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Magnetic properties of $(Ho,Y)_6Fe_{23}$ intermetallic compounds

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Abstract

Intermetallic ingots of $Ho_{6-x}Y_xFe_{23}$ alloys were synthesized with compositions $x=0$, 0.47, 0.92, 1.86, 4.85 and 6. Magnetization $M(H, T)$ measurements were performed on the samples from 4 K to above Curie temperature T_C(~500 K) in a magnetic field up to 17 kOe. Magnetic properties near T_C are weakly influenced by yttrium substitution, in agreement with preponderant Fe–Fe magnetic interactions. In contrast, when x increases the magnetic compensation temperature T_{comp} is shifted to low temperature and vanishes when x~1.5. At 4.2 K, the magnetization of the compounds increases at a rate of ~9.3 μ_B per at. Ho substituted, close to the free Ho^{3+} value. The magnetic properties $M(H, T, x)$ are discussed within the frame of the molecular field theory model of Herbst and Croat which takes into account canted magnetic structures present in R–T compounds. The mean canting angle θ between Ho and Fe moments is found greater than its value in pure Ho_6Fe_{23} but remains less than 10° for the most canted structures corresponding to $x=0.92$ and 1.86. The calculated temperature dependences of the magnetization of the compounds, assuming a linear variation of the parameters of the Fe sublattice from Ho_6Fe_{23} to Y_6Fe_{23}, are in fairly good agreement with experimental data.

Keywords: $(Ho, Y)_6Fe_{23}$ intermetallic compounds; Magnetic properties; Molecular field theory

1. Introduction

The rare earth intermetallic derived compounds R_6Fe_{23} (R=Gd to Yb) with a magnetic compensation temperature T_{comp} present a great interest for applications such as amorphous thin films for high density magnetic and magnetooptic information storage media [1], as well as fundamental studies. Recently, a crystal field analysis gives new insight on the magnetic anisotropy properties of bulk alloys R_6Fe_{23} (R=Dy to Tm) which share a common [111] direction of 'easy' magnetization [2]. All R_6Fe_{23} compounds crystallize in the cubic (*Fm3m*) Th_6Mn_{23} structure, R being located in site (24e) and Fe occupying the four distinct positions (4b, 24d, $32f_1$ and $32f_2$) [3]. Magnetic properties of pure R_6Fe_{23} were well studied in contrast to substituted derived compounds. We present here, the results of magnetic properties of yttrium-substituted Ho_6Fe_{23} intermetallic alloys. The 'non magnetic' yttrium, which does not possess the large orbital magnetic moment and magnetic anisotropy of R atoms, substitutes Ho on the unique rare earth site for all the compounds of formula $Ho_{6-x}Y_xFe_{23}$. Concerning the magnetic properties of the end members of the system, Ho_6Fe_{23} and Y_6Fe_{23}, neutron diffraction experiments [4–7] show that the Fe moments are coupled ferromagnetically to each other in both compounds and antiferromagnetically to the rare earth in the case of Ho_6Fe_{23}. The resultant magnetic moment of Fe is slightly greater in Ho_6Fe_{23} than in Y_6Fe_{23} [8]. At low temperature, the magnetic moment of Ho is close to its free ion Ho^{3+} value (10 μ_B at^{-1}). Finally, it is to be noted that, in contrast to Ho_6Fe_{23}, the 'easy' magnetic axis is [100] for Y_6Fe_{23} [2,9].

The magnetic properties of Ho_6Fe_{23} arise from the three types of magnetic interactions between the two sublattices: the magnetic interactions Fe–Fe among the iron 3d electrons are the strongest and determine mainly the high temperature properties particularly in the vicinity of the Curie temperature T_C, the Ho–Ho interactions are the weakest, and ferrimagnetic Ho–Fe interactions have intermediate strength. It is well known that non collinearity is present in rare-earth transition metal compounds as the exchange coupling between rare-earth (R) and transition-metal (T) moments in R–T compounds is not large enough to hold the R and T moments rigidly antiparallel for heavy rare earth elements [10]. The purpose of this work is thus to investigate the influence of the yttrium substitution to holmium in the rare earth sublattice on the magnetic properties of Ho_6Fe_{23}. The experimental data are analyzed within the frame of the molecular field theory model of Herbst and Croat [8] which takes canting into account.

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2. Experimental

Intermetallic ingots of $Ho_{6-x}Y_xFe_{23}$ alloys were prepared by radio frequency induction melting of the constituent metals in a water-cooled copper crucible, under a purified Ar atmosphere. The samples were remelted 5 times and vacuum annealed at 1100°C for 7 days in order to achieve homogeneity. The chemical composition was checked by X-ray diffraction and electron microprobe analysis. The samples studied were obtained for $x=0$, 0.47, 0.92, 1.86, 4.85, and 6. Magnetization $M(H, T)$ measurements were performed on the powder samples from 4 K to above Curie temperature T_C (~500 K) in a magnetic field up to 17 kOe using DSM8 magnetometer under pure He atmosphere. The Curie temperature was determined from magnetization versus T at low field ($H<1$ kOe).

3. Results and discussion

3.1. Low temperature magnetization results

The influence of yttrium substitution on the magnetic properties is evidenced in the low temperature region. We plotted in Fig. 1 the 4.2 K magnetization curves $M(H)$ as a function of the applied field for different yttrium content x. As x increases, the low temperature magnetization first decreases and then increases strongly to its value in Y_6Fe_{23}. The magnetic values of Ho_6Fe_{23} and Y_6Fe_{23} are in good agreement with literature data [3,8,9,11–14]. Using the standard approach of $1/H$, the saturation magnetizations σ_s ($T=4.2$ K) are deduced from Honda plots and plotted in Fig. 2 as a function of x. The line representing the linear variation of $\sigma_s(x)$ from Ho_6Fe_{23} to Y_6Fe_{23} has a slope of ~9.3 μ_B (at. Ho substituted)$^{-1}$, close to the value of the free ion Ho^{3+}. The experimental points are close to this line with noticeable deviations for $x=0.92$ and 1.86. These results may be related to variations of crystallographic properties and/or variations of the canting of magnetic moments. Indeed, variation of the lattice parameters could affect the strength of the interaction between magnetic ions [15], or a decrease of interatomic distances can also induce an increase of the crystal field which would result in a slight quenching of the rare earth moment [16].

Concerning the influence of canting on the magnetic properties of R_6Fe_{23}, Herbst and Croat interpreted the magnetization results of pure rare earth compounds on the basis of a Néel molecular field model for a two sublattices ferrimagnet with the introduction of a canting angle θ [8]. Using this model, the resultant magnetization of the compound M_{tot} is given by:

$$\vec{M}_{tot}(T) = \vec{M}_{Fe}(T) + \vec{M}_R(T) \quad (1)$$

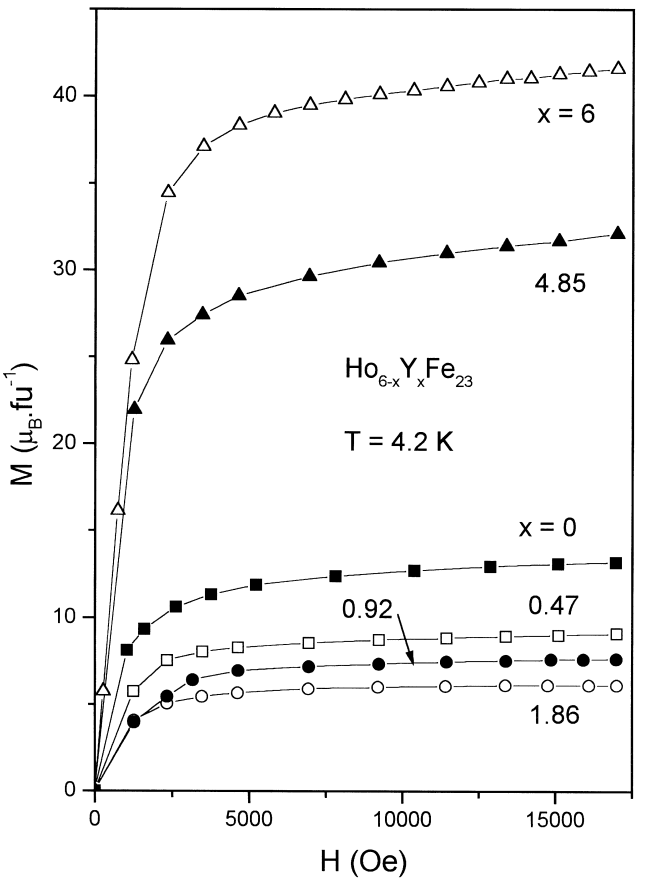

Fig. 1. Magnetization versus applied field at 4.2 K of $Ho_{6-x}Y_xFe_{23}$ compounds.

where $\vec{M}_{Fe}$ and $\vec{M}_R$ are the sublattices magnetizations deviating from anticollinearity by a temperature-independent canting angle θ. The value of θ is comprised between 0 (anticollinearity) and θ_{max} corresponding to the largest canting angle allowing $\vec{M}_{tot}$, $\vec{M}_R$ and $\vec{M}_{Fe}$ to form a closed triangle, i.e.:

$$\theta_{max} = \sin^{-1}(M_{tot}/M_R) \quad (M_R(T=0) > M_{Fe}(T=0)) \quad (2)$$

The value of θ is determined by fitting M_{exp} (T) data using Eq. (1) [8]. In a first approximation, this model may be extended to the pseudo binary system $Ho_{6-x}Y_xFe_{23}$:

$$\vec{M}_{tot}(T, x) = \vec{M}_{Fe}(T, x) + \vec{M}_R(T, x) \quad (3)$$

the sublattice where the substitution takes place (here Ho and Y) being treated as one sublattice [17] of magnetization:

$$M_R(0, x) = (6 - x)\, g\, J \quad (4)$$

where $g=5/4$ and $J=8$ of free Ho^{3+} ion, and θ corresponding to the mean canting angle of the Ho moments relative to M_{Fe} influenced by yttrium substitution. The slightly different values of M_{Fe} in Ho_6Fe_{23} and Y_6Fe_{23} are taken into account by assuming a linear variation:

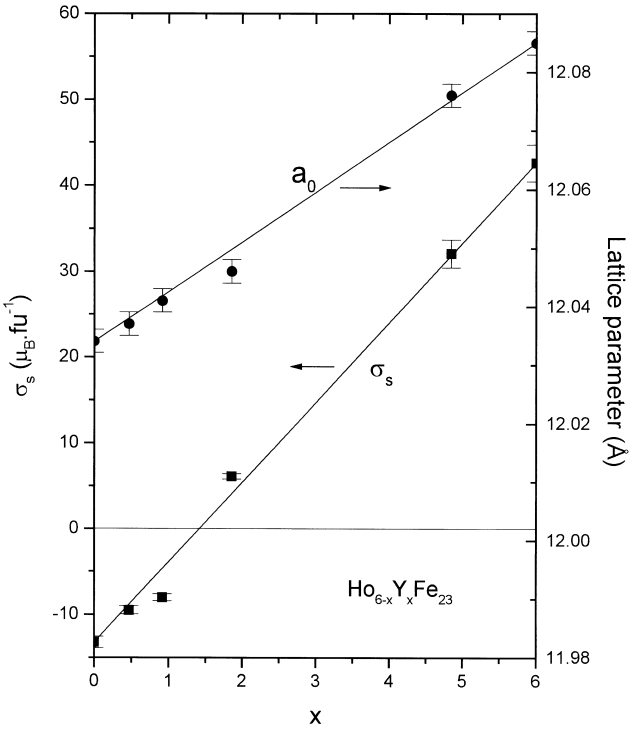

Fig. 2. $Ho_{6-x}Y_xFe_{23}$ lattice parameters a_0 and saturation magnetizations σ_s at 4.2 K versus yttrium concentration x (negative σ_s values correspond to compounds with a magnetic compensation point). Solid lines correspond to linear variations.

$$M_{Fe}(0, x) = [(6 - x)/6]M_{Fe}(0, 0) + (x/6)\, M_{Fe}(0, 6) \qquad (5)$$

In order to compare to experimental data, using Eq. (3)–(5), we plotted in Fig. 3 the concentration dependence of calculated $|M_{tot}|$ for different values of θ. We observe that the experimental σ_s correspond to θ values less than 10° (Table 1), with maximum values obtained for $x = 0.92$ (8°) and $x = 1.86$ (6°). Another interesting comparison is to compute the magnetization moment $M_{tot}(\theta_{max})$ corresponding to the maximum possible canting angle compatible with the experimental σ_s using Eq. (2) (for $x = 1.86$, M_{Fe} replaces M_R in Eq. (2), whereas due to $M_{Fe} \gg M_{Ho}$, θ for $x = 4.85$ is not determined) (Fig. 3 and Table 1). For all studied compounds, σ_s are smaller than $M_{tot}(\theta_{max})$, but close to these values for $x = 0.92$ and $x = 1.86$. The deviations observed in Fig. 2 for these values may thus be related to greater mean canting angles of Ho moments relative to Fe moments. These yttrium substitution rates are in the vicinity of $x \sim 1.5$ which is the alloy composition corresponding to the compensation temperature $T_{comp} = 0$. Due in part to small net magnetization, the compensation point is a zone of canted magnetic structures [10,17]. Note that a large canting angle $\theta = 20.2°$ was obtained for pure Tm_6Fe_{23} for which $T_{comp} = 0$ [8].

3.2. Magnetization temperature dependence

The experimental temperature dependence of the magnetization of the compounds are plotted in Fig. 4 and Fig. 5 for different x. They were measured at 16 kOe as a function of temperature which led to slightly different values than saturation σ_s.

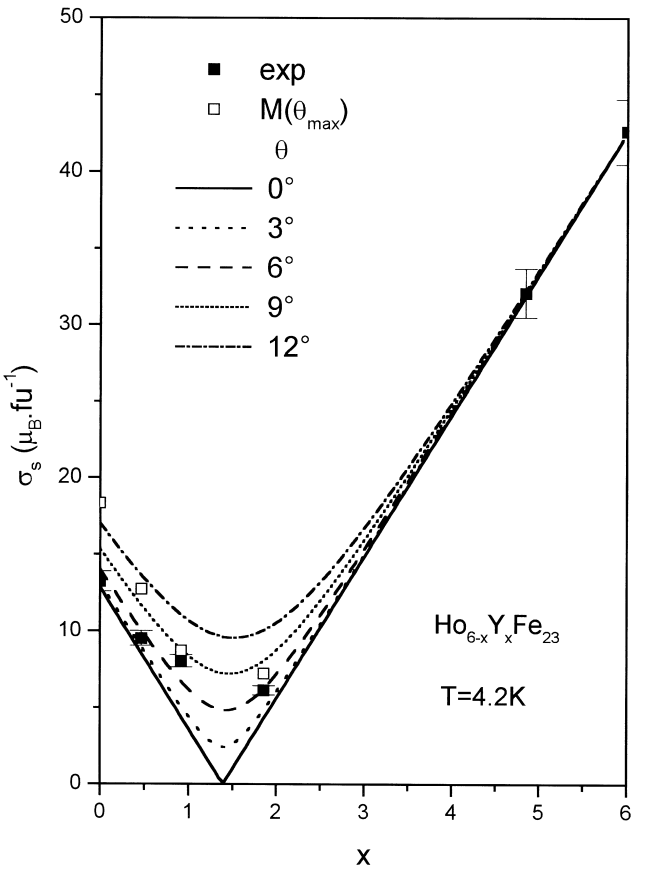

Fig. 3. Saturation magnetization σ_s at 4.2 K versus calculated values for different values of canting angle θ. Open squares are calculated magnetizations for the maximum canting angle θ_{max}.

For compounds with a compensation point (Fig. 4), when x increases, T_{comp} is shifted to low temperature at a decreasing rate of ~100 K (at. Ho subst.)$^{-1}$. In agreement with canted structures, the experimental spontaneous value of magnetization at T_{comp} is different from 0 as it should be for pure ferrimagnetism of the samples ($\theta = 0$). The magnetization at T_{comp} is greater for $x = 0.92$ than for $x = 0.47$ or $x = 0$, in agreement with the greater value of θ (8° vs. 3.5°) deduced from 4.2 K results.

In the temperature region close to T_C, the magnetization curves present very similar results (Figs. 4 and 5) and Curie temperatures of all the samples from $x = 0$ to $x = 6$ fall in a ~20 K temperature interval near 500 K (Fig. 4 and Table 1). In this temperature region, the magnetic properties are dominated by the Fe–Fe interactions very similar to Ho_6Fe_{23} and Y_6Fe_{23}, which explains the observed results. In the intermediate temperature range ($T_{comp} < T < T_C$), the magnetization increases drastically when the yttrium substitution increases.

The magnetic properties $M(H, T, x)$ are interpreted within the frame of the molecular field theory model of Herbst and Croat [8]:

Table 1
Experimental data and parameters used for calculation of the magnetization of $Ho_{6-x}Y_xFe_{23}$

x	T_{comp}(K)	T_C(K)	$\sigma_s(\mu_B.fu^{-1})$	$\mu_{Fe}(\mu_B.at^{-1})$	θ (°)	θ_{max}(°)	N_{Fe-Fe}	N_{Ho-Fe}	N_{Ho-Ho}
0	188	515	13.2	2.05	3.5	13	5200	−750	230
0.47	150	515	9.5	2.03	3.5	10	5314	”	”
0.92	99	513	7.9	2.02	8	9	5424	”	”
1.86	–	508	6.2	1.99	6	8	5653	”	”
4.85	–	495	32.1	1.89	0	–	6380	”	”
6	–	496	42.5	1.85	–	–	6660	–	–

$$M_i(T) = M_i(T=0)\, B_{Ji}(u_i), \quad i = \text{Ho, Fe} \tag{6}$$

where $M_i(T) = n_i \mu_i(T)$ represents the magnetization of the n_i magnetic ions of moment μ_i at temperature T in units of the Bohr magneton (μ_B), B_{Ji} being the Brillouin function, $J_{Fe} = 1$ [8], $J_{Ho} = 8$ (Ho^{3+}), and

$$u_i = \mu_i(0) H_i(T)/kT \tag{7a}$$

$$H_i(T) = H_a + (N\mu_B \rho / M_w)\, \Sigma_j n_i N_{ij} \mu_j(T) \tag{7b}$$

where H_a represents the applied field, N is Avogadro's number, ρ the density in g cm^{-3}, and M_w is the molecular formula weight of the compound. N_{ij} are the molecular field coefficients ($N_{ij} = N_{ji}$ when $i \neq j$). From the sublattice magnetizations $M_i(T)$ deduced from Eqs. (6)–(7), the temperature magnetizations of the compounds M_{tot} are calculated using Eq. (1) for the canting angles θ obtained previously. θ is a function of the substitution rate and, in order to have a minimum of parameters, we keep the same molecular field coefficients N_{HoFe} and N_{HoHo} as those of Ho_6Fe_{23} (The different parameters corresponding to our experimental values are reported in Table 1).

For N_{FeFe}, we assume that it varies linearly from Ho_6Fe_{23} to Y_6Fe_{23} compounds:

$$N_{FeFe}(x) = [(6-x)/6]\, N_{FeFe}(0) + (x/6)\, N_{FeFe}(6) \tag{8}$$

As can be observed in Figs. 4 and 5, the agreement is rather good indicating that the different assumptions used in the model are reasonable. Particularly at T_{comp}, the

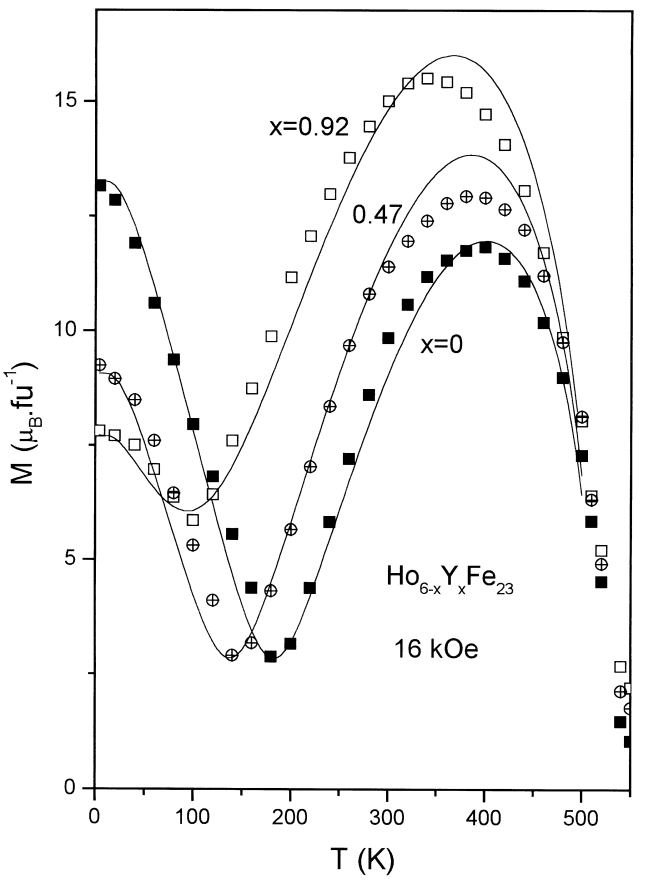

Fig. 4. Temperature variations of magnetization at 16 kOe of compounds with a magnetic compensation point. Solid lines are calculated values (See text).

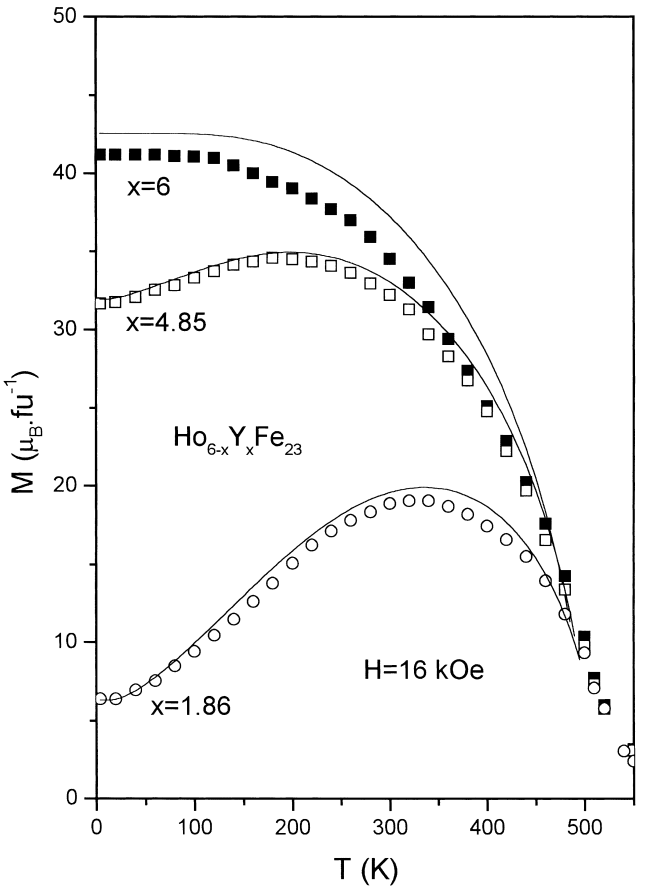

Fig. 5. Temperature variations of magnetization at 16 kOe of $Ho_{6-x}Y_xFe_{23}$ compounds without compensation temperature. Solid lines are calculated values.

calculated $M(T_{comp})$ moment is close to its experimental value, in agreement with the assumed temperature independency of θ. Small discrepancies are observed mainly in high temperature region (~250 K to ~450 K). We do not try to improve the fit by using adjustable parameters.

4. Conclusion

A possible mechanism for canting is competition between sublattice magnetic anisotropies [10]. Substitution of yttrium in place of magnetic holmium may decrease the magnetic anisotropy of the rare earth sublattice, leading to more canted structures than in pure Ho_6Fe_{23}. This is more evidenced in the vicinity of $x \sim 1.5$ corresponding to $T_{comp} = 0$, where rare earth and Fe sublattice magnetizations are comparable. It is to be noted also that the 'easy' axis is different in the end members of our system, Ho_6Fe_{23} and Y_6Fe_{23}, which may contribute to increase canting in the intermediate compositions.

The mean canting angle θ between R and Fe moments is found greater than its value in pure Ho_6Fe_{23} but remains lower than 10° and close to its maximum value allowed by the molecular field model of Herbst and Croat for $x = 0.92$ and 1.86. θ may reflect equally the crystallographic disorder introduced by yttrium substitution in the Ho sublattice. The calculated temperature dependence of magnetizations of the compounds, assuming a linear variation of the parameters of the Fe sublattice from Ho_6Fe_{23} to Y_6Fe_{23}, are in fairly good agreement with experimental data.

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