Heterogeneous Yb$^{3+}$-Yb$^{2+}$ mixed valency and unusual Kondo ground state in Yb$_4$As$_3$


To cite this version:


HAL Id: jpa-00246933
https://hal.archives-ouvertes.fr/jpa-00246933
Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Heterogeneous Yb$^{3+}$-Yb$^{2+}$ mixed valency and unusual Kondo ground state in Yb$_4$As$_3$

P. Bonville (1,*), A. Ochiai (2), T. Suzuki (3) and E. Vincent (1)

(1) CEA, C.E. Saclay, DSM/DRECAM, Service de Physique de l’Etat Condensé, 91191 Gif-sur-Yvette, France
(2) The Oarai Branch, I.M.R., Tohoku University Oarai, Ibaraki 311-13, Japan
(3) Department of Physics, Tohoku University, Sendai 980, Japan

(Received 29 November 1993, accepted 15 December 1993)

Résumé. — Des mesures de spectroscopie Mössbauer sur $^{170}$Yb, dans le domaine de tempéra-
ture 0,045-50 K, et de susceptibilité magnétique et amputation, dans le domaine de tempéra-
ture 0,6-50 K, ont été réalisées dans le composé fermon lourd Yb$_4$As$_3$. La présence de $\sim$ 20\% d’ions Yb$^{3+}$ est détectée dans les spectres Mössbauer lorsqu’on applique un champ magnétique de 7 T, ce qui constitue une preuve microscopique de l’existence d’un état de valence mixte hétérogène contenant les ions Yb$^{2+}$ et Yb$^{3+}$. On n’a pas détecté d’ordre magnétique du sous-réseau Yb$^{3+}$ (avec des moments supérieurs à 0,15 $\mu_B$) jusqu’à 0,045 K. On a montré que la remontée à basse température de la susceptibilité magnétique est une caractéristique intrinsèque de Yb$_4$As$_3$, ce qui suggère que l’état fondamental est un réseau Kondo d’un type inhabituel.

Abstract. — We present $^{170}$Yb Mössbauer spectroscopy data in the temperature range 0.045-
50 K and magnetic susceptibility and isothermal magnetisation measurements in the tempera-
ture range 0.6-50 K in the heavy fermion compound Yb$_4$As$_3$. The presence of $\sim$ 20\% of Yb$^{3+}$
ions is detected in the Mössbauer spectra with an applied magnetic field of 7 T, yielding a
microscopic proof of the existence of a heterogeneous mixed valence state containing Yb$^{3+}$ and
Yb$^{2+}$ ions. No magnetic ordering of the Yb$^{3+}$ sublattice (with moments bigger than 0.15 $\mu_B$) is
detected down to 0.045 K. The low temperature upturn of the magnetic susceptibility is shown
to be an intrinsic feature of Yb$_4$As$_3$, suggesting that the ground state is of an unconventional
Kondo lattice type.

1. Introduction.

The phenomenon of charge ordering in metallic materials has seldom been observed because of
the charge screening effect due to the conduction electrons. Among rare earth intermetallics

(*) Email: bonville@amoco.saclay.cea.fr.
with definite metallic character, only cubic YbPd is known to undergo a charge ordering transition. A specific heat anomaly is observed in this compound at $T_{tr} = 110$ K [1], which was identified by $^{170}$Yb Mössbauer spectroscopy measurements [2] as due to Yb charge ordering; the low temperature phase of YbPd contains Yb$^{3+}$ and an intermediate valent Yb state in equal quantities, and the Yb$^{3+}$ sublattice orders magnetically below 1.9 K. Charge ordering could be present in metallic hexagonal Yb$_3$Si$_3$, with a 3 : 2 ratio of Yb$^{3+}$ and Yb$^{5+}$ ions, as suggested by the magnetic susceptibility measurements [3].

Among rare earth compounds with semiconducting or low carrier metallic character, a well known example of charge ordering is Eu$_3$S$_4$ [4] which contains the Eu$^{2+}$ and Eu$^{3+}$ ions in the ratio 2 : 1 below $T_{tr} = 186$ K. Recently, charge ordering has been observed in Eu$_4$As$_3$ by $^{151}$Eu Mössbauer spectroscopy below $T_{tr} = 340$ K with a 3 : 1 ratio of Eu$^{2+}$ and Eu$^{3+}$ ions [5]. In Yb$_4$As$_3$, a structural phase transition has been observed at $T_{tr} = 295$ K, with discontinuities of the resistivity and of the Hall coefficient [6]. The high temperature phase is cubic (anti-Th$_3$P$_4$ structure, space group $I43d$), and in the low temperature phase, the lattice has trigonal symmetry (space group $R3c$) as in Eu$_4$As$_3$. The magnetic susceptibility shows a Curie-Weiss behaviour between 250 K and 80 K, with an effective moment corresponding approximately to one Yb$^{5+}$ ion per formula unit and a paramagnetic Curie temperature $\Theta_p \approx -60$ K [6]. This behaviour can be interpreted by the hypothesis of a low temperature charge ordered phase with a 3 : 1 ratio of Yb$^{2+}$ and Yb$^{3+}$ ions. In such a case, a likely ionic arrangement in the rhombohedral unit cell has two Yb$^{3+}$ ions on the (111) axis separated by a distance $\frac{\sqrt{3}a}{4} \approx 3.8$ Å, and six Yb$^{2+}$ ions.

The transport and specific heat data [6, 7] have shown that, in its low temperature phase, Yb$_4$As$_3$ has an extremely low carrier concentration of 0.001 per Yb atom and that the assumed Yb$^{3+}$ component shows the properties of a heavy-electron material (or Kondo lattice) [8]: the magnetic resistivity shows a $T^2$ thermal variation up to 50 K usually ascribed to electron-electron interactions within the heavy quasi-particle band, and the Sommerfeld coefficient $\gamma$ of the specific heat $C_{el}$ has the relatively high value of 160-200 mJ/mol K$^2$ in zero magnetic field. Application of a magnetic field larger than 3 T reduces the $\gamma$ coefficient at low temperature, which suggests that the heavy-electron behaviour in Yb$_4$As$_3$ is perturbed by the presence of a relatively small magnetic field.

The low temperature behaviour of the magnetic susceptibility is peculiar: as the temperature decreases, there appears a deviation from a Curie-Weiss law followed by a plateau below 15 K, with a value $\chi_0 \approx 2.75 \times 10^{-2}$ emu/mole; below 10 K, the susceptibility starts increasing anew, and this was first attributed to the presence of "impurity" Yb$^{3+}$ ions, such as is observed in the intermediate valence compounds Yb$_4$Sb$_3$ and Yb$_4$Bi$_3$ [6].

All the measured properties, especially the transport properties, show a marked sample dependence; the specific heat and magnetic susceptibility seem to be less sample sensitive [7], which could indicate that the carrier concentration can vary appreciably according to sample preparation.

In this work, we report on low temperature $^{170}$Yb Mössbauer spectroscopy and magnetic measurements in Yb$_4$As$_3$. The present sample has a lattice constant of $a = 8.789$ Å in the cubic high temperature phase. The Mössbauer data will be shown to give a microscopic proof of the existence of a heterogeneous mixed valence state at low temperature in this compound. Unlike for the isotope $^{151}$Eu, Mössbauer spectroscopy with $^{170}$Yb does not allow the two Yb valence states to be distinguished by the isomer-shift value: the natural linewidth is indeed 10 times larger than the isomer-shift difference between the Yb$^{2+}$ and Yb$^{3+}$ valence states [9]. The valence states can be unambiguously distinguished through the quadrupolar hyperfine interaction in non-cubic compounds, or by their magnetic properties like in YbPd: Yb$^{3+}$ is
paramagnetic with $J = 7/2$ (spin-orbit ground state of the $4f^{13}$ configuration) whereas Yb$^{2+}$ is diamagnetic with $J = 0$ ($4f^{14}$ configuration). In Yb$_4$As$_3$, we could evidence the presence of Yb$^{3+}$ ions by detecting their polarisation in a strong magnetic field at very low temperature.

The magnetic measurements down to 0.5 K are performed to investigate the low temperature upturn of the magnetic susceptibility, which is visible in the data of reference [6] down to 4.2 K; combining the results obtained by the local Mössbauer technique and the bulk magnetic measurements, we show that this upturn is intrinsic and we discuss the implications concerning the ground state of the paramagnetic fraction in Yb$_4$As$_3$.

2. Mössbauer measurements with the $^{170}$Yb isotope.

2.1 Spectra in zero magnetic field. — The spectra, which were recorded in the temperature range $0.045 \leq T \leq 60$ K in zero magnetic field, show very little thermal variation. They consist of a slightly asymmetrical line which can be very satisfactorily fitted to an axial quadrupolar hyperfine Hamiltonian:

$$\mathcal{H}_Q = \frac{eQV_{zz}}{8} [I_2^2 - \frac{I(I + 1)}{3}]$$

where $Q = -2.11$ barn and $I = 2$ are respectively the electric quadrupole moment and the spin of the excited $^{170}$Yb nuclear state (the ground nuclear state has $I_g = 0$), and $V_{zz}$ is the main component of the axial Electric Field Gradient tensor at the Yb site. The fitted value of $eQV_{zz}/8$ is $\approx 0.5$ mm/s in the whole temperature range and corresponds to $V_{zz} \approx 53 \times 10^{23}$ erg cm$^{-1}$ cm$^{-2}$. This indicates that the Yb ions lie at a site with non-cubic axial symmetry, in agreement with the trigonal distortion observed in the low temperature phase of Yb$_4$As$_3$. The relatively small value and the absence of thermal variation of $eQV_{zz}/8$ show that the electric field gradient mainly arises from lattice charges and not from the electrons of an incomplete 4f shell. This fact, together with the isomer-shift value of $-0.12$ mm/s (with respect to a TmB$_{12}$ γ-ray source), shows that the spectra arise mainly from Yb$^{2+}$ ions [9]. It is not possible, in these zero field spectra, to resolve two components that would correspond to the two valence states Yb$^{3+}$ and Yb$^{2+}$, which have very slightly different isomer shifts. The spectrum at $T = 0.045$ K, represented in figure 1a, does not show any hint of a magnetic hyperfine interaction; this means that there is no magnetic ordering in Yb$_4$As$_3$ down to 0.045 K with magnetic moments bigger than 0.15 $\mu_B$, which is the resolution limit with the $^{170}$Yb isotope.

The presence of this axially symmetric E.F.G. tensor at a Yb site also quantitatively accounts for the upturn of the specific heat $C_\text{cl}$ observed below 0.2 K [10]. The high temperature tail of the nuclear quadrupolar Schottky anomaly due to the $^{173}$Yb isotope ($I = 5/2, Q = 3.1$ barn), calculated using the above measured $V_{zz}$ value, indeed satisfactorily reproduces the observed increase of $C_\text{cl}/T$ in the 100 mK range.

2.2 Spectra with applied magnetic field. — Spectra were recorded between $T = 0.045$ K and 4.2 K with an external magnetic field of 7 T oriented perpendicularly to the direction of propagation of the γ-rays. The polycristalline sample was mixed with an epoxy ligand to prevent rotation of the grains in the magnetic field. The spectrum at $T = 0.045$ K, represented in figure 1b, reveals a small difference with respect to the zero field spectrum at the same temperature (Fig. 1a): an extra absorption is visible on the wings of the central line, symmetrical with respect to the center of the velocity (or energy) range. This component is interpreted as arising from paramagnetic Yb$^{3+}$ ions polarised by the external field $H$, the resulting spectrum
Fig. 1. $^{170}$Yb Mössbauer absorption spectra at $T = 0.045$ K in Yb$_4$As$_3$. a) Spectrum in zero magnetic field; the continuous line is a fit to the quadrupolar hyperfine Hamiltonian (1). b) Spectrum with a field of 7 T applied perpendicularly to the γ-ray direction of propagation; the continuous lines show the contributions of the Yb$^{2+}$ (single line) and of the Yb$^{3+}$ (four line spectrum) ions (see text).

As the trigonal distortion in the temperature phase of Yb$_4$As$_3$ is small, we can reasonably assume that the crystalline anisotropy at the Yb$^{3+}$ site is weak and therefore that the field induced Yb$^{3+}$ magnetic moment $\mu$ is close to parallel to the external field $\mathbf{H}$. In this case, $\theta = 90^\circ$ and, according to expression (3), the Yb$^{3+}$ spectrum consists of the four $m_I = \pm 1$, ±2 lines with equal intensities, the central $m_I = 0$ line being absent. We mention that the choice of a perpendicular geometry ($\mathbf{H} \perp \mathbf{k}$) yields a better resolution in the case of a small magnetic polarisation; in a parallel geometry ($\mathbf{H} \parallel \mathbf{k}$) with $\theta = 0$, only the two $m_I = \pm 1$ lines are present, and for a given hyperfine field, the spectrum extension is half that obtained with $\theta = 90^\circ$.

The two-component fit shown in figure 1b is a superposition of a magnetic hyperfine spectrum with $\theta = 90^\circ$ and of a quadrupolar hyperfine spectrum corresponding respectively to the contribution of the Yb$^{3+}$ and Yb$^{2+}$ ions. Similar fits were performed for the spectra at $T = 0.1$ K, 0.6 K and 4.2 K, which also show the contribution due to the polarised Yb$^{3+}$ ions. In

\[ \mathcal{H}_{\text{mag}} = -g_n\mu_n \mathbf{I} \cdot \mathbf{H}_{\text{hf}} \]  

where $g_n$ is the excited nuclear state gyromagnetic ratio and $\mathbf{H}_{\text{hf}}$ the hyperfine field proportional to the field induced Yb$^{3+}$ magnetic moment: $\mathbf{H}_{\text{hf}} = C\mu(H)$. The intensities of the five nuclear transitions $|I_S = 0 > \leftrightarrow |I = 2, m_I >$ depend on the angle $\theta$ between $\mathbf{H}_{\text{hf}}$ (or $\mu$) and the direction $\mathbf{k}$ of propagation of the γ rays and are given by the following expressions:

\[
\begin{align*}
I(m_I = \pm 2) &= \frac{1}{2}\sin^2 \theta(1 + \cos^2 \theta) \\
I(m_I = \pm 1) &= \frac{1}{2}(\cos^2 \theta + \cos^2 2\theta) \\
I(m_I = 0) &= \frac{3}{4}\sin^2 2\theta
\end{align*}
\]  

As the trigonal distortion in the temperature phase of Yb$_4$As$_3$ is small, we can reasonably assume that the crystalline anisotropy at the Yb$^{3+}$ site is weak and therefore that the field induced Yb$^{3+}$ magnetic moment $\mu$ is close to parallel to the external field $\mathbf{H}$. In this case, $\theta = 90^\circ$ and, according to expression (3), the Yb$^{3+}$ spectrum consists of the four $m_I = \pm 1$, ±2 lines with equal intensities, the central $m_I = 0$ line being absent. We mention that the choice of a perpendicular geometry ($\mathbf{H} \perp \mathbf{k}$) yields a better resolution in the case of a small magnetic polarisation; in a parallel geometry ($\mathbf{H} \parallel \mathbf{k}$) with $\theta = 0$, only the two $m_I = \pm 1$ lines are present, and for a given hyperfine field, the spectrum extension is half that obtained with $\theta = 90^\circ$.

The two-component fit shown in figure 1b is a superposition of a magnetic hyperfine spectrum with $\theta = 90^\circ$ and of a quadrupolar hyperfine spectrum corresponding respectively to the contribution of the Yb$^{3+}$ and Yb$^{2+}$ ions. Similar fits were performed for the spectra at $T = 0.1$ K, 0.6 K and 4.2 K, which also show the contribution due to the polarised Yb$^{3+}$ ions. In
these fits, the Yb$^{3+}$ component is found to be identical to the zero field spectrum. For the Yb$^{3+}$ component, the following parameters are obtained: at $T = 0.1$ K, $H_{hf} = 66(6)$ T and a relative weight $(21 \pm 3)$%; at $T = 4.2$ K, $H_{hf} = 58(10)$ T and a relative weight $(19 \pm 5)$%. Using the $^{170}$Yb$^{3+}$ hyperfine constant $C = 102T/\mu_B$, this yields the following induced moment per Yb$^{3+}$ ion for $H = 7$ T: $\mu(T = 0.1 \text{ K}) \approx 0.65(7) \mu_B$ and $\mu(T = 4.2 \text{ K}) \approx 0.56(10) \mu_B$. These magnetic moment values are reported in figure 3 together with the magnetisation measurements. Although the error bars are relatively large, they show a systematic trend to increase as temperature is lowered.

These measurements therefore show the presence of $(20\pm5)$% of Yb$^{3+}$ ions at low temperature in Yb$_4$As$_3$; within experimental uncertainty, this percentage is close to that $(25 \%)$ derived from the value of the high temperature effective magnetic moment [6]. As all spectroscopic techniques, Mössbauer spectroscopy is sensitive to electronic fluctuations within a given frequency window; for the isotope $^{170}$Yb, the lower end of the window is at a frequency of $\sim 10$ MHz; consequently, our measurements show that, if any fluctuations do occur between the Yb$^{3+}$ and Yb$^{2+}$ states in Yb$_4$As$_3$, they occur at a frequency lower than 10 MHz. Very probably, at $T = 4.2$ K and below, any charge fluctuations should be frozen and we can state that we have observed a static array of Yb$^{3+}$ and Yb$^{2+}$ ions.

It must be mentioned that, as the Yb$^{3+}$ and Yb$^{2+}$ ions could occupy different crystallographic sites in the low temperature phase, their respective Lamb-Mössbauer f-factors for resonant $\gamma$-ray absorption could be different. In such a case, the weights of the two spectral components could not exactly reflect the atomic percentages of the two charge states. We think however that any f-factor difference should be small because the distortion from cubic symmetry is small, and that its magnitude should lie within the error bars.

### 3. Magnetic measurements.

#### 3.1 Magnetic Susceptibility.

The magnetic susceptibility, measured by a standard extraction technique with a field of 0.1 T between 0.6 K and 53 K, is represented in figure 2, the insert showing the low temperature part in greater detail. As temperature decreases, a first plateau is found around 10 K, with \( \chi_1 \approx 2.8 \times 10^{-2} \text{ emu/mole} \), in agreement with previous measurements [6, 7]. After a small increase, a second smaller plateau occurs between 2 K and 4 K, with \( \chi_2 \approx 3.2 \times 10^{-2} \text{ emu/mole} \). Below 2 K, the susceptibility increases according to a Curie-Weiss law:

$$\chi(T) = \frac{\mu_{\text{eff}}^2}{3k_B(T + \Theta_p)},$$

with $\Theta_p \approx -0.84$ K and $\mu_{\text{eff}} \approx 0.88 \mu_B$, assuming one Yb$^{3+}$ ion per formula unit. The thermal variation of $\chi(T)$ down to 10 K is reminiscent of a Kondo behaviour, which occurs in the presence of 4f electron-band electron hybridisation [11]. The ground state of a Kondo system is a magnetic singlet and therefore the magnetic susceptibility saturates, well below a characteristic temperature $T_K$, towards a value $\chi(0K) \approx \frac{\mu_{\text{eff}}^2}{3k_B T_K}$. For Yb$_4$As$_3$, taking the first plateau value $\chi_1$ as $\chi(0)$, one gets a Kondo temperature $T_K \approx 70$ K. However, the Kondo picture does not account for the low temperature upturn of $\chi(T)$ which, as is shown in the next section, is an intrinsic feature of the Yb$^{3+}$ sublattice. The Curie-Weiss behaviour observed below 2 K indicates a breakdown of the Kondo singlet, the Yb$^{3+}$ ions recovering paramagnetic moments of the order of 1 $\mu_B$. 
Fig. 2. — Low temperature magnetic susceptibility in Yb$_4$As$_3$; the insert shows the thermal variation for $T < 10$ K with the same units as the main figure.

3.2 Isothermal Magnetisation. — The isothermal magnetisation measurements were performed at $T = 0.6$ K, 1.2 K and 4.2 K in fields up to 5 T. They are represented in figure 3, together with the moment values derived from the Mössbauer hyperfine field at 7 T. The insert of figure 3 shows the low field part of the $m$ vs. $H$ curves. In order to obtain the moment value per Yb$^{3+}$ ion, we assumed, consistently with the Mössbauer data, a fraction of 0.2 Yb$^{3+}$ per formula unit. At $T = 4.2$ K, the $m$ vs. $H$ curve is linear; below 1.2 K a downward curvature appears at low fields, the initial slope of the $m$ vs. $H$ curve increasing as temperature decreases. This corresponds to the Curie-Weiss increase of the susceptibility below 2 K. For higher fields, below 1.2 K, the increase of the magnetisation is linear with the field and no tendency to saturation is observed up to 5 T, nor even up to 35 T at 4.2 K [12].

The Mössbauer derived moment values at 7 T can be compared with the magnetisation data by linearly extrapolating the $m$ vs. $H$ curves at 0.6 K and 4.2 K, assuming that the field variation is linear in the small interval between 5 and 7 T. This linear extrapolation intersects the lower part of the Mössbauer error bars at $T = 0.6$ K and 4.2 K (not shown in the figure for clarity). This shows that the 20% of Yb$^{3+}$ per formula unit, observed by Mössbauer spectroscopy, are those giving rise to the low temperature susceptibility increase, i.e. that this feature is an intrinsic property of Yb$_4$As$_3$. The coherence between the two types of measurements must be underlined: Mössbauer spectroscopy is a local technique, which can measure the modulus of the individual magnetic moments, and their concentration in the present case, whereas the measured magnetisation is that of the bulk and was converted into moment per Yb$^{3+}$ using the Mössbauer derived content in Yb$^{3+}$ ions.

4. Discussion.

The present experiments cannot distinguish between a charge-ordered phase where the Yb$^{3+}$ ions would occupy regular crystallographic sites, and a heterogeneous mixed valence state where the Yb$^{3+}$ ions would be located at random in the lattice. The Mössbauer derived percentage of Yb$^{3+}$ ions ($\approx 20\%$) in the low temperature phase of Yb$_4$As$_3$ is somewhat smaller than the expected fraction (25%) based on crystallographic considerations in the case of a charge-
ordered state, as in Eu₄As₃. This could be an indication in favour of a disorder of the two charge states in the lattice. However, a definitive proof of the existence of a charge ordered state could be provided by a neutron diffraction study with a large applied magnetic field. At 4.2 K with \( H = 7 \) T, the individual Yb\(^{3+}\) magnetic moments are \( \approx 0.55 \) \( \mu_B \), which is large enough for magnetic Bragg peaks to be detected in the case of a charge-ordered state.

The low temperature upturn of the magnetic susceptibility has been attributed, in a first analysis, to the presence of a small fraction (0.001) of Yb\(^{3+}\) ions, by analogy with Yb₄Sb₃ and Yb₄Bi₃ where the same phenomenon is observed [6]. However, these two compounds contain homogeneously intermediate valent Yb ions, with a weak paramagnetic susceptibility, and therefore the presence of a small amount of normal paramagnetic “impurity” Yb\(^{3+}\) ions is very likely. In a \(^{75}\)As NQR investigation of Yb₄As₃ [13], the quantity \( \frac{1}{T_1T} \), where \( 1/T_1 \) is the nuclear spin lattice relaxation rate of \(^{75}\)As, was found to follow a thermal variation very close to that of the magnetic susceptibility, with a sharp increase below 4 K. This suggested that the low temperature upturn of the magnetic susceptibility is an intrinsic feature of the Yb\(^{3+}\) fraction of Yb₄As₃. Indeed, the spin lattice relaxation of the \(^{75}\)As nuclei is very likely to be driven by the Yb\(^{3+}\) spin fluctuations through a transferred hyperfine interaction and there would be no reason why \( \chi(T) \) and \( \frac{1}{T_1T} \) follow similar thermal variations if the Yb\(^{3+}\) ions were present only as impurities. In the present work, by comparing the response to a magnetic field of these Yb\(^{3+}\) ions using both a local technique and a bulk measurement, we could demonstrate that the low temperature Curie-Weiss like behaviour of the susceptibility observed between 0.6 K and 2 K is an intrinsic feature of the ground state of the Yb\(^{3+}\) sublattice and is not due to isolated impurity Yb\(^{3+}\) ions. Eventually, a concentration of 0.001 Yb\(^{3+}\) could not have been detected in the Mössbauer spectra.

Down to 10 K, the behaviour of the Yb\(^{3+}\) sublattice is that of a dense Kondo material, with a high Kondo temperature \( T_K \sim 70 \) K and a heavy-fermion like electronic specific heat with \( \gamma = 160-200 \) mJ K\(^{-2}\) mole\(^{-1}\). However, its ground state is clearly not of a conventional Kondo lattice type, at least as concerns its magnetic properties. For low applied magnetic

Fig. 3. — Isothermal magnetisation curves in Yb₄As₃ below 4.2 K \( (H \leq 5 \) T) and Yb\(^{3+}\) magnetic moment derived from the \(^{170}\)Yb Mössbauer hyperfine field for \( H = 7 \) T. The error bars for \( H = 7 \) T and \( T = 0.05 \) and 4.2 K are not shown for clarity; they are of the same magnitude as the represented ones. The insert shows the low field \( m \) vs. \( H \) curves with the same units as the main figure.
fields below 2 K, the Yb\textsuperscript{3+} sublattice has sizeable paramagnetic moments (\(\sim 1\mu_B\)) which could be antiferromagnetically correlated with a characteristic energy of 1 K, as deduced from the \(\Theta_K\) value (\(\sim -0.9\) K) and from the onset temperature (1 K) of a downward curvature of the low field magnetisation curves. The fact that no magnetic ordering is observed down to 0.045 K suggests that the Yb\textsuperscript{3+} ions could be distributed at random in the lattice, inhibiting long range magnetic correlations to develop. An alternative explanation for this behaviour could be the existence at low temperature of a Kondo coupling with a small Kondo temperature (< 1 K), resulting in quantum spin fluctuations hindering the establishment of magnetic order.

The small magnitude of the paramagnetic moments below 2 K could be caused by the crystal electric field interaction, which is probably also responsible for the deviation from the Curie-Weiss law observed below 80 K. However, all of the cubic eigenstates of Yb\textsuperscript{3+} (neglecting the small trigonal distortion) have effective paramagnetic moments bigger than 1 \(\mu_B\) and therefore the observed moment reduction remains an open question. The crystal electric field level scheme in Yb\textsubscript{4}As\textsubscript{3} is being presently investigated by neutron inelastic scattering [14].

5. Conclusion.

The \(^{170}\)Yb Mössbauer measurements with an external magnetic field of 7 T have provided a microscopic proof of the existence of a heterogeneous mixed valence state in Yb\textsubscript{4}As\textsubscript{3} at low temperature. The two charge states Yb\textsuperscript{2+} and Yb\textsuperscript{3+} are present in the lattice, with \(\sim 20\%\) Yb\textsuperscript{3+} ions. Combining the Mössbauer data with magnetisation and susceptibility measurements, it was shown that the low temperature susceptibility increase, which had first been attributed to impurity Yb\textsuperscript{3+} ions, is an intrinsic feature of the Yb\textsuperscript{3+} sublattice. The physics of this Yb\textsuperscript{3+} sublattice, in the low temperature phase, can tentatively be described, for low applied magnetic fields, as consisting of two regimes, the crossover being around \(T = 2\) K. The high temperature regime is that of a Kondo lattice with a large Kondo temperature \(\sim 70\) K, and probably a sizeable Crystal Electric Field interaction. As temperature decreases, the magnetic degrees of freedom of the Yb\textsuperscript{3+} ground state start to freeze into a Kondo singlet around 10 K. Below 2 K, the Kondo singlet is broken and the magnetic degrees of freedom are released; the paramagnetic Yb\textsuperscript{3+} moments, of the order of magnitude of 1 \(\mu_B\), are coupled by an antiferromagnetic interaction of magnitude 1 K, but the system shows no long range magnetic ordering, with magnetic moments larger than 0.15 \(\mu_B\), down to 0.045 K. For moderate applied magnetic fields (> 2 T), the low temperature heavy electron behaviour is destroyed and surprisingly, the “high field” magnetic susceptibility drops markedly with respect to the low field value. The ground state of the Yb\textsuperscript{3+} sublattice in Yb\textsubscript{4}As\textsubscript{3} is therefore of an unconventional type and its elucidation needs more experimental work, especially at very low temperature.

References