Investigation of the Direction of Spontaneous Magnetisation at 0 K in HoCo$_2$ and TmFe$_2$

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ABSTRACT: The direction of spontaneous magnetisation at 0 K across a phase orientation boundary in rare-earth laves phase compounds is computed as a function of the ratio of magnetic to electrostatic interactions. The phase boundary and range of parameters used for the computation correspond to the portion of the orientational phase diagram where experimental data can be obtained. In the series of pseudo-binary compounds ($Gd_x Ho_{1-x}$)Co_2 and ($Y_x Ho_{1-x}$)Co_2 the range of parameters covers the continuous transition from the <100> to the <110> orientations. The nmr measurements on this series show that the direction of spontaneous magnetisation is at intermediate orientation between the <100> and <110> directions. The material *TmFe$_2$*, which is in the vicinity of a discontinuous orientational boundary, is also discussed.

Keywords: Lanthanides; Crystal field; Laves phase; Phase transition.

دراسة الاتجاه للتمغنط التلقائي عند الصفر المطلق (ok) لمركبي HoCo$_2$ و TmFe$_2$

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ملخص: تم حساب اتجاه التمغنط التلقائي عند درجة الحرارة K 0 (الصفر المطلق) عبر حد توجيه الطور المغناطيسي في مركبات العناصر الأرضية النادرة والتي لها أطوار لافز (laves phases) – باعتباره دالة في نسبة التفاعلات الكهربية إلى التفاعلات المغناطيسية. حد الطور المغناطيسي ومدى المعاملات التي تم استخدامها في الحساب تخص ذلك الجزء من بياني الطور التوجيهي الذي يمكن استخلاص نتائج تجريبية منه. أما بالنسبة لسلسلة المركبات التي يطلق عليها(pseudo – binary) مثل(Co_2 ($Gd_x Ho_{1-x}$) فإن مدى المعاملات يغطي الإنتقال المتصل من الإتجاه <100>. الى الا تجاه <110>). ان قياسات الرنين النووي المغناطيسي لهذه السلسلة من المركبات توضح أن اتجاه التمغنط التلقائي يكون متوسطا بين الاتجاهين <100> و <110>

تناقش هذة الورقه أيضا المادة $Tm Fe_2$ والتي تقع على مقربة من حد توجيه الطور المغناطيسي المنقطع.

كلمات مفتاحية: انتقال طوري ، طور لافز ، الحقل البلوري ، لاثينيدات.

1. Introduction

One of the characteristics of rare-earth ions is that the spin-orbit coupling in the 4-*f* shell is much larger than the interactions experienced by the ion when embedded in a crystal. As a result **J**, the total angular momentum of the 4*f* shell, remains, in a first approximation, a good quantum number in the solid [1]. The states of the ion subjected to the crystal-field and the magnetic interactions experienced in the solid are well described to first order by the simple effective electronic Hamiltonian [2].

$$\mathcal{H}_{el} = \mathcal{H}_{cf} + \mathcal{H}_z \tag{1}$$

where $\mathcal{H}_z$ stands for the magnetic interaction of the 4*f* shell with the host crystal and $\mathcal{H}_{cf}$ is the crystal-field interaction which is the electrostatic interaction of the 4*f* shell with the electric field gradients due to the surrounding ions. In the Zeeman representation, the eigenstates of the electronic Hamiltonian are expressed as linear combinations of $|M_J\rangle$ states. Since at room temperatures and below only the ground *J*-manifold is populated the index *J* is dropped and the electronic states are written

$$|E_n\rangle = \sum_M \lambda_M |M\rangle$$

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Each electronic state $|E_n\rangle$ has a magnetic moment associated to the expectation value $\langle E_n | J_z | E_n \rangle$ of the z-component of the angular momentum $\boldsymbol{J}$ tied to the corresponding aspherical distribution of the $4f$ electrons. The $4f$ shell and therefore the magnetic moment have a preferred orientation with respect to the electric field gradients at the ion's site in the crystal. Different states have different preferred orientations. This feature is responsible for the wealth of magnetic structures and magnetic transitions displayed by rare-earth compounds. In particular, when a low-lying excited state has a strongly preferred orientation conflicting with that of the ground state, a change in the orientation of spontaneous magnetization can occur as the temperature is increased and the excited state becomes populated [3]. We note in passing that the gadolinium ion Gd^{3+} being in an S state, the crystal-field interaction is zero in first order and therefore, in first order, Gd^{3+} has no preferred orientations.

At zero-temperature, the direction of spontaneous magnetization in magnetic rare-earth compounds is determined solely by the ground state of the $4f$ shell. The nature of the ground state depends of course on the parameters in the Hamiltonian in equation 1; as the parameters are varied, the direction of spontaneous magnetisation may change. For ions at a site of cubic symmetry the Hamiltonian can be expressed in the dimensionless form given in equation 7 below which it depends on two parameters only. Al-Abry *et al.* [4, 5] have done a systematic investigation of the direction of spontaneous magnetization at zero temperature in the two-parameter space for all the values of J found in the ground state of lanthanide ions. In the present paper we discuss the direction of spontaneous magnetization in two compounds, $HoCo_2$ and $TmFe_2$. In these compounds the rare-earth ion is at a site of cubic symmetry and the parameters for these compounds place them near a boundary between two regions in the parameter space with different orientations of spontaneous magnetization for the ground state.

The crystal-field Hamiltonian is expressed as a linear combination of the Steven's operators $\boldsymbol{O}_n^m$ [6].

$$\mathcal{H}_{cf} = \sum_{n=0}^{6} \sum_{m \leq n} B_n^m \boldsymbol{O}_n^m$$

The B_n^m are the crystal-field parameters. At a site of cubic symmetry there are only four non-vanishing terms in the expansion: B_4^0, B_4^4, B_6^0 and B_6^4 are the non-zero parameters. Furthermore there is a relation between the two fourth order and between the two sixth order terms; therefore only two parameters are required to describe the crystal field [7]. The crystal-field Hamiltonian is written

$$\mathcal{H}_{cf} = B_4 \boldsymbol{O}_4 + B_6 \boldsymbol{O}_6 \tag{2}$$

with $\boldsymbol{O}_4 = \boldsymbol{O}_4^0 + 5\boldsymbol{O}_4^4$ and $\boldsymbol{O}_6 = \boldsymbol{O}_6^0 - 21\boldsymbol{O}_6^4$

Following Lea, Leask and Wolf [6] the Hamiltonian is recast in the form

$$\mathcal{H}_{cf} = W \left\{ x \frac{\boldsymbol{O}_4}{F_4} + (1 - x) \frac{\boldsymbol{O}_6}{F_6} \right\} \tag{3}$$

where W is an energy scale factor and the unitless parameter x gives the ratio of the fourth to sixth order crystal-field terms.

$$B_4 F_4 = W x$$

$$B_6 F_6 = W(1 - |x|)$$

F_4 and F_6 are numerical factors depending on the particular value of J [7];
the magnetic interaction is

$$\mathcal{H}_Z = -\boldsymbol{B}_R \cdot \boldsymbol{\mu}_R = -g_J \mu_B \boldsymbol{B}_R \cdot \boldsymbol{J} \tag{4}$$

where $\boldsymbol{B}_R$ is a vector that represents the sum of all the effective magnetic fields acting on the rare-earth ion; these can arise because of exchange, the dipolar field or an externally applied field. g_J is the Landé g-factor and μ_B is the Bohr magneton. Following McMorrow *et al.* [8] we introduce the vector $\boldsymbol{\alpha}$

$$\boldsymbol{\alpha} = -g_J \mu_B \boldsymbol{B}_R \tag{5}$$

and write the electronic Hamiltonian

$$\mathcal{H}_{el} = \boldsymbol{\alpha} \cdot \boldsymbol{J} + W \left\{ x \frac{\boldsymbol{O_4}}{F_4} + (1-x) \frac{\boldsymbol{O_6}}{F_6} \right\} \tag{6}$$

This Hamiltonian involves three parameters, W, x and the vector $\boldsymbol{\alpha}$. For the purpose of the present work which is concerned with the direction of spontaneous magnetization, it is more convenient to recast the Hamiltonian in a two-parameter dimensionless form by dividing by the energy factor W. The Hamiltonian becomes

$$\mathcal{H}_{el} = \boldsymbol{R} \cdot \boldsymbol{J} + \left\{ x \frac{\boldsymbol{O_4}}{F_4} + (1-x) \frac{\boldsymbol{O_6}}{F_6} \right\} \tag{7}$$

The magnitude of the vector parameter $\boldsymbol{R} = \boldsymbol{\alpha}/W$ represents the relative strength of the magnetic to the electrostatic interactions; the balance between the relative strengths of $|\boldsymbol{R}|$ and x determines the direction of spontaneous magnetization [4, 5].

Given the values of x and $|\boldsymbol{R}|$ and the orientation (θ, ϕ) of $\boldsymbol{R}$, the direction of spontaneous magnetization which is the direction of the angular momentum $\boldsymbol{J}$ can be in principle computed by diagonalising the Hamiltonian 7. However, for arbitrary values of (θ, ϕ) the computed direction of $\boldsymbol{J}$ will not in general be parallel to the input direction of $\boldsymbol{R}$. To be the direction of spontaneous magnetization, the value of (θ, ϕ) must satisfy the two conditions that the computed direction of $\boldsymbol{J}$ is parallel to $\boldsymbol{R}$, and that the energy of the state is at a minimum with respect to (θ, ϕ) [4, 5].

2. Results and discussion

In this work the evolution of the direction of spontaneous magnetization in the parameter space was computed as in reference [4] by varying systematically the parameters x and $|R|$ and finding for each value of $(x, |R|)$ which values of the polar angles (θ, ϕ) give the lowest energy for the ground state and the computed orientation of $\boldsymbol{J}$ parallel to the input $\boldsymbol{\alpha}$.

Table 1 gives a summary of the values of W, x and R for $HoCo_2$ and $TmFe_2$ derived from data published by various authors. The different experimental techniques used by the authors lead to a scatter in the values of the parameters. In most cases such an uncertainty in the parameters is not a problem. However, in the cases of Ho^{3+} in $HoCo_2$ and Tm^{3+} in $TmFe_2$, because these compounds are close to a boundary between regions of different directions of spontaneous magnetization in the $\{R, x\}$ parameter space, a small variation in the values of the parameters can lead to an erroneous direction of spontaneous magnetization.

Table 1. The parameters for $HoCo_2$ and $TmFe_2$ derived from published data. *a*: Gignou *et al.*[9], *b*: Aubert *et al.* [10], *c*: Castets and Gignoux [11], *d*: Germano and Butera [12], *e*: Martin *et al.*[13] derived values of B_4 and B_6 from the data of Atzimony *et al.*[14], *f*: Yanovsky *et al.* [15], *g* and *h* derived by Bleaney [18] from Rhyne and Koon [16] and Koon and Rhyne [17], i: Bleaney [18].

Ion	J	Compound	W (K)	x	$|R|$	ref
Ho^{3+}	8	$HoCo_2$	0.60	-0.4687	46.6	*a*
			0.60	-0.4665	45.8	*b*
			0.30	-0.4839	60.2	*c*
Tm^{3+}	6	$TmFe_2$	0.59	0.555	99	*d*
			0.58	0.649	89	*e*
			0.54	0.721	86	*f*
			0.59	0.353	78	*g*
			0.61	0.627	76	*h*
			0.44	0.64	105	*i*

The relevant portions of the orientational phase diagram for the two ions Ho^{3+} ($J = 8$) and Tm^{3+} ($J = 6$) are given in Figures 1-A and 1-B. The published parameters for the two compounds given in table 1 are also shown in the figures. In the notation of Al-Abry *et al* (4, 5), the boundary in the case of $J = 6$ is of the type *Da* where the transition is discontinuous across the boundary. At a critical value of the parameters the two orientations (110) and (111) have the same energy but all the orientations in the plane containing these two directions have a higher energy. There is a sudden change of direction of spontaneous magnetization at the critical value. For $J = 8$ the boundary is of the type *C* where there are two critical values for the parameters; between these two values the direction of spontaneous magnetization is at an intermediate orientation between the (100) and the (110) axis. There is a continuous rotation of the direction of spontaneous magnetization. Figures 1-C and 1-D show the computed directions of spontaneous magnetization across the boundary for the two cases.
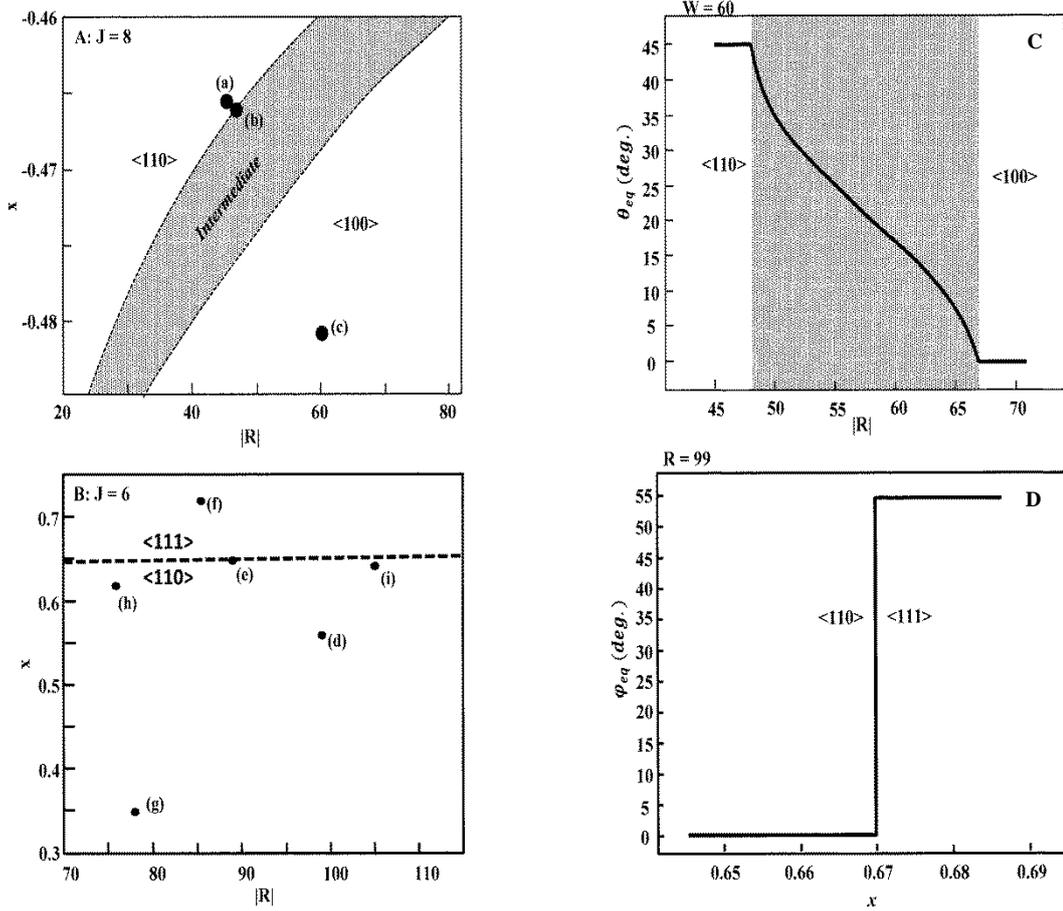
Figure 1. *A* and *B*: the relevant areas of the orientational phase diagrams for J = 6 and *J* = 8; the letters in brackets refer to the references in table 1. *C* and *D* are the computed direction of spontaneous magnetisation across the phase boundary.
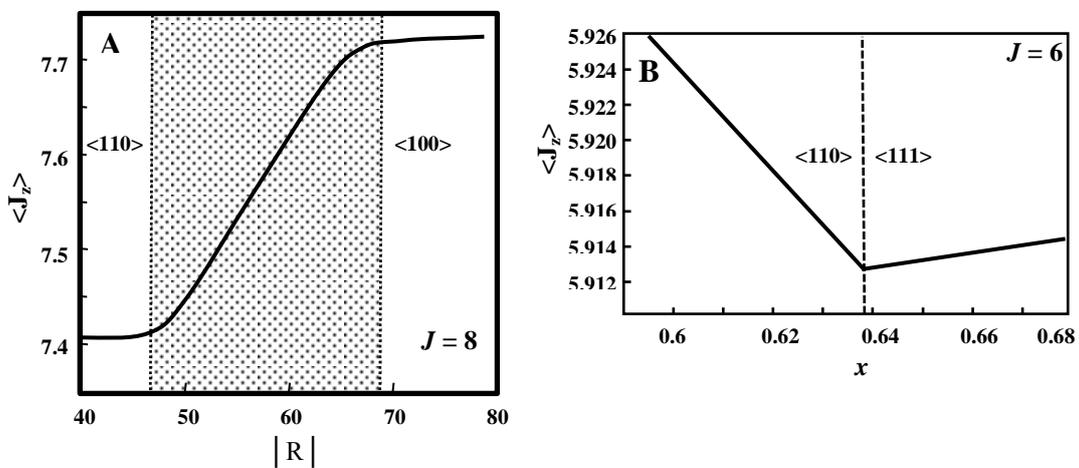
Figure 2. The variation of $<J_z>$ across the boundary. A: for $J = 8$ and B for $J = 6$.

The computed values of $\langle J_z \rangle$ corresponding to figures 1-C and 1-D are shown in figure 2-A and 2-B. As one might expect, in figure 2-A for the case of Ho^{3+}, the value of $\langle J_z \rangle$ varies continuously across the boundary and the first derivative is continuous. For Tm^{3+}, $\langle J_z \rangle$ is continuous through the boundary but there is a discontinuity with a change of sign in the first derivative. We note that for $J = 8$ the change in the value of $\langle J_z \rangle$ across the boundary is about 3%, whereas in the case of $J = 6$ the variations of $\langle J_z \rangle$ in the vicinity of the boundary are of the order of 0.02%.

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We consider first the case of $HoCo_2$. The direction of spontaneous magnetization was investigated experimentally by [165]Ho:Ho^{3+} NMR. The holmium nucleus has spin 7/2, the NMR spectrum presents seven quadrupole-split lines. The frequency a_t of the central line of the spectrum is directly related to the expectation value $\langle J_z \rangle$ which can be computed from the Hamiltonian in equation 7 [1, 2]

$$a_t = a_o \frac{\langle J_z \rangle}{J} + a''$$

(8)

Where a_0 is the free-ion dipolar hyperfine coupling constant ($a_0 = 6497$ MHz for holmium); a'' is the contribution arising from the direct interaction of the nucleus with the surroundings in the crystal and a'' is a small contribution that can be treated as a free parameter. Because of the large value of a_0, any small change in the value of $\langle J_z \rangle$ results in a large shift in the NMR frequencies. In materials where the value of $\langle J_z \rangle$ depends strongly on the orientation of the ion with respect to the crystal axis, the NMR spectrum is a powerful tool to determine the direction of magnetization [19].
In practice it is difficult to control experimentally the parameters $|R|$ and x. However, in the case of $HoCo_2$, the value of $|R|$ can be decreased by doping the compound with non-magnetic yttrium or increased by doping with gadolinium which has a larger spin than holmium and, as mentioned in the introduction, does not contribute to the anisotropy because Gd^{3+} is in an S state.
A series of compounds $(Ho_{1-y}Gd_y)Co_2$ (y = 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.97) was prepared by arc-melting. Assuming for the sake of computation that the value of $|R|$ is 46.6 for pure $HoCo_2$ (table 1) the concentrations of gadolinium chosen correspond to $|R|$ = 46.6, 48.1, 49.8, 54.0, 58.1, 62.0, 85.4 respectively. To obtain lower values of $|R|$ a compound doped with 5% of yttrium corresponding to the value of $|R|$ = 44.3 was prepared. The value of the molecular field experienced by the Ho^{3+} ion in the pseudo-binary compounds was estimated following McMorrow et al [8]. It is expected that these values of $|R|$ take the compound across the orientational phase boundary.
The NMR spectra were taken on the 2-8 GHz spectrometer at the University of Manchester (UK) [20] at liquid helium temperatures. A preliminary outcome of some of the still unpublished measurements on some of the $(Ho,Gd)Co_2$ compounds was presented at the XIII Congress Ampere [21]. In the concentrated $HoCo_2$ compound and in the $(Ho,Gd)Co_2$ compounds with low gadolinium concentration two overlapping spectra are observed. For concentrations of gadolinium above 50% a single spectrum is observed which is consistent with the <100> orientation of spontaneous magnetisation. The NMR spectrum of [165]Ho:$HoCo_2$ is shown in figure 3. The presence of two spectra indicates that there are two inequivalent sites with slightly different strengths of the exchange interaction. In the transition region this results in a significant shift of the NMR spectrum. The explanation for the two sites has not yet been unequivocally established. The two obvious possible causes, an impurity in the starting materials for the sample preparation or closure domains or domain walls were discarded by repeating the measurements with specimens of $HoCo_2$ prepared at other institutions including a single crystal on loan from Laboratiore Louis Neel, Grenoble. An 8 T field was applied to the single crystal specimen. In all experimental conditions two spectra are observed in $HoCo_2$. We will not attempt here to give any plausible explanations for the presence of the two sites.
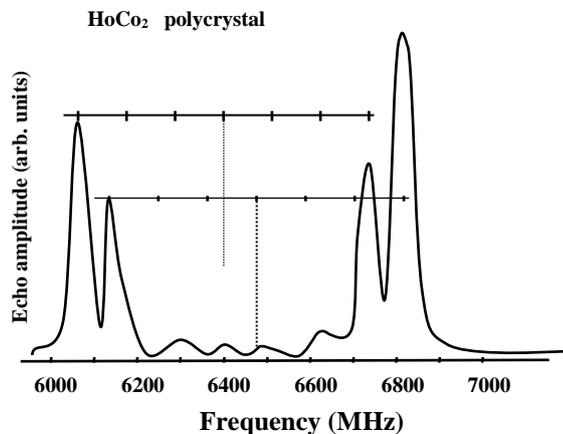
Figure 3. The observed spectrum for $HoCo_2$ is the superposition of two 7-lines spectra.

For each compound we have derived the values of a_t of each of the two overlapping spectra. In figure 4 we have plotted all the measured values of a_t as a function of concentration. The conclusion than can be drawn from the figure 5 is that two spectra are observed only for compounds with a value of $|R|$ that places them in the transition region. Therefore, the pure compound $HoCo_2$ is inside the transition region.
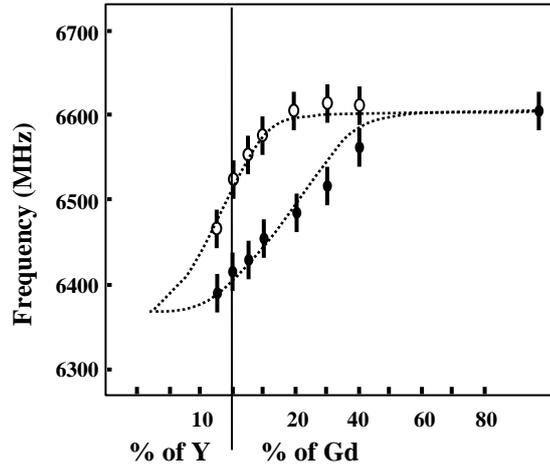
Figure 4. Summary of the frequency of the central line of all the spectra observed. The dashed line is a guide to the eye; the vertical line corresponds to the $HoCo_2$ compound.

In order to obtain a comparison between computation and experiment we have derived the values of $<J_z>$ using equation 8. We have considered a'' as a free parameter for each compound and allowed a'' to vary linearly with concentration from 392 MHz in the concentrated compound to 356 MHz in the compound with 40% gadolinium. We have also assumed that the low frequency spectrum corresponds to the values of $|R|$ estimated for the specimen preparation and that the high frequency spectrum corresponds to a site with a value of $|R|$ increased by 9. The values of $<J_z>$ thus obtained are compared to the values computed using the parameters of Aubert et al (10). The figure shows a very good agreement between the measurements and the computation.
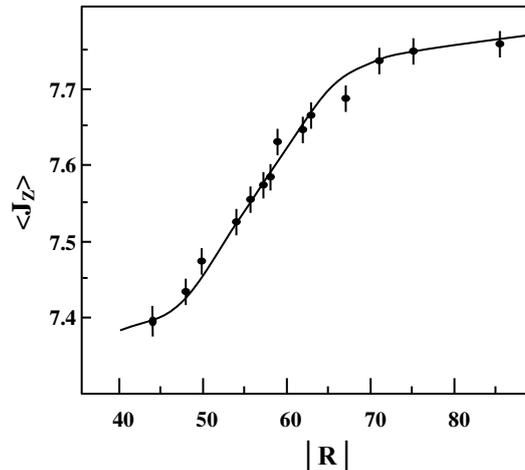
Figure 5. The values of $<J_z>$ derived from the measurements are compared to the computed values (solid line).

Turning now to $TmFe_2$ we note that some of the parameters given in table 1 give the <111> as direction of spontaneous magnetisation for the ground state, while others give the <110>. The parameters of Germano and Butera (12) give a reorientation of the spontaneous magnetisation as a function of temperature from the <110> at low temperatures to <111> above 55 K.

As noted in Figure 3, there is only a small (0.02%) change in $<J_z>$ across the phase boundary. Therefore, nmr cannot be used to ascertain the direction of spontaneous magnetisation at low temperatures. The direction of magnetisation can be obtained from the ^{57}Fe Mössbauer spectrum since the iron sites are not magnetically equivalent [14]. A detailed study of the ^{57}Fe Mössbauer spectrum by Al-Sariri (22) confirmed that the direction of magnetisation in $TmFe_2$ is <110> at all temperatures. The specimen used for the Mössbauer measurements by Al-Sariri was a crushed single crystal obtained from University of Birmingham (UK).

3. Conclusion

This work has shown that a boundary in the orientational phase diagram can place constraints in the range of the values for the parameters of the Hamiltonian. These constraints make it possible to refine the values of the parameters. The nmr data shows that $HoCo_2$ is just inside the intermediate region on the <110> side of the boundary. Therefore, the parameters that describe best the Ho^{3+} ion in this compound are those of Abert et al [4]. For $TmFe_2$ most of the experimental data available would indicate that the <110> is the orientation of spontaneous magnetization at all temperatures; therefore the parameters given by Yanovsky et al. [15] are probably incorrect. However, the analysis given by Sariri, based on unpublished high field $^{169}Tm:TmFe_2$ nmr [23] and in some pseudo-binary alloys would indicate that magnetostriction is not negligible. An extra term needs to be included in the crystal-field Hamiltonian in order to take the magnetostriction distortion into account.

4. Acknowledgements

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