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Nonpareil Yb Behavior in $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$

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We investigate the temperature dependence of the Yb valence in $\text{YbMn}_6\text{Ge}_{1.8}\text{Sn}_{4.2}$ and $\text{YbMn}_6\text{Ge}_{1.6}\text{Sn}_{4.4}$ using resonant inelastic x-ray scattering experiments. Yb is found to be in an intermediate valent state in the whole investigated temperature range (10–450 K). We thus prove that the unusually high magnetic ordering temperature of Yb (~ 60 and 90 K for $x = 4.2$ and 4.4 , respectively) involves an intermediate valent Yb, an unprecedentedly observed phenomenon. Further, an anomalous increase in the Yb valence is observed upon cooling. A scenario is proposed to explain this unusual behavior. It is based on the presence of magnetically ordered Mn moments and on an Anderson Hamiltonian with a Zeeman term modeling the magnetic interactions.

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Exotic electronic properties (Kondo, intermediate valent, heavy fermion or nonconventional superconductivity behaviors, etc.) can be encountered in Ce, Yb, and U intermetallic compounds [1]. These properties result from an interplay between very large intra-atomic Coulomb interactions in the f shell and a partial delocalization due to the hybridization of f states with the conduction electrons. Heavy fermion or Kondo compounds are characterized by the formation at low temperature of a correlated Fermi liquid state with a usually large effective electron mass. For a single impurity, the ground state is a singlet state (nonmagnetic) resulting from a $4f$ moment screened by conduction electrons. This Kondo picture can be described by the Anderson impurity model which shows that the Coulomb interaction (charge fluctuation energy scale) and hybridization strength yield an emergent low energy scale (Kondo energy $k_B T_K$) associated with spin fluctuations which control the universal behavior of the thermodynamical properties. The main signature of these universal laws is a crossover around T_K from a high-temperature localized moment regime to a low-temperature Fermi liquid regime with large effective mass and screened $4f$ moment. Concerning the $4f$ occupation number, the hybridization leads to an intermediate valent ground state, whereas in the high-temperature regime, a variation towards an integer value is expected [2]. Such a picture remains valid for many Ce or Yb dense compounds in a first approximation [3], and scaling behaviors have been evidenced in thermodynamical [4] and spectroscopic quantities [5].

In Yb-based materials, valence fluctuations involve trivalent magnetic $4f^{13}$ ($J = 7/2$) and divalent nonmagnetic $4f^{14}$ ($J = 0$) states. The Yb valence varies with pressure, temperature, magnetic field, or chemical doping. In intermetallics, the magnetic nature of the ground state results

from the competition between Kondo interactions and magnetic exchange interactions. In compounds with nonmagnetic elements, a magnetic ground state with a usually low ordering temperature, a reduced magnetic moment, and a valence close to 3 can be stabilized. A typical example is YbPd, which orders ferromagnetically at 1.9 K with a valence of $\nu \sim 2.8$ [6]. When magnetic transition elements are present, supplementary and stronger $4f$ - $3d$ interactions play a role. However, the situation of coexisting intermediate valence Yb and magnetically ordered transition metal sublattice has rarely been observed. Recently, unusual magnetic behaviors have been reported in the new $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ series [7]. The Yb ordering temperature was found to be ~ 60 and 90 K for $x = 4.2$ and 4.4 , respectively (exceptionally high ordering temperatures in Yb compounds), while the Mn moments order near ~ 340 K in both cases. In the ground state, Yb is in a ferromagnetic Mn sublattice and carries a substantial magnetic moment ($\sim 1.5\mu_B$) antiferromagnetically coupled with the Mn moments. Moreover, there is some indirect indication that Yb could be in an intermediate valent state [7]. These compounds exhibit unique physical properties with the interplay of Kondo interactions which reduce the Yb magnetic moment and the evidence of an astonishingly high magnetic ordering temperature of the Yb sublattice.

In this Letter, we present a resonant inelastic x-ray scattering (RIXS) study at the Yb $L3$ edge of two alloys in the $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ series, namely, $x = 4.2$ and 4.4 . These measurements prove the intermediate valent character of Yb previously conjectured [7] and further evidence a temperature dependence of the $4f$ electron number which decreases upon increasing temperature, in contrast to the usual observation in intermediate valent Yb materials [2]. A scenario is proposed to explain this surprising and

counterintuitive temperature dependence. It correlates this anomalous temperature dependence with the presence of a magnetically ordered Mn sublattice, in particular, with the breakdown of the singlet nonmagnetic Kondo state. We propose a very simple model based on a single-impurity Anderson model with an intermediate valent ground state augmented by a Zeeman term to qualitatively describe the magnetic interactions. This term can produce the valence change, which is experimentally observed. We also point out the lattice contraction upon cooling, which could play a role in the valence change.

The polycrystalline $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ samples with $x = 4.2$ and 4.4 were prepared from high-purity elements in closed Mo crucibles to avoid losses of Yb during annealing, as described in Ref. [7]. The precise chemical composition of the two alloys was determined by microprobe measurements. The RIXS measurements were carried out on beam line ID16 at European Synchrotron Radiation Facility (Grenoble, France). X-ray diffraction experiments were performed in the 300–15 K temperature range using a Philips X'Pert Pro diffractometer ($\lambda = 1.540\,56\text{ \AA}$).

Figure 1(a) shows Yb L_3 x-ray absorption spectroscopy (XAS) spectra of $\text{YbMn}_6\text{Ge}_{1.6}\text{Sn}_{4.4}$, measured at different temperatures, in the partial fluorescence yield (PFY) mode associated with the radiative $2p^53d^{10} \rightarrow 2p^63d^9$ decay. The main structure at 8.947 keV and the shoulder at 8.941 keV correspond to transitions from the initial intermediate valent state to final states of mainly $2p^54f^{13}$ (3+ valence) and $2p^54f^{14}$ (2+ valence) character. By the usual

assumption that their relative intensities reflect the weight of the corresponding configurations in the initial state, it is possible to deduce the $4f$ occupation number and then the Yb valence. The temperature dependence of the Yb valence can also be probed by RIXS [8–10]. This resonant spectroscopy couples the initial state with $3d^94f^{13}$ and $3d^94f^{14}$ final states. The weak Yb^{2+} contribution can be enhanced by tuning the resonant excitation energy corresponding to the Yb^{2+} shoulder in the PFY spectrum ($h\nu = 8.941\text{ keV}$). This is illustrated in Fig. 1(b), which reports the RIXS spectra normalized at the resonant Yb^{2+} feature ($3d^94f^{13}$ final state) recorded at different temperatures. Because of the resonant character, the Yb valence cannot be obtained from a simple ratio of the two structures. Then, following a standard procedure previously proposed [8], we have normalized the RIXS ratio of these two structures with the ratio obtained from the L_3 XAS data. The temperature dependence of the Yb valence obtained from RIXS has been reported in Fig. 1(d). This dependence evidences a decrease in the Yb valence upon heating. RIXS spectra of another alloy of the series ($x = 4.2$) are shown in Fig. 1(c), and the temperature dependence of the Yb valence is also reported in Fig. 1(d). Yb is found in an intermediate valence state over the whole investigated temperature range in both alloys. Hence, our measurements unambiguously demonstrate that the high-temperature magnetic ordering of the Yb sublattice in the $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ series involves intermediate valent Yb. This unprecedented phenomenon is most likely due to the interaction with the strongly magnetized Mn sublattice. There are a few other systems where intermediate valent Yb and a magnetically ordered transition metal are simultaneously present, but they do not show magnetic order of Yb [11,12]. In the latter phases, the valence of Yb is significantly lower ($v \sim 2.5$) and the transition metal sublattice is either weakly magnetized [11] or antiferromagnetically arranged [12].

In addition to their singular magnetic properties, $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ ($x = 4.2$ and 4.4) exhibit an anomalous temperature dependence of the Yb valence. Indeed, in intermediate valent compounds, the Yb valence usually increases with increasing temperature. This behavior can be understood in the framework of the single-impurity Anderson model. At low temperature ($T \ll T_K$), only the ground state is populated and its hybridized character leads to a valence smaller than 3. With increasing temperature ($T \sim T_K$), the magnetic and purely trivalent states are thermally populated, leading to an increase in the average valence. In conclusion, a valence increase is observed following a scaling behavior as a function of T/T_K . The temperature dependence in this series is completely different since a significant decrease is observed [Fig. 1(d)].

The Yb intermediate valent state results from the interplay of large Coulomb interaction and hybridization between $4f$ and conduction states. In the Anderson

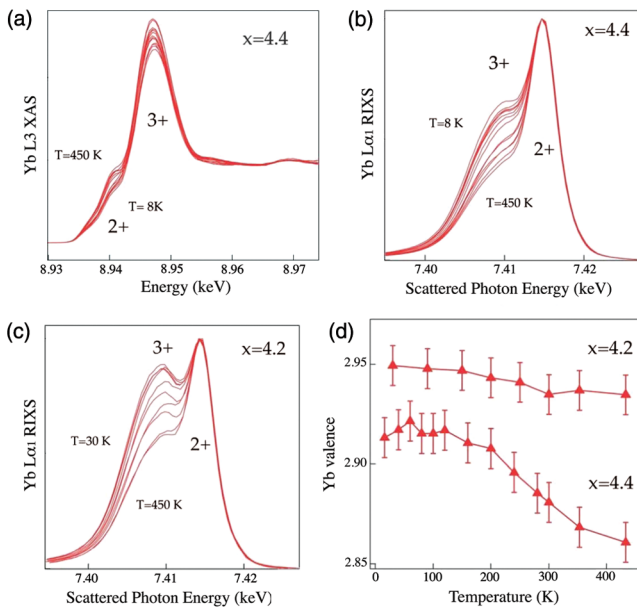


FIG. 1 (color online). (a) XAS spectra at different temperatures in the PFY mode for the $x = 4.4$ alloy. (b), (c) RIXS spectra at different temperatures for $x = 4.4$ and 4.2 alloys, respectively. (d) Temperature dependence of the valence deduced from RIXS.

impurity model, the ground state is a nonmagnetic singlet ($n_f > 13$) which can be written as a quantum admixture of N electron states corresponding to the different electronic configurations of the Yb impurity. In the infinite U limit, only two configurations contribute and the ground state can be schematically written [2,13]:

$$|\Psi_{\text{GS}}\rangle = c_{13}|4f^{13}\rangle + c_{14}|4f^{14}\rangle,$$

where the $|4f^{13}\rangle$ state represents a many body singlet state describing the corresponding Yb configuration screened by conduction electrons with opposite moment (Kondo ground state). In the Kondo limit (small hybridization), $|c_{14}| \ll |c_{13}|$ and the valence is close to 3 ($n_f \approx 13$). The thermodynamical properties are then characterized by the Kondo scaling behavior associated with spin fluctuations. With increasing hybridization, the valence admixture increases and charge fluctuations start to play a role. The singlet ground state is separated from a manifold of excited states corresponding to magnetic $|4f^{13}\rangle$ states [2]. In this picture, the temperature population of the excited states leads to an increase in n_f . This temperature dependence obeys a scaling behavior controlled by the Kondo scale and it has been evidenced from spectroscopic measurements in Ce- and Yb-based compounds [8,14–17].

The opposite temperature dependence of the Yb valence is observed in the $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ alloys. However, this series exhibits another very unusual behavior with a high-temperature magnetic ordering of the Yb sublattice. To account for the appearance of a magnetic moment on Yb atoms, the Kondo screened singlet state must be broken, and that could be achieved by the exchange interaction of $4f$ states with Mn $3d$ states. To describe qualitatively such an effect, we propose a toy model where the system is simply represented by one $S = 1/2$ impurity state with energy $\varepsilon_i < 0$ for Yb atoms, while an infinitely narrow band at energy $\varepsilon_0 = 0$ corresponds to the itinerant electron gas. There is a hybridization term (V) mixing both kinds of states and Coulomb interactions (U) on the impurity. The Hamiltonian is then a single-impurity Anderson Hamiltonian:

$$H = \sum_{\sigma} \varepsilon_i n_{i,\sigma} + \varepsilon_0 \sum_{\sigma} n_{0,\sigma} + V \sum_{\sigma} (a_{i,\sigma}^{\dagger} a_{0,\sigma} + \text{c.c.}) + U n_{i,\sigma} n_{i,-\sigma} + g_i \mu_B \sigma_{i,z} B, \quad (1)$$

with an additional Zeeman-like term (last term) describing the magnetic interactions involving the localized spin [18]. In the infinite U limit, the double occupancy of the impurity orbital is forbidden and the basis states are $|0\rangle$ for the unoccupied impurity state and the $|\eta, \eta'\rangle$ with $\eta, \eta' = \uparrow$ or \downarrow for, respectively, the spin of the impurity and itinerant electrons. In the zero field limit, the energy spectrum is a singlet nonmagnetic ground state $[c_0|0\rangle + c_1(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}]$ at $\varepsilon_i - \delta$, a triplet excited level corresponding to the spin-one states at ε_i , and a high energy singlet state corresponding mainly to the non-occupied impurity state [Fig. 2(a)]. $|c_0|$ and δ increase with

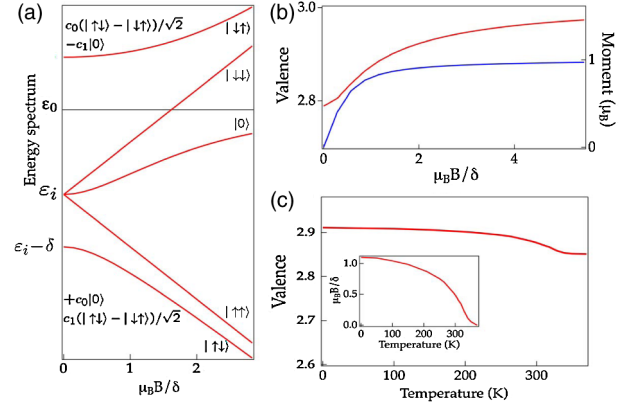


FIG. 2 (color online). (a) Energy spectrum as a function of the magnetic energy ($\mu_B B$) normalized by the characteristic energy (δ) corresponding to the stabilization energy of the Kondo singlet state. The states at the right part of the figure represent the infinite B limit. (b) Valence and magnetic moment as a function of the normalized magnetic energy. (c) Valence and normalized magnetic energy (in the inset) as a function of temperature.

increasing the hybridization parameter V . A finite magnetic field leads to a breakdown of the nonmagnetic character of the ground state due to the admixture with excited states. At very high fields, the ground state is a doublet ($|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$) corresponding to the magnetically polarized impurity. The field dependences of the impurity valence ($v = 2 + |c_1|^2$) and the magnetic moment are presented in Fig. 2(b). With increasing magnetic field, the weight of the $|\uparrow\downarrow\rangle$ component in the ground state increases whereas the weight of the unoccupied orbital $|0\rangle$ decreases. Moreover, a parallel evolution from a nonmagnetic state to a completely polarized magnetic state occurs. Although the hybridization leads to an intermediate valent ground state (quantum admixture between different occupation number $n_i = 0$ and 1 of the impurity orbital), the magnetic field favors the magnetic $n_i = 1$ configuration. Such a behavior obtained in this very crude model is also found in more elaborate calculations which clearly indicate a splitting of the Kondo resonance induced by magnetic fields [19,20]. From an experimental point of view, an increase in the Yb valence upon increasing the external magnetic field has been observed in YbAgCu_4 [21].

We have shown that the Yb valence exhibits an anomalous temperature dependence in the $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ alloys. This could be due to the exchange interactions with ordered Mn moments. It is reasonable to model these complex interactions by a temperature dependent effective magnetic field which vanishes above the ordering temperature. Thus, we introduce a temperature dependence of the Zeeman term in our toy model to take into account the disappearance of Mn ordering with increasing temperature. For simplicity, we choose a monotonic temperature dependence [insert of Fig. 2(c)] neglecting the complex changes in the Mn magnetic order with temperature [7]. The simple

model yields a good qualitative description of the unusual experimental temperature dependence. This is shown in Fig. 2(c) for $\varepsilon_i = -2.75\delta$, $V = 1.36\delta$ (all parameters are expressed in terms of δ the energy difference between singlet and triplet states at zero field). A value $B \sim k_B T_K / \mu_B \sim 100$ T can be roughly estimated in these materials. This is the order of magnitude of the exchange field reported in similar intermetallic compounds: 200 and 90 T in $R_2\text{Fe}_{14}\text{B}$ and $R\text{Fe}_2$, respectively [22]. Therefore, this simple approach in the framework of the Anderson model with an applied field provides a description of the anomalous temperature dependence of the valence and the breakdown of the nonmagnetic character of Yb atoms. Our model well describes the behavior recently reported for $\text{Yb}_{0.88}\text{Fe}_4\text{Sb}_{12}$ within which the anomalous increase in the intermediate valence of a nonmagnetically ordered Yb is concomitant with the ferromagnetic ordering of Fe below 20 K [11]. In $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ ($x = 4.2$ and 4.4), the anomalous thermal dependence of the Yb valence still persists above the Mn ordering temperature (~ 340 K). This behavior could be due to fluctuation effects above the ordering temperature.

Although our simplified model seems able to capture the essential physics, it cannot be excluded that the high sensitivity of the Yb valence *vis-à-vis* the lattice contraction in these alloys might also participate in the anomalous temperature variation of the Yb valence. In Yb-based systems, the increase in the external [11,12,23] or chemical pressure [24], which reduces the interatomic distances, favors the trivalent state due to the smaller radius of trivalent Yb compared with that of divalent Yb. With Yb valence around $\nu \sim 2.9$, as in the present cases, a significant valence variation requires a ~ 10 GPa pressure corresponding to a $\sim 10\%$ volume reduction [23,25]. From electronic structure calculations, different mechanisms have been proposed for these pressure-induced effects [26,27]. As expected, upon replacing part of the Sn atoms by Ge atoms of smaller radius on going from $x = 4.4$ to $x = 4.2$, the lattice of $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ shrinks ($\delta V/V = -1.43\%$ at 300 K). This modest volume reduction yields, however, a perceptible increase in the Yb valence from $\nu \sim 2.88$ to $\nu \sim 2.93$, showing that in the vicinity of these Sn contents, the Yb valence is very sensitive to the interatomic distances. On the other hand, upon cooling from room temperature down to 15 K, the volume reduction of standard magnitude [23] ($\Delta V/V_0 = -1.27\%$ and -1.31% for $x = 4.2$ and 4.4 , respectively, where V_0 is the cell volume at 300 K) and the concomitant measured valence increase ($\Delta \nu \sim +0.02$ and $+0.03$ for $x = 4.2$ and 4.4 , respectively) are of the same order of magnitude as those induced by the chemical pressure effect. We therefore suggest that the lattice contraction upon cooling might play a role in the observed anomalous increase in the Yb valence, due to the strong sensitivity of the Yb valence upon interatomic distance changes in these phases.

In this Letter, we have shown that the high-temperature magnetic ordering of Yb in $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$ ($x = 4.2$ and 4.4) takes place while Yb is in an intermediate valent state with $\nu \sim 2.9$, a not yet reported behavior that likely finds its origin in the interaction with the magnetized Mn sublattice. We have also evidenced a rarely observed increase in the Yb valence upon cooling. A possible explanation has been tentatively put forward to account for this unusual thermal dependence of the Yb valence. It is based on the breakdown of the singlet state by the exchange field arising from the ordered Mn moments. This coupling, simply described by a Zeeman term, leads both to the emergence of a Yb magnetic moment and to the anomalous temperature dependence of the valence. We also pointed out the strong dependence of the Yb valence upon the interatomic distance variation which could contribute through lattice contraction upon cooling to the anomalous variation of the Yb valence with temperature. A better understanding of the highly puzzling properties of Yb in $\text{YbMn}_6\text{Ge}_{6-x}\text{Sn}_x$, seldom or never observed before, now requires theoretical approaches allowing us to treat intermediate valence in the presence of complex magnetic interactions.

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