Magnetic Anisotropy and Spin Rotations in Ho$_x$Tb$_{1-x}$Fe$_2$ Cubic Laves Compounds

U. Atzmony and M. P. Dariel

Nuclear Research Centre—Negev, Beer Sheva, Israel

and

E. R. Bauminger, D. Lebenbaum, I. Nowik, and S. Ofer

*The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel**

(Received 8 December 1971)

The directions of the easy magnetization in the Ho$_x$Tb$_{1-x}$Fe$_2$ system have been determined by means of the Mössbauer effect in ^{57}Fe. If the direction of magnetization of the system is described by an (x,T) spin-orientation diagram, it is found that the (x,T) plane is divided into three regions, in each of which the direction of magnetization is along a different major crystal axis. The diagram is interpreted by simple cubic-crystalline-field theory.

The magnetic properties of the cubic iron–rare-earth Laves-phase compounds (type MgCu$_2$) have been extensively investigated in recent years by various methods including the Mössbauer effect on ^{57}Fe.[1-3] In these compounds the rare-earth ions are situated on a diamond sublattice and the iron ions on a corner-sharing network of regular tetrahedra. The site symmetry of the iron ions is $\bar{3}m$. All iron ions are crystallographically equivalent, and the threefold axes lie in the [111] directions. Even though all the RFe$_2$ compounds are structurally identical, various types of Mössbauer spectra were observed. The different spectra were interpreted in terms of the direction of the easy magnetization axis in the respective compounds. With the direction of easy magnetization ($\vec{n}$) along the [100] axis, all iron atoms are equivalent and a simple six-line spectrum is expected, as was observed for HoFe$_2$ and DyFe$_2$. If $\vec{n}$ is along the [111] direction, two magnetically inquivalent iron sites with relative population 3:1 exist,[4] giving rise to a spectrum which is a superposition of two six-line patterns, as observed for YFe$_2$, ErFe$_2$, TbFe$_2$, and TmFe$_2$.[3] With $\vec{n}$ parallel to the third major cubic axis, namely [110], two magnetically inequivalent iron sites with a population ratio 2:2 are present. This situation is believed to prevail in SmFe$_2$ at low temperatures.[3]

According to Bowden et al.,[3] the occurrence of different easy directions of magnetization in the various RFe$_2$ compounds is due to the rare-earth's single-ion anisotropy. Calculations based on Bleaney's simple point-charge model could explain the direction of easy magnetization in most of the binary iron Laves compounds.

We have carried out a series of Mössbauer-effect measurements on ^{57}Fe in ternary $(R_x^1 R_{1-x}^2$Fe$_2)$ compounds, as function of concentration x and temperature T. This Letter reports the results for the Ho$_x$Tb$_{1-x}$Fe$_2$ system.

Whereas the magnetization of TbFe$_2$ between 4.2 and 300 K is in the [111] direction and that of HoFe$_2$ is in the [100] direction, the compounds Ho$_x$Tb$_{1-x}$Fe$_2$ behave in a more complicated way. For certain values of x and T the easy magnetization is in the [110] direction. If one describes the direction of magnetization of the system in terms of an (x, T) spin-orientation diagram (Fig. 1), one finds that the (x, T) plane is divided into three regions. In each of these regions the direction of magnetization is along one of the major crystal axes ([111], [100], or [110]). The transitions
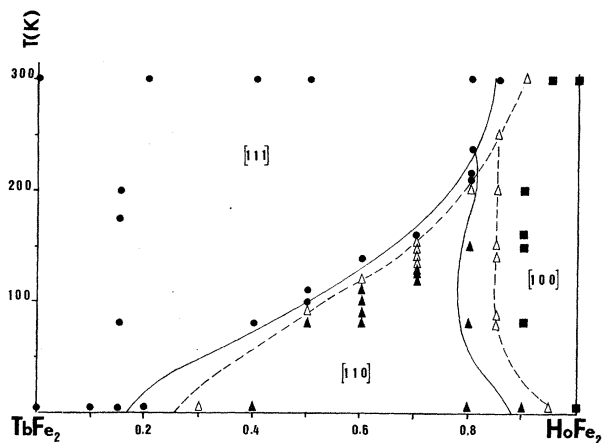

FIG. 1. Spin-orientation diagram in the Ho$_x$Tb$_{1-x}$Fe$_2$ system. Filled circles, filled triangles, and filled squares correspond to experimentally determined spectra characteristic of the [111], [110], and [100] axes of magnetization, respectively. Open triangles correspond to intermediate types of spectra. The broken lines are the experimentally, and the solid lines the theoretically, determined boundaries of regions with different directions of magnetization.

between the three regions are not sharp. In the transition regions, the direction of magnetization does not coincide with one of the three major crystal axes.

We have calculated theoretical (x, T) spin-orientation diagrams by taking into account the cubic crystalline field and exchange field acting on the rare-earth ions. A proper choice of the field parameters gave good agreement between the experimental and theoretical spin-orientation diagrams.

The two cubic Laves compounds $HoFe_2$ and $TbFe_2$ form a continuous solid solution. The ternary Laves compounds were prepared by arc-melting 99.9%-pure rare earths and 99.99%-pure iron under an argon atmosphere. Metallographic and x-ray powder diffraction measurements showed that the samples contained less than 5% of foreign phases. In some of the samples the composition was verified by electron-microprobe analysis. This showed that the samples were homogeneous, with x constant to better than 2%.

The measurements were performed with [57]Co-in-Pd sources at room temperatures, and with absorbers of $Ho_xTb_{1-x}Fe_2$ with $x = 0$, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.85, 0.9, 0.95, and 1.0. Measurements were carried out for absorber temperatures of 4.2, 80, and 300 K. For some of the samples measurements were performed at various intermediate temperatures between 80 and 300 K. For this purpose the samples were held in a variable-temperature cryostat. The temperature stability in each measurement was better than 1 K, and the absolute temperature was measured to an accuracy of 1 K.

Some of the spectra obtained at 4.2 and 300 K

FIG. 2. Mössbauer spectra at 4.2 K. Spectrum g is a simple six-line spectrum corresponding to the presence of only one site of iron atoms. It is characteristic of the [100] direction of easy magnetization. Spectra d and e are characteristic of a [110] direction of magnetization, which gives rise to two inequivalent iron sites with a population ratio of 2:2, and thence to a superposition of two six-line spectra of equal intensity. Actually this appears in the form of the splitting of some peaks (i.e., the second and the sixth of spectrum g) into two peaks of equal intensity. In spectra a and b the same peaks are split into two peaks with an intensity ratio of 3:1, indicating the existence of two inequivalent iron sites with that population ratio. This is characteristic of the [111] direction of magnetization. Spectra c and f are of intermediate types. The splitting of the peaks results from the slightly different hyperfine interactions magnetically inequivalent iron sites.

are shown in Figs. 2 and 3. Three main types of spectra, characteristic of samples with the easy direction of magnetization along one of the major cubic axes ([111], [110], or [100]), are observed. Visual inspection allows one to determine in a straightforward manner the direction of the axis of magnetization of the absorber.

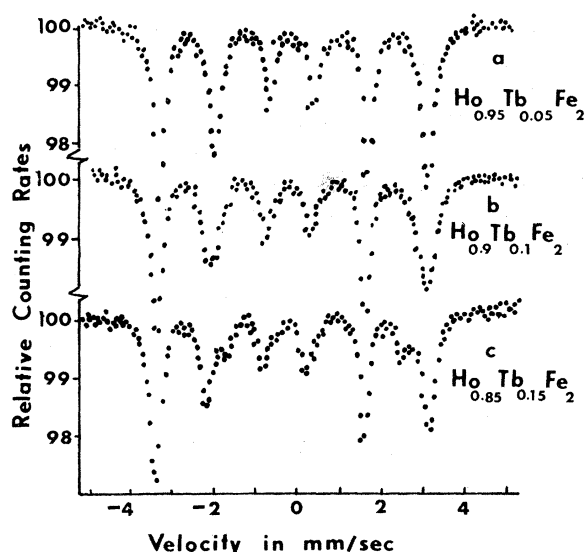The significant results are those related to the

Velocity in mm/sec
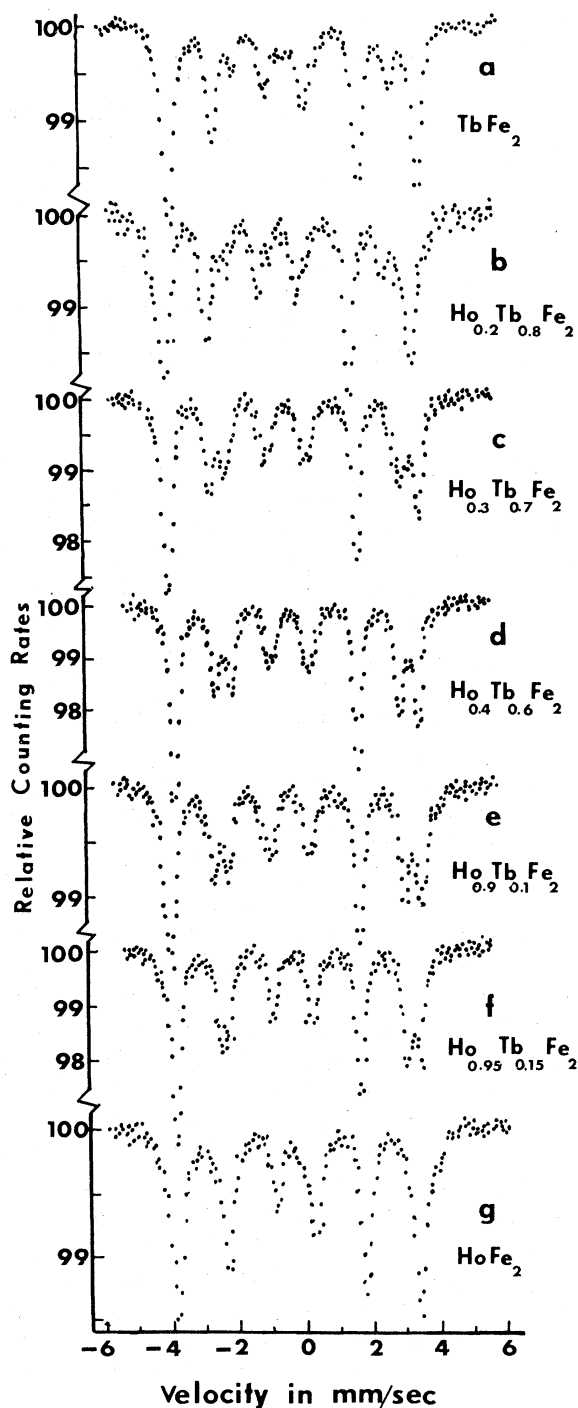
FIG. 3. Mössbauer spectra at 300 K. Spectrum a is characteristic of the [100], and spectrum c of the [111], axis of magnetization. Spectrum b is of an intermediate type.

rotation of the spin direction from one major cubic axis to another. The transition from one kind of spectrum to another seems to be a continuous process, taking place within $\Delta x \sim 0.1$ and $\Delta T \sim 30$ K. Inside these intervals, however, the Mössbauer spectra possess an intermediate character, the nature of which will be discussed later. All the experimental results are summarized in the (x, T) spin-orientation diagram shown in Fig. 1.

For the theoretical analysis it was assumed that the major contribution to the magnetic anisotropy is due to the crystalline electric field acting on the rare-earth ions. It was further assumed that the R-R exchange interactions are small compared to R-Fe interactions. The last assumption is supported by Mössbauer-effect measurements on ^{169}Tm in $TmFe_2$,[5] and on ^{161}Dy in $DyFe_2$[6]: The temperature dependences of the hyperfine fields acting on the rare-earth nuclei in these compounds can be fitted by Brillouin functions with $\vec{J}$ appropriate to the respective rare-earth ion, and exchange fields proportional to the hyperfine fields acting on the iron nuclei at the various temperatures. The fact that the magnetic ordering temperatures of all RFe_2 compounds are much higher than the respective temperatures for isostructural RCo_2 and RNi_2 compounds also proves that the R-Fe exchange interactions are much stronger than the R-R interactions.

The single-rare-earth-ion Hamiltonian can therefore be expressed as

$$\mathcal{3C} = V_4 + V_6 + 2(g - 1)\beta_B H_e \vec{J} \cdot \vec{n},$$

where

$$V_4 = A_4 \langle r^4 \rangle \langle J \| \beta \| J \rangle (O_4{}^0 + 5O_4{}^4)$$

and

$$V_6 = A_6 \langle r^6 \rangle \langle J \| \gamma \| J \rangle (O_6{}^0 - 21 O_6{}^4),$$

where H_e is the exchange field acting on the rare-earth ion, $O_n{}^m$ are the operator equivalents, and β and γ the reduced matrix elements tabulated by Hutchings.[7] The values of $\langle r^n \rangle$ used were those calculated by Freeman and Watson.[8] A_4 and A_6 are constants independent of the rare-earth ions involved (except for the small shielding correction calculated by Freeman and Watson[9]).

Using various values of the parameters A_4, A_6, and H_e, we calculated the eigenvalues of the Hamiltonian for the three possible directions of magnetization. This then enables us to calculate the free energy F of the binary Laves compounds as a function of x, T, and $\vec{n}$. The easy direction of magnetization of a given compound $Ho_xTb_{1-x}Fe_2$ at a certain temperature was taken as the direction for which the expression $xF_{Ho}(\vec{n}) + (1 - x)F_{Tb}(\vec{n})$ had the lowest value. This procedure was carried out for a series of temperatures between 4.2 and 300 K for various values of x. The results were used to determine theoretical spin-orientation diagrams as shown in Fig. 1. Comparison with the experimental results indicates that A_6 cannot be neglected and that the ratio A_6/A_4 $= -0.04a_0{}^{-2}$ best fits the experimental data. The calculated results are quite sensitive to the values of the ratio A_6/A_4, but not to the values of A_4 and H_e. The experimental results can be fitted with values of A_4 between $(1 \text{ K})/a_0{}^4$ and $(30 \text{ K})/a_0{}^4$ and values of $\beta_B H_e$ between 110 and 150 K. These values of $\beta_B H_e$ are in good agreement with those derived from the previously mentioned Mössbauer-effect measurements.[5,6]

From the knowledge of the free energy in the three directions of magnetization, one can calculate the bulk anisotropy constants. Using the values of the free energy determined with the set of parameters A_4, A_6/A_4, and H_e that gave good agreement between the experimental and theoretical spin-orientation diagrams, one gets, for instance, at 4.2 K for $HoFe_2$, $K_1 = 2.5 \times 10^6$ erg/cm³ and $K_2 = 111.4 \times 10^6$ erg/cm³, and for $TbFe_2$, K_1 $= -15.7 \times 10^6$ erg/cm³ and $K_2 = 13.9 \times 10^6$ erg/cm³. The bulk anisotropy constants are strongly depen-

dent on the exact values of the parameters A_4 and A_6/A_4. Since in the present system A_4 could not be given a definite value, the calculated values of K_1 and K_2 are only approximate.

The theoretical model predicts a first-order phase transition between the regions of different spin orientation. This prediction is in apparent contradiction with the presence of the transition regions in the spin-orientation diagram. The appearance of the transition regions may be due to the following factors:

(1) The inhomogeneity of the samples. This however cannot be the main factor, as some of the experimental spectra (e.g., spectrum f in Fig. 2) cannot be interpreted as a superposition of two spectra corresponding to magnetizations along two different major crystalline directions.

(2) The existence of additional, noncubic anisotropic terms due to distortions, dipolar fields, and anisotropic exchange that have been neglected in Eq. (1). As a result of these terms, the magnetization may not coincide with the direction of one of the major crystalline axes, and in the transition region $\tilde{n}$ may deviate significantly from these axes. Thus, for example, spectrum f in Fig. 2 corresponds to a direction of magnetization lying in the (100) plane, but not parallel to one of the major ([100] or [110]) crystalline axes.

In Fig. 1 a slight shift between the experimental and the theoretical boundaries of the three regions is observed. This shift may be due to several factors, the main one being the neglect of an anisotropy term contributed by the Fe-Fe interaction, which favors the [111] direction. Smaller shifts may be caused by the uncertainty in the values of some of the parameters ($\langle r^n \rangle$, antishield-

ing factors) used in the calculations. Furthermore, the possibility of mixing higher ionic J states into the ground state was neglected. As the exchange fields acting on the rare-earth ions in $R\mathrm{Fe}_2$ compounds are quite large, the contribution of this mixing to the anisotropy may be non-negligible. Finally, the previously mentioned noncubic anisotropic terms, that were not taken into account in Eq. (1), could also contribute somewhat to the shift of the boundaries.

We are carrying out similar measurements and calculations for the systems $R_x{}^1R_{1-x}{}^2\mathrm{Fe}_2$ with $R^1 = \mathrm{Dy}$, Ho and $R^2 = \mathrm{Er}$, Tb, and Tm. The experimental results and a detailed comparison with theoretical predictions will be published elsewhere.

[1]W. E. Wallace, J. Chem. Phys. 41, 3857 (1964).
[2]G. K. Wertheim and J. H. Wernick, Phys. Rev. 125, 1937 (1962).
[3]G. J. Bowden, D. St. P. Bunbury, A. P. Guimaraes, and R. E. Snyder, J. Phys. C: Proc. Phys. Soc., London 2, 1367 (1968).
[4]G. K. Wertheim, V. Jaccarino, and J. H. Wernick, Phys. Rev. 135, A151 (1964).
[5]R. L. Cohen, Phys. Rev. 134, A94 (1964).
[6]E. Segal, Ph.D. thesis, Hebrew University, 1967 (unpublished).
[7]M. T. Hutchings, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1966), Vol. 16, p. 277.
[8]A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).
[9]A. J. Freeman and R. E. Watson, Phys. Rev. 139, A1606 (1965).

Observation of α - Particle Core-Excited Threshold States in Light Nuclei

H. R. Weller
Department of Physics, University of Florida, Gainesville, Florida 32601
(Received 6 December 1971)

The nuclei $^{15}\mathrm{N}$, $^{15}\mathrm{O}$, and $^{19}\mathrm{Ne}$ are examined in terms of the appearance of α-particle core-excited threshold states. It is shown that this simple model can account for most of the α-particle states seen above the threshold for α-particle emission. We discuss the most striking features of these states.

Recent work of Gillet[1] and Middleton, Garrett, and Fortune[2] has stressed the importance of quartet structures in the interpretation of nuclear excited states. One expects resonances in the α channel at compound-system energies correspond-

ing to these states. It is the intent of this Letter to summarize and correlate a series of studies which have revealed the existence of α-particle states at high energies in light nuclei. These states have spins, parities, and energies which