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Local properties of Tm$^{3+}$ and Yb$^{3+}$ in TmAsO$_4$ and ordering in YbAsO$_4$ from $^{169}$Tm and $^{170}$Yb Mössbauer measurements

J. A. Hodges, P. Imbert and G. Jéhanno

DPh-G/PSRM, C.E.N. Saclay, 91191 Gif-sur-Yvette Cedex, France

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Abstract. — Mössbauer measurements are reported on $^{169}$Tm in TmAsO$_4$ and on $^{170}$Yb diluted into TmAsO$_4$ and in YbAsO$_4$. For TmAsO$_4$ we establish a set of crystal field parameters for Tm$^{3+}$ in the tetragonal phase, above the Jahn-Teller transition temperature ($T_D = 6.0$ K). The same parameters also account for the essential features of the observed ground state $g$-values for Yb$^{3+}$ in TmAsO$_4$ both above and below $T_D$. From the Tm$^{3+}$ line shape analysis we find that the degeneracy of the lowest non Kramers doublet in the tetragonal phase is lifted by local distortions. Magnetic ordering is observed in YbAsO$_4$ below about 0.3 K.

1. Introduction. — At room temperature TmAsO$_4$ and YbAsO$_4$ crystallize in the tetragonal Zircon structure (space group D$_{4d}^{2}$) the rare earth ions being at sites with D$_{2d}$ symmetry. At 6.0 K TmAsO$_4$ suffers a Jahn-Teller distortion to an orthorhombic structure (space group D$_{2h}^{2}$) with the local symmetry now D$_2$. According to these symmetries which are based on bulk averaged X-ray measurements, the Tm$^{3+}$ non-Kramers ground doublet should be degenerate above $T_D$ and non degenerate below $T_D$. No information is presently available to show whether YbAsO$_4$ also undergoes a crystallographic transition at low temperatures. In fact YbAsO$_4$ has been the subject of little attention compared to that paid the model Jahn-Teller compound TmAsO$_4$ [1-8].

Here we use $^{169}$Tm and $^{170}$Yb Mössbauer spectroscopy to study Tm$^{3+}$ in TmAsO$_4$, Yb$^{3+}$ diluted into TmAsO$_4$ and Yb$^{3+}$ in YbAsO$_4$. The use of a microscopic probe means that in TmAsO$_4$ we can sample the local environment on either side of the Jahn-Teller bulk transition temperature for both the host lattice ion provoking the structural transition and for a particular substitutional impurity ion.

In TmAsO$_4$ the hyperfine parameters obtained from the Mössbauer absorption line positions are interpreted within a crystalline electric field (CEF) model. The Mössbauer absorption line shapes are also exploited to provide information concerning the local properties. In particular they provide evidence showing that in TmAsO$_4$, the degeneracy of the Tm$^{3+}$ non-Kramers ground doublet is, in fact, lifted above $T_D$.

2. TmAsO$_4$. — Mössbauer measurements on $^{169}$Tm ($I_e = 3/2, I_f = 1/2, 8.4$ keV) were made from 1.4 to 300 K. A marked difference was observed between the line shapes above and below $T_D$ (Fig. 1). For $T < T_D$ the quadrupole doublet is symmetric and for $T > T_D$ it is asymmetric.

The data was fitted to a Hamiltonian made up of two terms. The first term represents the quadrupole hyperfine interaction linking the nuclear quadrupole moment of the $I_e = 3/2$ level and the electric field gradient. The second term represents the magnetic hyperfine interaction within the non Kramers ground doublet influenced by electronic relaxation within these levels. Below $T_D$ the quadrupole hyperfine interaction alone is sufficient to explain the data whereas above $T_D$ both the quadrupole hyperfine interaction and the magnetic hyperfine interaction are required the latter being treated in terms of a pseudo-quadrupole interaction.

In section 2.1 we discuss the information obtained concerning the Tm$^{3+}$ CEF parameters provided by the analysis of the thermal variation of the quadrupole...
hypertine interaction. This analysis is chiefly based upon the Mössbauer absorption line positions. In section 2.2 we discuss the analysis relating to the absorption line shapes. This provides information concerning the presence of local distortions and relaxation effects.

2.1. Tm$^{3+}$ CRYSTALLINE ELECTRIC FIELD PARAMETERS. — The thermal variation of the total quadrupole hyperfine splitting $\alpha$ is shown in figures 2a and 2b. A marked change in slope occurs at the bulk structural transition temperature. The electric field gradient which interacts with the nuclear quadrupole moment to create the observed quadrupole hyperfine splitting, is chiefly due to the electronic quadrupole moments of the Tm$^{3+}$ 4f levels. In turn these electronic quadrupole moments depend on the crystalline electric field (CEF) parameters. It is thus possible to establish a set of the electronic CEF parameters based on the observed thermal variation of the quadrupole hyperfine splitting $\alpha$. In this analysis we ignore any contribution to the electric field gradient arising from the non spherical distribution of distant charges as this is probably small.

The $^3H_6$ term of the Tm$^{3+}$ is split by a crystal field as described by

$$\mathcal{K} = \sum_{m,n} B_n^m \theta_n^m O_n^m.$$ 

Above $T_D$ for $D_{2d}$ symmetry, $B_2^0$, $B_4^0$, $B_6^0$, $B_4^4$ and $B_6^6$ are non zero. To obtain values for these five CEF parameters from the measured quadrupole hyperfine splittings it is necessary to take a number of thermal averages. Consequently this fitting procedure alone does not lead to a unique set for the CEF parameters. To circumvent this difficulty we also constrained the parameters to give the correct energy separations between the ground state electronic doublet and the next two lowest levels which are both singlets with energies 13.8 cm$^{-1}$ [7] and 86.5 cm$^{-1}$ [3]. The various parameters obtained were $B_2^0 = -37$, $B_4^0 = 15.7$, $B_6^0 = \pm 680$, $B_2^4 = -42$ and $B_6^4 = \pm 60$ cm$^{-1}$ with an accuracy of near 10% $B_2^4$ and $B_6^4$ probably have the same sign as otherwise we were unable to obtain agreement with the experimental data. These values can be considered to be reliable in that they explain all the available data and are also close to those obtained by optical spectroscopy on the neighbouring system Er$^{3+}$ in YAsO$_4$ [9].

The wave functions of the degenerate non Kramers ground doublet derived from the above CEF parameters are

$$\psi \mid \pm \rangle = 0.878 \mid \pm 5 \rangle - 0.437 \mid \pm 1 \rangle + 0.194 \mid \mp 3 \rangle$$

which have an associated value $g_z = 9.18$. This agrees closely with the measured value:

$$g_z = 9.1 \pm 0.2 \quad [10],$$

Fig. 2a-b. — Thermal variation of $\alpha$ the quadrupole hyperfine splitting for Tm$^{3+}$ in TmAsO$_4$ from 10 to 295 K (Fig. 2a) and from 1.4 to 24 K (Fig. 2b). The solid line is calculated for the tetragonal phase using the crystal field parameters given in the text. A marked difference exists between the extrapolation of these calculated values to low temperatures (dashed line) and the measured values in the orthorhombic phase.
supporting the credibility of the proposed set of CEF parameters in the tetragonal phase.

Below $T_D$ in the orthorhombic phase, the quadrupole hyperfine splitting increases rapidly as the temperature is lowered to reach a value which is over 50% higher than the extrapolated saturated value for the tetragonal phase (Fig. 2b). In contrast to the behaviour above $T_D$, the origin of the observed variation of $\alpha$ below $T_D$ is due both to a temperature dependence of the CEF parameters resulting from the bulk deformation of the lattice, as well as to thermally driven population changes within the CEF levels.

In the orthorhombic phase the number of CEF parameters increases to nine. The amount of experimental information available is not sufficient to establish a unique set of values for these nine parameters. We have observed that keeping the CEF values of the tetragonal phase and simply adjusting the second order orthorhombic term $B_2^0$ does not provide simultaneous agreement at $T \rightarrow 0$ with the measured quadrupole hyperfine splitting and the separation between the two lowest levels (9.1 cm$^{-1}$) [1]. In view of this, it is probable that the five CEF parameters which are present both above and below $T_D$ have different values in the two phases.

2.2 INFORMATION OBTAINED FROM THE LINE SHAPES.

- Experimentally two different effects are observed in the two crystallographic phases. As shown in figure 1 above $T_D$, the right hand component is broader than the left hand component, the two components however, having the same surface areas. This line width asymmetry is still present as the temperature is increased at least up to about 40 K where the two lines coalesce following the reduction in the average quadrupole hyperfine splitting. Below $T_D$, the line widths of the two components are equal but this common line width progressively decreases as the temperature is lowered to reach a saturated value. Both the line shape asymmetry above $T_D$ and the line width variation below $T_D$ are used here to obtain information on $\Delta$ the local energy separation between the two $\text{Tm}^{3+}$ ground state electronic levels.

2.2.1. Line shape asymmetry for $T > T_D$ — The line shape asymmetry observed just above $T_D$ is due to the presence of a magnetic hyperfine interaction and to the effects of relaxation. This relaxation essentially concerns only the levels of the non Kramers ground doublet as these are the only levels significantly populated just above $T_D$. As the line shape asymmetry is independent of temperature this shows that the relaxation rate is also independent of temperature indicating that the driving mechanism for the relaxation is spin-spin coupling between neighbouring $\text{Tm}^{3+}$ ions.

The magnetic hyperfine interaction within the doublet levels can be conveniently treated in two limits. In the first approach the ground doublet is taken to remain degenerate and the interaction, written in the form $A_s S_s(t) J_s$, can be treated in first order perturbation. The other magnetic hyperfine components are zero in this Ising-like system. As a numerical value for $A_s$ is already available from the wave functions of the ground doublet, as given in section 2, the (stochastic) relaxation model fit at 7.0 K (Fig. 1) then provides a well defined value for the relaxation rate. The value obtained is $W = 3.2 \times 10^5$ MHz. This value however is unphysically high. It is in fact roughly two orders of magnitude higher than the relaxation rate observed between the ground doublet levels of $\text{Yb}^{3+}$ in $\text{YbAsO}_4$ as described in section 4. As the driving mechanism is the same in both systems (spin-spin interactions of comparable strengths), it is unreasonable for the rate to be so much higher in $\text{TmAsO}_4$ than in $\text{YbAsO}_4$. This means that the interpretation in terms of a degenerate non Kramers doublet cannot be retained.

For the case where the degeneracy of the ground doublet is lifted a second approach in terms of the pseudo-quadrupole interaction can be used. In this approach the magnetic hyperfine interaction is treated in second order perturbation within the non degenerate levels of the doublet [11]. The criterion for establishing which of the two approaches is more relevant depends on the size of $\Delta$, the energy separation between the doublet levels, compared to a characteristic energy which here is the $\text{Tm}^{3+}$ magnetic hyperfine splitting ($E_{hf} \sim 0.1$ cm$^{-1}$). When $\Delta < E_{hf}$ the treatment in terms of a degenerate Ising doublet is appropriate and when $\Delta > E_{hf}$ the treatment in terms of a pseudo-quadrupole interaction is appropriate.

The interpretation in terms of a pseudo-quadrupole interaction entails that $\Delta$ is not zero whereas according to the bulk X-ray established symmetry the doublet should be degenerate. It is however not surprising that the local value of $\Delta$, which is that probed by the Mössbauer measurements, is not zero. This is because the non Kramers ground doublet is very sensitive to strains which act directly to lift the degeneracy. Evidence has previously been presented showing the presence of local random dynamic strains in the tetragonal phase of $\text{TmAsO}_4$ [12]. This evidence related to the coupling between the local strains and the excited doublet at near 100 cm$^{-1}$. Here the coupling evidenced is between the local strains and the ground state doublet.

For the two non degenerate levels $|a>$ and $|b>$ separated by an energy $\Delta$, the Mössbauer line shapes in terms of the pseudo-quadrupole interaction depends on $\Delta$, on $\langle a | J_s | b \rangle$, which is the only non zero magnetic matrix element within the two level system, and on $W$ the relaxation rate. $\langle a | J_s | b \rangle$ is already known ($= 3.9$) as when $\Delta$ is not too large (roughly a few cm$^{-1}$ or less), it is the same as the matrix element of $J_z$ within either level of the degenerate doublet considered earlier. Within a stochastic model the fit shown on figure 1 was again obtained but now only provides interdependent values for $\Delta$ and $W$. Inde-
pendent values for $A$ and $W$ can in general only be obtained if $A$ remains small and measurements are made at temperatures $T \ll A$ [11]. This is impossible in the present case because of the phase transition at $T_D$. Identical fits to that shown on figure 1 at 7.0 K were obtained provided that $Wd^2 = 3.5 \times 10^{11}$ MHz$^3$ with an upper limit on $A$ of about $4.5 \times 10^4$ MHz (1.5 cm$^{-1}$). For comparison if we take the relaxation rate in TmAsO$_4$ to be the same as in YbAsO$_4$ then the observed line shape corresponds to a value $A \sim 0.3$ cm$^{-1}$. In this context it is interesting to note that EPR measurements on Tm$^{3+}$ diluted in YAsO$_4$ have been interpreted in terms of a similar value for $A$ ($\sim 0.3$ cm$^{-1}$) [13].

Up to now we have assumed that all of the Tm$^{3+}$ ions have the same properties that is there is no spatial distribution in the parameters. If it is assumed that $A$ can show a spatial distribution, then it is possible to choose this distribution such that, using the pseudo-quadrupole approach, the asymmetric line shape obtained above $T_D$ can be explained without introducing line broadening due to relaxation. Consequently allowing the possibility of a distribution in $A$ would lead to a less well defined relaxation rate.

The essential information obtained from this treatment in terms of a pseudo-quadrupole interaction is that $A$ (whether it is single valued or whether it shows a distribution) is not zero above $T_D$ and is typically higher than 0.1 cm$^{-1}$.

As the temperature is lowered down through $T_D$ the asymmetry in the line shape rapidly disappears (Fig. 1). This behaviour is due to the rapid increase in $A$ which occurs below $T_D$ as the crystal distorts macroscopically ($A$ has increased to near 6 cm$^{-1}$ at 5 K [8]). In other words as the temperature is lowered through $T_D$ the pseudo-quadrupole interaction, whose strength is inversely proportional to $A$, is quenched out and is no longer able to broaden the right hand line of the Mössbauer absorption spectra.

We note that in TmVO$_4$ which, like the present case TmAsO$_4$, has a non Kramers ground doublet, an asymmetric broadening of the Tm$^{3+}$ Mössbauer line shapes is also observed [14]. This again shows that non zero values of $A$ are present above $T_D$. However contrary to the present case, the line shape asymmetry changes progressively with decreasing temperature and in fact it disappears before $T_D$ is reached. This suggests for TmVO$_4$ that $A$ in the tetragonal phase is temperature dependent and that as the temperature is lowered, and before $T_D$ is reached, it grows to a value which is big enough to quench out the pseudo-quadrupole interaction.

2.2.2. Line width variation below $T_D$. — The (common) line width increases from the low temperature limiting value of 6.2 mm/s (42 MHz) observed at 1.4 K to 9.3 mm/s (63 MHz) at $T_D$. The left hand line whose width, to a first approximation is not influenced by the pseudo-quadrupole interaction, remains broadened at the same value (9.3 mm/s) above $T_D$. The variation in line width below $T_D$ is not due to the fact that the relaxation rate between the CEF levels is not fast enough to fully average the electric field gradient. This would have led also to a thermal dependence of the line width of the left hand line above $T_D$ which is not observed experimentally. We attribute the (common) line broadening to the presence of a spatial distribution in the local quadrupole hyperfine splittings. This distribution is linked to the distribution in local environments which in turn is linked to a distribution in the CEF parameters and in $A$. To obtain the width in the distribution of $A$ (called $\Delta A$) from the width of the experimentally available distribution in the quadrupole hyperfine splitting $\alpha$ (called $\Delta \alpha$), we scale the two parameters using the known experimental thermal variations of $\alpha$ and $A$ (Fig. 2 for $\alpha$ vs. $T$ and reference [8] for $L_1$ vs. $T$).

From this we obtain that, just below $T_D$, $\Delta A$ is of the order of 1 cm$^{-1}$ and that it decreases to zero as the temperature is lowered. The linked distributions in $\alpha$, $A$ and the CEF parameters have a common origin — the presence of random strains. When the temperature is lowered the influence of these random strains is weakened as the sample distorts to its saturated orthorhombic structure.

Combining the results above and below $T_D$ we see that the Mössbauer analysis has provided evidence for both the presence of a distribution in $A$ above and below $T_D$ and for non zero values of $A$ above $T_D$.

The above analysis was made in terms of a two level electronic system. In practice an excited singlet at 13.8 cm$^{-1}$ is present [7]. This will only have marginal impact on the analysis of the results near and below $T_D$ and its influence has been ignored.

3. TmAsO$_4$: Yb$^{3+}$. — Results were obtained from a source experiment on neutron activated TmAsO$_4$ using a YbB$_6$ absorber. As such, the ytterbium is present as $^{170}$Yb ($I_e = 2$, $I_a = 0$, $E = 84.4$ keV) at very low concentration levels so that the bulk structural transition temperature is expected to be at 6.0 K as for pure TmAsO$_4$. Figure 3 shows the results at 1.4 K, that is for $T < T_D$ where the local symmetry is orthorhombic. However the satisfactory fit shown was obtained using a slow relaxation limit Hamiltonian having tetragonal symmetry :

$$\mathcal{H} = \alpha (I_z^2 - 2) + A_x S_x I_x + A_\perp (S_x I_x + S_y I_y)$$

with $\alpha = -1.78 \pm 0.08$ mm/s ($-121 \pm 5$ MHz), $|A_x| = 1.5 \pm 0.2$ mm/s ($104 \pm 14$ MHz), and $|A_\perp| = 14.1 \pm 0.2$ mm/s ($958 \pm 14$ MHz)

and with the sign of the product of the three magnetic hyperfine parameters negative. From these results we obtain $|q_z| = 0.4$ and $|q_\perp| = 3.60$ which are similar to the values obtained for Yb$^{3+}$ in YAsO$_4$ [15].
Fig. 3. — $^{170}$Yb emission Mossbauer spectra at 1.4 K for a source of neutron activated TmAsO$_4$ against a YbB$_6$ single line absorber.

Just above $T_D$ in the tetragonal phase, the Yb$^{3+}$ Mossbauer spectrum is similar to that shown in figure 3 for the orthorhombic phase. The changing symmetry then has little influence on the static hyperfine parameters for the ground levels of Yb$^{3+}$ in TmAsO$_4$. We have observed that the hyperfine parameters for Yb$^{3+}$ in TmV$_4$O$_4$ are also the same either side of $T_D$.

On crossing $T_D$ there is also little change in the Yb$^{3+}$ Mossbauer line shapes which remain characteristic of that of the slow relaxation limit. There is thus no discernable cross relaxation between the Yb$^{3+}$ and Tm$^{3+}$ in either phase. Above about 10 K the Mossbauer line shapes are broadened by the effects of relaxation. As these are temperature dependent, they are attributed to coupling to phonons.

The $g$ values of the Yb$^{3+}$ ground state calculated using the same $B^{0*}$ that were established above for the Tm$^{3+}$ ion in the same matrix above $T_D$ are $|g_\parallel|=0.66$ and $|g_\perp|=3.64$. These have the same symmetry ($g_\parallel < g_\perp$) and approximately the same magnitudes as the measured values. This suggests that in TmAsO$_4$ the crystal field parameters for Yb$^{3+}$ are close to those for Tm$^{3+}$. In particular the second order crystal field parameter $B_2^0$ for Yb$^{3+}$ is negative and fairly small. For if $B_2^0$ were negative and large (more negative than $-120$ cm$^{-1}$ using the same fourth and sixth order CEF parameters given above) the Yb$^{3+}$ ground state would become

$$\psi |\pm\rangle = a |\pm 5/2\rangle + b |\mp 3/2\rangle$$

with $g_\parallel > g_\perp$. We have observed that such a ground state occurs for Yb$^{3+}$ in TmVO$_4$. Thus although the composition of the Tm$^{3+}$ ground doublet is the same in TmAsO$_4$ and in TmVO$_4$

$$\psi |T\rangle = a |\pm 5\rangle + b |\pm 1\rangle + c |\mp 3\rangle$$

the composition of the Yb$^{3+}$ ground doublet is different in the two matrices. This however is compatible with one common set of CEF parameters for both Tm$^{3+}$ and Yb$^{3+}$ in TmAsO$_4$ and one common set for both Tm$^{3+}$ and Yb$^{3+}$ in TmVO$_4$.

The limiting low temperature 4f contribution to quadrupole hyperfine interaction splitting $\alpha$, calculated from the Yb$^{3+}$ in TmAsO$_4$ tetragonal ground state wave function, is $-1.10$ mm/s ($-75$ MHz). This value is less negative than the experimental result of $-1.78$ mm/s ($-120$ MHz). The difference ($0.68$ mm/s ($-45$ MHz)) is due to the lattice contribution to the quadrupole hyperfine splitting which will be of the anticipated negative sign as $B_2^0$ is negative.

4. YbAsO$_4$. — From previous susceptibility data it had been observed that if any magnetic ordering occurs it was below 0.6 K [16]. We have observed that ordering does occur at lower temperatures and our initial estimates set $T_N$ near 0.3 K. It was not possible to obtain a more accurate value due to the presence of temperature dependent line broadening in the magnetically ordered region. At the lowest temperatures used (below 0.1 K) a complicated line shape is still observed. This arises because the exchange interaction is small enough so as to be comparable in size to the hyperfine interaction and further the quantization axis of the exchange interaction may be perpendicular to the quantization axis of the hyperfine interaction. A complete set of hyperfine constants has not yet been obtained from the data but we have obtained an approximate value for the saturated magnetic hyperfine field. This hyperfine field value is equivalent to a Yb$^{3+}$ 4f magnetic moment of near 1.9 $\mu_B$ which is close to that corresponding to the dominant $g$-value ($g_\parallel = 3.6$) for Yb$^{3+}$ diluted into TmAsO$_4$.

Above $T_N$ in the paramagnetic region, the line shapes show the effects of temperature independent magnetic relaxation. This relaxation is due to spin-spin coupling between neighbouring Yb$^{3+}$ ions. Some small discrepancies remain between the experimental and theoretical line shapes using a relaxation model [17] which applies to electronic relaxation within a uniaxially symmetric electronic doublet as pertains here. Consequently no exact value for the relaxation rate could be obtained. A rough estimate sets it at near $5.0 \times 10^3$ MHz. We have previously observed [18] that discrepancies exist between the experimental and theoretical relaxation line shapes when the driving mechanism for the relaxation is the spin-spin interaction. It is probable here also that the misfits are due to the particular nature of the spin-spin interaction.

As well as providing an approximate value for the relaxation rate, the line shape analysis in the paramagnetic region gave a value for the quadrupole hyperfine interaction parameter $\alpha$. The value obtained

$$\alpha = -2.0 \pm 0.1 \text{ mm/s} (-136 \pm 7 \text{ MHz})$$
is close to that observed for Yb$^{3+}$ diluted in TmAsO$_4$: $-1.78 \pm 0.08$ mm/s ($-121 \pm 5$ MHz). This again demonstrates the similarity of the Yb$^{3+}$ ground state wave functions in TmAsO$_4$ and YbAsO$_4$.

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References