

Magnetic structure of β -ErD₂: Long-range and short-range order from powder neutron diffraction

P. Vajda,¹ G. André,² T. J. Udovic,³ R. W. Erwin,³ and Q. Huang³

¹Laboratoire des Solides Irradiés, Ecole Polytechnique, F-91128 Palaiseau, France

²Laboratoire Léon-Brillouin, CEA-Saclay, F-91191 Gif/Yvette, France

³NIST Center for Neutron Research, Gaithersburg, Maryland 20899-8562, USA

(Received 19 October 2004; published 25 February 2005)

Two parallel neutron powder diffraction investigations were performed on different specimens of ErD₂ at the LLB (CEN, Saclay) and at NIST for the determination of its magnetic structure. It comprises, below $T_N=2.23$ K, two coexisting sinusoidally modulated antiferromagnetic (AF) configurations, M' and M'' , with the respective incommensurate propagation vectors, $\mathbf{k}'=(0.275,0.275,0.750)$, together with its third harmonic $3\mathbf{k}'$, and $\mathbf{k}''=(0.120,0.120,0.750)$. Contrary to other heavy rare-earth dideuterides, no commensurate AF configuration could be detected down to 120 mK. On the other hand, similar to earlier observations on HoD₂ and TbD₂, magnetic short-range order (SRO) shows up near 1.5 K in ErD₂ after the disappearance of certain M'' lines. This SRO seems to correlate with the hexagonal γ -phase of the trideuteride and suggests an electronic phase separation with memory effects.

DOI: 10.1103/PhysRevB.71.054419

PACS number(s): 75.30.-m, 75.40.-s, 75.50.Ee

I. INTRODUCTION

β -ErH₂ is the heaviest of the magnetically ordering cubic rare-earth (*R*) dihydrides; TmH₂ is a van Vleck paramagnet with a nonmagnetic ground state and the atypical (orthorhombic) YbH₂ is nonmagnetic because of the divalency of the Yb ion and its filled 4*f* shell. It is also the last where reliable qualitative and quantitative magnetic scattering data down to the lowest temperatures have been lacking. (For a general review of the situation in *R*-H systems up to 1995 see, e.g., Ref. 1.) Magnetic ordering in ErH₂ was first observed by specific heat² and Mössbauer³ measurements at 2.1 to 2.3 K and attributed to antiferromagnetism (AF). An ill-defined nonstoichiometric sample of ErH_{2.08} exhibited a $T_N=2.6$ K in magnetic susceptibility experiments.⁴ This field was then extended to superstoichiometric systems through the whole β -phase range, β -ErH_{2+x} up to its limit of $x_{\max}=0.09$ (Refs. 1 and 5), by susceptibility⁶ and resistivity⁷ measurements showing the striking influence of the excess (*x*) H atoms on octahedral (*O*) sites—the two other H atoms filling ideally the two tetrahedral (*T*) sites of the CaF₂-type cell—and explaining in part the variations in T_N of the earlier results. (The latter work had also revealed metal-semiconductor transitions, for *x*-rich specimens, driven by H-sublattice order/disorder phenomena.) Finally, the excitations due to the crystal electric field were studied by inelastic neutron scattering⁸ and its influence upon the spin-disorder resistivity in the paramagnetic (PM) state by electrical measurements.⁹

The magnetic structure of ErD₂ was investigated, together with an exploratory series of other heavy *R*-dideuterides, in a neutron-powder diffraction (NPD) study down to 1.5 K by Shaked *et al.*¹⁰ They confirmed the transition at $T_N=2.15$ K and attempted to determine the magnetic configurations present. Contrary to three other investigated systems, RD₂, with *R*=Tb, Dy, and Ho, they had not been able to fit the low-temperature spectra of ErD₂ with a unique structure

based on the chemical lattice and, therefore, suggested the simultaneous presence of both commensurate and incommensurate components. It was, thus, essential to pursue the NPD experiments pushing to still lower temperatures in the hope of separating the possibly coexisting and/or overlapping magnetic structures and to determine their configurations, similarly to what we had already done in refined form with TbD₂,¹¹ DyD₂,¹² and HoD₂.¹³ In what follows, we are presenting NPD results obtained with two different specimens of ErD₂ and down to a *T* of 120 mK. We have established the simultaneous presence of two incommensurate magnetic structures below 2.23 K and determined their configurations; no commensurate AF structure as suggested by Shaked *et al.*¹⁰ could be detected above 120 mK. In addition, magnetic short-range order (SRO) stable up to 4 to 5 times T_N is observed and compared with similar phenomena in TbD₂ (Ref. 11) and HoD₂ (Ref. 13). Its significance is discussed in the context of possible electronic phase separation.

II. EXPERIMENT

Two sets of powder specimens were prepared for the work at LLB Saclay on the one hand and at NIST on the other hand. The former used Er of 99.9% metallic purity as starting material, the latter had purer, 99.99% Er as basis. The loading procedure was identical in both cases and has been described earlier, for example, in Ref. 7, absorption of a calibrated volume of D₂ at 600 °C–650 °C to fill the available *T*-sites, with subsequent pumping off eventual excess *O*-site atoms at 400 °C–450 °C. The final LLB sample corresponded to a composition of ErD_{1.93} and contained—as will be seen later—several % of Er₂O₃; the NIST sample was ErD_{1.99}.

The neutron diffraction was performed at LLB (Saclay) at the cold neutron guide of the Orphée reactor (spectrometer G4.1) employing a wavelength of $\lambda=2.425$ Å and taking

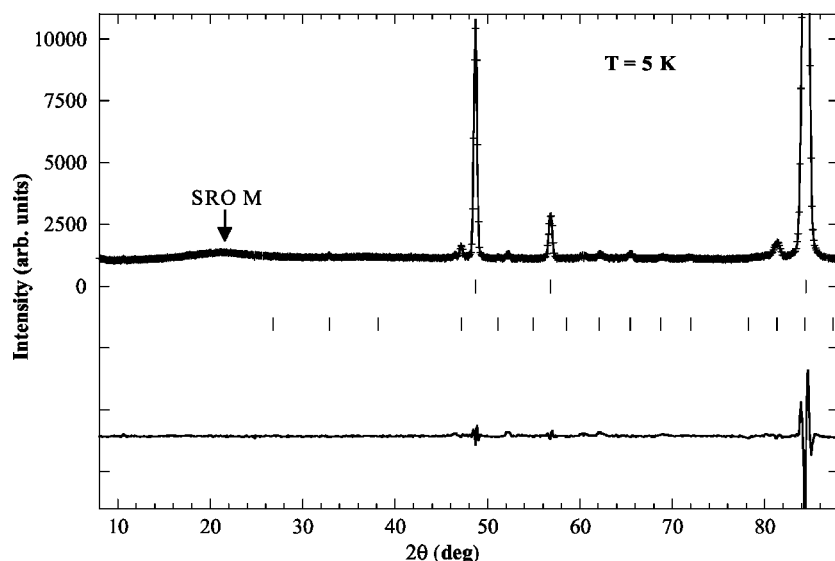


FIG. 1. Neutron powder diffraction spectrum at $T=5$ K of the LLB ErD_2 specimen exhibiting also some nuclear reflections of Er_2O_3 . The ticks indicate a fit with $\text{ErD}_{1.93}$ as main refined structure and 5%–10% Er_2O_3 as additional contribution; the difference between calculated and observed spectra is shown at the bottom. Note the magnetic SRO structure near $2\Theta \sim 21$ deg to be discussed later.

spectra for $8 \leq 2\Theta \leq 88$ deg in 0.1 deg steps, in the T -range 1.4 to 5 K. At NIST, we had used a Cu(311) monochromator at a wavelength $\lambda=1.540$ Å, covering a spectral range of $3 \leq 2\Theta \leq 168$ deg, taking steps of 0.05 deg and working between 0.120 and 3.5 K. The data were analyzed and refined using the Fullprof program¹⁴ at LLB and the GSAS program¹⁵ at NIST.

III. RESULTS

A. Nuclear reflections

The results of the two experiments at LLB and at NIST were identical as concerns the observed ErD_2 line positions on the diffraction spectra when taking into account the difference in wavelengths. However, as mentioned in Sec. II, it was discovered that the LLB sample contained between 5% and 10% of the oxide Er_2O_3 (probably formed during the preparation), which had to be taken care of in the analysis. No oxide lines were visible on the NIST spectra.

Figure 1 presents the NPD spectrum of the LLB sample at $T=5$ K, well above the PM-AF transition temperature of ~ 2.2 K. The exhibited nuclear reflections were fitted with two chemical unit cells, the matching ticks and the difference spectra in the lower part of Fig. 1 indicating satisfactory qualitative agreement. We had used, for ErD_2 , a CaF_2 -type ($Fm3m$) unit cell, with a cell parameter of $a(\text{ErD}_2)=5.116(1)$ Å, yielding a reliability factor $R_N(\text{ErD}_2)=2.93\%$. The oxide reflections were fitted by pattern matching, employing the cubic Ti_2O_3 -type ($Ia3$) cell, with a parameter of $a(\text{Er}_2\text{O}_3)=10.553(3)$ Å. Already now we wish to draw attention towards the broad SRO peak visible around $2\Theta=20$ deg and to which we shall come back later.

B. Magnetic reflections

Figure 2 shows again a spectrum of the LLB sample, this time at the lowest temperature taken, $T=1.42$ K. The accumulated intensity (low background) and the large neutron

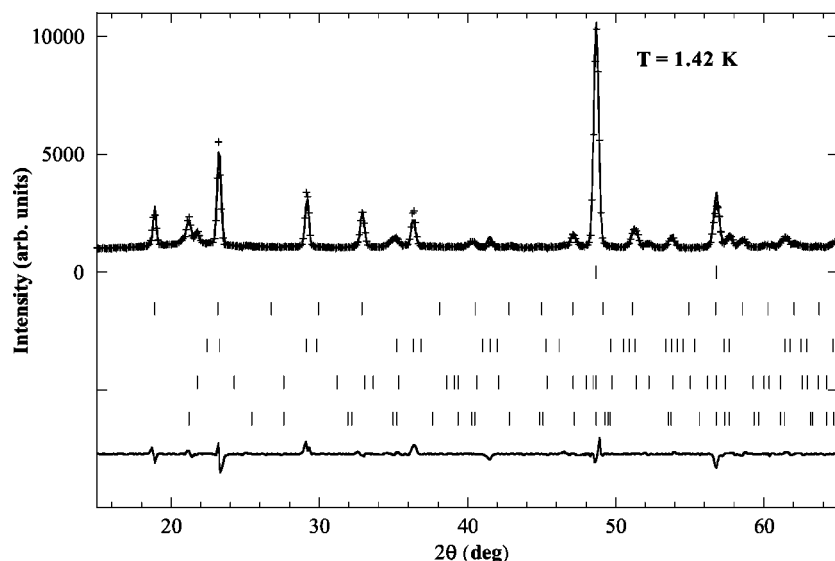


FIG. 2. NPD spectrum at 1.42 K of the LLB ErD_2 specimen exhibiting the nuclear and magnetic reflections of $\text{ErD}_{1.93}$ and Er_2O_3 . The ticks represent the calculated reflections of the following contributions (in decreasing order): $\text{ErD}_2(N)$, $\text{Er}_2\text{O}_3(N+M)$, $\text{ErD}_2(M')$, $\text{ErD}_2(3M')$, $\text{ErD}_2(M'')$ (see text).

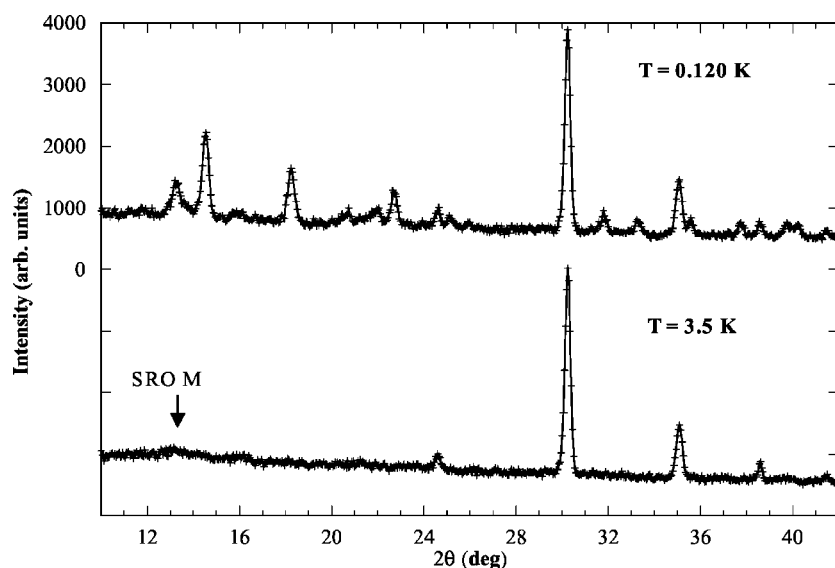


FIG. 3. NPD spectra of the NIST specimen taken at 3.5 K and at 120 mK, showing the same magnetic reflections as the LLB sample of Fig. 2 at 1.42 K. The x axis was expanded by the factor $\lambda_{\text{LLB}}/\lambda_{\text{NIST}}=1.575$, for easier comparison. Note also the magnetic SRO structure near $2\theta \sim 13$ deg in the 3.5 K spectrum to be compared with that of Fig. 1.

wavelength permit a clear separation of the nuclear and the magnetic lines and the corresponding matching. The five series of ticks indicate the nuclear and the magnetic (Bragg) reflections of the erbium dideuteride and the erbium oxide. The magnetic structure of Er₂O₃ was obtained by profile matching and corresponds nicely to the noncollinear AF as determined by Moon *et al.*¹⁶ we shall only consider its contribution to the magnetic intensity and shall show the temperature dependence further on in Fig. 4

The magnetic structure of the erbium dideuteride was best fitted as consisting of two coexisting configurations.

(1) A sinusoidally modulated AF, M' , with a propagation vector $\mathbf{k}'=(0.275,0.275,0.750)$, which is close to a commensurate configuration with $\mathbf{k}=1/4(113)$, with a fourfold larger unit cell than the nuclear matrix. It also contains its third harmonic, $3M'$, squaring up with the propagation vector $3\mathbf{k}'=(0.825,0.825,0.750)$; the reliability factor was $R_{M'}=16\%$.

(2) Another sinusoidally modulated AF, M'' , with a propagation vector $\mathbf{k}''=(0.120,0.120,0.750)$, i.e., close to $1/8(116)$.

Configuration M' corresponds to the higher-temperature, intermediate structure, postulated by Shaked *et al.*¹⁰ and indeed observed and determined by two of the authors of this paper in DyD₂ (Ref. 12) and HoD₂ (Ref. 13) but not in TbD₂. On the other hand, the second configuration, M'' , resembles that of the intermediate structure in TbD₂ determined in Ref. 11 as close to $1/8(116)$, namely $\mathbf{k}=(0.123,0.137,0.754)$. Neither of those, however, corresponded to the searched for configuration which would be *really commensurate* with the quadruple of the chemical cell $(0.250, 0.250, 0.750)$. We had hoped to see it when going to even lower temperatures, to justify the appellation intermediate, such as was the case with TbD₂ (Ref. 11) and HoD₂.¹³ For DyD₂,¹² the intermediate configuration was followed by another at lower T , which was closer to $1/4(113)$ but not quite commensurate yet, namely $(0.258, 0.273, 0.750)$.

The crucial experiment performed at NIST with another ErD₂ specimen down to 120 mK did not show any additional lines nor any significant line shift to represent a commensurate structure. Figure 3 shows the spectra of the NIST sample in the paramagnetic region, at 3.5 K, and that at the lowest temperature taken, $T=120$ mK, selected in an angular region such as to be directly comparable to the interesting range of the LLB spectrum of Fig. 2. Thus, ErD₂ seems to defend its special position in the group of the heavy RD₂'s by refusing to transform its incommensurate magnetism into a commensurate one even as low as 120 mK.

Figure 4 exhibits the temperature dependence of selected magnetic reflections, the $2\theta \sim 23$ deg line representing the most intensive magnetic (113) peak for ErD₂ (M') and $2\theta \sim 33$ deg for Er₂O₃, of the LLB experiment [Fig. 4(a)]; the $2\theta \sim 14.6$ deg line of NIST (corresponding to the $2\theta \sim 23$ deg line of LLB) down to the lowest T [Fig. 4(b)]. We note a final approach towards saturation at 120 mK, with an absolute value for the Er moment, calculated taking into account the contributions of the M' -line intensity and that of the SRO, as $M=(5.5 \text{ to } 6)\mu_B$; close to that observed in the oxide Er₂O₃ by Moon *et al.*¹⁶ The Néel temperature of ErD₂ is $T_N=2.23(1)$ K, for the LLB specimen, slightly bigger than that of NIST, $T_N=2.0(1)$ K, which could indicate minor traces of octahedral x-atoms (less than 1%) in the latter; T_N was shown before to be quite sensitive to the stoichiometry of the sample.⁷ An attempt to fit the data in the form of $M \propto (1-T/T_N)^\beta$ was not very satisfactory and depended on the T -range used; the obtained critical exponent $\beta=0.2$ to 0.4 was closer to the $1/3$ of a 3D Ising model than to the $1/2$ of the mean field one. The data concerning the interesting structural and magnetic results have been collected in Table I. The ordering temperature of the oxide, $T_N(\text{Er}_2\text{O}_3)=3.5(1)$ K, is in agreement with that determined by Moon *et al.*¹⁶ to 3.4 K.

C. Magnetic SRO

As already noted above the spectrum in Fig. 1 contained a broad SRO structure near $2\theta \sim 20$ deg at a temperature well

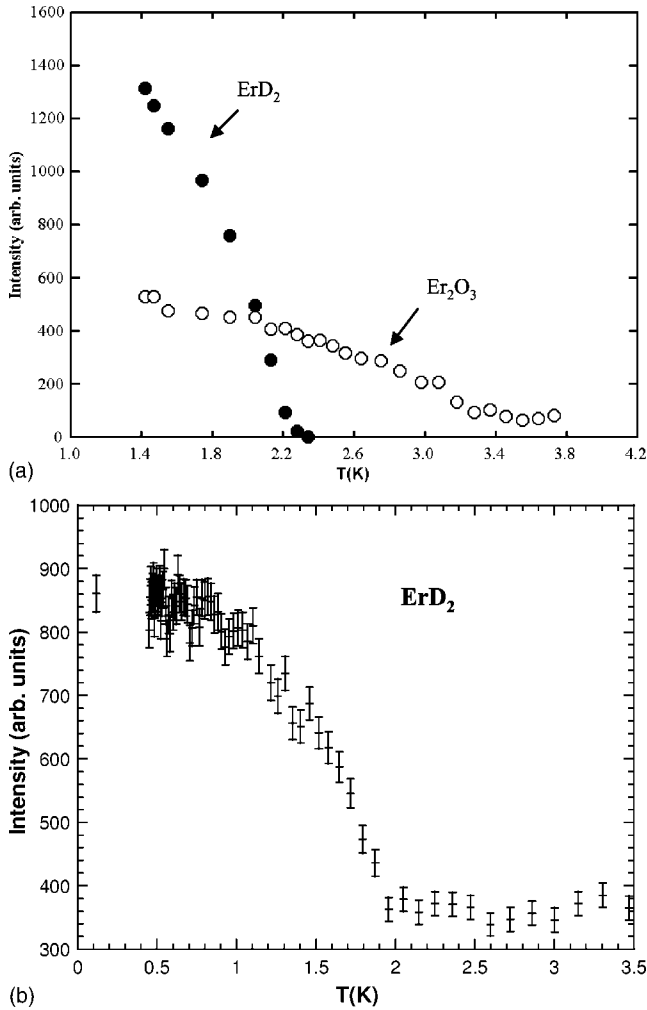


FIG. 4. Temperature dependence of the integrated intensities of several magnetic lines, (a) the (113) $2\Theta \sim 23$ deg line for ErD_2 (filled circles) and the $2\Theta \sim 33$ deg line for Er_2O_3 (empty circles), of the LLB experiment between 1.4 and 4 K; (b) the $2\Theta = 14.6$ deg line from the NIST experiment (corresponding to the $2\Theta \sim 23$ deg line of the LLB) between 0.12 and 3.5 K.

above T_N . We decided to explore this somewhat closer in a wide temperature range, a selected view of which is presented in Fig. 5. Here, we have chosen to represent the spectra as a function of the wave vector, $Q = 2\Theta/\lambda$, to be able to plot the results of both experiments, LLB and NIST, on the same graph, for immediate comparison. A clear bump is visible at $Q \sim 0.95 \text{ \AA}^{-1}$ after the disappearance of the magnetic lines belonging to the configuration M' (mainly at $Q = 0.95 \text{ \AA}^{-1}$); the separation from M'' is less evident, the latter seems rather to transform to SRO around 2 K. A second smaller but still distinct asymmetric bump exists at $Q \sim 1.55 \text{ \AA}^{-1}$, also apparently transforming around 2 K from the complex peak containing M' and M'' lines. The NIST sample (presented as uppermost spectrum in Fig. 5) does not exhibit any SRO at the lowest temperature of 120 mK, but does so at 3.5 K (see Fig. 3), in the same respective spectral region. A comparison with this 120 mK spectrum permits, on the other hand, to note an indication for the presence of a weak SRO background already in the lowest- T LLB spec-

TABLE I. Structural and magnetic parameters obtained for ErD_2 (see text).

$a(\text{\AA})$	$R_N(\%)$	$T_N(\text{K})$	$\mathbf{k}(\text{AF})$	$R_M(\%)$	$M(\mu_B)$
5.116(1)	2.93	2.23	$\mathbf{k}' = (0.275, 0.275, 0.750)$ $\mathbf{k}'' = (0.120, 0.120, 0.750)$	16	5.5–6

trum at 1.4 K. The analysis of the peak width gave a correlation length ξ_M varying with increasing temperature from 50 to 30 $\text{\AA}$, up to $T \approx 10$ K, which is more than four times T_N !

The situation is strikingly reminiscent of the observations made earlier on the system HoD_{2+x} (Ref. 13) where two SRO peaks had shown up, for the pure dideuteride ($x=0$), after the disappearance of the low- T commensurate phase above T_1 (erroneously called T_2 in Ref. 13) and roughly on the same positions; in the case of the superstoichiometric $\text{HoD}_{2.12}$ specimen, the same but much more intense SRO peaks appeared immediately at the lowest T .

We have reconsidered the situation in view of the newly obtained results on ErD_2 and have retreated the temperature dependences of HoD_2 (Ref. 13) and also of TbD_2 from Ref. 11 in the interesting range around T_N , corresponding to T_2 in these papers. When doing this one notes the striking resemblance, mentioned above, between the spectra in Fig. 5 and those of the above systems, not only as concerns the positions of the SRO peaks but also their widths—giving correlation lengths ξ_M decreasing from 55 to 30 $\text{\AA}$ with increasing temperature—and even their asymmetric shape; the existence range of SRO in HoD_2 was determined to be between $T_1 \sim 3$ to 4 K and 40 to 45 K, more than six times $T_N \sim 7$ K. For TbD_2 , the peaks were broader but at the same positions and the existence range shifted to higher T 's like all the other magnetic manifestations (see Ref. 11); the correlation lengths are $\xi_M = 20$ to 15 $\text{\AA}$ between $T_1 \sim 16$ K and > 50 K, three times its T_N of 19 K.

IV. DISCUSSION

A. Magnetic structures

It has already been noted (e.g., Refs. 10 and 13) that great qualitative similarities (but also differences) existed between the four heavy R dihydrides (dideuterides) with $R = \text{Tb}$, Dy , Ho , and Er , in that they all presented sinusoidally modulated configurations with commensurate or incommensurate propagation vectors of the form $\mathbf{k} = (\zeta, \zeta, 1-\zeta)$ or $(\zeta, \zeta, 1-2\zeta)$, such as $1/4(113)$ and $1/8(116)$. [$\text{GdH}(\text{D})_2$ is sinusoidally modulated AF of the MnO -type with $\mathbf{k} = 1/2(111)$ (see Ref. 17) which can, formally, also be represented by $(\zeta, \zeta, 1-\zeta)$ but rather belongs, together with CeD_2 , PrD_2 , and SmD_2 , to the group of the light $\text{RH}(\text{D})_2$ systems.]

This was recognized in theoretical work by Liu¹⁸ who had connected the appearance of the above configurations with special features of Fermi-surface nesting and

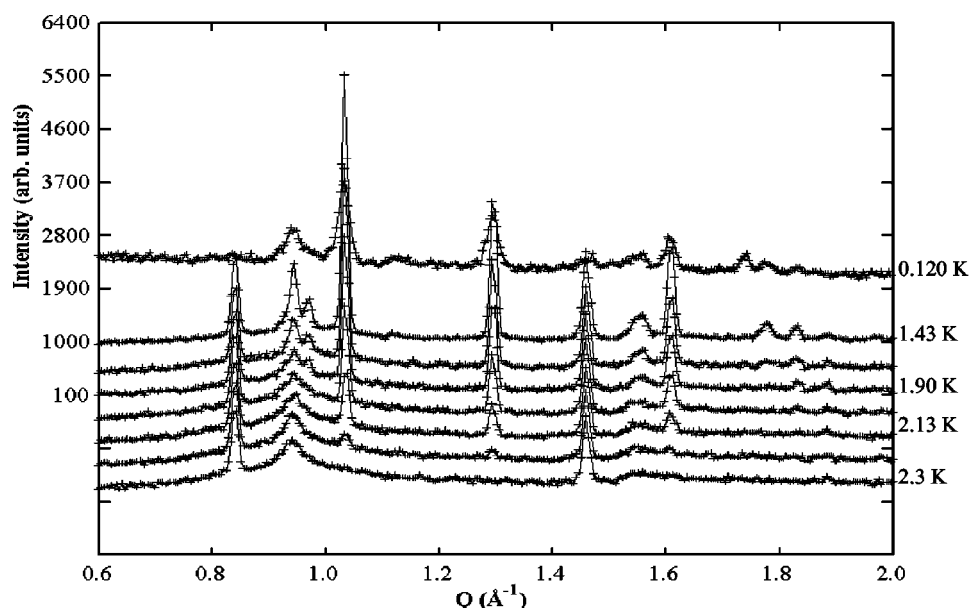


FIG. 5. NPD spectra of the LLB ErD₂ specimen at various temperatures between 1.4 and 2.3 K (in decreasing order) and the superimposed 120 mK spectrum of the NIST specimen, plotted as a function of the wave vector Q , to show the evolution of the SRO structure at $Q \sim 0.95 \text{ \AA}^{-1}$ and $1.55 \text{ \AA}^{-1}$.

reproduced part of the experimental observations such as the low- T commensurate structures. But neither the presence of coexisting or overlapping second intermediate structures nor their eventual incommensuracy have been predicted by theory and are most probably related to the frustrating interference of the RKKY polarization exchange interaction and the crystal electric field.

On the other hand, a formal analysis *via* a group-theoretical approach towards the symmetry of magnetically ordering crystals could be attempted, such as for example, discussed by Izyumov *et al.*¹⁹ There, the authors treat certain modulated phases as possible deviations from a Lifshitz star with wave vector $\mathbf{k}_0$ (by itself corresponding to a special point in the Brillouin zone and, thus, in the Fermi surface), in the form $\mathbf{k} = \mathbf{k}_0 + \delta\mathbf{k}$, which can be applied in our cases to yield

(i) for M' , $\mathbf{k}' = (0.275, 0.275, 0.750) = 1/4(113) + 1/40(110)$ where $\mathbf{k}_0 = 1/4(113)$ and $\delta\mathbf{k} = \mu(110)$ with $\mu = 1/40$;

(ii) for M'' , $\mathbf{k}'' = (0.120, 0.120, 0.750) = 1/4(113) - 13/100(110)$ where $\mathbf{k}_0 = 1/4(113)$ and $\delta\mathbf{k} = \mu(110)$ with $\mu = -13/100$;

The observed deviations from the Lifshitz star $\mathbf{k}_0 = 1/4(113)$, expressed in the form $\mu(110)$, would then represent a quantitative description of the interfering RKKY interaction.

B. Magnetic SRO

The magnetic SRO associated with the spectra in Fig. 5 for ErD₂, as well as with those of TbD₂ (Ref. 11) and HoD₂,¹³ had also been observed in Ref. 13 for the superstoichiometric β -HoD_{2.12}—but with bigger intensity, which had allowed to detect a third SRO structure at higher angles (near $Q \sim 2.9 \text{ \AA}^{-1}$) and, consequently, to attempt their analysis. We were surprised, at that time, not to be able to fit the three magnetic peaks within the cubic

β -dihydride lattice of the matrix but only when using the hexagonal γ -trihydride cell and its parameters. It was suggested in Ref. 13 that we were facing here a kind of memory effect such as observed in martensitic transformations, the more so as there exists an orientation relationship between the fcc β -phase and the hcp γ -phase in the form $[110]//[11\bar{2}0]$ and $(111)/(0001)$, with the parameters $a(\text{fcc})/\sqrt{2} = a(\text{hcp})$.

It was, therefore, quite encouraging that, in the meantime, experiments on switchable mirrors in the system $\text{La}_{1-z}\text{Y}_z\text{H}_x$ performed by van Gogh *et al.*²⁰ permitted to detect the presence of γ -YH₃ nuclei in β -YH₂ and *vice versa*, which could be considered as the origin of the strong hysteresis effects observed in their films. In addition, this could also be the basic mechanism for the electronic phase transformation (phase separation) which exists in the form of metal-semiconductor transitions in several superstoichiometric R -dihydrides near the phase boundary¹ and, more generally, serves to explain the colossal magnetoresistance effects in some magnetic oxides.²¹ In the present case of the magnetic R -hydrides, we apparently observe competing magnetic orderings in the β -phase (producing SRO), with the formation of large local R -moments (varying from site to site in size and orientation but correlated over tens of angstroms) and concomitant crystal field anisotropy. The latter would then be responsible for the described memory effects.

Finally, we wish to mention in this context—and supporting the above ideas—that preliminary results obtained by the authors at NIST on a γ -ErD₃ powder specimen indicate an asymmetric magnetic SRO structure in the spectral range in question, which disappears at $T_N = 590 \text{ mK}$, corresponding nicely to that estimated by Flood, $T_N \sim 0.6 \text{ K}$, from saturation-magnetization measurements.²²

V. CONCLUSIONS

We have determined the magnetic structure of ErD₂ and established that it contains, below $T_N = 2.23 \text{ K}$, two

coexisting sinusoidally modulated AF configurations incommensurate with the chemical lattice, which can be represented by

(1) $M':\mathbf{k}' = (0.275, 0.275, 0.750) = 1/4(113) + 1/40(110)$
and its third harmonic $3M'$ with $(0.825, 0.825, 0.750)$
 $= 3/4(111) + 3/40(110)$;

(2)
 $M'':\mathbf{k}'' = (0.120, 0.120, 0.750) = 1/4(113) - 13/100(110)$

Contrary to expectancy and to other heavy *R*-dideuterides, no

commensurate AF configuration could be detected down to 120 mK.

Magnetic SRO appears in ErD_2 around 1.5 K near $Q \sim 0.95 \text{ \AA}^{-1}$ and $1.55 \text{ \AA}^{-1}$ and is present up to ~ 10 K. It seems to transform out of certain M'' lines and is comparable to the magnetic SRO's observed earlier in HoD_2 and TbD_2 , where it had shown up after the vanishing of the low- T commensurate phases at T_1 . The correlation of this SRO observed in the cubic β -phase to the parameters of the hexagonal γ -phase suggests an electronic phase separation with memory effects.

-
- ¹P. Vajda, "Hydrogen in rare earth metals including RH_{2+x} phases," in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner (North Holland, Amsterdam, 1995), Vol. 20.
- ²J. Opyrchal and Z. Bieganski, *Solid State Commun.* **20**, 261 (1976).
- ³G. K. Shenoy, B. D. Dunlap, D. G. Westlake, and A. E. Dwight, *Phys. Rev. B* **14**, 41 (1976).
- ⁴R. L. Carlin and L. J. Krause, *Phys. Rev. B* **23**, 6149 (1981).
- ⁵T. J. Udovic, Q. Huang, and J. J. Rush, *J. Alloys Compd.* **356/7**, 41 (2003).
- ⁶A. Boukraa, P. Vajda, and J. N. Daou, *J. Magn. Magn. Mater.* **123**, L5 (1993).
- ⁷P. Vajda and J. N. Daou, *Phys. Rev. B* **49**, 3275 (1994).
- ⁸N. Shamir and H. Shaked, *Phys. Rev. B* **22**, 6463 (1980).
- ⁹J. N. Daou, P. Vajda, and J. P. Burger, *Phys. Rev. B* **37**, 5236 (1988).
- ¹⁰H. Shaked, D. G. Westlake, J. Faber, and M. H. Mueller, *Phys. Rev. B* **30**, 328 (1984).
- ¹¹P. Vajda, J. N. Daou, and G. André, *Phys. Rev. B* **48**, 6116 (1993).
- ¹²P. Vajda, G. André, and J. Hammann, *Phys. Rev. B* **55**, 3028 (1997).
- ¹³P. Vajda, G. André, and O. J. Zogal, *Phys. Rev. B* **57**, 5830 (1998).
- ¹⁴J. Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).
- ¹⁵A. C. Larson and R. B. Von Dreele, *General Structure Analysis Systems* (University of California, California, 1985).
- ¹⁶R. M. Moon, W. C. Koehler, H. R. Child, and L. J. Raubenheimer, *Phys. Rev.* **176**, 722 (1968).
- ¹⁷R. R. Arons and J. Schweizer, *J. Appl. Phys.* **53**, 2645 (1982).
- ¹⁸S. H. Liu, *Solid State Commun.* **61**, 89 (1987).
- ¹⁹Yu. A. Izyumov, V. E. Naish, and R. P. Ozerov, *Neutronografiya Magnetikov (Neutron Diffraction of Magnetism)* (Atomizdat, Moscow, 1981), Vol. 2.
- ²⁰A. T. M. van Gogh, D. G. Nagengast, E. S. Kooij, N. J. Koeman, and R. Griessen, *Phys. Rev. Lett.* **85**, 2156 (2000); *Phys. Rev. B* **63**, 195105 (2001).
- ²¹B. Raveau and A. Maignan, *Europhys. News* **34**, 238 (2003).
- ²²D. J. Flood, *J. Appl. Phys.* **49**, 1495 (1978).