Valence instability in $YbPd_2Si_2$:
Magnetic susceptibility, x-ray absorption, and photoemission studies

E. V. Sampathkumaran,* K. H. Frank, G. Kalkowski, G. Kaindl,
M. Domke, and G. Wortmann

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany
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The bulk and surface valence states of Yb were determined for the intermetallic compound $YbPd_2Si_2$ by magnetic susceptibility (χ), L_{III}-edge x-ray absorption, and valence-band photoemission measurements. In the susceptibility data this compound exhibits the characteristic features of homogeneously mixed-valent systems: enhanced Pauli paramagnetism at low temperatures, a maximum in χ at about 30 K, and Curie-Weiss behavior at high temperatures. The observed temperature dependence of χ is discussed in light of interconfigurational fluctuation (ICF) as well as Fermi-liquid models. The mixed-valent state of Yb is also borne out in the L_{III}-edge x-ray absorption spectra, which reveal a weak temperature dependence of the Yb mean valence $\bar{v}$, in agreement with the results from an analysis of the χ data in light of the ICF model. Valence-band photoemission spectra support our view of a homogeneously mixed-valent state of Yb; they further identify a valence transition to the divalent state in the outermost surface layer. $4f$ binding energies are found to be 0.80 ± 0.05 eV higher at the surface as compared to the bulk. All three methods suggest that—within the limits of accuracy—the room-temperature mean valence of Yb in $YbPd_2Si_2$ is close to the high-temperature limit given by the ionic ICF model.

I. INTRODUCTION

Ever since the structure of $ThCr_2Si_2$ was determined (BaAl₄-type, space group $I4/mmm$),[1] a large number of isotypic rare-earth (RE) compounds of the form RX_2Y_2 (R=RE, X=transition element, Y=B, Ga, Si, Ge, Sn, P, As, and Sb) have been reported.[2] These ternary compounds have attracted considerable attention in the recent past because of the interesting Kondo, valence-fluctuation,[3-5] superconducting,[6-8] and magnetic properties[9-10] which some of these compounds possess. Particularly, the recent characterization of $EuPd_2Si_2$ as a rather unique intermediate-valent system,[11] with a precipitous temperature- and pressure-induced valence transition,[11-15] aroused increased interest in the field of valence-fluctuation phenomena in these ternary compounds.

Systematic studies[2] of the lattice volume of these ternary RE compounds suggest a correlation between the valence state of a given RE ion (Ce, Eu, and Yb) and the position of the elements X and Y in the Periodic Table. In addition, any abnormality in the valence of Eu in a given compound seems to be indicative of the occurrence of a similar anomaly in the isotypic Yb compound. This prompted us to investigate the compound $YbPd_2Si_2$ for the occurrence of valence instabilities, although no anomaly for $YbPd_2Si_2$ is visible in the lattice volume data of the RPd_2Si_2 series.[2] L_{III}-edge x-ray absorption (XA) and $4d$ core-level x-ray photoemission (PE) studies have been reported previously for $YbPd_2Si_2$ at room temperature;[16] it was not possible, however, to decide from those results whether the observed valence mixing of Yb is static (inhomogeneous) or dynamic (homogeneous) in nature.

In this paper we report magnetic susceptibility (in the temperature range from 2.4 to 300 K), L_{III}-edge XA (16

to 300 K), and valence-band PE (at 300 K) studies of $YbPd_2Si_2$. These results conclusively prove the dynamic nature of the valence mixing in $YbPd_2Si_2$. We find a weak temperature dependence of the mean valence $\bar{v}$ of Yb, contrary to what is known for the mean valence of Eu in $EuPd_2Si_2$. In addition, we observe a shift of the $4f$ binding energy in the outermost surface layer by 0.80 ± 0.05 eV to higher values as compared to bulk Yb ions. This allows a separation of the $4f^{13}$ final-state spectral features originating from bulk and surface Yb^{2+} ions. As in other homogeneously mixed-valent compounds,[17-20] the observed surface and bulk intensities indicate that the outermost surface layer of $YbPd_2Si_2$ is in the divalent state.

II. EXPERIMENTAL METHODS

The $YbPd_2Si_2$ compound used for the present studies was prepared by melting the constituent elements in an arc furnace in an atmosphere of purified argon. By adding a slight excess of Yb, the loss due to vaporization of Yb while melting was compensated. The ingot thus obtained was homogenized by vacuum annealing at 700 °C for four days. From x-ray diffraction, the single-phase nature of the sample was confirmed, and the obtained values for the lattice constants were found to be in good agreement with those reported in the literature.[2]

The magnetic susceptibility measurements were performed in an external magnetic field of 5 kOe in the temperature range from 2.4 to 300 K using a vibrating sample magnetometer. For the XA experiments in the region of the Yb-L_{III} edges, performed in transmission geometry, the highly monochromatic tunable x-ray beam from the EXAFS-II spectrometer at the Hamburg Synchrotron-

strahlungslabor (HASYLAB, DESY, Hamburg) was employed. [The rocking-curve width is $\cong 2$ eV (full width at half maximum) at 8.9 keV.] XA coefficients were obtained by monitoring the intensities of the incident and transmitted x-ray beams with nitrogen-filled ionization chambers. A homogeneous sample was prepared by pressing the finely powdered material into paraffin. The valence-band PE experiments were performed at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY, Berlin) using the photon beam of the SX-700 monochromator. At 120-eV photon energy the combined-system resolution of the double-pass cylindrical-mirror analyzer and monochromator was about 0.5 eV. Clean surfaces were prepared by scraping the sample in a vacuum of 1×10^{-10} Torr with a metal-bonded diamond file; the cleanliness was checked via the O $2p$ PE signal.

III. RESULTS AND DISCUSSION

A. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility (χ) measured in an external field of 5 kOe is shown in Fig. 1. χ attains a peak at $T_{max} \cong 30$ K and tends to a constant value below 10 K. Above 120 K, χ^{-1} is a linear function of T, with a slope corresponding to an effective magnetic moment of $\mu_{eff} = 4.5 \pm 0.1 \mu_B$; this is very close to the moment expected for the free Yb^{3+} ion ($\mu_{eff} = 4.54 \mu_B$). From an extrapolation of the high-temperature behavior of χ^{-1}, we obtain a paramagnetic Curie temperature, $\Theta_p = -70$ K. Such a large negative Θ_p is characteristic of homogeneously mixed-valent compounds; its magnitude is much larger than the Θ_p values known[21] for other stable-valent RPd$_2$Si$_2$ compounds (GdPd$_2$Si$_2$: $\Theta_p = 2$ K; TbPd$_2$Si$_2$: -1 K; DyPd$_2$Si$_2$: -4 K; HoPd$_2$Si$_2$: -5 K; ErPd$_2$Si$_2$: -3 K). We have also studied the magnetization of YbPd$_2$Si$_2$ at 4.2 K in external fields up to 70 kOe and found it to be a linear function of the applied field. In the temperature range of investigation (2.4 to 300 K), there is no indication for magnetic order-
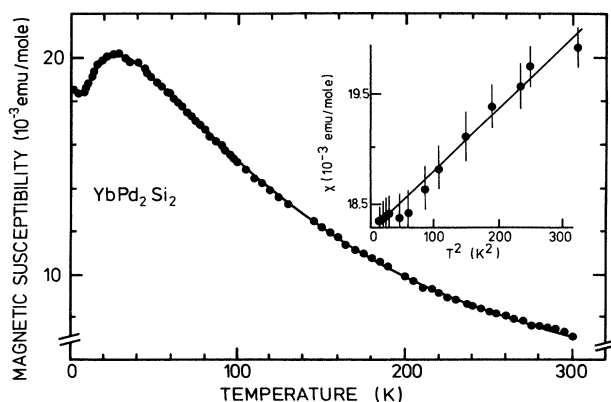

FIG. 1. Magnetic susceptibility of YbPd$_2$Si$_2$ as a function of temperature. The solid line is obtained from theory as described in the text. The inset shows the linear relationship between χ and T^2 for $T \ll T_{max}$.

ing. These features in the susceptibility data—high negative Θ_p, a maximum in the temperature dependence of χ, and nonmagnetic behavior at low temperatures—conclusively prove the homogeneously mixed-valent state of Yb in YbPd$_2$Si$_2$.

The observed temperature dependence of the magnetic susceptibility can be interpreted within the framework of an ionic interconfigurational fluctuation (ICF) model[22] as well as Fermi liquid models.[23-25] In the ICF model, expectation values of the measured physical quantities (valence, Mössbauer isomer shift, magnetic susceptibility, etc.) are calculated by averaging over the occupied $4f^n$- and $4f^{n-1}$-multiplet states. The energy difference between the lowest-lying ionic states of the $4f^{n-1}$ and $4f^n$ configurations is denoted by E_x and all ionic levels are assumed to have the same finite mixing width $\Gamma = k_B T_f$; T_f is called the characteristic fluctuation temperature. Applying this model to the case of Yb, we obtain for the normalized occupation probability of the Yb^{3+} state

$$p_3 = 8/[8 + \exp(E_x/T^*)] , \qquad (1)$$

where E_x is expressed in degrees Kelvin and $T^* = (T^2 + T_f^2)^{1/2}$. T^* is called the effective temperature,[26] and it takes both quantum and thermal fluctuations into account. This model qualitatively explains the observed maximum in χ if the Yb^{3+} ionic state is assumed at higher energy than the Yb^{2+} state. When the temperature is lowered, the Curie-Weiss increase in χ is then overcompensated by a decrease in χ due to increased population of the lower-lying nonmagnetic Yb^{2+} state. This ICF model has successfully explained the susceptibility behavior of a number of intermediate-valent Yb systems.[22] Quantitatively, the magnetic susceptibility of an intermediate-valent Yb system, neglecting crystal-field effects, is given by

$$\chi(T) = \frac{8N(4.54\mu_B)^2}{3k_B T^*[8 + \exp(E_x/T^*)]} . \qquad (2)$$

All symbols in Eq. (2) have their usual meanings. In this model, the high-temperature limit of $\bar{v}$ for Yb is obtained as 2.89 (assuming positive values for E_x).

We have least-squares fitted the theoretical form given by Eq. (2) to the measured χ data. For the temperature range above 33 K we obtain $E_x = 70 \pm 5$ K and $T_f = 100 \pm 5$ K. A good fit of the data measured in the temperature range 10 K $< T < 33$ K is obtained only if either E_x or T_f is assumed to be weakly temperature dependent. With a temperature-independent T_f, E_x takes the form $E_x = 154.6 - 4.64T + 0.07T^2$ (for $T < 33$ K); thus, at 10 K, $E_x = 115$ K. These parameters lead to a slightly temperature-dependent mean valence of Yb ($\bar{v} \cong 2.86$, 2.82, and 2.75 at 300, 85, and 16 K, respectively).

Recently it was shown that the maximum in the susceptibility of several mixed-valent Yb and Ce compounds may also be interpreted in a Fermi-liquid model.[23] This interpretation is based on the very similar scaling behavior of χ in these $4f$ systems and the strongly interacting Fermi-liquid ^{3}He. At low temperatures ($T \ll T_{max}$), the magnetic susceptibility should then have the form[23]

$$\chi(T) = \chi(0)(1 + \alpha T^2) .$$ (3)

For $T > T_{max}$ free-spin behavior is expected. This leads to a maximum in χ for positive values of α, as observed in several Ce and Yb compounds.

We have analyzed the χ data for YbPd$_2$Si$_2$ within this model, with the result that both a T^2 behavior of χ for $T < 16$ K as well as the scaling behavior characteristic of Fermi-liquid systems are observed. The first point is obvious from the inset in Fig. 1, where it is shown that χ varies linearly with T^2 at low temperatures. The scaling behavior, on the other hand, leads to a proportionality between $\chi(0)$, T_{max}, and Θ_p, which for Yb systems is given by the relation[23] $C/\chi(0)T_{max} \cong 5$, where C is the free-ion Curie constant. Our results for YbPd$_2$Si$_2$ are in agreement with such a ratio. In summary, we can say that YbPd$_2$Si$_2$ exhibits all the characteristic features of strongly interacting Fermi-liquid systems, like enhanced Pauli paramagnetism, T^2 behavior of χ at low temperatures, crossover to free-spin behavior at high temperatures, and scaling. It is therefore of interest to perform specific-heat measurements on YbPd$_2$Si$_2$ and verify the relation between $\chi(0)$ and the linear coefficient of specific heat known for such systems.[27]

B. L_{III}-edge x-ray absorption

In order to support the conclusions obtained from the susceptibility measurements regarding the temperature dependence of $\bar{v}$ of Yb in YbPd$_2$Si$_2$, L_{III}-edge measurements were performed at various temperatures. Figure 2

shows the L_{III} edge of Yb at the lowest and the highest temperature points studied (16 and 300 K). To derive values for the mean valence, a superposition of two identical L_{III}-edge profiles, separated by $\Delta E(2p) = 6.5$ eV, was least-squares fitted to the experimental data points. The L_{III}-edge profiles were analytically described as the sum of a Lorentzian line and an arctangent function convoluted with a Gaussian, representing the finite-energy resolution of the spectrometer. In agreement with similar work on other mixed-valent Yb compounds, the L_{III}-edge feature at lower excitation energy is assigned to $2p^5 4f^{14}$ and the intense feature to $2p^5 4f^{13}$ final core states,[28] originating from Yb^{2+} and Yb^{3+} ions, respectively.[29,30] The difference in the $2p$ excitation energies, $\Delta E(2p)$, used in the present analysis is the same as the one found for the mixed-valent high-pressure phase of Yb metal.[29] The best fits were obtained for $\Delta E(2p) = 6.5$ eV, but the resulting valences (given below) are the same within the given error bars for slightly different values of $\Delta E(2p)$.

From the relative intensities of the Yb^{2+}- and Yb^{3+}-derived L_{III}-edge features, the following values for the mean valence $\bar{v}$ were obtained: $\bar{v} = 2.89 \pm 0.08$ at 300 K and $\bar{v} = 2.82 \pm 0.08$ at 16 K. The absolute error bars are quoted as ± 0.08 corresponding to about five times the statistical errors in the data analysis. With such a conservative estimate of error bars we believe that possible systematic errors due to uncertainties in the line shape and possible differences in $2p \rightarrow 5d$ transition probabilities for the Yb^{2+} and Yb^{3+} ions, as well as possible effects from core-hole screening, are accounted for. Despite the relatively large absolute error bars, however, the achieved accuracy in the relative variation of $\bar{v}$ with temperature is estimated to be better than ± 0.02.

L_{III}-edge measurements were performed at five different temperatures. The results are presented in Fig. 3, where the difference $\Delta \bar{v}$ of the mean valence at a given temperature relative to the value at 300 K is plotted as a function of temperature. The data clearly show a small
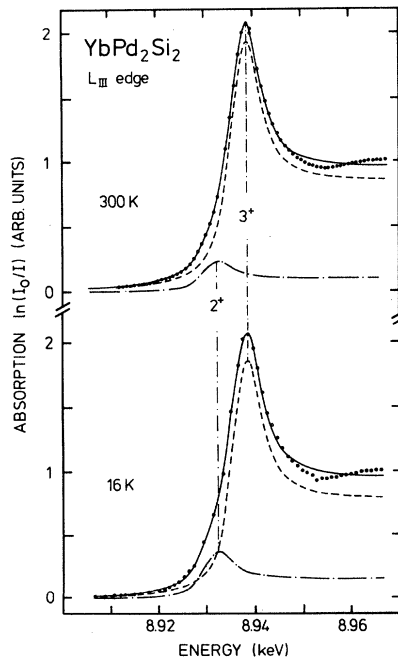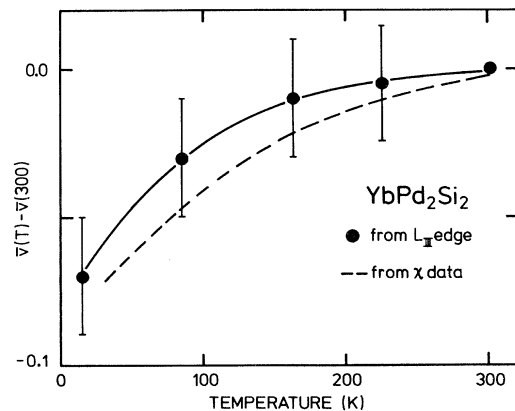

FIG. 2. Yb L_{III}-edge x-ray absorption of YbPd$_2$Si$_2$ at 16 and 300 K. The solid lines represent the results of least-squares-fit analyses as described in the text. The dash-dotted and dashed subspectra are assigned to Yb^{2+} and Yb^{3+} initial-ionic states, respectively.

FIG. 3. Temperature dependence of the Yb mean valence $\bar{v}$ as obtained from L_{III}-edge measurements (solid points); plotted is the difference between $\bar{v}(T)$ and the value at 300 K. The solid line through the data points serves as a guide to the eye. The dashed curve is obtained from an analysis of the χ data in the light of the ionic ICF model, as described in the text.

but distinct decrease of $\bar{v}$ by $\Delta\bar{v}=0.07$ when the temperature is lowered from 300 to 16 K. For comparison, we have also included in Fig. 3 (dashed curve) the variation of $\bar{v}$ as obtained with the ionic ICF model, using the parameters $E_x(T)$ and T_f as determined from an analysis of the temperature dependence of the magnetic susceptibility (see above).

The close agreement between the directly determined temperature variation of $\bar{v}$ from L_{III}-edge measurements and the one obtained from the ionic ICF model deserves special emphasis. It shows that the ICF model, in the form employed here, is suitable in describing the temperature variation of $\bar{v}$. In addition, the consistency of the $\bar{v}$ results from an analysis of the susceptibility and L_{III}-edge data suggests rather small final-state effects in the L_{III}-edge XA spectra of YbPd$_2$Si$_2$. Finally, we may say that the clearly observed variation of $\bar{v}$ with temperature confirms our view of a homogeneously mixed-valent state of Yb in YbPd$_2$Si$_2$.

C. Valence-band photoemission

A typical photoemission spectrum of YbPd$_2$Si$_2$ obtained at room temperature using synchrotron radiation at BESSY is shown in Fig. 4; it is recorded at a photon energy of 120 eV, where emission from Pd $4d$ states is strongly suppressed due to the well-known Cooper minimum in the photoelectric cross section.[31] The PE spectrum in Fig. 4 exhibits the $4f^{13}$ and $4f^{12}$ final-state multiplet structures originating from divalent ($4f^{14}$) and trivalent ($4f^{13}$) initial ionic Yb states, respectively.[18] The lowest-binding-energy components of the two multiplet structures are separated by a Coulomb correlation energy of $U=5.9\pm0.05$ eV.

As in Yb metal,[32,33] YbAl$_2$,[18] and other RE systems,[19,36] the divalent multiplet structure close to E_F is a superposition of two sets of bulk- and surface-derived spin-orbit-split $4f^{13}$ doublets (spin-orbit splitting 1.29 eV), shifted against each other by a surface core-level shift Δ_c. In agreement with observations in other RE systems, the structure close to E_F is assigned to emission from bulk Yb^{2+} ions, the other one to surface emission.
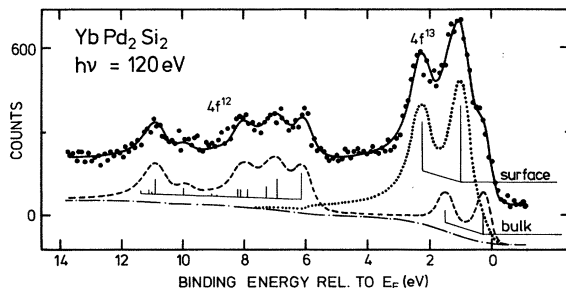

FIG. 4. Photoemission spectrum of YbPd$_2$Si$_2$ taken at $h\nu=120$ eV. The solid curve is obtained by a least-squares fit analysis of the data as described in the text. The subspectra of bulk Yb^{2+} and Yb^{3+} (dashed curve) and surface Yb^{2+} (dotted curve) obtained from the fitting, along with the background (dash-dotted), are also shown (transposed from the measured spectrum).

In the least-squares-fit analysis of the spectrum, the theoretical function was set equal to the sum of the $4f^{13}$ and $4f^{12}$ multiplet components with Doniach-Šunijć line shapes plus an inelastic background; this function was convoluted with a Gaussian for experimental resolution. The relative intensities of the $4f^{12}$ multiplet components were taken from the intermediate-coupling calculations of Gerken,[34] which are adjusted to the relative separations of the $4f^{12}$ multiplet lines known from optical absorption spectroscopy.[35] The results of the fit analysis are presented in Fig. 4. The values of the binding energy relative to E_F of the most weakly bound $^2F_{7/2}$-$4f^{13}$ multiplet components are determined as 0.2 eV for the bulk Yb^{2+} ions and 1.0 eV for the surface Yb^{2+} ions, respectively. This corresponds to a surface core-level shift of $\Delta_c=0.80\pm0.05$ eV for YbPd$_2$Si$_2$, and this value of Δ_c is quite similar in magnitude to those observed for Yb metal,[32,33] YbAl$_2$,[18] and YbZn$_2$.[36]

The fact that the least-bound bulk $4f^{13}$ multiplet component is observed in close vicinity of E_F is consistent with the homogeneously mixed-valent state of Yb in YbPd$_2$Si$_2$, and follows from the degeneracy of the $4f^{14}$ and $4f^{13}$ (plus conduction electron) states in such systems. The small 0.2-eV shift of the least-bound $4f^{13}$ multiplet component has been observed also in other homogeneously mixed-valent systems, and may be due to incomplete final-state screening and/or lattice relaxation effects.[18,19] The most striking feature in the PE spectrum of Fig. 4 is the large intensity of the surface $4f^{13}$ final-state doublet (dotted) as compared to the bulk peaks ($4f^{13}$ part of the dashed curve). Such a strong surface enhancement of the $4f^{13}$ emission cannot be explained on the basis of known electron-escape depths l for hot electrons with about 115-eV kinetic energy alone. Rather, one has to assume that a surface layer of thickness Δs undergoes a valence transition to the divalent state. Such surface valence transitions have been observed for a number of bulk-trivalent RE systems, like Sm metal,[37] EuPd$_x$,[38] YbAu$_2$,[39] TmS,[19] and SmAl$_2$;[36] they seem to be the rule for homogeneously-mixed-valent RE systems, as TmSe, Tm$_{1-x}$YSe,[19] EuPd$_2$Si$_2$,[17] and YbAl$_2$.[18]

In order to get a rough estimate of the thickness Δs of the divalent surface layer on YbPd$_2$Si$_2$, we assume identical PE cross sections for bulk and surface Yb atoms. This leads[18] to $I/I_B=\exp(\Delta s/l)$, where I is the total intensity of $4f$ emission (including surface multiplets) and I_B stands for the intensity of bulk emission ($4f^{12}$ and bulk-$4f^{13}$ multiplets). From a least-squares-fit analysis of the 120-eV spectrum of YbPd$_2$Si$_2$ we obtain $I/I_B=2.00\pm0.05$ and hence $\Delta s/l=0.70\pm0.03$. Assuming $l\cong6$ Å for photoelectrons with about 115-eV kinetic energy,[40] we obtain $\Delta s\cong4.2$ Å. If we compare this value for Δs with the shortest Yb-Yb distance in YbPd$_2$Si$_2$ (4.1 Å) we arrive at the conclusion that the outermost surface layer is divalent in YbPd$_2$Si$_2$.

We may derive a value of the mean valence of bulk Yb ions from the relative intensities of the Yb^{3+} and bulk-Yb^{2+} emission, taking the different numbers of $4f$ electrons in the initial state into account, and assuming a divalent surface layer on YbPd$_2$Si$_2$. The result is $\bar{v}=2.75\pm0.1$, which agrees reasonably well with the sus-

ceptibility and L_{III}-edge results at 300 K.

In Yb metal, the bulk- and surface-$^2F_{7/2}$ components are observed 1.2 and 1.8 eV below E_F, respectively,[32,33] whereas in YbPd$_2$Si$_2$, the corresponding values are 0.2 and 1.0 eV. Therefore, the chemical shift of the $2F_{7/2}$-binding energy between Yb metal and YbPd$_2$Si$_2$ is 1.0 eV for bulk Yb^{2+} ions, but only 0.8 eV for Yb^{2+} ions at the surface. The origin for the smaller chemical shift of surface atoms lies in differences in the cohesive energy, due to the reduced coordination of surface atoms. In general, the cohesive energy of the surface is only about 80% of that of the bulk.[41] If one compares a series of compounds of, say, a particular RE element, any difference in the chemical bonding will result in different cohesive energies and hence in chemical shifts for the bulk core-level binding energy. The surface core-level binding energy in such compounds will also be proportional to the surface cohesive energy of the compound. It is therefore natural—as observed in YbPd$_2$Si$_2$—that the surface chemical shift of a compound is about 20% smaller than that of the bulk.

IV. CONCLUSION

On the basis of magnetic susceptibility measurements, L_{III}-edge XA, and valence-band PE studies, we have shown that YbPd$_2$Si$_2$ is a homogeneously mixed-valent compound. The room-temperature mean valence of Yb in YbPd$_2$Si$_2$, determined in the present study, is close to the high-temperature limit of $\bar{v}$ for Yb in the ICF model.[22] The valence transition observed for the outermost surface layer of YbPd$_2$Si$_2$ is in accord with observations on other homogeneously mixed-valent materials,[17−19] and actually seems to be the rule for such materials with $4f$ instabilities. It is therefore striking that surface-induced changes in the $4f$ occupancy have not been identified in mixed-valent Ce compounds.

Both the L_{III}-edge XA data and the analysis of the magnetic susceptibility reveal a weak decrease of $\bar{v}$ by about 0.07 as the temperature is lowered from 300 to 16 K. This is quite different from the situation found for EuCu$_2$Si$_2$,[42] and particularly EuPd$_2$Si$_2$,[11−15] where strong valence changes as a function of temperature have been observed. In EuPd$_2$Si$_2$ the precipitous valence transition was explained in terms of cooperative effects arising from intersite coupling between the Eu ions.[13,15] In homogeneously mixed-valent Yb systems, however, one should bear in mind that the lowering of the temperature causes two opposite effects on the lattice volume: a shrinkage due to the usual anharmonic lattice contraction and an expansive effect due to the increased population of the larger Yb^{2+} ionic states at lower temperatures. This may cause very unusual lattice expansion properties as actually observed for Yb systems.[43] In this way, Yb-Yb intersite-coupling effects—even if present in YbPd$_2$Si$_2$—may not strongly influence the temperature dependence of $\bar{v}$. The question of cooperative versus single-ion aspects of the valence changes in YbPd$_2$Si$_2$ can be addressed further by investigating the dilute system Yb$_{1-x}$Lu$_x$Pd$_2$Si$_2$.

*Permanent address: Tata Institute of Fundamental Research, Bombay-40005, India.

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