



**HAL**  
open science

## **Tm-169 MÖSSBAUER STUDY OF THULIUM HYDRIDES (II) : TmH<sub>3</sub>**

G. Wortmann, G. Kalkowski, A. Heidemann, F. Wagner

► **To cite this version:**

G. Wortmann, G. Kalkowski, A. Heidemann, F. Wagner. Tm-169 MÖSSBAUER STUDY OF THULIUM HYDRIDES (II) : TmH<sub>3</sub>. Journal de Physique Colloques, 1980, 41 (C1), pp.C1-233-C1-234. 10.1051/jphyscol:1980176 . jpa-00219745

**HAL Id: jpa-00219745**

**<https://hal.science/jpa-00219745v1>**

Submitted on 4 Feb 2008

**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.

Tm-169 MÖSSBAUER STUDY OF THULIUM HYDRIDES (II) :  $\text{TmH}_3$ G. Wortmann, G. Kalkowski, A. Heidemann<sup>+</sup> and F.E. Wagner<sup>+</sup>*Institut für Atom- und Festkörperphysik, Freie Universität Berlin, 1000 Berlin, W. Germany.**+ Physik-Department, Technische Universität München, 8046 Garching, W. Germany.*Introduction

The aptitude of the 8.4 keV resonance of  $^{169}\text{Tm}$  for the study of thulium hydrides has been demonstrated in a preceding contribution to this conference [1]. The reason for this lies, beside the low gamma energy, in the resolution power of the  $^{169}\text{Tm}$  resonance for quadrupole interactions.  $^{169}\text{Tm}$ , a 100% isotope, is in its trivalent state a non-Kramers ion with a  $^3\text{H}_6$  configuration of the  $4f^{12}$  electron shell, which responds very sensitively to crystalline electric field (CEF) interactions. When the  $\text{Tm}^{3+}$  site symmetry is lower than cubic, rather large quadrupole splittings can be observed with the 8.4 keV  $3/2 \rightarrow 1/2$  transition of  $^{169}\text{Tm}$ . They may reach values up to 150 mm/s at liquid helium temperatures, where only the lowest CEF levels of the  $J=6$  4f-configuration are populated. At higher temperatures,  $eq_{4f}$ , the 4f contribution to the observed electric field gradient  $eq$ , is temperature averaged and the lattice contribution,  $eq_{\text{latt}}$ , becomes dominant. This behaviour has been observed and analysed in the early days of Mössbauer spectroscopy [2].

The information obtained from the present study of  $\text{TmH}_3$  will be used to discuss the controversial results of two recent studies of  $\text{Er}^{3+}$  in  $\text{YH}_3$  and  $\text{ErH}_3$ , respectively [3,4].

Sample Preparation and Experiments

The  $\text{TmH}_3$  sample was prepared by exposing

about 100 mg of Tm metal at 870 K to a  $\text{H}_2$  pressure of 1400 Torr for one hour. During the the cooling of the sample, the  $\text{H}_2$  pressure was raised to about 3000 Torr. The X-ray diffraction analysis showed only the hexagonal rare earth (R.E.) trihydride phase [5]. The gravimetric determination of the H content of the sample yielded a formula  $\text{TmH}_{3.1(2)}$ . The Mössbauer measurements were performed similar as described in [1].

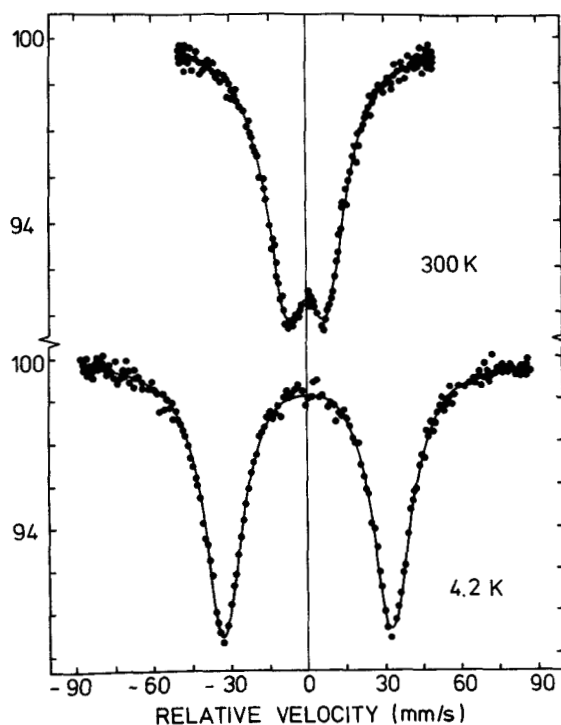


Figure 1:  $^{169}\text{Tm}$  Mössbauer spectra of  $\text{TmH}_3$  at various temperatures

### Results and Discussion

Fig. 1 shows two spectra of  $\text{TmH}_3$  at 300 K and 4.2 K. Both spectra reveal a typical quadrupole doublet, and, as in the  $^{169}\text{Tm}$  study of the Tm dihydrides [1], no indication of any magnetic hyperfine interactions. The temperature dependence of the quadrupole splitting,  $\Delta E_Q = e^2qQ/2$ , is given in Tab. 1 for a series of measurements between 4.2 K and 350 K. Measurements at  $T > 300$  K were followed by studies at lower temperatures to ensure that no hydrogen loss of the sample had occurred. A plot of the data of Tab. 1 shows that  $\Delta E_Q$  approaches a value of 14(1) mm/s at high temperatures.

From the quadrupole splittings observed in  $\text{TmH}_3$ , information on the CEF groundstate of the  $\text{Tm}^{3+}$  ion can be extracted by arguments similar to those applied recently to a Mössbauer study of  $\text{Er}^{3+}$  in  $\text{ErH}_3$  and  $\text{YH}_3$  [3] and to a susceptibility and magnetization study of  $\text{ErH}_3$  [4], respectively. It was assumed that in the isostructural R.E. trihydrides the CEF interaction of the R.E. ions can be described by hexagonal CEF parameters, although the H lattice actually lowers the point symmetry at the R.E. ions to  $C_2$ . This assumption is supported by a  $^{155}\text{Gd}$  Mössbauer study [6], where an axially symmetric  $eq_{\text{latt}}$  was observed, indicating that the hexagonal lattice of the R.E. ions is mainly responsible for  $eq_{\text{latt}}$ .

Using the CEF-level diagrams of Segal and Wallace [7] for hexagonal fields (which, however, use only fourth and sixth order CEF operators), Flood [4] derived from the magnetic data of  $\text{ErH}_3$  a negative value of  $x$ , the ratio of fourth order to sixth order CEF parameters. In contrast to this, Suits et al. [3] found from their Mössbauer data of  $\text{Er}^{3+}$  in  $\text{YH}_3$  a positive value of  $x$ . Transforming the  $\text{Er}^{3+}$  CEF parameters to the  $\text{Tm}^{3+}$  case, the negative sign (and the magnitude) of  $x$  from Ref. 4 would lead to two singlets with predominantly  $m_J = \pm 6$  character for the lowest CEF states in  $\text{TmH}_3$ , while the positive sign of  $x$  from Ref. 3

results in a  $\text{Tm}^{3+}$  singlet groundstate with  $m_J = \pm 3$  character [7]. Using a value of  $eq_{\text{latt}} = 5 \cdot 10^{17}$  V/cm<sup>2</sup> from Ref. 6 and the above CEF states (including the shielding parameters of Ref. 2), a rough estimate yields  $\Delta E_Q \cong 150$  mm/s at 4.2 K for the former and  $\Delta E_Q \cong 50$  mm/s for the latter case.

Together with our experimental results, this clearly favours the CEF parameters obtained from the  $^{166}\text{Er}$  Mössbauer study [3]. In principle, the temperature dependence of  $\Delta E_Q$  can be used to further elucidate the CEF levels of  $\text{Tm}^{3+}$  in  $\text{TmH}_3$ . However, since  $\Delta E_Q$  decreases quite fast in the low temperature region, additional data are needed for a more detailed analysis.

Finally, it should be noted that the high temperature value of  $eq$  ( $\Delta E_Q(T \rightarrow 400 \text{ K}) = 14$  mm/s corresponds to  $eq = 6 \cdot 10^{17}$  V/cm<sup>2</sup>, which most likely can be regarded as an approach to  $eq_{\text{latt}}$ ) is about 20% larger than the value obtained for  $\text{GdH}_3$  [6]. Such a small difference can easily be attributed to the smaller volume of the unit cell of  $\text{TmH}_3$ . This work will be continued.

**Table 1:** Temperature dependence of the  $^{169}\text{Tm}$  quadrupole splitting in  $\text{TmH}_3$

Temperature ( K )	$\Delta E_Q$ ( mm/s )
4.2	65.5(2)
55	56.2(2)
77	48.7(2)
260	18.1(6)
300	15.9(4)
330	15.4(6)
350	14.6(6)

### References

- 1) F. Waibel et al., contibuted paper to this conference.
- 2) R.G. Barnes, R.L. Mössbauer, E. Kankeleit, J.M. Poindexter, Phys. Rev. 136 (1964) A 175.
- 3) B. Suits, G.K. Shenoy, B.D. Dunlap, D.G. Westlake, J. Mag. Magn. Mat. 5 (1977) 34.
- 4) D.J. Flood, J. Appl. Phys. 49 (1978) 1495.
- 5) A. Pebler and W.E. Wallace, J. Phys. Chem. 66 (1962) 148; M. Mansmann and W.E. Wallace, J. Physique 25 (1964) 454.
- 6) S.J. Lyle, P.T. Walsh, A.D. Witts, J.W. Ross, J. Chem. Soc. Dalton (1975) 1406.
- 7) E. Segal, J. Sol. State Chem. 2 (1970) 347.