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Magnetic ordering in the heavy-electron compound YbSi

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Abstract. ^{170}Yb Mössbauer experiments in the heavy-electron compound YbSi are presented in the temperature range 0.045–100 K. Magnetic ordering of the Yb moments below 1.6 K is confirmed and a strong moment reduction in the magnetic phase is demonstrated. The crystal-field excitation is found to be of the order of 100 K and the low-temperature Kondo energy scale is estimated to be 2.5 K. YbSi is thus a heavy-electron material where Kondo-frustrated magnetic ordering occurs due to the competition between RKKY exchange and Kondo coupling.

1. Introduction

The heavy-electron materials are intermetallic compounds containing Ce, Yb or U where hybridisation between the f electrons and band electrons leads to unusual transport and magnetic properties [1]. The 'generic' feature of these compounds is the high value of the electronic specific heat coefficient γ or equivalently of the carrier effective mass, which can reach more than 100 times the free-electron mass. Another striking characteristic of these materials is the progressive quenching of the f-electron magnetic moments as the temperature decreases, which is attributed to the formation of a Kondo singlet ground state with an energy scale $k_B T_K$. In fact, the actual ground state of such systems is determined by a complex interplay between the Kondo coupling ($k_B T_K$), the RKKY exchange interaction ($k_B T_{RKKY}$) and the crystal electric field (CEF) acting on the rare-earth or U ion (Δ_{CEF}).

A magnetically ordered ground state can be expected in heavy-electron compounds when the following hierarchy of interactions holds: $k_B T_K \leqslant k_B T_{RKKY} \ll \Delta_{CEF}$. This can be understood as follows: the Kondo coupling favours a zero-moment ground state, whereas the RKKY exchange favours a magnetic ground state, and so the latter must dominate the Kondo energy scale for magnetic ordering to set in. The role of the CEF interaction is to lift the free-ion degeneracy and so to determine, in a given temperature range, the levels which will be involved in the hybridisation. It has been shown to

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influence greatly the strength of the Kondo energy scale [2, 3]. In the case of Yb^{3+} (ground spin–orbit multiplet with $J = \frac{7}{2}$) the CEF interaction splits the eightfold free-ion degeneracy into four Kramers doublets. If T_K^0 is the 'high-temperature' Kondo energy scale and Δ_{CEF} an order of magnitude of the energy separation between the lowest CEF states with degeneracy N_1 and the excited CEF states with degeneracy N_2, the effective low-temperature Kondo energy scale is expressed as: $T_K \simeq T_K^0(k_B T_K^0/\Delta_{CEF})^{N_2/N_1}$. This expression holds when $k_B T_K^0 \ll \Delta_{CEF}$. For a well isolated ground doublet, one obtains: $T_K/T_K^0 \simeq (k_B T_K^0/\Delta_{CEF})^3$, i.e. the effective low-temperature Kondo coupling can be reduced by a factor 10 or 100 with respect to the 'high-temperature' T_K^0. Then a magnetically ordered ground state is likely to occur when: $k_B T_K \leqslant k_B T_{RKKY} \ll k_B T_K^0 \ll \Delta_{CEF}$. Such a situation is encountered in the Yb monopnictides where our ^{170}Yb Mössbauer experiments have determined the features of a Kondo-frustrated antiferromagnetic ordering of the Yb^{3+} moments below about 0.5 K [4–6].

Generally speaking, Mössbauer spectroscopy, as a microscopic probe technique, can provide valuable information concerning the CEF splitting, the effective ordering temperature, the magnetic moments and eventually the strength of the RKKY interaction in magnetic Yb heavy-electron systems. We present here a ^{170}Yb Mössbauer study, down to 0.045 K, of the compound YbSi. Previous transport, specific heat and magnetic measurements [7, 8] have ascertained the heavy-fermion character of YbSi, which has one of the largest electronic specific heat coefficients observed to date in Yb compounds and a high-temperature Kondo energy scale T_K^0 of a few 10 K. Antiferromagnetic ordering below 1.6 K was inferred from the specific heat and resistivity kinks at that temperature [8]. Our Mössbauer data confirm the presence of magnetic ordering below 1.6 K and show that the spontaneous moment of the Yb^{3+} ion is quite small: $0.2–0.3\mu_B$. We could give a rough estimation of the CEF excitation which is found to be of the order of 100 K.

2. Experimental

2.1. Sample preparation

The compound was prepared from ytterbium(3N) and silicon(5N). Stoichiometric amounts of starting materials were put in an outgassed tantalum tube with both ends squeezed in high-current clamps and then melted for about one minute by resistance heating in a 10^{-5} Torr vacuum. During the melting the tube was mechanically vibrated and reversed several times in order to ensure good homogeneity. The sample is a single-phase polycrystal (except for a few percent of Yb_2O_3).

2.2. Crystal structure

The x-ray powder spectrum is characteristic of the orthorhombic CrB-type structure with parameters $a = 4.178$ Å, $b = 10.31$ Å and $c = 3.768$ Å [9]. The Cmcm (D_{2h}^{17}) space group implies the presence of two perpendicular mirror planes ($\boldsymbol{b}, \boldsymbol{a}$) and ($\boldsymbol{b}, \boldsymbol{c}$) at a Yb site. Figure 1 shows the orthorhombic lattice cell of YbSi which contains four molecular units. The Yb sites are crystallographically equivalent, as are the Si sites. The five Si nearest neighbours of an Yb atom form a pyramid with a rectangular base ($\boldsymbol{a}, \boldsymbol{c}$), as shown in figure 1.

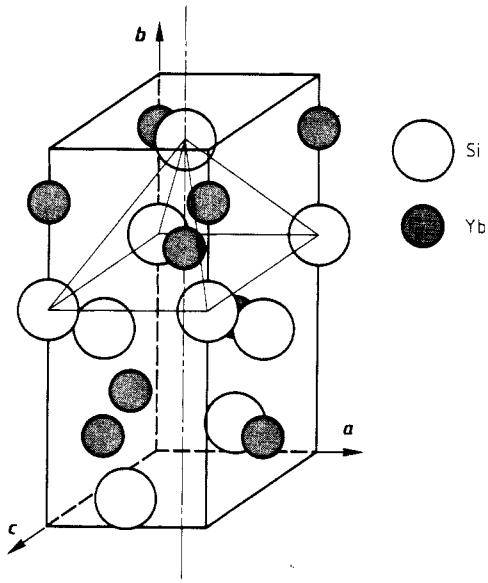

Figure 1. Orthorhombic lattice cell of YbSi. The chain axis is the assumed tetragonal axis (see text). The distances from the Yb ion at the centre of the Si pyramid to the Si ion on the axis is 2.95 Å and to the four Si ions on the pyramid base is 2.89 Å.

2.3. Mössbauer spectrometry

The ^{170}Yb Mössbauer spectra were recorded using a triangular Doppler velocity signal and a monochromatic γ-ray source of ^{170}Tm in TmB_{12}. The full width at half maximum (FWHM) of the line, as measured with a reference absorber of YbB_6, is 2.72 mm s^{-1} (1 mm s^{-1} corresponds to 68 MHz for ^{170}Yb). The low-temperature spectra were recorded using a ^{3}He–^{4}He refrigerator (0.045 K $\leqslant T \leqslant$ 1.6 K) and a standard ^{4}He cryostat at higher temperatures (1.6 K $\leqslant T \leqslant$ 100 K).

The 0^+–2^+ nuclear transition of ^{170}Yb has an energy of 84.3 keV and yields five transitions $\Delta I_z = 0, \pm 1, \pm 2$.

3. Mössbauer data

3.1. Paramagnetic phase

The absorption spectrum obtained at 4.2 K is shown in figure 2(*b*). Its general form is representative of the spectra we observe in the paramagnetic region, i.e. above 1.6 K. It corresponds to a quadrupolar electric hyperfine interaction:

$$\mathcal{H}_Q = \alpha_Q(I_z^2 - 2) + (\eta/6)(I_+^2 + I_-^2)$$

where $\alpha_Q = eQV_{zz}/8$ is the quadrupolar coupling constant and $\eta = |V_{xx} - V_{yy}|/V_{zz}$ is the asymmetry parameter of the electric field gradient (EFG) tensor $\{V_{xx}, V_{yy}, V_{zz}\}$, V_{zz} being its largest component. Q is the nuclear excited-state quadrupole moment. Fitting the spectrum at $T = 4.2$ K yields: $\alpha_Q = (-1.59 \pm 0.01)$ mm s^{-1} and $\eta < 0.05$. The EFG tensor thus has axial symmetry to a good approximation at the Yb site. The Cmcm space group of the YbSi lattice implies that the axes of the EFG tensor at the Yb site are the crystallographic axes ***a***, ***b*** and ***c***. As the nearest environment of an Yb ion is a Si pyramid with an approximately square base having the ***b*** axis as a fourfold symmetry axis (see

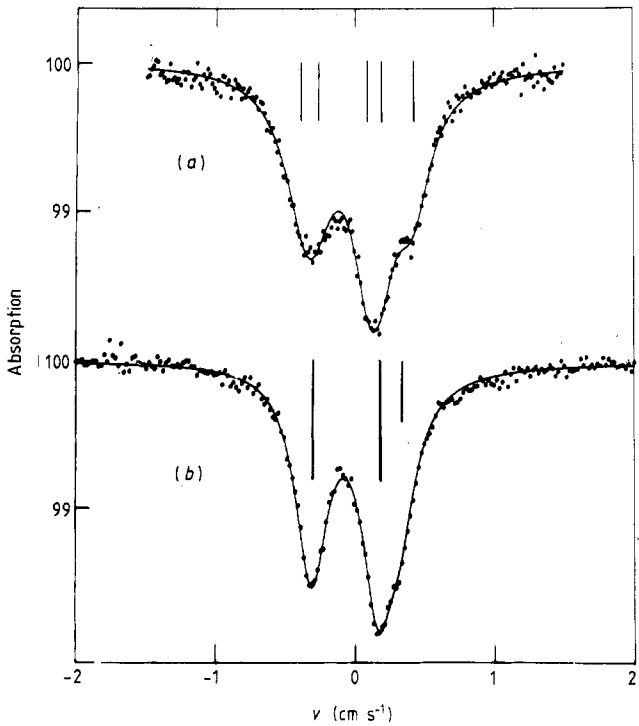

Figure 2. ^{170}Yb Mössbauer spectra in YbSi at $T = 0.045$ K (a) and $T = 4.2$ K (b). The full curves are fits as explained in the text. The vertical bars indicate the positions of the hyperfine energies, their length being proportional to the transition amplitude.

figure 1), our data suggest that the principal EFG axis is the crystal $\boldsymbol{b}$ axis. This in turn leads us to assume that the CEF interaction at the Yb site has approximately tetragonal symmetry around the $\boldsymbol{b}$ axis.

The quadrupolar coupling parameter α_Q decreases slowly with increasing temperature: at 55 K, we obtain: $\alpha_Q = -1.47$ mm s^{-1} and at 100 K: $\alpha_Q = -1.06$ mm s^{-1}. The 30% decrease of α_Q at 100 K with respect to its low-temperature value indicates that the overall CEF splitting is much larger than 100 K.

We also measured the thermal variation of the Mössbauer absorption fraction $f(T)$ in the temperature range 4.2–100 K. We find that it is in agreement with a Debye-type phonon dispersion law with a rather high Debye temperature $\theta_D = 266$ K.

3.2. Magnetic phase

The spectrum at $T = 0.045$ K (figure 2(a)) shows some noticeable differences compared to that at 4.2 K (extra line broadening, enhanced structure) indicative of the presence of a small magnetic hyperfine field $\boldsymbol{H}_{hf}$ at the nucleus site. It was fitted to an axial hyperfine Hamiltonian:

$$\mathcal{H}_{hf} = -g_n\mu_n \boldsymbol{I} \cdot \boldsymbol{H}_{hf} + \alpha_Q(I_z^2 - 2)$$

where $g_n\mu_n\boldsymbol{I}$ is the nuclear moment of the excited nuclear state. The quantisation axis z

Table 1. Hyperfine parameters used in the fits of the YbSi spectra at 0.045, 4.2, 55 and 100 K. G is the FWHM of the individual lines, the other parameters having their meaning as defined in the text. A bold-face parameter means that it was fixed in the fitting procedure. When fitting the $T = 0.045$ K spectrum with all the linewidths left as free parameters, the widths of the $\Delta I_z = 0, \pm 1$ transitions converge towards unphysically small values (below 2.8 mm s^{-1}). That is why they are kept fixed at the value of the minimal experimental width.

	G(mm s^{-1}) versus ΔI_z							
T(K)	−2	+2	−1	+1	0	α_Q (mm s^{-1})	H_{hf} (kOe)	θ (deg)
0.045	3.65 ±0.2	3.47 ±0.2	**2.80**	**2.80**	**2.80**	−1.56	240	70
4.2			2.82			−1.59	—	—
55			2.88			−1.47	—	—
100			2.54			−1.06	—	—

is the principal axis of the EFG tensor and the direction of $\boldsymbol{H}_{hf}$ is given by an angle θ with respect to z.

Fits using a unique linewidth for the five transitions are not satisfactory. In order to reproduce correctly the observed lineshape, it is necessary to allow for an inhomogeneous broadening of the individual spectral lines: the two lines corresponding to the $\Delta I_z = \pm 2$ transitions (unresolved less energetic line) show a mean FWHM of 3.56 mm s^{-1}, which is 30% higher than that of the lines corresponding to $\Delta I_z = 0, \pm 1$, which have the minimum linewidth of 2.8 mm s^{-1}. The quadrupolar parameter has a value of (-1.58 ± 0.02) mm s^{-1}, very close to that at 4.2 K, and the hyperfine field is found to be 240 kOe and at an angle $\theta = 70°$ with respect to the z axis (this fit corresponds to the full curve in figure 2(a)). Table 1 gives the values of the Mössbauer parameters used in the fits of the $T = 0.045$ K spectrum, together with those of the paramagnetic phase.

The presence of a hyperfine field at 0.045 K confirms the existence of magnetic ordering of the Yb^{3+} moments in YbSi at very low temperature. The saturated spontaneous moment derived from the obtained value of H_{hf} is quite low: $0.23\mu_B$ per Yb^{3+} ion. The magnetic moments are almost perpendicular to the principal axis of the EFG tensor, which is likely to be the $\boldsymbol{b}$ crystal axis (see § 3.1). The thermal variation of the hyperfine field between 0.045 K and 1.6 K, and the mean-field curve corresponding to $S = \frac{1}{2}$, $H_0 = 240$ kOe and $T_N = 1.6$ K are shown in figure 3. The hyperfine field is seen to decrease smoothly from 0.045 K to 1.6 K, slightly above the mean-field curve. In fact, the 1.6 K spectrum can also be satisfactorily fitted to a pure quadrupolar hyperfine Hamiltonian with vanishing hyperfine field. The Néel temperature is thus close to 1.6 K, in agreement with the previously published value [8].

As the fits were obtained allowing for inhomogeneous broadenings of the different lines, it is of interest to consider the possible origin of such broadenings. The mean linewidth of the two lines corresponding to the $\Delta I_z = \pm 2$ transitions decreases with temperature along with the hyperfine field. This suggests the presence of a distribution of the magnitudes and/or of the directions of the hyperfine field. Now, in the presence of a small hyperfine field almost perpendicular to the principal axis of the EFG tensor ($\theta = 70°$), the quadrupolar hyperfine levels are not shifted in energy at first order, and the degeneracy of the two $\Delta I_z = \pm 2$ lines is not lifted to second perturbation order. So a distribution of the magnitudes of a hyperfine field remaining close to perpendicular to the principal EFG axis cannot explain the observed broadening. We found in fact that

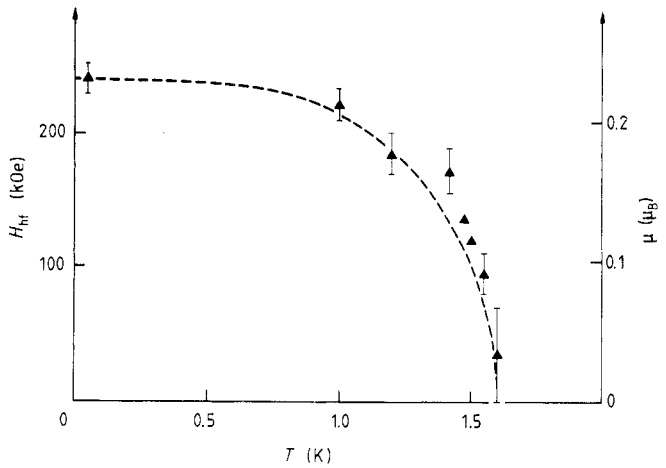

Figure 3. Thermal variation of the hyperfine field (left-hand scale) and of the spontaneous Yb^{3+} moment (right-hand scale) in YbSi. The broken curve is the mean-field curve corresponding to $S = \frac{1}{2}$, $H_0 = 240$ kOe and $T_N = 1.6$ K.

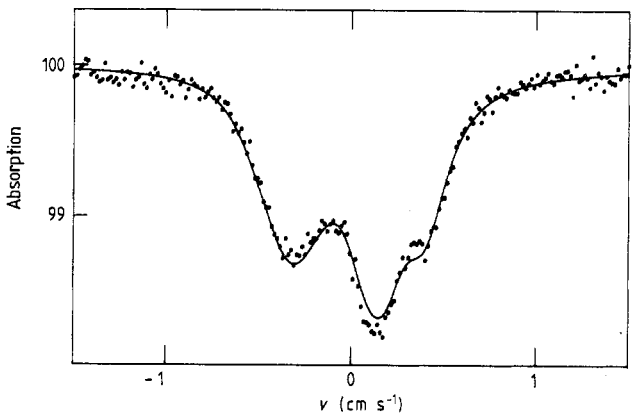

Figure 4. Fit of the $T = 0.045$ K Mössbauer spectrum in YbSi using a correlated distribution of hyperfine fields and angles θ (see text). The FWHM of the individual lines was fixed at 2.8 mm s^{-1} in this fitting procedure.

the best multi-component fit to the experimental spectrum at $T = 0.045$ K must allow for a correlated distribution of the angle θ (between 45° and 90°) and of the field magnitude (full curve in figure 4). The obtained angular distribution is almost isotropic with field values ranging from 375 kOe for $\theta = 45°$ to 200 kOe for $\theta > 60°$. This fitting procedure, although it does not exactly reproduce the observed spectrum, could reflect the presence in YbSi of a complex magnetic structure with small magnetic moments falling in the range $0.2–0.3\mu_B$.

4. Discussion

Reduced magnetic moments and modulated antiferromagnetic structures are characteristic features of magnetically ordered heavy-electron materials as has been experimentally demonstrated in Ce compounds by neutron diffraction techniques [10]. Such

a Kondo-frustrated ordering occurs when the effective Kondo coupling and the RKKY exchange are of the same order of magnitude. However, it is well known that the CEF interaction alone leads to a moment reduction with respect to the free-ion value. Using the information about the Yb site symmetry and electronic parameters we obtained in this paper, we can discuss the nature of the ground CEF state of Yb^{3+} in YbSi in order to check whether the observed small magnetic moment can be explained in terms of the CEF interaction.

As we have shown, the CEF interaction at the Yb site has tetragonal symmetry to a good approximation. In this case, the ground wavefunction must be built with $|J_z = m\rangle$ states separated by $|\Delta J_z| = 4$. The quadrupolar coupling parameter is the sum of an unknown (small) lattice contribution and of a dominant 4f electron contribution α_{4f}, and furthermore its value can be somewhat reduced by the hybridisation. However, the experimental value and sign of α_Q (-1.58 mm s^{-1}) imply that the ground wavefunction contains predominantly the state $|J_z = \pm\frac{1}{2}\rangle$ ($\alpha_{4f} = -4$ mm s^{-1}) or the state $|J_z = \pm\frac{3}{2}\rangle$ ($\alpha_{4f} = -2.4$ mm s^{-1}), rather than $|J_z = \pm\frac{7}{2}\rangle$ or $|J_z = \pm\frac{5}{2}\rangle$ which have positive EFG contributions. Calculations show in this case that the saturated magnetic moment, perpendicular to the z axis, must be of order $2\mu_B$, which is much bigger than the observed moment of 0.2–0.3μ_B. Thus the strong moment reduction we observe in YbSi does not seem to have its origin in the CEF interaction, but is likely to be a genuine hybridisation effect. The modulation in size and direction of the magnetic moment we propose to explain the observed inhomogeneous line-broadening can also be a consequence of the frustration induced by the presence of hybridisation, which is substantiated by the set of transport and magnetic bulk measurements made in [7] and [8].

Assuming that the first CEF excitation Δ_{CEF} is of the order of 100 K, one can obtain an estimation for the low-temperature Kondo energy scale in YbSi (the high-temperature T_K^0 is taken to be 40 K following [8]): $T_K = T_K^0(k_B T_K^0/\Delta_{CEF})^3 \simeq 2.5$ K. This value is of the same order of magnitude as the RKKY coupling in YbSi (and more generally in Yb systems) and supports the assumption of the presence of a Kondo-frustrated magnetic ordering in YbSi.

5. Conclusion

Low-temperature ^{170}Yb Mössbauer experiments have confirmed the occurrence of magnetic ordering below 1.6 K in the heavy-electron compound YbSi. The Yb^{3+} spontaneous magnetic moments are found to be unusually small (0.2–0.3μ_B) and are possibly arranged in a complex and modulated structure. The observed moment reduction is assumed to originate in 4f-band electron hybridisation. Further Mössbauer experiments in an applied magnetic field are in preparation in order to measure the strength of the RKKY interaction.

The symmetry of the crystal electric field at the Yb site is found to be approximately axial, probably tetragonal around the crystal ***b*** axis. The overall CEF splitting has been estimated to be much greater than 100 K, which supports the assumption derived in [8] of a $J = \frac{1}{2}$ hybridisation occurring in YbSi at low temperature. Mössbauer spectroscopy appears therefore as a powerful technique, complementary to neutron scattering and μSR spectroscopy, to detect and characterise the low-temperature frustrated magnetic ordering occurring in Yb magnetic heavy-electron systems, like YbSi and the Yb monopnictides [4–6].

References

[1] For an experimental review, see Ott H R 1987 *Prog. Low Temp. Phys.* **11** 215; for a theoretical review, see Newns D M and Read N 1987 *Adv. Phys.* **36** 799
[2] Gunnarsson O and Schönhammer K 1985 *Theory of Heavy Fermions and Valence Fluctuations* ed. T Kasuya and T Saso (Berlin: Springer) p 100
[3] Okiji A and Kawasaki N 1985 *Theory of Heavy Fermions and Valence Fluctuations* ed. T Kasuya and T Saso (Berlin: Springer) p 46
[4] Bonville P, Hodges J A, Hulliger F, Imbert P and Ott H R 1987 *J. Magn. Magn. Mater.* **63 & 64** 626
[5] Bonville P, Hodges J A, Hulliger F, Imbert P, Jéhanno G, Marimon da Cunha J B and Ott H R 1988 *Hyperfine Interact.* **40** 381
[6] Bonville P 1988 *Hyperfine Interact.* **40** 15
[7] Jaccard D and Sierro J 1982 *Valence Instabilities* ed. P Wachter and H Boppart (Amsterdam: North-Holland) p 409
[8] Engkagul C, Selim R, Mihalisin T and Schlottmann P 1987 *Phys. Rev.* B **35** 3686
[9] Iandelli A, Palenzona A and Olcese G L 1979 *J. Less-Common Met.* **64** 213
[10] Vettier C, Burlet P and Rossat-Mignod J 1987 *J. Magn. Magn. Mater.* **63 & 64** 18