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Low temperature Mössbauer study and magnetic susceptibility measurements on YbMo_6S_8 and TmMo_6S_8

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Résumé. — L'étude par effet Mössbauer sur Yb^{170} et les mesures de susceptibilité magnétique ont montré que YbMo_6S_8 contient en proportions sensiblement équivalentes des ions Yb^{2+} et Yb^{3+} . Les ions Yb^{2+} sont soumis à un très fort gradient de champ électrique axial et se meuvent préférentiellement dans le plan perpendiculaire à l'axe de ce gradient (vraisemblablement l'axe hexagonal *c*). Les moments magnétiques des ions Yb^{3+} s'ordonnent perpendiculairement à l'axe *c* au-dessous de $T_N = 2,75$ K et valent $1,7 \mu_B$ près de zéro Kelvin. Les impuretés d'ytterbium apparaissent également sous les formes Yb^{2+} et Yb^{3+} dans TmMo_6S_8 , où les ions Yb^{3+} présentent un tenseur *g* légèrement anisotrope ($g_{\parallel} = 2,32$, $g_{\perp} = 3,64$). Des mesures par effet Mössbauer sur Tm^{169} montrent la présence d'un seul site de Tm.

Abstract. — Mössbauer study on Yb^{170} and magnetic susceptibility measurements show that YbMo_6S_8 contains both Yb^{2+} and Yb^{3+} ions with nearly equal proportions. The Yb^{2+} ions are submitted to a very strong electric field gradient with axial symmetry and move preferentially in the plane perpendicular to the gradient axis (which is probably the hexagonal axis *c*). The Yb^{3+} magnetic moments order perpendicularly to the *c* axis below $T_N = 2.75$ K and their magnitude is $1.7 \mu_B$ near zero Kelvin. Ytterbium impurities also appear as Yb^{2+} and Yb^{3+} ions in TmMo_6S_8 , where the Yb^{3+} *g*-tensor is slightly anisotropic ($g_{\parallel} = 2.32$, $g_{\perp} = 3.64$). Tm^{169} Mössbauer measurements on TmMo_6S_8 show that only one Tm site is present.

The superconducting ternary compounds RMO_6X_8 , where R is a metal (Sn, Pb, Rare Earth,...) and X represents S or Se, have been intensively studied during past years, from the point of view of their superconducting as well as their magnetic properties (see [1] for a review).

In this paper we report on the results of a low-temperature study of YbMo_6S_8 and of Yb impurities diluted in TmMo_6S_8 , using the Mössbauer effect on Yb^{170} ($I_g = 0$, $I_e = 2$).

We also report on the preliminary results of the study of TmMo_6S_8 using the Mössbauer effect on Tm^{169} ($I_g = \frac{1}{2}$, $I_e = \frac{3}{2}$).

Finally, we have measured the thermal variation of the powder magnetic susceptibility of YbMo_6S_8 between 4.2 K and 50 K.

The compounds YbMo_6S_8 and TmMo_6S_8 have the same crystallographic structures (space group : $R\bar{3}$) [2] and the local symmetry at the rare-earth site

is trigonal. The ternary axis is the *c* axis of the hexagonal cell.

The critical superconducting temperatures are : $T_c \simeq 8.5$ K for YbMo_6S_8 and $T_c \simeq 2$ K for TmMo_6S_8 [2].

Susceptibility measurements on YbMo_6S_8 suggested the existence of a mixture of Yb^{2+} and Yb^{3+} ions [2]; furthermore, specific heat measurements in this compound showed a peak at about 2.7 K, which was interpreted as being due to the appearance of antiferromagnetic ordering [3].

1. Experimental results. — An X Ray check of our samples showed that they are single phase compounds, containing less than 1 % of Mo_2S_3 . The Mössbauer experiments and the susceptibility measurements were performed on the same sample.

1) Neutron irradiation of TmMo_6S_8 creates Tm^{170} , which decays to Yb^{170} . The Mössbauer emission spectrum of the Yb^{170} impurities created this way shows two components between 1.5 K and 40 K (Fig. 1) : — a triplet, characteristic of a pure quadrupole

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Fig. 1. — Emission Mössbauer spectrum of Yb^{170} in TmMo_6S_8 at 1.5 K and fitted curve. (Dashed vertical lines : Yb^{2+} component.)

hyperfine interaction with axial symmetry ($\eta < 0.2$), corresponding to :

$$\alpha = \frac{3 e Q V_{zz}}{4 I(2I - 1)} = + 1.78 \text{ mm} \cdot \text{s}^{-1}$$

(for Yb^{170} : $(1 \text{ mm} \cdot \text{s}^{-1} = 2.8 \times 10^{-6} \text{ eV})$).

This triplet, which we attribute to Yb^{2+} ions (see the discussion below), shows a strong anomaly of the relative line intensities : 0.81 : 2 : 0.91 instead of 1 : 2 : 2. In our case, this anomaly cannot be due to sample thickness effects nor to inhomogeneous line broadenings. Calculations show that the observed intensities are very well accounted for by an anisotropy of the atomic vibrations that is by the Goldanski-Karyagin effect, which is observed here for the first time with the Yb^{170} isotope. The anisotropy constant $a = K^2[\langle z^2 \rangle - \langle x^2 \rangle]$, where $\langle z^2 \rangle$ and $\langle x^2 \rangle$ are respectively the quadratic mean vibrations of Yb atoms parallel and perpendicular to the principal axis of the electric field gradient (EFG), is found to be : $a \simeq - 3.2$ at low temperature.

This Yb^{2+} component shows no variation between 1.5 K and 40 K.

— a spectrum, attributed to Yb^{3+} , with an axial magnetic and quadrupole hyperfine interaction :

$$H_{\text{hf}} = A_z I_z S_z + \frac{A_{\perp}}{2} (I^- S^+ + I^+ S^-) + \alpha(I_z^2 - 2),$$

in presence of slow relaxation of the Yb^{3+} moment within the ground Kramers doublet ($S = \frac{1}{2}$: effective spin of the doublet ; I : nuclear spin). The spectrum obtained at 1.5 K allows the magnetic (A_z and $A_{\perp}$) and quadrupole (α) hyperfine constants to be obtained. The fitted values are :

$$A_z = 9.05 \text{ mm} \cdot \text{s}^{-1}, \quad A_{\perp} = 14.20 \text{ mm} \cdot \text{s}^{-1}$$

and

$$\alpha = - 0.5 \text{ mm} \cdot \text{s}^{-1}.$$

At higher temperature ($T > 20$ K), speeding up of relaxation produces broadening of the lines of the spectrum.

These two components have nearly equal relative intensities between 1.5 K and 40 K.

2) The Mössbauer absorption spectrum of Yb^{170} in YbMo_6S_8 also consists of two components between 60 mK and 40 K (Fig. 2) :

— a Yb^{2+} triplet, presenting nearly the same features as that observed in TmMo_6S_8 ($\alpha \simeq 1.85 \text{ mm} \cdot \text{s}^{-1}$; $a \simeq - 2$), and showing no variation between 60 mK and 40 K ;

— a spectrum attributed to Yb^{3+} in the presence of an effective field between 60 mK and 2.75 K (Fig. 2a) according to the hamiltonian :

$$H_{\text{hf}} = - g_n \mu_n \mathbf{I} \cdot \mathbf{H}_{\text{eff}}(T) + \alpha(I_z^2 - 2)$$

[$g_n \mu_n I$: nuclear moment of Yb^{170}].

Above 2.75 K (Fig. 2b) this component transforms into a pure quadrupole spectrum. Fitting the spectra below and above 2.75 K gives the following values :

$$\alpha \simeq - 1 \text{ mm} \cdot \text{s}^{-1}, \quad \mathbf{H}_{\text{eff}}(0) = 1770 \text{ kG}.$$

$\mathbf{H}_{\text{eff}}$ is found to be perpendicular to the principal axis of the EFG tensor, that is to the ternary c axis.

Fig. 2. — Absorption Mössbauer spectra of Yb^{170} in YbMo_6S_8 and fitted curves at 60 mK (a) and at 4.2 K (b). (Dashed vertical lines : Yb^{2+} component.)

The Yb^{2+} and Yb^{3+} components have intensities roughly 40 %-60 % in the YbMo_6S_8 spectra. As the Mössbauer recoil-free fraction is probably weaker for the ion Yb^{2+} which shows a large vibrational anisotropy, the real Yb^{2+} ionic proportion is likely to exceed 40 % in the sample.

3) Magnetic susceptibility measurements between 4.2 K and 40 K show that $1/\chi(T)$ follows a Curie-Weiss law with a slope corresponding to an effective moment per Yb atom :

$\mu_{\text{eff}} = 2.03 \mu_B/\text{at. Yb}$, in good agreement with measurements by Alekseevski *et al.* [3].

2. Discussion and interpretation. — 1) The existence of a cation site showing an anisotropy of atomic

vibrations with $a = K^2[\langle z^2 \rangle - \langle x^2 \rangle] < 0$ has been observed by Mössbauer effect on Sn¹¹⁹ in SnMo₆S₈ [4, 5]. Besides this, an X-Ray study with single crystals suggests the existence in the RMo₆S₈ phases of a more or less pronounced delocalization of the cation in a plane perpendicular to the ternary *c* axis [6].

An interesting feature of Yb¹⁷⁰ Mössbauer spectrometry is that, unlike Sn¹¹⁹ spectrometry, it offers the possibility of measuring the asymmetry parameter η of a pure quadrupole spectrum. The finding of a vanishing η for the Yb²⁺ ions suggests that the EFG axis *Oz* (which is also the direction of the vibrational anisotropy) is certainly parallel to the *c* axis. This result is not compatible with the presence of a static delocalization of the Yb²⁺ ions, which would destroy the local trigonal symmetry; a dynamical delocalization preserving this symmetry is also very unlikely to occur at such low temperatures.

Another important result is the diamagnetic character of the Yb atoms presenting such a vibrational anisotropy. This statement is derived from the absence of any effective field on the nucleus for this kind of ions in YbMo₆S₈ below T_N , as well as from the absence of any slow relaxation magnetic hyperfine interaction at low temperature for these ions diluted in TmMo₆S₈. This diamagnetic character allows the assignation of Yb²⁺ to these ions.

The abnormally high value of the quadrupole constant ($\alpha \simeq 1.80$ mm/s) with respect to values usually found for Yb²⁺ [8] ($\alpha \simeq 0.5$ mm/s) might be related to the trigonal deformation of the surroundings which is also responsible for the observed vibrational anisotropy.

2) The slow relaxation Mössbauer spectrum of Yb³⁺ ions in TmMo₆S₈ is not very different from the classical pattern obtained in a cubic site for a Γ_7 -like ground Kramers doublet [7]. The *g*-tensor deduced from the measurement of the magnetic hyperfine constants is : $g_z = 2.32 \pm 0.20$ and $g_{\perp} = 3.64 \pm 0.08$ and the measured quadrupole constant is :

$$\alpha = -0.5 \pm 0.5 \text{ mm} \cdot \text{s}^{-1}.$$

These values allow the assignment of the following approximate wave function to the ground doublet of Yb³⁺ in TmMo₆S₈ (*Oz* : trigonal local axis $\parallel c$) :

$$|\psi\rangle = -0.566 |J_z = \frac{7}{2}\rangle \pm 0.733 |J_z = \frac{1}{2}\rangle + 0.376 |J_z = -\frac{5}{2}\rangle,$$

which compares with the Γ_7 wave-function :

$$|\psi\rangle_{\Gamma_7} = -0.623 |\frac{7}{2}\rangle \pm 0.745 |\frac{1}{2}\rangle + 0.235 |-\frac{5}{2}\rangle.$$

3) The Yb³⁺ spectra in YbMo₆S₈ confirm the existence of a magnetic ordering of the electronic moments below $T_N = 2.75$ K, in the superconducting phase, in agreement with the measurements of Alek-

seevski *et al.* [3]. Moreover, they show that the moments are perpendicular to the ternary *c* axis, and that the value of the saturation moment, derived from the value of $H_{\text{eff}}(0)$, is : $\mu_{\text{sat}} = 1.70 \mu_B$, which indicates a strong reduction relatively to the free ion value. It should be noted that other REMo₆S₈ compounds (RE = Gd, Tb, Dy, Er) show antiferromagnetic ordering at low temperature with the Rare Earth moments parallel to the ternary *c* axis [9-13].

The ground doublet of Yb³⁺ in YbMo₆S₈ must not be very different from that of Yb³⁺ in TmMo₆S₈ : the observed *g*-tensor anisotropy in TmMo₆S₈ matches with an easy direction of magnetization perpendicular to the *c* axis and the value $g_{\perp} = 3.64$ is compatible with a saturation moment of $1.70 \mu_B$ in YbMo₆S₈.

Above the magnetic transition temperature T_N , the quadrupole Yb³⁺ spectrum in YbMo₆S₈ is reasonably accounted for without any vibrational anisotropy ($a = 0$), in contrast with the Yb²⁺ site results.

4) The value of the effective magnetic moment measured by susceptibility ($\mu_{\text{eff}} = 2.03 \mu_B/\text{at. Yb}$) in YbMo₆S₈ is in good agreement with the value calculated using the *g*-tensor of Yb³⁺ ($S = \frac{1}{2}$) in TmMo₆S₈, when assuming equipopulation of Yb²⁺ and Yb³⁺ ions :

$$\mu_{\text{eff}} = \sqrt{0.5 \frac{g_z + 2g_{\perp}}{3}} \times \sqrt{S(S+1)} \mu_B \Rightarrow \Rightarrow \mu_{\text{eff}} = 1.96 \mu_B/\text{at. Yb}.$$

Yb²⁺ and Yb³⁺ equipopulation is not incompatible with the Mössbauer spectra which show that the proportion of the Yb²⁺ ions is larger than 40 %.

5) Preliminary results of a Mössbauer study of TmMo₆S₈ with the isotope Tm¹⁶⁹ show a unique quadrupole doublet ($\Delta E = 3.2 \text{ cm} \cdot \text{s}^{-1}$) at low temperatures.

3. Conclusion. — Mössbauer effect study with Yb¹⁷⁰ and powder magnetic susceptibility measurements on YbMo₆S₈ revealed the presence of two types of Ytterbium atoms, with nearly equal proportions. First, diamagnetic Yb²⁺ ions, submitted to a very strong axial EFG, which evidence a strong anisotropy of the Mössbauer recoil free fraction and which vibrate preferentially within a plane perpendicular to the EFG axis (which is probably the ternary *c* axis). Second, magnetic Yb³⁺ ions, submitted to a predominant cubic crystal field with a small trigonal component, and whose ground electronic doublet is close to a Γ_7 doublet; the vibrations in this site are quite isotropic. Their magnetic moments are ordered perpendicularly to the ternary *c* axis below $T_N = 2.75$ K in the superconducting state. Neutron diffraction experiments are in preparation in order to determine the nature of the magnetic ordering in this compound.

The presence of Yb²⁺ ions probably accounts for the high superconducting transition temperature of

YbMo_6S_8 with respect to other REMo_6S_8 compounds [2].

In TmMo_6S_8 , the Mössbauer study with Tm^{169} did not show the presence of two different types of ions or sites. On the contrary, the study of dilute Yb^{170} impurities created by radioactive decay of Tm^{170} after neutron irradiation of TmMo_6S_8 reveals again the presence of Yb^{2+} and Yb^{3+} ions with

comparable proportions, and whose single-ion properties are similar to those observed in YbMo_6S_8 .

In both samples, crossing the superconducting transition temperature does not involve any change, in first approximation, in Mössbauer spectra, confirming the weak interaction existing in REMo_6X_8 superconductors between d superconducting electrons and 4f electrons of the Rare Earth.

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