Heterogeneous mixed valence in $YbPd_3S_4$: evidence from ^{170}Yb Mössbauer and x-ray L_{III}-edge absorption measurements

LETTER TO THE EDITOR

Heterogeneous mixed valence in YbPd₃S₄: evidence from 170Yb Mössbauer and x-ray L_III-edge absorption measurements

P Bonville[1], C Godart[2], E Alleno[2], F Takahashi[3], E Matsuoka[3] and M Ishikawa[3]

[1] CEA, Centre d'Etudes de Saclay, Service de Physique de l'Etat Condensé, 91191 Gif-sur-Yvette, France
[2] LCMTR-CNRS, Groupe des Laboratoires de Thiais, 94320 Thiais, France
[3] Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan

Abstract
The intermetallic bronze YbPd₃S₄ is shown to be a heterogeneous mixed-valence system, by means of 170Yb Mössbauer spectroscopy and x-ray L_III-edge absorption and magnetic measurements. Two valence states coexist in this compound: Yb³⁺ and close-to-divalent Yb. The trivalent fraction (about 50%) undergoes a transition to magnetic ordering at about 2 K, with the Γ_7 doublet as the ground crystal field state. The possibility of charge (or valence) ordering is discussed.

1. Introduction

Among rare earths, the Sm, Eu, Tm, and Yb ions are known to have the possibility of existing in the trivalent or the divalent charge state in intermetallic compounds. A coexistence of these two charge states occurs in some materials, called heterogeneous mixed-valence systems. These must be distinguished from homogeneous mixed-valence materials, where the rare-earth electronic state is the same throughout the lattice, but presents a non-integer valence due to hybridization of the 4f wavefunction with conduction band electrons [1]. Of special interest are the heterogeneous mixed-valence materials where the rare-earth sites occupied by the two valence states are equivalent in the high-temperature phase: in this case, a charge (or valence) ordering is expected to occur, accompanied by a small lattice distortion and a symmetry lowering in the low-temperature phase [2]. The resistivity in such materials can be either of semiconducting type, like in Eu₃S₄ [3], or of metallic type, like in YbPd [4]. For Yb intermetallic compounds, the trivalent state ($4f^{13}$) is paramagnetic, with one hole in the 4f shell, and the other state is either divalent diamagnetic or close to divalent, but weakly paramagnetic.

The reverse is true for Eu compounds: $Eu^{2+}(4f^7)$ is paramagnetic, and $Eu^{3+}(4f^6)$ is weakly paramagnetic.

Recently, magnetic measurements on the rare-earth palladium bronze $YbPd_3S_4$, where the unit cell contains two equivalent Yb sites, have suggested that this compound is a heterogeneous mixed-valence material. Transport and specific heat measurements have shown that its conductivity is of metallic type and that the Yb^{3+} fraction orders magnetically below about 2 K [5, 6]. In the present work, we apply microscopic techniques, i.e. ^{170}Yb Mössbauer and x-ray L_{III}-edge absorption spectroscopies, to characterize the mixed-valence state in $YbPd_3S_4$ and to determine the proportions of the two valence states. We also infer the ground crystal field state of the Yb^{3+} ion from the magnetic moment value obtained from the Mössbauer and magnetic susceptibility data. Finally, we discuss the problem of charge ordering in this compound.

2. Crystal structure, samples, and experimental details

$YbPd_3S_4$ crystallizes into the cubic $NaPt_3O_4$-type structure, with space group $Pm3n$. The unit cell contains two Yb ions in crystallographically equivalent sites (2a), with cubic $m3$ point symmetry. From an x-ray diffractogram at room temperature, a least-squares fitting of the lattice parameter leads to $a = 6.626(1)$ Å. A Rietveld refinement of the site occupancies using the Fullprof program [7] yields 1.01, 1.00, and 0.99 for the Yb, Pd, and S sites respectively, which presents no significant difference from full occupancy. Therefore, no local distortions can be generated by vacancies, contrary to the situation in UPd_3S_4, where a deficiency in U-site occupancy (0.92) has been reported [8].

The Mössbauer transition of the ^{170}Yb isotope links the ground nuclear state, with spin $I_g = 0$, to the first excited nuclear state, with spin $I_e = 2$, at an energy 84.3 keV. The frequency equivalent for the Mössbauer 'velocity unit' is 1 mm s^{-1} = 68 MHz. The γ-ray source is neutron-activated Tm^*B_{12}; it yields a single Lorentzian-shaped line with half-width at half-maximum (HWHM) $g = 1.30$ mm s^{-1}, against a $YbAl_3$ standard absorber. All the spectra were recorded in zero magnetic field, and those below 1.5 K were recorded in a spectrometer coupled to a ^{3}He–^{4}He dilution refrigerator.

The L_{III}-edge x-ray absorption measurements were carried out at the LURE synchrotron facility (Orsay, France).

Two samples, prepared as described in [5], were used in this study, differing in their impurity content. The x-ray absorption and the magnetic data were taken for a sample with about 5 wt% of Yb_2O_2S, whereas the Mössbauer spectra were recorded with a purer sample, containing about 2.5 wt% of Yb_2O_2S.

3. ^{170}Yb Mössbauer absorption data

^{170}Yb Mössbauer spectra were recorded at various temperatures between 0.09 and 4.2 K (see figure 1). At the lowest temperature (0.09 K), the spectrum consists of two components with almost equal weights: a single line and a five-line spectrum, with respectively 45(5) and 55(5)% relative intensity. The single line has an isomer shift of -0.30 mm s^{-1} with respect to that of the TmB_{12} source, characteristic of a divalent or close-to-divalent Yb ion [9].

The five-line subspectrum is attributed to magnetically ordered Yb^{3+} ions, for which a hyperfine field is present at the nucleus. This hyperfine field is, to a good approximation, proportional to the spontaneous electronic moment for rare earths. In the case of $^{170}Yb^{3+}$, the proportionality constant is $C \simeq 102$ T/μ_B. At 0.09 K, the hyperfine field is 150(10) T,

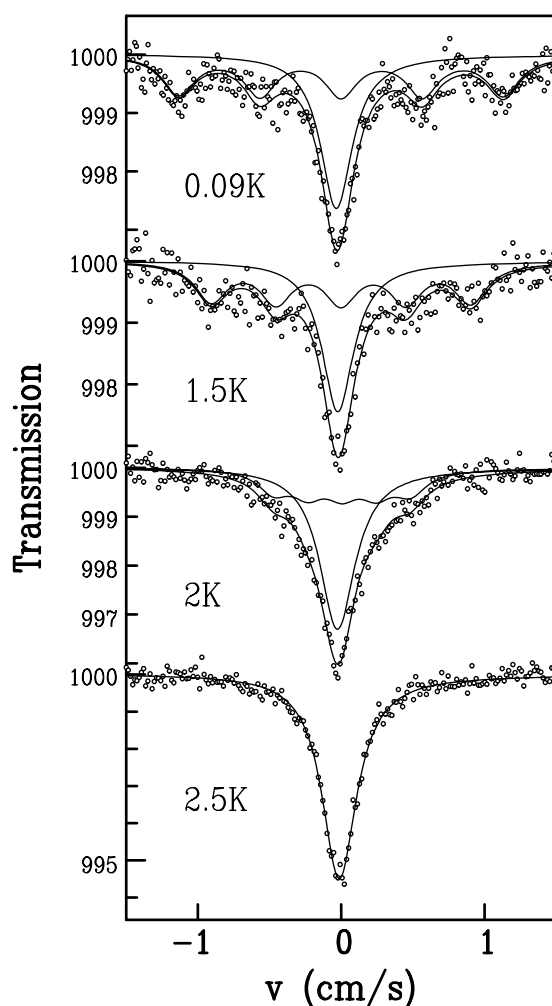**Figure 1.** ^{170}Yb Mössbauer absorption spectra for YbPd$_3$S$_4$ at selected temperatures.

and the derived saturated Yb^{3+} moment is $m_0 \simeq 1.5\ \mu_B$. In cubic symmetry, the crystal electric field ground state of the Yb^{3+} ion can be either the Γ_7 doublet ($m_0 = 1.715\ \mu_B$), the Γ_6 doublet ($m_0 = 1.33\ \mu_B$), or the Γ_8 quartet ($1.7\ \mu_B \leqslant m_0 \leqslant 2.1\ \mu_B$ according to the direction of the moment with respect to the cubic axes). In contrast to the Γ_6 and Γ_7 doublets, the Γ_8 quartet gives rise to a sizable quadrupolar hyperfine interaction in the magnetically ordered phase; it can be discarded from consideration as the ground state because the Yb^{3+} subspectrum in YbPd$_3$S$_4$ shows a vanishingly small quadrupolar interaction. As there are several effects that can cause slight deviation of the hyperfine field value from its bare crystal field value (enhancement through the exchange field, depletion by s-type conduction electron contribution, . . .), it is not possible at this stage to ascertain the crystal field Yb^{3+} ground state in YbPd$_3$S$_4$ since the measured moment value lies between those associated with Γ_6 and Γ_7.

The presence of about 2.5 wt% of the Yb$_2$O$_2$S impurity in the sample used for the Mössbauer measurements corresponds to an atomic Yb fraction of 1.9%. The ratio of the Mössbauer spectral intensities of an impurity phase and of the main phase is equal to the Yb

atomic ratio in the two phases corrected by the ratio of the Debye–Waller factors (Mössbauer f-factors). The f-factor depends on the Debye temperature Θ_D of the material and, near 0 K, it is given by $f = \exp(-\frac{3E_0^2}{4Mc^2\Theta_D})$, where E_0 is the energy of the nuclear transition, M is the mass of the Mössbauer nucleus, and c is the speed of light. The Debye temperature of Yb_2O_2S has been estimated to be about 300 K [10], and that of $YbPd_3S_4$ about 245 K [6]. Then, the spectral weight of Yb_2O_2S in the sample would be about 2.5%, i.e. it is negligible and the magnetic subspectrum observed below 2 K can be safely attributed to the main $YbPd_3S_4$ phase.

In a similar way, the ratio of the spectral intensities of the two valence states is equal to the atomic ratio corrected by the ratio of the f-factors for the two sites. These can have different Debye temperatures, which can be evaluated through the thermal variation of the spectral intensities. In $YbPd_3S_4$, such a procedure is not possible because the two subspectra are not resolved above 2 K. Mössbauer measurements have been performed on the isotypical compound $EuPd_3S_4$ [11], which shows properties very similar to those of $YbPd_3S_4$: a heterogeneous mixed-valence state, with equal quantities of Eu^{3+} and Eu^{2+}, and a metallic conductivity. ^{151}Eu Mössbauer spectroscopy allows the thermal behaviour of the two valence states to be followed up to high temperature. In $EuPd_3S_4$, it is found that the two states have slightly different Debye temperatures, yielding however an f-factor ratio at low temperature very close to 1. Then, the spectral intensity ratio at low temperature reflects the atomic ratio within experimental uncertainty. Assuming that this also holds for $YbPd_3S_4$, then the spectrum at 0.09 K shows the presence of two Yb valence states, with almost equal spectral weights: Yb^{2+} or close-to-divalent Yb and magnetically ordered Yb^{3+}. This is microscopic proof of a heterogeneous mixed-valence state, where the two configurations coexist statically on different Yb sites in the sample. As the timescale characteristic of ^{170}Yb Mössbauer spectroscopy is 10^{-8} s, this sets a lower limit for any time of fluctuation between the two valence states.

As temperature increases, the hyperfine field of the magnetic component decreases, the spectral weights remaining unchanged within experimental uncertainty. At 2 K, the Yb moment within the magnetic component is 0.6 μ_B. This is in agreement with a magnetic transition close to 2 K: the specific heat anomaly is rather broad and peaked at 1.8 K, and the magnetic susceptibility shows a maximum at 2.2 K [5].

Above 2 K, the spectra are no longer resolved and consist of a single line, somewhat broader than the individual line-widths below 2 K. This corresponds to the superposition of the Yb^{2+} line and of a line due to paramagnetic Yb^{3+}, because trivalent Yb in a cubic site shows no quadrupole hyperfine interaction in the paramagnetic phase. The extra broadening can be accounted for by the fact that the two valence states have different isomer shifts (-0.3 mm s^{-1} for Yb^{2+} and $\simeq 0.1$ mm s^{-1} for Yb^{3+}).

4. X-ray L$_{III}$-edge absorption data

The x-ray absorption spectrum at the Yb L$_{III}$ edge at 10 K is shown in figure 2. Two peaks are observed, one at 8935 eV corresponding to Yb^{2+}, and the other at 8942 eV corresponding to Yb^{3+}.

In order to extract the mean Yb valence, the spectrum was fitted to the superposition of two identical L$_{III}$-edge profiles, each being the sum of a Lorentzian-shaped line and a background arctangent function, and the two profiles being separated by an energy of 7.4 eV. The mean valence obtained is $v = 2.7(1)$. The spectrum at room temperature is identical and yields the same mean valence. The presence of about 5 wt% of Yb_2O_2S in the sample, corresponding to an atomic Yb^{3+} fraction of 3.8%, contributes a negligible weight to the trivalent peak.
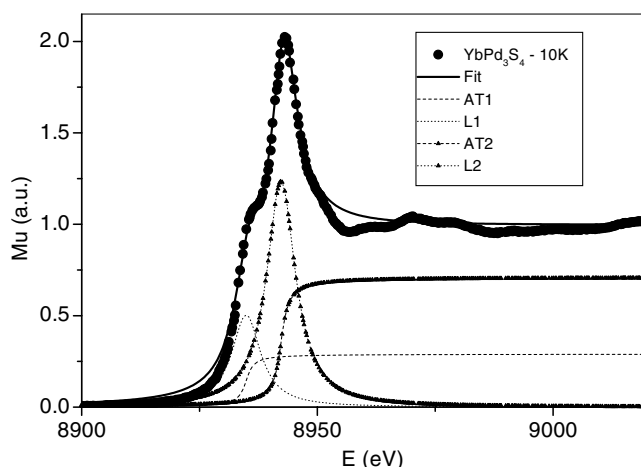
Figure 2. The x-ray L_{III}-edge absorption spectrum at 10 K for $YbPd_3S_4$ showing the two peaks corresponding to Yb^{3+} and Yb^{2+}.

With the assumption of a heterogeneous mixture of Yb^{2+} and Yb^{3+} ions in $YbPd_3S_4$, the measured valence yields 70(10)% of trivalent Yb, which is in agreement within experimental uncertainty with the fraction measured by Mössbauer spectroscopy, but somewhat higher than the mean Mössbauer value (55%). If one assumes an equal number of 'non-magnetic' Yb ions (associated with the single line in the Mössbauer spectrum at 0.09 K) and of trivalent Yb ions, then this yields a valence of 2.4 for the former. Such a non-integer valence close to 2 means that the corresponding Yb ions are in a homogeneous mixed-valence state, like for instance in Yb_4Sb_3 [12], with a small paramagnetic susceptibility which is quasi-independent of temperature. The combination of the x-ray L_{III}-edge and Mössbauer data gives thus the most probable picture for the heterogeneous mixed-valence state in $YbPd_3S_4$: equal quantities of trivalent, fully paramagnetic, Yb ions and of Yb ions with an intermediate valence of 2.4, weakly paramagnetic. The L_{III}-edge data also show that the proportion of the two valence states is temperature independent (at least up to 300 K).

5. Magnetic measurements

The magnetic susceptibility $\chi(T)$ was measured in a field of 150 G in the temperature range 2.5–320 K. The thermal variation of $1/\chi$, shown in figure 3, follows a Curie–Weiss law above 150 K, with an effective moment $\mu_{eff} \simeq 3.5\ \mu_B/Yb$ ion, and a paramagnetic Curie temperature $\theta_p \simeq -120$ K. At high temperature where the magnetic susceptibility is weak, the determination of the effective moment is hampered by the possible presence of a small paramagnetic susceptibility arising from the Yb_2O_2S impurity, and possibly from the intermediate-valence Yb ions discussed in the previous section. We checked however that addition of a small constant term to the Curie–Weiss law mainly affects θ_p without drastically changing the effective moment value. As the free ion effective moment for Yb^{3+} is 4.54 μ_B, the smaller measured value 3.5 μ_B corresponds to 60% of a trivalent ion per formula unit. This figure is in rather good agreement with the trivalent fraction derived from the Mössbauer spectra (55%). In the low-temperature region ($T < 40$ K), a Curie–Weiss law is also obeyed (see the inset in figure 3), with $\mu_{eff} \simeq 2.35\ \mu_B$ and $\theta_p \simeq -4.2$ K. Using the Yb^{3+} fraction obtained from the high-temperature data (60%), one obtains an effective moment of 3 μ_B/Yb^{3+} ion.
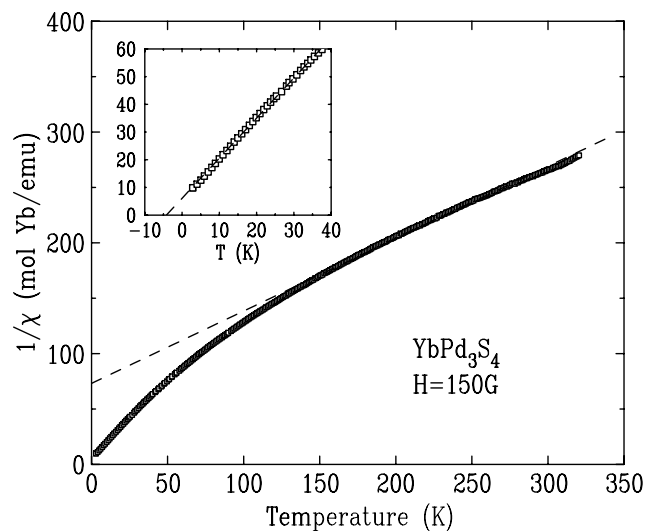
Figure 3. The thermal variation of the inverse magnetic susceptibility in YbPd$_3$S$_4$, measured with a field of 150 G. The inset shows the low-temperature part. The dashed lines represent Curie–Weiss laws (see the text).

The low-temperature Curie–Weiss law characterizes the behaviour of the ground crystal field doublet: the paramagnetic Curie temperature (-4.2 K) is compatible with a Néel temperature of 1.8 K, and the effective moment (3 μ_B) corresponds to the Γ_7 doublet (those of Γ_6 and Γ_8 are respectively 2.31 and 2.66 μ_B).

6. Discussion

Yb-based intermetallic compounds where two charge or valence states coexist are rather scarce. A few examples have been characterized by ^{170}Yb Mössbauer spectroscopy and γ–γ perturbed angular correlation measurements. Two cases are known where the two valence states occupy different sites in the unit cell: metallic Yb$_5$Si$_3$ [13] and semiconducting Yb$_3$S$_4$ [14]. Two other cases, where the Yb site is unique at high temperature, are metallic YbPd [4] and Yb$_4$As$_3$ [15, 16]. These two latter materials undergo a charge-ordering phase transition, at 110 K for YbPd and at 295 K for Yb$_4$As$_3$, accompanied by a distortion of the high-temperature cubic crystal structure. Magnetic ordering of the Yb^{3+} sublattice is found in YbPd ($T_N = 1.9$ K), whereas in Yb$_4$As$_3$ the Yb^{3+} fraction, arranged in ionic chains, is a one-dimensional antiferromagnet with no long-range magnetic ordering.

The problem of charge ordering cannot be addressed directly by Mössbauer spectroscopy itself, which is a local investigation technique. For YbPd$_3$S$_4$, a hint is given by the presence of magnetic ordering of the Yb^{3+} fraction, and by the observation of magnetic Bragg peaks at 1.6 K in the neutron diffraction pattern [5]. In our opinion, this implies that the Yb^{3+} ions lie on an ordered sublattice. A direct proof of the presence of charge ordering could be obtained by neutron diffraction experiments with a magnetic field at low temperature above T_N, because the Yb^{3+} ions will show a sizable induced magnetic moment and the non-magnetic (intermediate-valence) Yb ions will not.

A charge-ordering transition is accompanied by a lowering of the symmetry of the lattice, and the change in lattice constant can be very small (a few 0.1%). The charge-ordering

transition appears in principle as an anomaly in the thermal variation of several thermodynamic or transport quantities. In YbPd$_3$S$_4$, like in EuPd$_3$S$_4$, however, no structural distortion from the cubic structure could be detected up to 600 K, and no anomaly in the resistivity could be seen up to 550 K [6]. Then, we are left with the puzzling result that magnetic Bragg peaks are observed below $T_N \simeq 2$ K for YbPd$_3$S$_4$, but no hint of a lattice ordering of the Yb^{3+} ions can be found. A possibility for resolving this contradiction could be that charge ordering takes place at the same temperature as magnetic ordering of the trivalent fraction. This hypothesis is also probably borne out for EuPd$_3$S$_4$.

7. Conclusions

We have taken ^{170}Yb Mössbauer spectra, down to 0.09 K, and x-ray L$_{III}$-edge absorption and magnetic measurements for the cubic bronze YbPd$_3$S$_4$. Our data provide microscopic evidence that YbPd$_3$S$_4$ is a heterogeneous mixed-valence material, containing equal quantities of trivalent Yb ions and Yb ions with an intermediate valence of 2.4. The trivalent fraction orders magnetically below about 2 K, and the crystal field Yb^{3+} ground state is the cubic Γ_7 doublet. No charge-ordering transition could be detected up to high temperature, leaving the possibility that charge and magnetic ordering occur simultaneously at the Néel temperature. This question remains an incompletely resolved issue.

References

[1] Wachter P and Boppart H (ed) 1982 *Proc. Int. Conf. on Valence Instabilities (Zürich)* (Amsterdam: North-Holland)
[2] Morán-López J L and Schlottmann P 1980 *Phys. Rev.* B **22** 1912
[3] Berkooz O, Malamud M and Shtrikman S 1968 *Solid State Commun.* **6** 185
[4] Bonville P, Hammann J, Hodges J A, Imbert P and Jéhanno G 1986 *Phys. Rev. Lett.* **57** 2733
[5] Matsuoka E, Takahashi F, Kitagawa J, Ohoyama K, Yoshizawa H and Ishikawa M 2001 *J. Magn. Magn. Mater.* **231** L23
[6] Kitagawa J, Takabatake T, Matsuoka E, Takahashi F, Abe K and Ishikawa M 2002 *J. Phys. Soc. Japan* **71** 1630
[7] Rodriguez-Carvajal J 1993 *Physica* B **192** 55
[8] Daoudi A *et al* 1986 *Inorg. Chim. Acta* **117** 183
[9] Bonville P, Imbert P, Jéhanno G and Gonzalez-Jimenez F 1978 *J. Phys. Chem.* **39** 1273
[10] Rossat-Mignod J, Quezel G, Berton A and Chaussy J 1972 *Phys. Status Solidi* b **49** 147
[11] Wakeshima M, Doi Y, Hinatsu Y and Masaki N 2001 *J. Solid State Chem.* **157** 117
[12] Ochiai A, Nakai S, Oyamada A, Suzuki T and Kasuya T 1985 *J. Magn. Magn. Mater.* **47/48** 570
[13] Rams M, Królas K, Bonville P, Alleno E, Godart C, Kaczorowski D and Canepa F 1997 *Phys. Rev.* B **56** 3690
[14] Rams M, Królas K, Bonville P, Kwon Y S and Gonzalez-Jimenez F 1999 *Physica* B **259–261** 271
[15] Bonville P, Ochiai A, Suzuki T and Vincent E 1994 *J. Physique* I **4** 595
[16] Kohgi M, Iwasa K, Mignot J-M, Fak B, Gegenwart P, Lang M, Ochiai A, Aoki H and Suzuki T 2001 *Phys. Rev. Lett.* **86** 2439