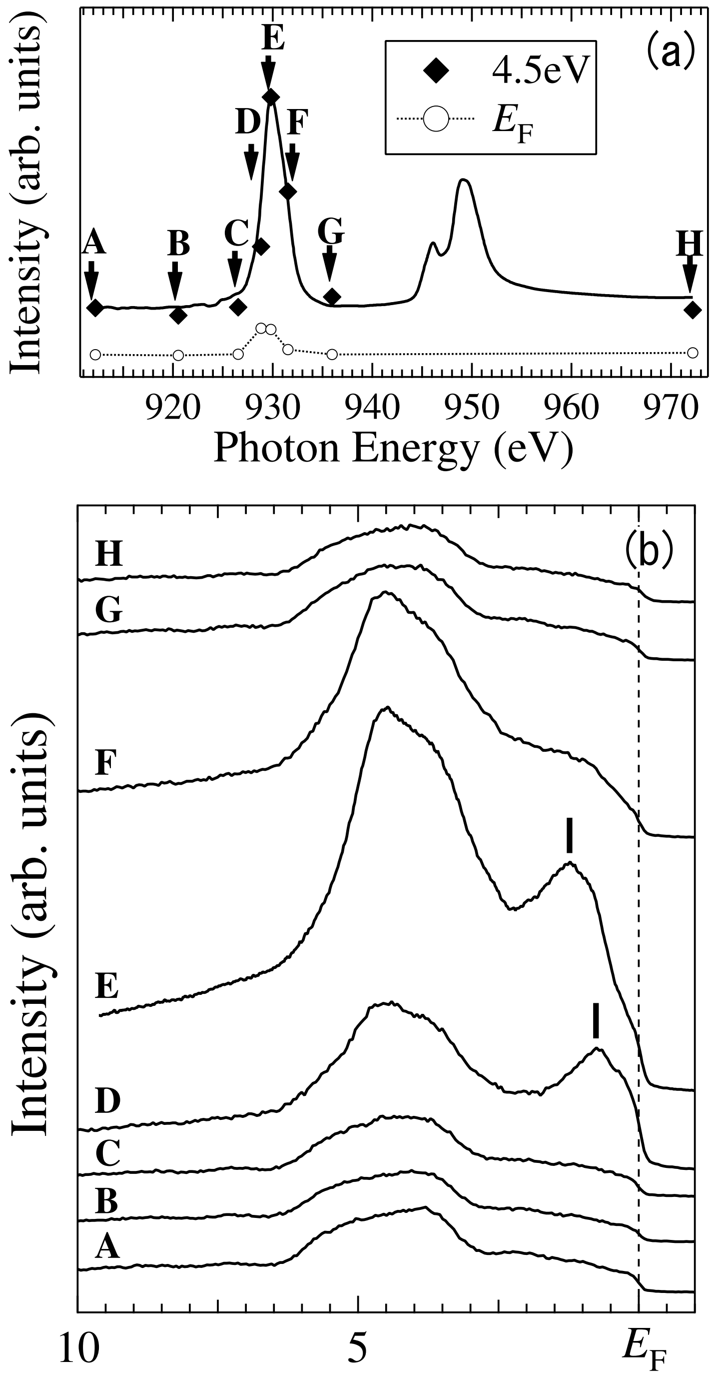

Fig. 2. (a) Pr $3d \rightarrow 4f$ x-ray absorption spectrum and (b)Resonant photoemission spectra of $PrPt_4Ge_{12}$ across Pr $3d \rightarrow 4f$. RPES spectra denoted with A-H are measured at photon energies indicated by arrows A to H on the XAS spectrum, respectively. Open circles and filled diamonds are the intensities at E_F and 4.5 eV binding energy of the RPES spectra.

References

1) B. C. Sales: in Handbook on the Physics and Chemistry of Rare Earths, ed K.A. Gschneidner, Jr., J.-C. G. Bunzli, and V.K. Pecharsky (Elsevier, Amsterdam, 2003) Vol. 33, pp. 1-34, and references therein.
2) Y. Aoki, H. Sugawara, H. Hisatomo and H. Sato: J. Phys. Soc. Jpn. **74** (2005) 209, and reference therein.
3) E. Bauer, A. Grytsiv, Xing-Qiu Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, R. Podloucky, and P. Rogl: Phys. Rev. Lett. **99** (2007) 217001.
4) R. Gumeniuk, W. schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, Yu. Grin: Phys. Rev. Lett. **100** (2008) 017002.
5) D. Kaczorowski and V. H. Tran: Phys. Rev. B **77** (2008) 180504.
6) E. Bauer, X.-Q. Chen, P. Rogl, G. Hilscher, H. Michor, E. Royanian, R. Podloucky, G. Giester, O. Sologub, and A. P. Gonçalves: Phys. Rev. B **78** (2008) 064516.
7) A. Maisuradze, M. Nicklas, R. Gumeniuk, C. Baines, W. Schnelle, H. Rosner, A. Leithe-Jasper, Yu. Grin, and R. Khasanov: Phys. Rev. Lett. **103** (2009) 147002.
8) M. Toda, H. Sugawara, K. Magishi, T. Saito, K. Koyama, Y. Aoki, and H. Sato: J. Phys. Soc. Jpn **77** (2008) 124702.
9) F. Kanetake, H. Mukuda, Y. Kitaoka, K. Magishi, H. Sugawara, K. M. Itoh and E. E. Haller: J. Phys. Soc. Jpn. **79** (2010) 063702. J. Phys. Soc. Jpn. **79** (2010) 063702.
10) H. Sato, Y. Abe, H. Okada, T. D. Matsuda, K. Abe, H. Sugawara, and Y. Aoki: Phys. Rev. B **62** (2000) 15125.
11) A.Yamasaki, S. Imada, T. Nanba, A. Sekiyama, H. Sugawara, H. Sato, C. Sekine, I. Shirotani, H. Harima, and S. Suga: Phys. Rev. B **70** (2004) 113103.
12) J. J. Yeh and I. Lindau: Atomic Data and Nuclear Data Tables **32** (1985) 1.
13) H. Rosner, J. Gegner, D. Regesch, W. Schnelle, R. Gumeniuk, A. Leithe-Jasper, H. Fujiwara, T. Haupricht, T. C. Koethe, H.-H. Hsieh, H.-J. Lin, C. T. Chen, A. Ormeci, Yu. Grin, and L. H. Tjeng: Phys. Rev. B **80** (2009) 075114.
14) B. T. Thole, G. van der Laan, and J. C. Fuggle: Phys. Rev. B **32** (1985) 5107.
15) Yu. Kucherenko, M. Finken, S. L. Molodtsov, M. Heber, J. Boysen, G. Behr, and C. Laubschat: Phys. Rev. B **66** (2002) 165438.
16) P. A. Cox, J. K. Lang and Y. Bear: J. Phys. F: Metal Phy. **11** (1981) 113-119.
17) M. Weinelt, A. Nilsson, M. Magnuson, T. Wiell, N. Wassdahl, O. Karis, A. Föhlisch, and N. Mårtensson: Phys. Rev. Lett. **78** (1997) 967-970.
18) S. Imada, Y. Fukuda, A. Yamasaki, A. Sekiyama, H. Sugawara, H. Sato, A. Ochiai and S. Suga: J. Elect. Spec. Relat. Phenom. **144 – 147** (2005) 651-653.
19) H. Sato, D. Kikuchi, K. Tanaka, M. Ueda, H. Aoki, T. Ikeno, S. Tatsuoka, K. Kuwahara, Y. Aoki, M. Kohgi, H. Sugawara, K. Iwasa, and H. Harima: J. Phys. Soc. Jpn. **77** (2010) Suppl. A 1.
20) PES measures one electron removal spectra, which are to be exact different from the ground state. However, structures near E_{F} of a PES spectrum correspond to well-screed states that may be similar to the ground state. Final state multiplet structures of Pr $4f^2$ states have only small contribution to the intensity near E_{F}, as the first excited states is located at 300 meV binding

energy, which is larger than the half of energy resolution of RPES studies (100 meV). These considerations suggest that the observed enhancement at E_{F} may be able to be discussed in relation to superconductivity that is a ground state property.