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Tm-169 MÖSSBAUER STUDY OF THULIUM HYDRIDES (II) : TmH_3 G. Wortmann, G. Kalkowski, A. Heidemann⁺ and F.E. Wagner⁺*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}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}Tm resonance for quadrupole interactions. ^{169}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 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}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_{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 TmH_3 will be used to discuss the controversial results of two recent studies of Er^{3+} in YH_3 and ErH_3 , respectively [3,4].

Sample Preparation and Experiments

The TmH_3 sample was prepared by exposing

about 100 mg of Tm metal at 870 K to a H_2 pressure of 1400 Torr for one hour. During the the cooling of the sample, the 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].

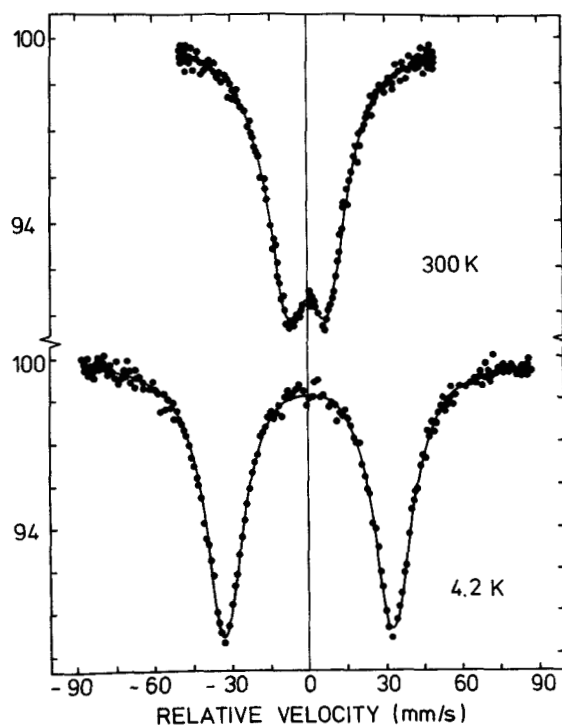


Figure 1: ^{169}Tm Mössbauer spectra of TmH_3 at various temperatures

Results and Discussion

Fig. 1 shows two spectra of TmH_3 at 300 K and 4.2 K. Both spectra reveal a typical quadrupole doublet, and, as in the ^{169}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 ΔE_Q approaches a value of 14(1) mm/s at high temperatures.

From the quadrupole splittings observed in TmH_3 , information on the CEF groundstate of the Tm^{3+} ion can be extracted by arguments similar to those applied recently to a Mössbauer study of Er^{3+} in ErH_3 and YH_3 [3] and to a susceptibility and magnetization study of 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}Gd Mössbauer study [6], where an axially symmetric eq_{latt} was observed, indicating that the hexagonal lattice of the R.E. ions is mainly responsible for eq_{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 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 Er^{3+} in YH_3 a positive value of x . Transforming the Er^{3+} CEF parameters to the 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 TmH_3 , while the positive sign of x from Ref. 3

results in a Tm^{3+} singlet groundstate with $m_J = \pm 3$ character [7]. Using a value of $eq_{\text{latt}} = 5 \cdot 10^{17}$ V/cm² 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}Er Mössbauer study [3]. In principle, the temperature dependence of ΔE_Q can be used to further elucidate the CEF levels of Tm^{3+} in TmH_3 . However, since ΔE_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/cm², which most likely can be regarded as an approach to eq_{latt}) is about 20% larger than the value obtained for GdH_3 [6]. Such a small difference can easily be attributed to the smaller volume of the unit cell of TmH_3 . This work will be continued.

Table 1: Temperature dependence of the ^{169}Tm quadrupole splitting in TmH_3

Temperature (K)	ΔE_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)

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