Magnetic structure of β-DyD_{2+x}: Modulated phases for $x=0$ and short-range order for $x=0.135$

P. Vajda
Laboratoire des Solides Irradiés, CNRS-CEA, Ecole Polytechnique, F-91128 Palaiseau, France

G. André
Laboratoire Léon-Brillouin, CNRS-CEA Saclay, F-91191 Gif/Yvette, France

J. Hammann
Service de Physique de l'Etat Condensé, CEA Saclay, F-91191 Gif/Yvette, France

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The magnetic transitions in the stoichiometric dideuteride β-$DyD_{2.00}$ have been studied by cold-neutron diffraction and low-field magnetization measurements. We observe, below $T_2=5.0(2)$ K, two sinusoidally modulated configurations, one for $T\leqslant T_1$, the other for $T_1\leqslant T\leqslant T_2$, with a partial overlap of about 0.5 K between them. The transition at T_1 presents a thermal hysteresis between 2.5 and 3.5 K. The magnetic structure below T_1 is nearly commensurate, with a propagation vector close to (1/4,1/4,3/4), $\mathbf{k}_1=(0.258,0.273,0.750)$, that between T_1 and T_2 is more incommensurate, with a $\mathbf{k}_2=(0.275,0.275,0.750)$. The β-$DyD_{2.135}$ specimen shows no magnetic long-range order but exhibits a broad bump in its spectrum, disappearing at 4–6 K and attributed to short-range ordered domains of $\sim$30 Å correlation length, confirming earlier resistivity and susceptibility measurements. [S0163-1829(97)04105-2]

I. INTRODUCTION

Dysprosium dihydride is one of the β-phase rare-earth hydrides, β-RH_2, crystallizing in the fcc fluorite-type structure (with all tetrahedral sites ideally occupied) and exhibiting magnetic ordering at low temperature. Moreover, it is well known that additional hydrogen atoms, x, sitting in octahedral interstitial sites, H_o, and forming superstoichiometric β-RH_{2+x} compounds, exert a significant influence upon the magnetism of these systems, leading sometimes to the vanishing of magnetic configurations and/or to the appearance of new ones (for a detailed review, see, e.g., Ref. 1). Thus it was shown recently[2] that, in β-TbD_{2+x}, the magnetic phase diagram consisted of various overlapping commensurate and incommensurate antiferromagnetic (AF) regions, depending on the concentration of the x-hydrogen atoms and also on their ordering state. Therefore, it has been recognized during the past decade that the precise characterization of x was essential for the reproducibility and correct description of experimental results.

The first reliable observations of magnetic transitions in the ''pure'' ($x=0$) dihydride DyH_2 were made by Bieganski, Opyrchal, and Drulis[3] in specific-heat measurements. They noted a λ-type transition at $T_N=3.30$ K, attributed to AF ordering, and a broader one, peaking at $T_C=4.5$ K, which remained unidentified. Friedt *et al.*[4] observed a well-defined hyperfine pattern in their Mössbauer spectrum below 3.3 K and a curious distribution with broad lines between 3.3 and 6 K, assigning the former to long-range-ordered (LRO) and the latter to short-range-ordered (SRO) magnetism. The first neutron-diffraction study of DyD_2 was performed by Shaked *et al.*[5] who used short-wavelength neutrons ($\lambda\sim1$ Å) because of the rather high absorption cross section of Dy. They noted magnetic reflections at 4.2 K and at 1.6 K but were unable to determine transition temperatures because of weak intensities; the lines were attributed to a sinusoidally modulated AF structure, with a propagation vector $\mathbf{k}$ along [113] and a period of $4a_0/\sqrt{11}$, where a_0 is the parameter of the unit cell. Traces of an ''intermediate'' magnetic structure [similar to that suggested for TbD_2 (Ref. 6)] were signaled in the 4.2 K spectrum.

As concerns the superstoichiometric β-$DyH(D)_{2+x}$ compounds, very little work had been done until quite recently. Mössbauer measurements on an ill-characterized $DyH_{2.14}$ specimen[7] indicated a magnetic transition at a temperature as high as 20 K, while a $DyH_{2.04}$ specimen exhibited a flat susceptibility maximum near 6 K, attributed by the authors to magnetic SRO.[8] The $DyD_{2.06}$ sample of Shaked *et al.*[5] showed no magnetic reflections and no hyperfine structure down to 1.4 K. Finally, complete low-temperature investigations of the DyH_{2+x} system were performed through the whole β-phase region, $0\leqslant x\leqslant x^{\beta}_{\max}$ [with $x^{\beta}_{\max}=0.23(1)$ at. H/at. Dy as determined by x-ray lattice parameter measurements[9]], using electrical resistivity[10] and susceptibility[11] experiments. They showed the extreme sensitivity of the magnetic manifestations to a variation of x, a direct result of the modifications of the crystal-field environment due to the H_o-H_o and H_o-H_T interactions, such as measured for example by inelastic neutron scattering.[12] A tentative magnetic phase diagram was proposed,[13] which contained a SRO region down to 1.3 K for intermediate x values, $x\sim0.1$, surrounded by two commensurate AF-ordered regions for smaller and for larger x, which were preceded by incommensurate or SRO structures.

In this work, we present a detailed neutron-diffraction study (combined with low-field magnetization measure-

ments) of the pure dihydride, $DyD_{2.00}$, and of an x-doped specimen, $DyD_{2.135}$, undertaken to clarify various contradictions in former work. In particular, we wanted to complete Shaked's data[5] using subthermal neutrons ($\lambda \sim 2.4$ Å) and characterize more precisely the magnetic structures for $x=0$, as well as to check their preliminary result concerning an intermediate x value. We have established, for $x=0$, an incommensurate AF structure below 5 K, which is overlapping with a nearly commensurate AF component; the latter order-order transition presents a rather strong hysteresis effect. All long-range magnetism appears destroyed for $x=0.135$; on the other hand, a magnetic SRO configuration is observed, which vanishes between 4 and 6 K.

II. EXPERIMENT

Approximately 1 g bulk Dy pieces of 99.99 at. % nominal purity, purchased from the Ames Laboratory (Ames, Iowa), were loaded with hydrogen after degassing at 650–700 °C for several hours until reaching a vacuum of $\sim 10^{-8}$ Torr. The hydrogenation procedure took place in two parts: (i) preparation of the ''pure'' dideuteride, filling all available tetrahedral sites by heating in a controlled deuterium atmosphere at 550–600 °C and (ii) addition of the octahedral x-deuterium atoms at 350–400 °C. This separation of the hydrogenation procedures ensures the precise determination of the concentration x in the case of an understoichiometry of the pure dihydride. In our case, due to the high purity and the thorough preparation of the starting metal, the composition of the dideuteride reached stoichiometry, $DyD_{2.00(1)}$. The second sample was doped to $x=0.135$ at. D/at. Dy. After preparation, the specimens were crushed to powder for the diffraction experiments.

Neutron-diffraction measurements were performed on the G4.1 spectrometer located at the cold-neutron guide of the Orphée reactor of the Laboratoire Léon-Brillouin at Saclay, using an 800 cell multidetector in the range $12° \leqslant 2\Theta \leqslant 92°$. Neutron spectra were taken employing a wavelength of $\lambda = 2.425$ Å, in the interval $1.4 \leqslant T \leqslant 12$ K. To minimize the effect of the high absorption cross section of Dy, a small (3 mm diameter) cylindrical sample holder was used for the experiments. The diagrams were analyzed employing the Rietveld program FULLPROF.[14]

dc magnetization measurements were made on a $DyH_{2.00}$ sample using a superconducting quantum interference device magnetometer (from Cryogenic Ltd) in fields as low as 1 Oe and in a temperature range from 300 K down to 2 K. Special care was taken in the interval between 2 and 10 K to determine the critical temperatures and the possible onset of low-T irreversibilities. The usual procedures were used, in which the sample is first zero-field-cooled (ZFC) down to the lowest temperatures before applying the field and measuring the magnetization as a function of T (ZFC magnetization). The field is kept constant and other measurements are taken, with the sample again being cooled down [field-cooled (FC) magnetization] or heated back up [field-heated (FH) magnetization]. The differences in the observed data serve to detect any irreversible effects.

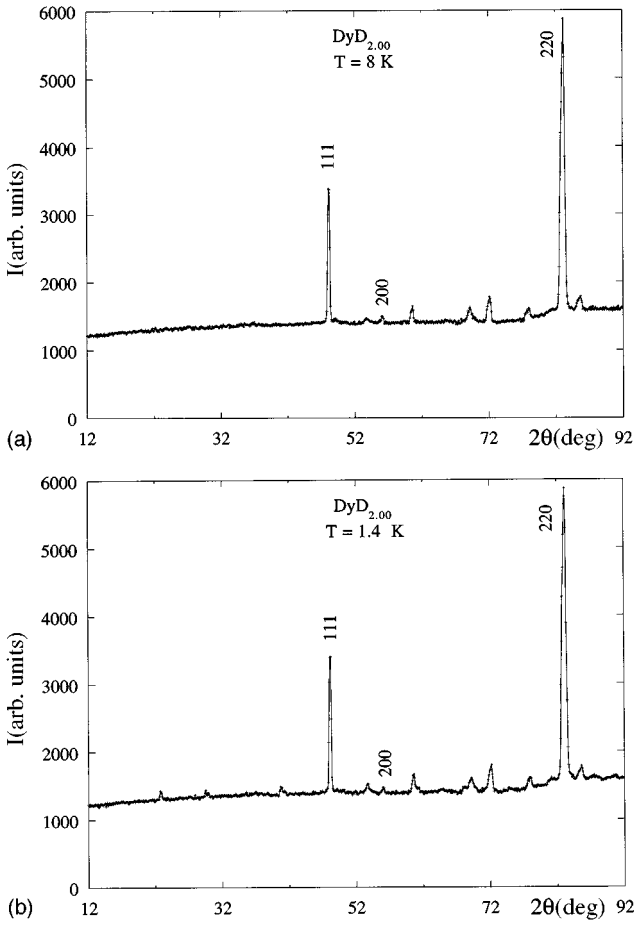

FIG. 1. Diffraction spectra of $DyD_{2.00}$ taken at 8 K (upper part) and at 1.4 K (lower part), indicating the nuclear structure lines and revealing the incommensurate magnetic phase at small angles in the low-T spectrum. The other peaks are due to impurities and to the sample environment.

III. RESULTS AND DISCUSSION

A. $x=0$

We present in Fig. 1 the measured neutron-diffraction spectra of $DyD_{2.00}$ in the paramagnetic region, at $T=8$ K (upper part), and in the magnetically ordered region, at $T=1.4$ K (lower part). A first comparison with the spectra of Shaked *et al.*[5] shows essentially a better resolution, mainly due to the longer wavelength neutrons in our case, allowing a finer analysis. This was obtained by treating the difference patterns as exhibited in Fig. 2 at various measuring temperatures and referred to the $T=8$ K spectrum.

Two main features have to be noted: (i) the appearance, below $T_2 = 5.0(2)$ K, of a series of narrow magnetic reflections close to but not exactly at the corresponding positions indicated in Ref. 5; (ii) the emergence, below $T_1 \sim 3$ K, of new magnetic lines slightly overlapping with the former spectrum. They exhibit a striking thermal hysteresis as seen in Fig. 3, $T_1(\text{down}) = 2.5(2)$ K and $T_1(\text{up}) = 3.5(2)$ K, indicating a first-order transformation.

It was not possible to fit correctly the series of small lines between T_2 and T_1 with any commensurate AF configuration, in particular along [113], if following the analysis for

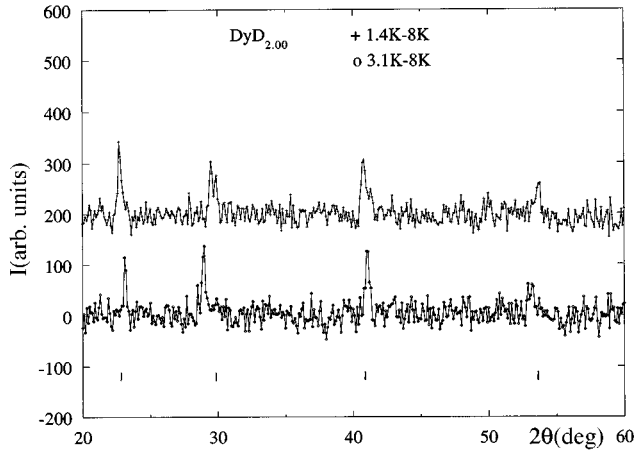

FIG. 2. Difference spectra of $DyD_{2.00}$ taken at 1.4 K (+) and at 3.1 K (○) with decreasing T and compared with that at $T=8$ K. Note the different positions of the magnetic lines and the vertical marks indicating the calculated positions of the commensurate (1/4, 1/4,3/4) configuration.

TbD_2 in Refs. 2 and 5. The best fit to the data presented here is an *incommensurate*, sinusoidally modulated configuration, with a propagation vector

$$\mathbf{k}_2=(0.275,0.275,0.750),$$

close to but not exactly along [1/4,1/4,3/4]. On the other hand, the fit indicates that the low-temperature phase below T_1 has practically locked into the commensurate configuration, its wave vector being

$$\mathbf{k}_1=(0.258,0.273,0.750).$$

Actually, the splitting visible on the magnetic peaks of the 1.4 K spectrum in Fig. 2 is indicative of the small but significant difference between the k_x and the k_y components of $\mathbf{k}_1$, in contrast to $\mathbf{k}_2$.

The smallness of the magnetic signals (Fig. 4) precludes any precise quantitative analysis. Nevertheless, a qualitative

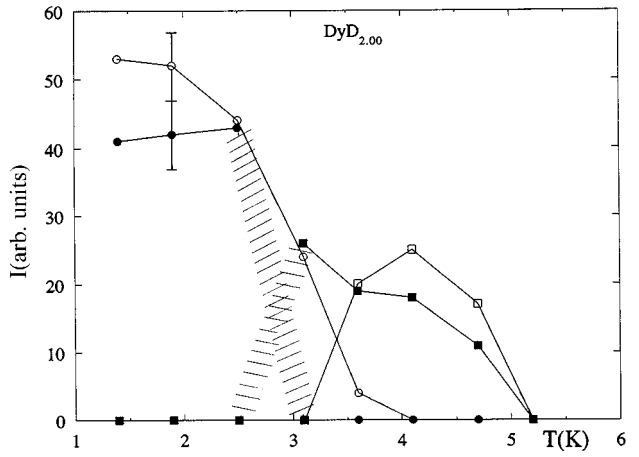

FIG. 3. Temperature dependence of the intensities for the two magnetic configurations taken with decreasing (full signs) and increasing (open signs) temperature. Note the hysteresis and the overlap region between them.

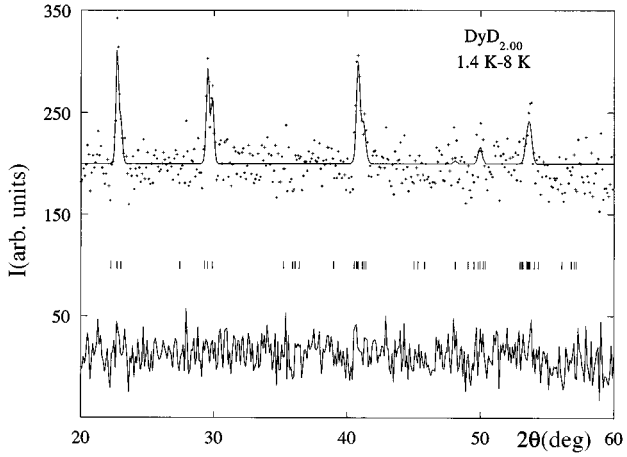

FIG. 4. Difference spectrum of $DyD_{2.00}$ between 1.4 and 8 K, indicating the calculated best fit with the propagation vector $\mathbf{k}_1=(0.258,0.273,0.750)$ and showing the positions of the corresponding reflections.

examination of the relative intensities of the different magnetic peaks seems to indicate a spin orientation along [001] like in TbD_2,[5,2] confirming the earlier suggestion.[5]

Thus the transition between the two AF configurations in DyD_2 seems to be relatively smooth as concerns their structure, though it remains energetically strong enough to give rise to a first-order transformation due to competition between the two phases. The latter is even more pronounced in the case of TbD_2,[2] resulting not only in higher values for T_1 and T_2 and a wider overlap interval, but principally in a different propagation vector: $\mathbf{k}_{ic}(TbD_2)\sim[1/8,1/8,3/4]$. The estimated magnetic moment on the Dy ion was $|\mu|=(3.5\pm0.5)\mu_B$, which corresponds to that given in Ref. 5, $(3-4)\mu_B$, and to the Mössbauer results of Friedt *et al.*,[4] $3.8\mu_B$; it is strongly quenched from the free-ion value of $10\mu_B$ by the cubic crystal field as had been discussed earlier.[4]

As a support for the above discussion, we show in Fig. 5 low-field magnetization measurements of $DyH_{2.00}$, prepared in the same manner as $DyD_{2.00}$. The results can be compared with the susceptibility data of Ref. 11, confirming the transitions near 5.5 and 3.5 K, but are yielding, in addition, a thermal hysteresis around T_1 in agreement with the above

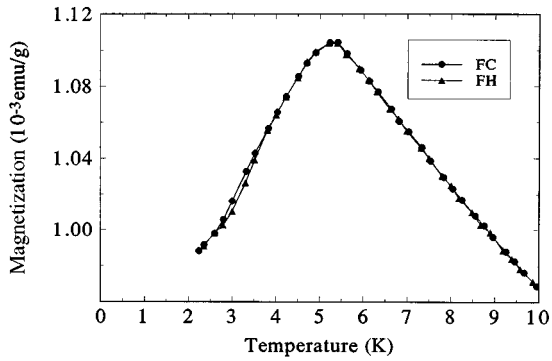

FIG. 5. Field-cooled (FC) and field-heated (FH) dc magnetizations for $DyH_{2.00}$ as a function of temperature for an applied field $H=1$ Oe.

neutron data. This irreversible effect is, however, very small and should be taken with care. It appears on top of a much larger irreversibility showing up above 30 K (with maximum amplitude near 60 K) below which the ZFC and the FC magnetizations yield quite different values. The low-T irreversible behavior between the FC and the FH magnetizations in Fig. 5 is confirmed by the observation of hysteresis effects on the field dependence of the magnetizations at 2.5 K. The absolute values of the magnetization given in Fig. 5 strongly depend on the 60 K irreversibility and possible kinetic effects and should not be taken as reference.

The (partly simultaneous) presence of two close AF configurations explains the complexity of the earlier experimental observations, such as the unusual distribution with broad lines in the Mössbauer spectra between 3.3 and 6 K.[4] Moreover, the specific-heat results of Bieganski, Opyrchal, and Drulis[3] and the recent resistivity[10] and susceptibility[11] data clearly indicate two transitions: one at $T_2=5-5.5$ K, the other at $T_1=3.3-3.4$ K, the difficulty of an unambiguous attribution being related to the overlap of the two existing configurations over a certain temperature range. In hindsight, we should like to recall the $T^{3.95}$ dependence of the $\rho_{\mathrm{mag}}(T)$ curve below 3 K for DyH_2 in Ref. 10, close to the expected T^4 dependence of the resistivity in a ''normal'' antiferromagnet,[15] which flattens out at higher T in the incommensurate region.

B. $x=0.135$

As expected, the nuclear structure of $DyD_{2.135}$ corresponds to a slightly contracted CaF_2 lattice as compared to the pure dihydride:

$$a_0(DyD_{2.135})=5.1888(16)\ \text{Å},$$

$$a_0(DyD_{2.00})=5.1935(14)\ \text{Å},$$

at $T=10$ K, with a reliability factor of $R_N=2.5\%$. These values can be related to the lattice constants of the corresponding hydrides measured at 90 K:[9]

$$a_0(DyH_{2.135})=5.194\ \text{Å},$$

$$a_0(DyH_{2.00})=5.199\ \text{Å},$$

at $T=90$ K.

The difference between the neutron spectra taken at 12 K and at 1.6 K (Fig. 6) does not show any lines corresponding to LRO magnetic configurations; the only significant structure is a broad flat bump centered near $2\Theta\sim39°$, which disappears in the region 4–6 K. It can be attributed to SRO domains, with a correlation length estimated from its linewidth to $\xi\sim30$ Å. On the other hand, the absence of net magnetic reflections conforms with the negative observations by Shaked *et al.*[5] in $DyD_{2.06}$, the latter corresponding to $x\sim0.10$, in view of the actual composition $DyD_{1.96}$ for their pure dideuteride. Similarly, susceptibility measurements on $DyH_{2.04}$ (Ref. 8) and on the series of DyH_{2+x} specimens in the interval $0.1\leqslant x\leqslant0.2$ (Ref. 11) presented flat ill-defined maxima between 6 and 10 K attributable to SRO. As for the resistivity measurements,[10] the magnetic ordering maximum seen at 3–4 K, for $x\leqslant0.05$, disappeared for higher x values, leaving just a minimum typical for magnetic fluctuations

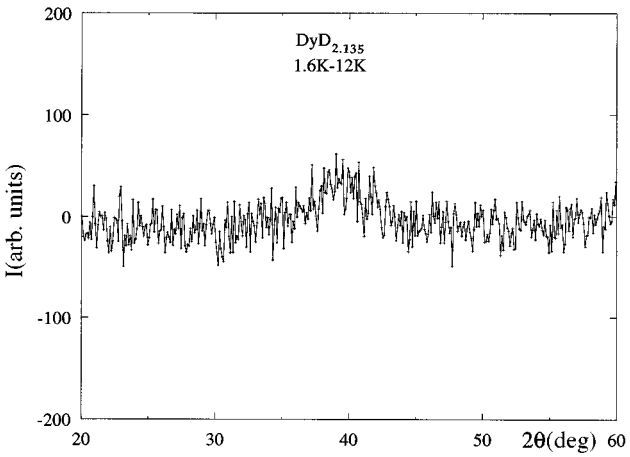

FIG. 6. Difference spectrum of $DyD_{2.135}$ between 1.6 and 12 K, indicating the SRO structure near $2\Theta=39°$.

(SRO); it was only for $x\geqslant0.2$ that new magnetic ordering transitions began to be manifest following LRO in the octahedral (x) hydrogen sublattice. Furthermore, the H_o vibrational line shapes measured in the incoherent-inelastic-neutron scattering experiments by Udovic, Rush, and Anderson[12] for $DyH_{2.15}$ can be interpreted in terms of an ordered H_o sublattice, in support of the above arguments. The latter phenomenon is also the probable reason for the appearance of magnetic LRO in $DyH_{2.14}$ ($x\sim0.2$, in view of $DyH_{1.94}$ as their base) signaled in the Mössbauer experiments.[7]

IV. CONCLUSIONS

High resolution neutron diffraction experiments performed on two β-DyD_{2+x} compositions, with $x=0$ and 0.135, yield additional information with respect to the work of Shaked *et al.*[5] allowing the magnetic structure to be established below $T_2=5.0$ K in the former specimen and the absence of magnetic LRO down to 1.6 K in the latter. The main results are as follows:

(i) The results for the $x=0$ specimen exhibit below $T_2=5.0(2)$ K an incommensurate AF structure, sinusoidally modulated with a propagation vector $\mathbf{k}_2=(0.275, 0.275, 0.750)$ roughly along a [113] axis, which transforms below ~3 K toward a more commensurate AF configuration of $\mathbf{k}_1=(0.258, 0.273, 0.750)$. The latter appears below $T_1=2.5-3.5$ K, following a strongly hysteretic transition. Hence, generally speaking, it is interesting to note, considering that Dy is situated between Tb and Ho in the rare-earth series, that the direction of the spin axis for DyD_2 is closer to that of TbD_2 rather than to HoD_2 as determined by Ref. 5. On the other hand, while the propagation vector $\mathbf{k}_1$ of the commensurate AF phase is for both cases, DyD_2 and TbD_2,[2] parallel to [1/4,1/4,3/4], that of the incommensurate phase, $\mathbf{k}_2$, is close to [1/4,1/4,3/4] in the case of DyD_2 but rather close to [1/8,1/8,3/4] for TbD_2.[2]

(ii) The $x=0.135$ sample lacks any LRO magnetism but exhibits a hump in the region $2\Theta\sim39°$, attributed to SRO magnetic structures disappearing between 4 and 6 K.

Thus, after specifying the magnetic phase diagram of the β-DyH_{2+x} system at low and at intermediate x values, it

seems highly desirable to clarify the situation for high x, where new structures show up caused by different crystal-field symmetries driven by hydrogen sublattice ordering.

In a broader outlook, we should like to emphasize that the general picture proposed by Shaked *et al.*[5] for the four heavy RH_2 hydrides ($R=\mathrm{Tb,Dy,Ho,Er}$), where a more commensurate AF structure is preceded by an incommensurate ''intermediate'' AF configuration, is confirmed by the present results for the cases $R=\mathrm{Tb}$ and Dy, allowing for a partial overlap of the two phases. It remains to specify the incommensurate phases for the systems HoD_2, which seems to be more complex than for the two former,[16] and ErD_2, and to verify the existence of low-temperature commensurate magnetism for the latter. Work along these lines is in progress.

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