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## MAGNETIC AND ELECTRIC PROPERTIES OF $R_2Fe_{17}$ COMPOUNDS STUDIED BY MEANS OF THE MÖSSBAUER EFFECT

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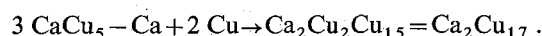
Philips Research Laboratories, Eindhoven, the Netherlands

**Résumé.** — Les propriétés magnétiques et électriques des composés  $R_2Fe_{17}$  ( $R =$  terre rare, yttrium ou thorium) ont été étudiées à l'aide de l'effet Mössbauer. Dans la région magnétiquement ordonnée, tous ces composés intermétalliques, sauf  $Tm_2Fe_{17}$ , présentent une anisotropie dans le plan de base. En dessous de 72 K l'anisotropie magnétique de  $Tm_2Fe_{17}$  est parallèle à l'axe  $c$ .

**Abstract.** — The magnetic and electric properties of the  $R_2Fe_{17}$  compounds ( $R =$  rare earth, yttrium, or thorium) have been studied by using the Mössbauer effect. In the magnetically ordered state all these intermetallic compounds except for  $Tm_2Fe_{17}$  have a basal plane anisotropy. This last compound has a  $c$ -axis anisotropy at 4 K and most likely an  $a$ -axis anisotropy at 80 K.

**1. Introduction.** — The rare earth-iron intermetallic compounds of the type  $R_2Fe_{17}$  the properties of which have been surveyed by Taylor [1], crystallize with hexagonal or with rhombohedral symmetry. Of all the rare earth-iron compounds, they have the lowest magnetic ordering temperatures and at the same time the highest moments per iron atom. Most of the  $R_2Fe_{17}$  compounds order either ferromagnetically or ferrimagnetically depending on whether  $R$  represents a light or a heavy rare-earth element.

The crystal structure of the  $R_2Fe_{17}$  compounds can be derived from the well-known hexagonal  $CaCu_5$ -type of structure by an ordered substitution of a pair of copper atoms at one-third of all the calcium sites

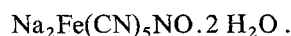


Largely depending on whether the rare-earth element is a light or a heavy one  $R_2Fe_{17}$  has a rhombohedral or a hexagonal structure which are, in fact, closely related. In the  $R_2Fe_{17}$  compounds, where  $R$  is a rare earth, yttrium or thorium, four crystallographically non-equivalent iron sites are present in the structure [2, 3]. According to Wyckoff's notation they are indicated by  $f(c)$ ,  $g(h)$ ,  $j(f)$ , and  $k(l)$ , where the symbols between brackets refer to the rhombohedral structure.

Mössbauer effect studies in the  $R_2Fe_{17}$  compounds have been made in order to determine the iron sublattice magnetization and to investigate the magnetic anisotropy properties of these intermetallic compounds.

**2. Experiments.** — The samples used in the present investigation were prepared by arc melting of the 99.9 % pure starting materials followed by vacuum annealing between 1000° and 1150 °C. In case more than one modification of  $R_2Fe_{17}$  is known to exist, we obtained the low temperature phase by vacuum annealing of the sample at temperatures between 850° and 950 °C. The high temperature phase could be obtained in some cases only by splat cooling. X-ray diagrams taken of the samples after grinding showed that  $R_2Fe_{17}$  is the only R-Fe phase being present.

The Mössbauer spectra of the samples, placed in a suitable cryostat, were obtained using a  $^{57}Co$  source in a Rh foil mounted on a constant acceleration drive system [4]. The velocity scale of the Mössbauer spectrometer was calibrated by measuring the hyperfine field of  $\alpha-Fe_2O_3$  at room temperature ( $H_{eff} = 515$  kOe). The isomer shift was measured relative to the NBS standard reference



The measured spectra were fitted by a least-squares analysis program of Lorentzian line shapes.

**3. Results and discussion.** — Mössbauer spectra of nearly all the  $R_2Fe_{17}$  compounds have been measured at various temperatures between 3 and 500 K. The shape of the Mössbauer spectra of the samples in the magnetically ordered state is largely dependent upon

the easy direction of magnetization. This is due to the fact that the Mössbauer hyperfine spectrum also includes the electric quadrupole interaction. The latter can be written in terms of the quadrupole splitting  $2e' = \frac{1}{4}e^2qQ(3\cos^2\theta - 1)$  where  $\theta$  is the angle between the direction of magnetization and the the axially symmetrical electric field gradient which is along the axis of local symmetry.

The f-site iron atoms in  $R_2Fe_{17}$  appear as a dumbbell with its axis parallel to the  $c$ -axis. This f-site has the highest point symmetry; it involves pairs of Fe atoms occurring at a distance that is significantly shorter than the interatomic distances within the other sublattices of the crystal.

The local symmetry at the iron atoms on the g sites most likely is along the  $c$ -axis, whereas the j-site iron atoms have their symmetry axis in the basal plane through the middle of the dumbbell. The symmetry axis of the k-site iron atoms has been chosen through the nearest f-site iron atom.

In general the Mössbauer spectra of the  $R_2Fe_{17}$  compounds could be resolved into subspectra associated with the four non-equivalent iron sites. Whenever the magnetic anisotropy is along the  $c$ -axis, a single hyperfine pattern can be assigned to each iron site. However, when the magnetization is in the basal plane the hyperfine pattern associated with the j- and the k-site iron nuclei splits up as a consequence of which the Mössbauer spectra had to be analysed into six different subspectra. In the spectra of  $R_2Fe_{17}$  measured below  $T_c$ , the highest hyperfine field is associated with the iron nuclei that form part of the dumbbell mentioned before, which henceforth we will denote f-site iron nuclei. It is possible to assign the other subspectra to the different iron sites in a consistent way making use of the measured quadrupole splitting in connection with the local symmetry and the magnetic anisotropy. Axial symmetry of the electric field gradient has been assumed in the analysis.

In figure 1 the hyperfine fields obtained at the f-site iron nuclei are given together with the weighted average of the hyperfine fields,  $H_{av}$ , at the other iron sites in the  $R_2Fe_{17}$  compounds at  $T = 15$  K. It turns out that in most of the  $R_2Fe_{17}$  compounds the corresponding hyperfine fields are about the same, and furthermore that the hyperfine field at the f-site iron nuclei is systematically larger than  $H_{av}$  by about 20%. It further appears that there is no essential difference between the corresponding hyperfine fields in  $R_2Fe_{17}$  compounds of a rhombohedral and a hexagonal structure.

Both hyperfine fields in  $Ce_2Fe_{17}$  and in  $Th_2Fe_{17}$  [5] are considerably smaller, whereas the hyperfine field at the f-site iron nuclei in  $Tm_2Fe_{17}$  of 420 kOe is unusually large. It is well-known that both cerium and thorium have four instead of three conduction electrons. Most likely the extra conduction electron partially fills up the d band of the iron atoms as a consequence of which the hyperfine fields at the iron

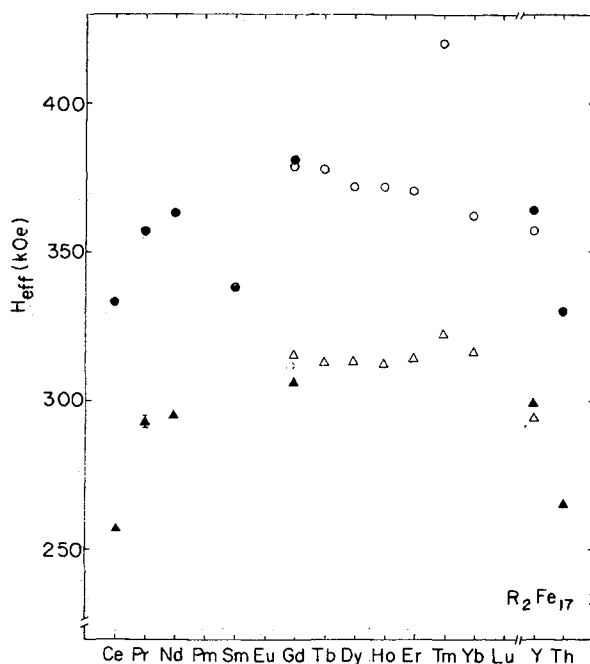


FIG. 1. — Effective hyperfine fields at iron nuclei in  $R_2Fe_{17}$  at  $T = 15$  K. The circles refer to the hyperfine fields associated with the dumbbell iron atoms, and the triangles refer to the weighted average of the hyperfine fields associated with the other iron atoms in the crystal. The compounds with a rhombohedral structure are indicated with closed symbols and those with a hexagonal structure are indicated with open symbols.

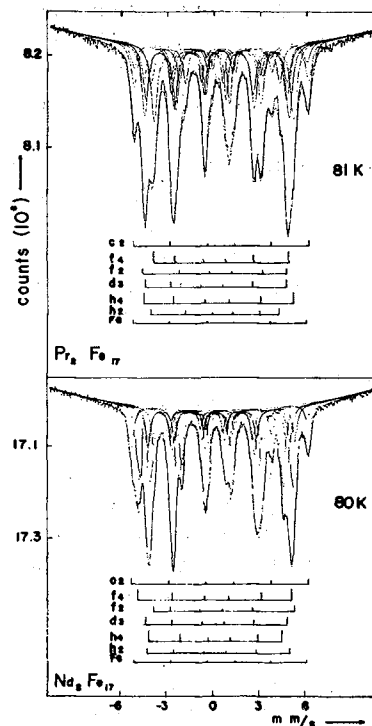


FIG. 2. — Mössbauer spectra of  $Pr_2Fe_{17}$  and  $Nd_2Fe_{17}$  at 80 K. The measured spectra, given by the data points, are fitted to a superposition of a number of hyperfine spectra each of which has been associated with one of the crystallographic iron sites as indicated underneath the spectra. The hyperfine spectrum due to a small contamination of metallic iron is also indicated. —

nuclei are small compared to those in the other  $R_2Fe_{17}$  compounds.

From our investigation it follows that the Mössbauer spectra of  $R = Pr, Dy, Er$  and  $Y$  are substantially different from those of  $R = Nd, Tb$  and  $Ho$ . The spectra of  $Pr_2Fe_{17}$  and  $Nd_2Fe_{17}$  at 80 K as shown in figure 2 do not change in the temperature range from 80 K down to 3 K. The results of the analysis of the two spectra which have to be interpreted in terms of six subspectra is different; a computer fit made for the spectra of the  $Pr$  compound cannot be used to interpret the spectra of the  $Nd$  compound and vice versa. Consequently the anisotropy is in the basal plane, most likely along the  $b$ - and  $a$ -axis for  $Pr_2Fe_{17}$  and for  $Nd_2Fe_{17}$  respectively. In addition, the Mössbauer spectra of  $Tm_2Fe_{17}$  at temperatures below 70 K have to be analysed in still another way as shown in figure 3. On the base of this information we conclude

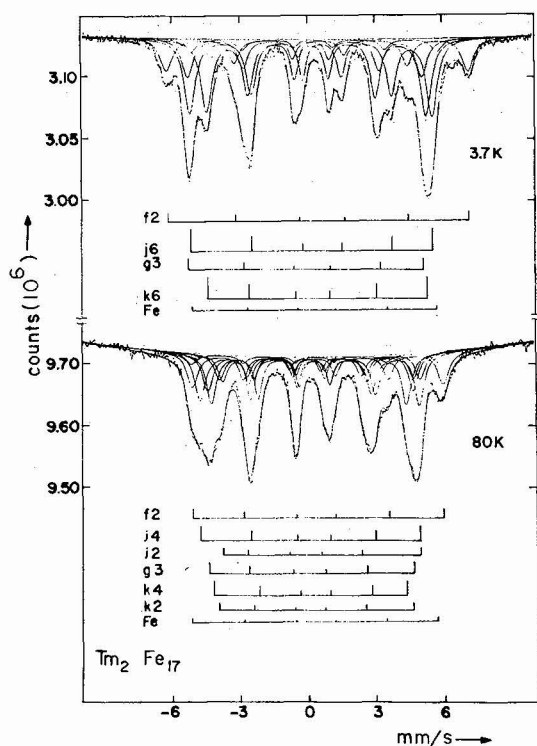


FIG. 3. — Mössbauer spectra of  $Tm_2Fe_{17}$  obtained below and above the magnetic phase transition at 72 K. The measured spectra, given by the data points, are fitted to a superposition of a number of hyperfine spectra each of which has been associated with one of the crystallographic iron sites as indicated underneath the spectra. The hyperfine spectrum due to a small contamination of metallic iron is also indicated.

that the anisotropy of the  $Pr, Nd$  and  $Tm$  compounds differ from each other and it is to be expected that the anisotropy properties of these compounds at low temperatures are mainly determined by the rare earth.

The magnetization in  $Tm_2Fe_{17}$  has a rather sharp maximum near 72 K indicating a change in magnetic structure at lower temperatures [6]. Furthermore the shape of the Mössbauer spectra of  $Tm_2Fe_{17}$  below 72 K

is quite different from that measured at temperatures above 72 K. The Mössbauer spectrum of  $Tm_2Fe_{17}$  at 3.7 K can be resolved into four different subspectra, each of which being associated with one of the four iron sublattices as shown in figure 3. From this result it immediately follows that the easy axis of magnetization is along the  $c$ -axis in close agreement with neutron diffraction experiments by Givord [7], who found a  $c$ -axis anisotropy at  $T = 4.2$  K and a basal plane anisotropy at 115 K. A possible analysis of the Mössbauer spectrum at 80 K has been given which is similar to that used for  $Nd_2Fe_{17}$ . A computer fit as used to interpret the spectra of  $Pr_2Fe_{17}$  turns out to be less successful. Moreover from crystal field theory, Elliott [8] has shown that the crystal field parameter determining the anisotropy in the basal plane is the same for  $Nd, Tb, Ho$  and  $Tm$  and different from  $Pr, Dy$  and  $Er$ .

Ray and Strnat [9], and Narasimhan *et al.* [10] found that of the  $R_2Co_{17}$  compounds only those with  $R = Sm, Er, Tm$  and  $Yb$  have an uniaxial anisotropy or a cone anisotropy.

Greedan and Rao [11] in their calculations on the magnetic anisotropy predicted a  $c$ -axis anisotropy for these four  $R_2Co_{17}$  intermetallic compounds and furthermore they found that the thulium sublattice in  $Tm_2Co_{17}$  has the highest stabilization energy for a  $c$ -axis anisotropy. On the other hand, both the  $Co$ -sublattice in  $Y_2Co_{17}$  and the  $Fe$ -sublattice in  $Y_2Fe_{17}$  have a basal plane anisotropy.

From the Mössbauer effect studies it follows that only  $Tm_2Fe_{17}$  has a  $c$ -axis anisotropy at temperatures below 72 K, whereas in all the other  $R_2Fe_{17}$  compounds there is a basal plane magnetic anisotropy down to 3 K. Apparently, the basal plane anisotropy seems to be more pronounced in the  $R_2Fe_{17}$  than in the  $R_2Co_{17}$  compounds.

In figure 4 we have plotted the isomer shift at the  $f$ -site iron nuclei in both  $Tm_2Fe_{17}$  and  $Er_2Fe_{17}$  versus the temperature. It turns out that the isomer shift at the  $f$ -site iron nuclei in  $Tm_2Fe_{17}$  at temperatures below 70 K is systematically higher than that at the corresponding nuclei in  $Er_2Fe_{17}$ , whereas at temperatures

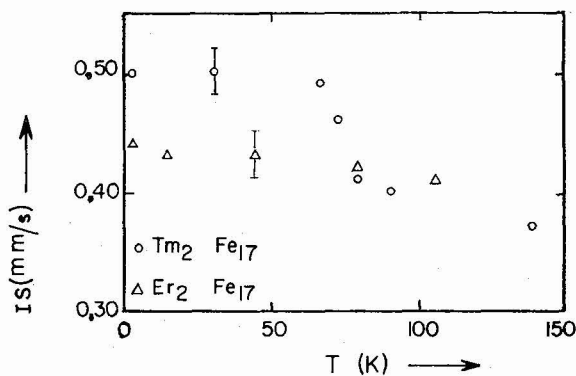


FIG. 4. — Isomer shifts measured at the  $f$ -site iron nuclei in  $Tm_2Fe_{17}$  and  $Er_2Fe_{17}$  plotted versus the temperature.

above 80 K, the isomer shifts in both compounds are the same. At the magnetic phase transition in  $\text{Tm}_2\text{Fe}_{17}$  around 72 K, the isomer shift increases by about 0.10 mm/s with decreasing temperature, which means that the electron charge density at the f-site iron nucleus rather abruptly becomes smaller. We have already shown [6] that at this phase transition the hyperfine field at the f-site iron nuclei suddenly increases by more than 10 % on lowering the temperature, and this indicates that the electron spin density at the nuclear site must have increased. It is, therefore, most likely that both phenomena are closely related to the change in magnetic anisotropy which has been discussed before.

In general the electron spin density at the f-site iron nuclei in  $\text{R}_2\text{Fe}_{17}$  is unusually high (Fig. 1) and the electron charge density is remarkably low compared to metallic iron. This anomalous behaviour is even more pronounced in  $\text{Tm}_2\text{Fe}_{17}$  below 72 K. The distance between the pair of iron atoms belonging to the dumbbell is very small, 2.39 Å, for most of the  $\text{R}_2\text{Fe}_{17}$  compounds compared to the interatomic distance of 2.51 Å in metallic iron. It is to be expected that the

wave functions of the iron atoms of the same dumbbell strongly overlap with the result that the 3d core polarization becomes higher probably due to a deformation of the 3d band. Simultaneously this apparently gives rise to a more effective shielding of the 4s electrons, lowering therefore the electron charge density at the f-site iron nucleus. From the results obtained with  $\text{Tm}_2\text{Fe}_{17}$  below 72 K it appears that these effects are even more pronounced when the magnetization is along the *c*-axis for which the crystal field of the thulium is responsible.

We may conclude that the iron atoms that form part of a dumbbell in  $\text{R}_2\text{Fe}_{17}$  to a large extent are responsible for the basal plane anisotropy in these intermetallic compounds, and that only in an exceptional case as  $\text{Tm}_2\text{Fe}_{17}$ , the strong anisotropy properties of this rare earth element make the anisotropy uniaxial at low temperatures. Though the unusual electron spin and charge densities at the f-site iron nuclei found in the Mössbauer effect studies are qualitatively explained by assuming a deformation of the d band, a further study e. g. applying polarized neutron scattering techniques seems to be appropriate.

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