Tm\textsuperscript{3+} and Yb\textsuperscript{3+} in TmXO\textsubscript{4} and YbXO\textsubscript{4} (X = P, V) from 169Tm and 170 Yb Mössbauer measurements

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**Tm\(^{3+}\) and Yb\(^{3+}\) in TmXO\(_4\) and Yb\(^{3+}\) in YbXO\(_4\) (X = P, V) from \(^{169}\)Tm and \(^{170}\)Yb Mössbauer measurements**

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Résumé. — A partir des paramètres hyperfins mesurés par effet Mössbauer sur \(^{169}\)Tm\(^{3+}\) dans TmPO\(_4\) et sur \(^{170}\)Yb\(^{3+}\) dans TmXO\(_4\) et YbXO\(_4\) (X = P, V) nous étudions les propriétés électroniques des ions de terres rares. Nous dégageons un jeu de paramètres de champ cristallin pour Tm\(^{3+}\) dans TmPO\(_4\) et nous réexaminons celui déjà proposé pour Tm\(^{3+}\) dans TmVO\(_4\). Dans les réseaux des deux phosphates les propriétés des ions Tm\(^{3+}\) et Yb\(^{3+}\) s'interprètent bien à l'aide des paramètres de champ cristallin très voisins. Il en va de même pour le cas des deux vanadates. Dans YbXO\(_4\) la relaxation provoquée par les interactions spin-spin est mesurée et analysée. YbVO\(_4\) s'ordonne à 0,15 K et YbPO\(_4\) est ordonné dans une zone de température comparable.

Abstract. — Mössbauer measurements are reported on \(^{169}\)Tm\(^{3+}\) in TmPO\(_4\) and on \(^{170}\)Yb\(^{3+}\) in TmXO\(_4\) and in YbXO\(_4\) (X = P, V). The measured hyperfine parameters are used to provide information concerning the electronic properties of the rare earth ions. A set of crystalline electric field (CEF) parameters is obtained for Tm\(^{3+}\) in TmPO\(_4\) and previously proposed CEF parameters for Tm\(^{3+}\) in TmVO\(_4\) are discussed. The measured ground state properties of Yb\(^{3+}\) diluted into the two TmXO\(_4\) can be generated by sets of CEF parameters close to those obtained for Tm\(^{3+}\) in the corresponding matrix. Spin-spin relaxation rates were measured in the paramagnetic YbXO\(_4\) and the origin of the rate in YbVO\(_4\) is discussed. Magnetic ordering is observed in YbVO\(_4\) below about 0.15 K and also in YbPO\(_4\) in a comparable temperature zone.

1. **Introduction.**

The rare earth compounds crystallizing in the zircon structure have been the subject of considerable attention. This has been chiefly directed towards examining the spectroscopic properties of the various rare earth ions and in examining the magnetic and crystallographic phase transitions which occur in certain of these compounds at low temperatures.

In the same spirit as for a previous paper which dealt with the thulium and ytterbium arsenates [1], here we investigate the properties of Tm\(^{3+}\) and Yb\(^{3+}\) in the phosphates and vanadates. For each of the two systems (PO\(_4\), VO\(_4\)) in turn, the results, which were obtained on polycrystalline samples, are presented and discussed in the following order:

a) \(^{169}\)Tm Mössbauer measurements in TmXO\(_4\) and the CEF analysis of the Tm\(^{3+}\) ion.

b) \(^{170}\)Yb Mössbauer measurements of Yb\(^{3+}\) diluted into TmXO\(_4\) and the analysis of the single ion Yb\(^{3+}\) characteristics and comparison with the CEF analysis for Tm\(^{3+}\) in the same matrix.

c) \(^{170}\)Yb Mössbauer measurements in the magnetically concentrated systems YbXO\(_4\) and an analysis in terms of the previously established Yb\(^{3+}\) single ion properties. This provides information concerning electronic relaxation rates and magnetic ordering.

2. **2.1 TmPO\(_4\).** — A considerable amount of information is already available concerning the properties of Tm\(^{3+}\) in this matrix [2-7]. The electronic ground state is known to be a singlet with a highly anisotropic Van Vleck susceptibility [7] and it is relatively well separated from the nearest excited levels. No Jahn-Teller transition occurs in this compound as the non-Kramers doublet levels whose coupling with lattice strain could drive such a transition do not remain sufficiently populated at low enough temperatures.

The thermal dependence of the \(^{169}\)Tm\(^{3+}\) quadrupole hyperfine splitting when combined with previous data existing in the literature, enables a more complete description to be given of the Tm\(^{3+}\) properties. In particular we obtain a set of values for the CEF...
parameters and specify the wave functions of the electronic levels.

Mössbauer absorption measurements on $^{169}$Tm ($I_g = \frac{1}{2}$, $I_e = \frac{3}{2}$, 8.4 keV, 1 mm/s $\equiv$ 6.78 MHz) were made from 1.4 to 850 K using a source of neutron activated $^{168}$Er in Al at room temperature. The data was fitted to a Hamiltonian having the appropriate tetragonal symmetry:

$$\mathcal{H} = \alpha \left( I_e^2 - \frac{I(I+1)}{3} \right)$$

(1)

which links the quadrupole moment of the $I_e = \frac{3}{2}$ level and the electric field gradient (EFG). The latter is comprised of a dominant component arising from the non-spherical charge distribution of the Tm$^{3+}$ electronic levels and a small component arising from the neighbouring and distant lattice charges.

The observed quadrupole doublet was symmetric at all temperatures, each component having the same line width. This contrasts with the case of both TmVO$_4$ and TmAsO$_4$ where an asymmetric doublet was observed above $T_d$ the bulk Jahn-Teller transition temperature. The origin of this difference lies with the fact that in both TmVO$_4$ and TmAsO$_4$ the ground level above $T_d$ is a non-Kramers doublet. In these doublet levels the pseudo-quadrupole interaction and relaxation both can give rise to a line-shape asymmetry [1]. However in TmPO$_4$ such effects are absent as the ground level is an isolated singlet.

The thermal variation of the $^{169}$Tm quadrupole hyperfine interaction is shown on figure 1. The observed temperature dependence is due to thermally driven population changes within the various 4f crystal field levels which have differing associated electric field gradients. There is an indication that the measured quadrupole splitting goes through a minimum near 500 K but, taking into account the experimental errors, this is not definitely established. In systems with tetragonal symmetry the simultaneous presence of a (temperature dependent) EFG due to the 4f levels and a (temperature independent) EGF due to lattice charges can lead to the total EFG (and the total quadrupole splitting) crossing through a zero value at some compensation temperature. This however does not happen here. As it is not established that the EFG due to the lattice charges effectively contributes to the total quadrupole splitting, it was not included in the subsequent analysis.

As far as the bare experimental results of figure 3 are concerned, they can be accurately accounted for by many different sets of CEF parameters. The quadrupole hyperfine interaction data alone is thus not sufficient to provide the actual CEF parameters. However by using, in addition, various other known properties of the Tm$^{3+}$ ion in TmPO$_4$ (Van Vleck susceptibility at $T = 0$ K and positions of the excited energy levels) we have established a relatively well defined set of CEF parameters. These parameters reproduce: (1) the Van Vleck susceptibilities of the ground singlet, (2) all the presently known energy levels of the excited states and (3) the low temperature limiting value of the quadrupole hyperfine interaction. In addition they approximately reproduce the thermal variation of the quadrupole hyperfine interaction as shown in figure 1. The discrepancies remaining in figure 1 have three origins: first that the lattice contribution to the EFG was not included in the analysis, second that the CEF parameters may themselves vary slightly with temperature and third that the various atomic and nuclear parameters entering into the analysis are only known to within an accuracy of about 10% [8].

In terms of a CEF described by

$$\mathcal{H} = \sum_{nm} B^n_m \sigma^m_n O^m_n$$

(2)

and with $B^0_2 = 132$, $B^2_0 = 4.1$, $B^4_0 = 642$, $B^6_0 = -44$, and $B^8_0 = 10.9$ cm$^{-1}$ we calculate:

$$\chi^A(T = 0) = 0.012 \text{ emu/g. atom} ; \quad (0.013, \text{ ref. [6]})$$
$$\chi^\Delta(T = 0) = 0.456 \text{ emu/g. atom} ; \quad (0.456, \text{ ref. [6]})$$
$$\Delta(\text{ground singlet-first excited doublet}) = 29 \text{ cm}^{-1} ; \quad (29, \text{ ref. [7]})$$
$$\Delta(\text{ground singlet-first excited singlet}) = 86 \text{ cm}^{-1} ; \quad (84, \text{ ref. [7]})$$
$$\Delta(\text{ground singlet-second excited doublet}) = 137 \text{ cm}^{-1} ; \quad (138, \text{ ref. [7]})$$
$$\Delta(\text{ground singlet-third excited doublet}) = 278 \text{ cm}^{-1} ; \quad (280, \text{ ref. [7]})$$

$$2 \alpha^\Delta(T = 0) = 7.4 \text{ cm/s} ; \quad (2 \alpha^\text{total}(T = 0) = 7.7 \text{ (this work)})$$

where the experimental values are given in brackets.
For the quadrupole hyperfine analysis the following relation between the constants was used:

\[(1 - R_q) Q < r^{-3} > = -87.7 \text{ cm}^{-1}\.

The accuracy of the proposed CEF parameters is estimated to be roughly 10%.

The wave function of the ground singlet is

\[|\psi\rangle = -0.32| + 4 > + 0.90| 0 > - 0.32| - 4 > \]

and those of the first excited doublet

\[|\psi\rangle = -0.46| \pm 5 > + 0.82| \pm 1 > - 0.34| \mp 3 > \]

The total calculated energy splitting of the \(^3H_6\) configuration is 323 cm\(^{-1}\).

2.2 \(\text{Yb}^{3+}\) in \(\text{TmPO}_4\). — The limiting low temperature \(^{170}\text{Yb}\) Mössbauer emission spectrum (\(I_g = 0, I_e = 2, 84 \text{ keV}, 1 \text{ mm/s} \equiv 67.95 \text{ MHz}\)) obtained from a source of neutron activated \(\text{TmPO}_4\) against a \(\text{YbB}_6\) absorber held at 4.2 K is shown in figure 2.

![Figure 2. \(^{170}\text{Yb}^{3+}\) Mössbauer emission spectrum for a source of neutron activated \(\text{TmPO}_4\) at 10 K against a \(\text{YbB}_6\) single line absorber.](image)

In addition to the main spectrum some unidentified impurities are also present. In terms of the tetragonal Hamiltonian:

\[\mathcal{H} = \alpha \left( I_x^2 - \frac{I(I+1)}{3} \right) + A_x S_x I_x + A_z (S_z I_x + S_y I_y) \quad (3)\]

and in the slow relaxation limit, the adjustment shown corresponds to

\[\alpha = -1.97 \pm 0.05 \text{ mm/s},\]
\[|A_x| = 4.7 \pm 0.5 \text{ mm/s},\]
\[|A_z| = 12.5 \pm 0.2 \text{ mm/s}\]

with the sign of the product of the three magnetic hyperfine components negative.

The ground state magnetic parameters correspond to \(g_x = 1.20\) and \(g_z = 3.19\). The values for \(\text{Yb}^{3+}\) in \(\text{YPO}_4\) are 1.52 and 3.13 respectively [9]. The symmetry (\(g_x < g_z\)) is the same as for the \(\text{Yb}^{3+}\) ground state in \(\text{TmAsO}_4\) (\(g_x = 0.4, g_z = 3.60\)) and opposite (\(g_x > g_z\)) to that for \(\text{Yb}^{3+}\) in \(\text{TmVO}_4\) (\(g_x = 6.45, g_z = 0.6\)).

From the derived \(g\)-values and the measured value of \(\alpha\) it is not possible to identify the ground state wave function from between the two possibilities \(a | \pm 7/2 > + b | \mp 1/2 >\) or \(a | \pm 5/2 > + b | \mp 3/2 >\). However when the CEF parameters established above for \(\text{Tm}^{3+}\) in \(\text{TmPO}_4\) are applied to \(\text{Yb}^{3+}\), the ground state is found to be of the form \(a | \pm 5/2 > + b | \mp 3/2 >\) with \(g_x = 1.55\) and \(g_z = 3.20\). These values are close to those observed experimentally which is evidence that the CEF parameters are similar for both \(\text{Yb}^{3+}\) and \(\text{Tm}^{3+}\) in the phosphates and also that the \(\text{Yb}^{3+}\) ground state is of the form \(a | \pm 5/2 > + b | \mp 3/2 >\). With these CEF parameters the first excited doublet of \(\text{Yb}^{3+}\) is calculated to be at 103 cm\(^{-1}\).

Above about 20 K the Mössbauer line-shapes begin to be broadened by (phonon induced) relaxation.

2.3 \(\text{YbPO}_4\). — The \(^{170}\text{Yb}\) Mössbauer absorption spectrum at 4.2 K using a source of \(\text{TmB}_{12}\) held at near 4.2 K is shown on figure 3 and represents the low temperature limiting the line-shape in the paramagnetic phase. The presence of magnetic relaxation, which acts to wipe out the influence on the line-shape of the magnetic hyperfine parameters, is clearly evident in comparison with the line shape for the dilute counterpart of figure 2. In the low temperature paramagnetic region, the line-shape is independent of temperature showing that the driving mechanism is spin-spin interactions between neighbouring \(\text{Yb}^{3+}\) ions. Above about 25 K the line-shape changes due to the onset of phonon driven relaxation. The line fit shown on figure 3 was obtained using a relaxation model [10] which applies to relaxation within an uniaxially symmetric electronic doublet as is the case here. Using the static magnetic hyperfine parameters \((A_x, A_z)\) as obtained for \(\text{Yb}^{3+}\) diluted in \(\text{TmPO}_4\), the fit on figure 3 corresponds to a relaxation rate of \(2.0 \times 10^{10} \text{ s}^{-1}\). This is close to that \((3.0 \times 10^{10} \text{ s}^{-1})\) previously obtained within the \(\text{Yb}^{3+}\) ground electronic doublet in \(\text{YbAsO}_4\) [1]. The quadrupole hyperfine interaction parameters \(\alpha\) obtained from this fit was \(-1.55 \text{ mm/s}\) which has the same sign and is roughly 25% smaller in magnitude than for \(\text{Yb}^{3+}\) diluted in \(\text{TmPO}_4\).

As far as the measured relaxation rate \((2.0 \times 10^{10} \text{ s}^{-1})\) is concerned, we have examined whether it is possible...
to estimate the relative importance of the contributions of the classical dipole-dipole interaction and of the exchange interaction to the total relaxation rate. To do this we have examined whether it is possible to calculate the dipole-dipole relaxation rate using a method that we have previously described and which is based on a «Golden Rule» approach. This approach works well when the magnetic ion has Ising-like characteristics \((g_d > g_i)\) [11] as then the dipolar Hamiltonian can be directly factorized into two parts, the off-diagonal elements of the dipolar Hamiltonian yielding the matrix elements of the spin-flip transition probability and the diagonal elements yielding the density of states of the spin bath. In the phosphates however, the \(\text{Yb}^{3+}\) ground doublet does not have Ising-like characteristics as \(g_d < g_i\) and thus a physically meaningful factorization of the dipolar Hamiltonian is not feasible. There thus seems to be no reliable way at present of calculating the dipole-dipole relaxation rate in this system. Because of this we cannot identify the driving mechanism of the observed spin-spin relaxation in \(\text{YbPO}_4\).

In the case of \(\text{YbVO}_4\) (sect. 3.3), \(\text{Yb}^{3+}\) has Ising-like characteristics and the «Golden Rule» approach leads to a reliable identification of the driving mechanisms.

At lower temperatures the Mössbauer line-shapes show the influence of magnetic ordering. For example at 0.065 K the total width of the spectrum has increased by approximately 40% compared to that of figure 3. This broadening corresponds to the presence of an electronic moment of roughly 1 \(\mu_B\). It is not presently known if this is the low temperature saturated moment, nor has it been possible to accurately specify the ordering temperature.

3.

3.1 \(\text{TmVO}_4\). — \(\text{TmVO}_4\) is a model Jahn-Teller compound with the tetragonal to orthorhombic phase transition occurring at \(T_d = 2.15\) K [12]. Measurements of the \(^{169}\text{Tm}\) quadrupole hyperfine splittings in this system have been reported by Tripllett et al. [13] and were not repeated here. As for \(\text{TmPO}_4\) in section 2.2, we examine the Mössbauer data, as well as the other available results in this system, with a view to specifying the CEF properties. A set of CEF parameters derived from optical spectroscopy measurements on \(\text{Tm}^{3+}\) diluted into \(\text{YVO}_4\) has been reported by Knoll [2] and was later refined by Wortmann et al. [14]. Using the parameters proposed in reference [14]: \(B_2^0 = -87.3, B_2^q = 42.2, B_4^0 = 870.1, B_4^q = -38.3\) and \(B_6^q = -35.2\text{ cm}^{-1}\), we calculate the limiting low temperature tetragonal phase quadrupole hyperfine splitting due to the EFG arising from the f-levels to be 4.25 cm/s which compares with the experimental value of near 3.5 cm/s [13]. The difference between the two values (−0.75 cm/s) has two origins. First, it is due to the lattice contribution to the EFG. To roughly estimate this contribution we can take the value directly measured on \(\text{Gd}^{3+}\) in \(\text{GdVO}_4\) [15] and apply it to \(\text{Tm}^{3+}\). This leads to a value of near −0.4 cm/s. This is of the correct sign but it is smaller than the observed difference. A second origin of the difference lies with the fact that the set of CEF parameters above is probably not correct in all detail, as it does not accurately account for all the optically measured energy levels of the ground \(^{3}\text{H}_6\) configuration [14].

The ground state doublet wave functions in the tetragonal phase derived from the above CEF parameters are:

\[
|\psi\rangle = 0.89|\pm 5\rangle - 0.42|\pm 1\rangle + 0.19|\mp 3\rangle.
\]

The value of \(g_d\) calculated from these wave functions is 9.4 and is smaller than the measured value of 10.2 obtained for \(\text{Tm}^{3+}\) both in \(\text{YVO}_4\) [16] and in \(\text{TmVO}_4\) [17]. This difference would disappear if the wave function given above were slightly richer in the \(|\pm 5\rangle\) component. Increasing the coefficient of this component would also bring the calculated value for the quadrupole hyperfine splitting closer to the experimental value.

The quadrupole hyperfine splitting does not change much in going across \(T_d\) [13], showing that the wave functions of each of two ground state singlets in the orthorhombic phase are essentially derived from linear combinations of the ground state doublet wave functions in the tetragonal phase. The changing lattice symmetry thus introduces very little admixture with the excited states which is in keeping with the fact that the nearest of these is relatively well separated at near 54 cm\(^{-1}\) [2]. This behaviour is different to that observed in \(\text{TmAsO}_4\) [1] where the first excited state above the ground doublet is at near 14 cm\(^{-1}\) and where crossing \(T_d\) from above leads to considerable mixing of the low lying excited states into the ground state. Another difference between the two Jahn-Teller compounds \(\text{TmVO}_4\) and \(\text{TmAsO}_4\) relates to the Mössbauer line-shapes. Whereas for \(\text{TmAsO}_4\) the quadrupole doublet is asymmetric down to \(T_d\) where it then becomes abruptly symmetric, for \(\text{TmVO}_4\), the asymmetry progressively decreases to disappear before \(T_d\) is reached. This difference is related to the lifting (by local strains) of the degeneracy of the ground state doublet above \(T_d\) and its interplay with the pseudo-quadrupole interaction [1]. In \(\text{TmAsO}_4\), just above \(T_d\) the amount of local degeneracy lifting \(\Delta\) does not vary significantly with temperature whereas in \(\text{TmVO}_4\) \(\Delta\) increases progressively as \(T_d\) is approached from above [1].

3.2 \(\text{Yb}^{3+}\) in \(\text{TmVO}_4\). — The \(^{170}\text{Yb}\) Mössbauer emission spectrum was obtained using a source of neutron activated \(\text{TmVO}_4\) against a \(\text{YbB}_4\) moving absorber. In this way the \(\text{Yb}^{3+}\) concentration is very low so that the characteristics of the matrix and in particular the bulk Jahn-Teller transition temperature is expected to be the same \((T_d = 2.15\) K\) as in pure \(\text{TmVO}_4\). The spectrum at 1.4 K that is, in the ortho-
rhombic phase is shown in figure 4. Identical data was obtained at 4.2 K that is in the tetragonal phase. The changing lattice symmetry has no discernable influence on the properties of the Yb$^{3+}$ ground state which, on both sides of $T_d$, are well accounted for by the tetragonal Hamiltonian given in equation (3). The fitted parameters were:

$$\alpha = 3.4 \pm 0.1 \text{ mm/s},$$
$$|A_z| = 25.2 \pm 0.2 \text{ mm/s},$$
$$|A_\perp| = 2.5 \pm 0.8 \text{ mm/s}$$

with the product of the three magnetic hyperfine negative components. The magnetic hyperfine parameters correspond to $g_z = 6.45 \pm 0.05$ and $g_\perp = 0.6 \pm 0.2$. The values for Yb$^{3+}$ in YVO$_4$ are the $g_z = 6.08, g_\perp = 0.85$ [18]. This Ising-like behaviour is very different to that observed for Yb$^{3+}$ in both TmPO$_4$ and TmASO$_4$ where $g_z > g_\perp$. From the present $g$-values, the wave function of the ground doublet can be derived:

$$|\psi\rangle = 0.91 |+/2\rangle + 0.41 |\mp 1/2\rangle.$$

The experimentally observed $g$-values can be generated with the tetragonal CEF Hamiltonian of equation (2) with the fourth and sixth order parameters kept the same as for Tm$^{3+}$ in YVO$_4$ as cited in section 3.1 and with $B_2^0 = -145 \text{ cm}^{-1}$ that is, with $B_2^0$ more negative than for Tm$^{3+}$ in YVO$_4$.

The Yb$^{3+}$ quadrupole hyperfine parameter associated with the above wave function is calculated to be 4.2 mm/s. This has the same (positive) sign, but is bigger than as, the experimental value of 3.4 mm/s. The difference ($-0.8$ mm/s) can be associated with the contribution of the lattice charges to the EFG which has the expected negative sign in keeping with the negative sign of $B_2^0$. As the temperature is increased above 15 K, the quadrupole hyperfine interaction begins to decrease as the excited Yb$^{3+}$ CEF levels begin to be populated. However from about 20 K to about 60 K accurate values of $\alpha$ cannot be obtained due to the influence on the line-shapes of (thermally dependent) magnetic relaxation. At, and above 70 K, the magnetic relaxation rate is fast enough to almost wipe out the magnetic hyperfine structure and $\alpha$ can again be accurately obtained. At 70 K the measured value of $\alpha$ is 1.9 mm/s. The decrease in $\alpha$ between 4.2 and 70 K is thus 1.5 mm/s. Using the CEF parameters given above (that is with the parameters established for Tm$^{3+}$ in YVO$_4$ but with $B_2^0 = -145 \text{ cm}^{-1}$), the decrease in $\alpha$ over the same temperature range is calculated to be 1.3 mm/s. The reasonable agreement with experiment supports the credibility of the CEF parameters given above.

On both sides of $T_d$ the Mössbauer line-shapes are characteristic of the slow relaxation limit. There is thus no magnetic cross-relaxation visible between Yb$^{3+}$ and Tm$^{3+}$ in either the orthorhombic or tetragonal phases. This same behaviour was also observed for Yb$^{3+}$ in TmAsO$_4$ [1].

3.3 YVO$_4$. — The $^{170}$Yb Mössbauer absorption spectra at 0.07, 4.2 and 70 K are shown in figure 5. The results at 0.07 K were obtained using an isotopically enriched sample. These spectra correspond respectively to within the magnetically saturated region, to within the paramagnetic region where the line-shape is independent of temperature (relaxation driven by spin-spin processes) and to a temperature where the magnetic relaxation is governed chiefly by interaction with the phonons. We discuss first the fitted static hyperfine parameters and then discuss the dynamical aspects.

The line-shape at 0.07 K was fitted to an axial Hamiltonian including a quadrupole hyperfine interaction ($\alpha$) and an effective hyperfine field ($H_\text{eff}$) acting on the Yb$^{3+}$ nucleus

$$\mathcal{H} = \alpha (I_z^2 - (I + 1)/3) + g_n \beta_n H_\text{eff} I_z. \quad (4)$$

![Fig. 5. — $^{170}$Yb$^{3+}$ Mössbauer absorption spectra for YbVO$_4$ at a) 0.07, b) 4.2, and c) 70.0 K.](image)
The fitted values were: \( a = 3.50 \pm 0.05 \text{ mm/s} \) and \( H_z \) (colinear with the principal axis of the EFG) = 3 240 ± 80 kOe. This hyperfine field corresponds to a magnetic moment of 3.1 \( \mu_B \) which agrees with the value obtained from neutron diffraction measurements [19]. In the paramagnetic region at 42 K, \( \alpha = 3.65 \pm 0.05 \) mm/s and at 70 K, \( \alpha = 2.2 \pm 0.1 \) mm/s.

A number of elements point to the close correspondence between the single ion ground state properties of Yb\( ^{3+} \) in TmVO\(_4\) and in YbVO\(_4\). At temperatures such that only the ground doublet is populated, \( \alpha \) is the same in both matrices. The observed saturated hyperfine field in YbVO\(_4\) of 3 240 ± 80 kOe is directed along the principal axis of the electric field gradient and corresponds to a value of \( A_z = 24.0 \pm 0.6 \) mm/s. This is essentially the same as that directly measured for Yb\( ^{3+} \) in TmVO\(_4\): \( A_z = 25.2 \pm 0.2 \) mm/s which is also parallel to the principal axis of the electric field gradient. The similarities between the Yb\( ^{3+} \) properties in the two matrices also extend to the excited crystal field levels as is shown by the fact that the decrease in \( \alpha \) between 4.2 and 70 K is the same in both cases (1.45 mm/s in YbVO\(_4\) and 1.5 mm/s for Yb\( ^{3+} \) in TmVO\(_4\)).

The influence of relaxation is visible through the broadening of the absorption line shapes that it produces both in the magnetically ordered region just below \( T_N \) and also in the paramagnetic region up to about 70 K. Beyond this temperature the relaxation rate becomes fast enough to wipe out the magnetic hyperfine interaction leaving only a quadrupole line shape.

The relaxation broadened line-shape is independent of temperature at low temperatures in the paramagnetic region. The relaxation rate here is thus also independent of temperature. This behaviour identifies the driving relaxation mechanism as being spin-spin interactions between Yb\( ^{3+} \) ions. Using the relaxation model appropriate to uniaxial symmetry given in reference [9], we obtained the fit shown on figure 5b. At these temperatures (for example at 42 K) the fitted 70 K relaxation rate is near \( 2.0 \times 10^{11} \text{ s}^{-1} \). As the temperature is lowered through the Néel temperature, the line-shapes progressively change from the limiting low temperature paramagnetic line-shape of figure 5b to the saturated magnetic line-shape of figure 5a and the ordering temperature cannot be well defined. Using the temperature at which the line-shape begins to broaden as a guide, we estimate \( T_N \) to be in the neighbourhood of 0.15 K. This is somewhat higher than the value of 0.1 K as found by neutron diffraction [19].

### 4. Summary.

The CEF parameters (in cm\(^{-1}\)) relevant to Tm\(^{3+}\) and Yb\(^{3+}\) in TmPO\(_4\) and TmVO\(_4\) together with those obtained in reference [11] for TmAsO\(_4\) are given below. For Tm\(^{3+}\) the parameters concern the tetragonal phase (above the Jahn-Teller transition temperature if it exists). For Yb\(^{3+}\) the tetragonal CEF parameters also account for the ground state magnetic hyperfine parameters in the orthorhombic phase.

<table>
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<tr>
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<th>( B_2^0 )</th>
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<td>Tm(^{3+}) in TmAsO(_4) (ref. [1])</td>
<td>- 37</td>
<td>15.7</td>
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The fitted values were: \( a = 3.50 \pm 0.05 \text{ mm/s} \) and \( H_z \) (colinear with the principal axis of the EFG) = 3 240 ± 80 kOe. This hyperfine field corresponds to a magnetic moment of 3.1 \( \mu_B \) which agrees with the value obtained from neutron diffraction measurements [19]. In the paramagnetic region at 42 K, \( \alpha = 3.65 \pm 0.05 \) mm/s and at 70 K, \( \alpha = 2.2 \pm 0.1 \) mm/s.

A number of elements point to the close correspondence between the single ion ground state properties of Yb\( ^{3+} \) in TmVO\(_4\) and in YbVO\(_4\). At temperatures such that only the ground doublet is populated, \( \alpha \) is the same in both matrices. The observed saturated hyperfine field in YbVO\(_4\) of 3 240 ± 80 kOe is directed along the principal axis of the electric field gradient and corresponds to a value of \( A_z = 24.0 \pm 0.6 \) mm/s. This is essentially the same as that directly measured for Yb\( ^{3+} \) in TmVO\(_4\): \( A_z = 25.2 \pm 0.2 \) mm/s which is also parallel to the principal axis of the electric field gradient. The similarities between the Yb\( ^{3+} \) properties in the two matrices also extend to the excited crystal field levels as is shown by the fact that the decrease in \( \alpha \) between 4.2 and 70 K is the same in both cases (1.45 mm/s in YbVO\(_4\) and 1.5 mm/s for Yb\( ^{3+} \) in TmVO\(_4\)).

The influence of relaxation is visible through the broadening of the absorption line shapes that it produces both in the magnetically ordered region just below \( T_N \) and also in the paramagnetic region up to about 70 K. Beyond this temperature the relaxation rate becomes fast enough to wipe out the magnetic hyperfine interaction leaving only a quadrupole line shape.

The relaxation broadened line-shape is independent of temperature at low temperatures in the paramagnetic region. The relaxation rate here is thus also independent of temperature. This behaviour identifies the driving relaxation mechanism as being spin-spin interactions between Yb\( ^{3+} \) ions. Using the relaxation model appropriate to uniaxial symmetry given in reference [9], we obtained the fit shown on figure 5b. At these temperatures (for example at 42 K) the fitted 70 K relaxation rate is near \( 2.0 \times 10^{11} \text{ s}^{-1} \). As the temperature is lowered through the Néel temperature, the line-shapes progressively change from the limiting low temperature paramagnetic line-shape of figure 5b to the saturated magnetic line-shape of figure 5a and the ordering temperature cannot be well defined. Using the temperature at which the line-shape begins to broaden as a guide, we estimate \( T_N \) to be in the neighbourhood of 0.15 K. This is somewhat higher than the value of 0.1 K as found by neutron diffraction [19].

### 4. Summary.

The CEF parameters (in cm\(^{-1}\)) relevant to Tm\(^{3+}\) and Yb\(^{3+}\) in TmPO\(_4\) and TmVO\(_4\) together with those obtained in reference [11] for TmAsO\(_4\) are given below. For Tm\(^{3+}\) the parameters concern the tetragonal phase (above the Jahn-Teller transition temperature if it exists). For Yb\(^{3+}\) the tetragonal CEF parameters also account for the ground state magnetic hyperfine parameters in the orthorhombic phase.

<table>
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Derived Tm$^{3+}$ ground state wave functions:

Tm$^{3+}$ in TmAsO$_4$ (ref. [1]):  $0.88 | \pm 5 \rangle - 0.44 | \pm 1 \rangle + 0.19 | \mp 3 \rangle$

Tm$^{3+}$ in TmPO$_4$: $- 0.32 | + 4 \rangle + 0.90 | 0 \rangle - 0.32 | - 4 \rangle$

Tm$^{3+}$ in TmVO$_4$: $\sim 0.89 | \pm 5 \rangle - 0.42 | \pm 1 \rangle + 0.19 | \mp 3 \rangle$

but probably slightly richer in $| \pm 5 \rangle$

Yb$^{3+}$ experimental ground state g-values and wave functions:

Yb$^{3+}$ in TmAsO$_4$ (ref. [1]): $g_z = 0.4, \quad g_\perp = 3.60, \quad | \psi \rangle = a | \pm 5/2 \rangle + b | \mp 3/2 \rangle$

Yb$^{3+}$ in TmPO$_4$: $g_z = 1.2, \quad g_\perp = 3.19, \quad | \psi \rangle \text{ probably} = a | \pm 5/2 \rangle + b | \mp 3/2 \rangle$

Yb$^{3+}$ in TmVO$_4$: $g_z = 6.45, \quad g_\perp = 0.6, \quad | \psi \rangle = a | \pm 7/2 \rangle + b | \mp 1/2 \rangle$

It can be noticed that in TmAsO$_4$ and TmVO$_4$, Tm$^{3+}$ has approximately the same ground state wave function. However, the ground state wave functions for Yb$^{3+}$ are different in these two matrices. As mentioned in reference [1] this behaviour 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$_4$.

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References