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Crystal field and magnetic properties of ErH_2†

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The Mössbauser effect of the 80.6-keV resonance in ^{166}Er has been used to study the magnetic and electronic properties of ErH_2. The onset of magnetic hyperfine splitting shows a magnetic transition occurring at 2.4 ± 0.1 K. The extrapolated saturation hyperfine field is 2480 ± 20 kOe, corresponding to a magnetic moment of $(2.75 \pm 0.08)\mu_B$ on the Er ion in the ordered state. Measurements of the hyperfine splitting in an external magnetic field show that the crystal-field ground state is a Γ_6 Kramers doublet. These data, as well as an analysis of previously published magnetic-susceptibility data, indicate that the first excited crystal-field level is $\gtrsim 150$ K above the ground state. Measurements of the hyperfine spectra of Er as a solute in YH_2 give a Γ_7 ground state, which can arise from a small change in the ratio of fourth-order to sixth-order crystal-field parameters on going from this case to that of ErH_2. All of the above results can be understood on the basis of a "hydridic" (i.e., negatively charged) model for hydrogen in this compound.

INTRODUCTION

The rare-earth metals are known to readily form hydrides, and many studies have been made of these materials.[1] Compositions can be produced over a very wide range, with commensurate changes in physical properties. The dihydrides are known to form in the CaF_2 structure, and the resulting cubic coordination for the rare-earth ion surrounded by eight hydrogen ions is particularly favorable for crystal-field studies, since only two parameters are required to completely determine the crystal-field potential. A number of studies have focused on the crystal-field problem because it can be simply related to another problem of fundamental interest in hydrides: In a given metallic system does the hydrogen ion accept electrons to become negatively charged (the hydridic or anionic model) or does it donate electrons to the conduction band, becoming positively charged (protonic model)? In the following we will consider this question for the case of ErH_2.

In Fig. 1, the crystal-field diagram for Er^{3+} is shown, drawn in the style of Lea, Leask, and Wolf (LLW).[2] The parameters W and x defined by LLW are

$$\begin{aligned} Wx &= A_4\langle r^4\rangle \beta F(4)\,, \\ W(1-|x|) &= A_6\langle r^6\rangle \gamma F(6)\,, \end{aligned} \tag{1}$$

where A_4 and A_6 are crystal-field constants dependent on the system in question, $\langle r^4\rangle$ and $\langle r^6\rangle$ are electronic radial averages, β and γ are Steven's multiplicative factors, and $F(4)$ and $F(6)$ are numerical factors.

On the basis of simple models, one may attempt to calculate A_4 and A_6. A commonly used starting point is to assume that the ions in the material can be approximated by point charges and that only first nearest neighbors are of major importance. While this invariably gives an incorrect answer for the absolute magnitudes of the crystal-field

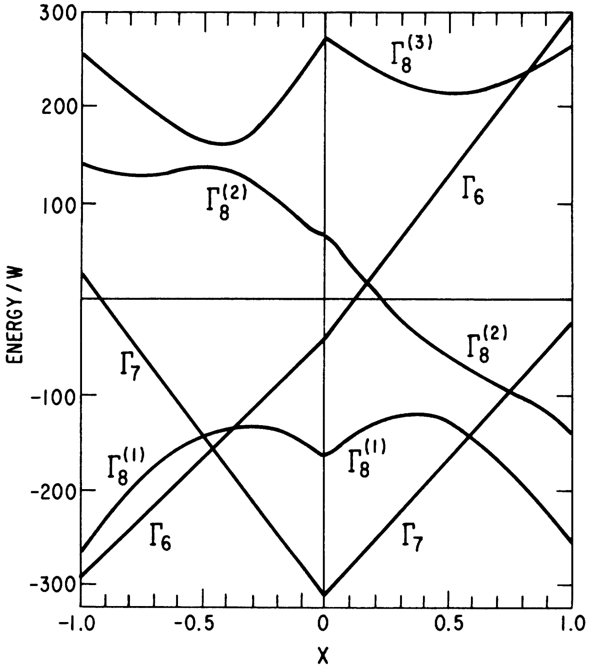

FIG. 1. Crystal-field diagram for Er^{3+} in a cubic environment, following the notation of Ref. 2.

parameters, it generally provides their *signs* correctly and thus allows one to determine in what region of the LLW diagrams (such as Fig. 1) one should concentrate his attention. In fact, for the present problem the sign determination is all that is required. For ErH_2 one can easily show[2] that x should be negative, and that W will be positive for the hydridic model and negative for the protonic model. As one sees from Fig. 1, the former case will yield either a Γ_6 or a Γ_7 ground state, and the latter a $\Gamma_8^{(3)}$ ground state. Hence, a determination merely of the electronic ground state can give the sign of the charge on the hydrogen ions within the framework of this model.

In the following we will present spectra of the Mössbauer effect for ErH_2 obtained from the 80.6-keV resonance in ^{166}Er, taken under varying conditions of temperature and applied external field. These data are interpreted to provide the ordering of the crystal-field states for this compound and, in addition, to show the presence of a cooperative magnetic transition.

EXPERIMENTAL

The source material for the 80.6-keV resonance consisted of 70 mg of natural abundance $Y_{0.61}Ho_{0.39}H_2$ irradiated in a flux of 5×10^{12} neutrons/cm^2 sec for a period of 3 h. The ^{166}Ho so obtained β decays with a mean life of 27 h to ^{166}Er. The above irradiation produced sufficient activity usable for approximately one week. Since the Ho is in a cubic site at the CaF_2 lattice, no quadrupole interactions are seen. Pure HoH_2 undergoes a magnetic transition at ~8 K,[3] which is somewhat lowered by the Y dilution. Nonetheless, at 4.2 K the source gave a linewidth of 10 mm/sec compared to 6.7 mm/sec at 10 K, when measured against a ErH_2 absorber at 4.2 K. While the broadened line at 4.2 K is still very usable, we have kept the source at 10 K whenever feasible.[4]

The hydrides were formed by reaction of either Er metal or the Ho-Y solid solution with purified hydrogen at 500 °C for 3 h. The hydrogen composition was determined both volumetrically and gravimetrically. The Er compound is thus determined to be ErH_{2+x}, where $x \leq 0.02$. Absorbers of this material were made with a thickness of 250 mg/cm^2 of total material. Spectra were obtained at 4.2 K with external fields applied up to 35 kOe, and in zero external field in the temperature range of 1.7–77 K.

DISCUSSION OF RESULTS

The results obtained in this study are relevant to the magnetic state and to the crystal-field ground state of the Er ion. We consider first the magnetic properties. Spectra taken at temperatures of 4.2 and 1.7 K are shown in Fig. 2. At the lower temperature, the spectrum consists of a five-line pattern typical of hyperfine splitting due to magnetic ordering. The magnetic transition temperature has been obtained by measuring the linewidth of the spectrum as the sample is cooled through the transition. In this way one obtains an ordering temperature of 2.4 ± 0.1 K. Using the measured hyperfine field of 2130 ± 20 kOe at 1.7 K and the measured transition temperature, and assuming a $J=\frac{1}{2}$ molecular-field dependence (see discussion below), we obtained a saturation hyperfine field of 2480 ± 75 kOe. From the calculated free-ion hyperfine field of 8100 kOe,[5] the free-ion electronic moment of $9\mu_B$, and an assumption of linearity between the hyperfine field and moment, we obtain a saturation magnetic moment of $(2.75 \pm 0.08)\mu_B$ for ErH_2 in the magnetically ordered state.

In order to obtain information on the crystal-field ordering, hyperfine spectra have been measured to provide the hyperfine field (and hence the electronic moment) as a function of external field. In essence, this provides a microscopic magnetization measurement, and we have previously shown the utility of such measurements for obtaining crystal-field parameters in Yb systems.[6] Typical results are shown in Fig. 3. The experimental arrangement is such that the γ ray is observed along the external field axis. If the ionic moment is well aligned along this direction, then the pure two-line

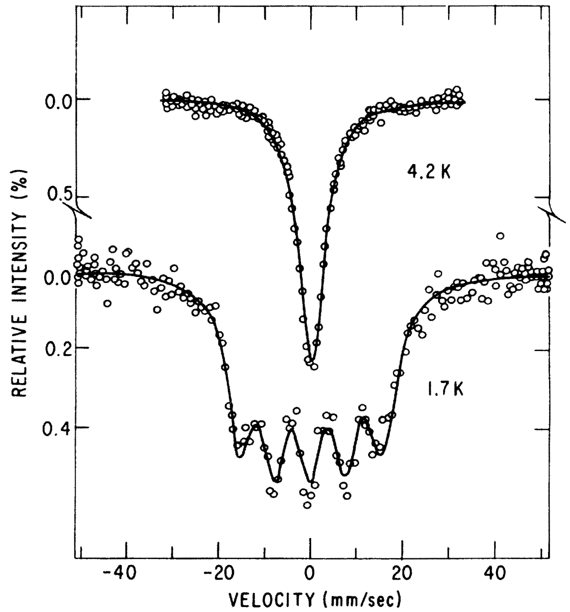

FIG. 2. Hyperfine spectra for ^{166}Er in ErH_2 at 4.2 and 1.7 K, with no external field.

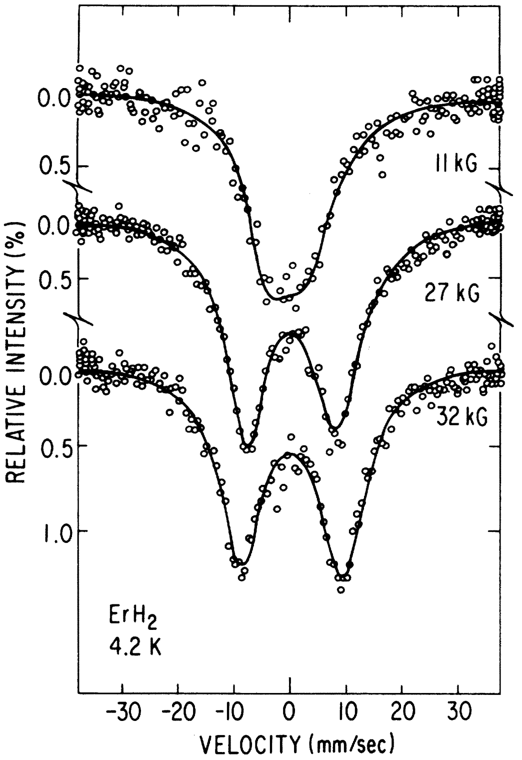

FIG. 3. Hyperfine spectra for ^{166}Er in ErH_2 at 4.2 K as a function of external field.

pattern (corresponding to transitions $\Delta I_z = \pm 1$) seen in the figure is anticipated.

From Fig. 1 and the discussion in the introduction, we see that Er in ErH_2 may have as a ground state either a Γ_6 or Γ_7 Kramers doublet, or a $\Gamma_8^{(3)}$ quartet. In the case in which the ground state is a doublet well separated from the first excited state, the hyperfine field (H_{hf}) will depend on the external field H_{ext} according to

$$H_{hf} = H_{sat} \tanh(g\mu_B S H_{ext}/kT)\,, \qquad (2)$$

where $H_{sat} = \frac{1}{18} g H_{free\ ion}$, $H_{free\ ion}$ being 8100 kOe, and $S = \frac{1}{2}$ for the Γ_6 or the Γ_7 ground states. For the Γ_6 state $g = -6$ and hence $H_{sat} = 2700$ kOe, and for the Γ_7 state $g = \frac{34}{5}$ and $H_{sat} = 3100$ kOe. The dependence given by Eq. (2) is shown by the solid lines in Fig. 4 labeled Γ_6 and Γ_7. If the ground state is anisotropic, Eq. (2) is not applicable. Thus if the anisotropic $\Gamma_8^{(3)}$ state is the lowest, the value of the hyperfine field will depend on the direction of the external field relative to the crystal axes. For a powder sample, this will result in some line broadening and some extra intensities, as was seen in the Yb cases.[6,7] However, the limiting possibilities can be calculated and this is indicated by the shaded region labeled Γ_8 in Fig. 4. If the crystal-field splittings are very small compared to the electronic Zeeman energy, the hyperfine field is given by the Brillouin function

$$H_{hf} = H_{free\ ion} B_{15/2}(9\mu_B H_{ext}/kT) \qquad (3)$$

shown by the line labeled "free ion" in the Fig. 4. If the crystal-field and Zeeman energies are comparable, the hyperfine field will show some intermediate value between the Γ_6 and free-ion limits, depending on the details of level ordering and splitting.

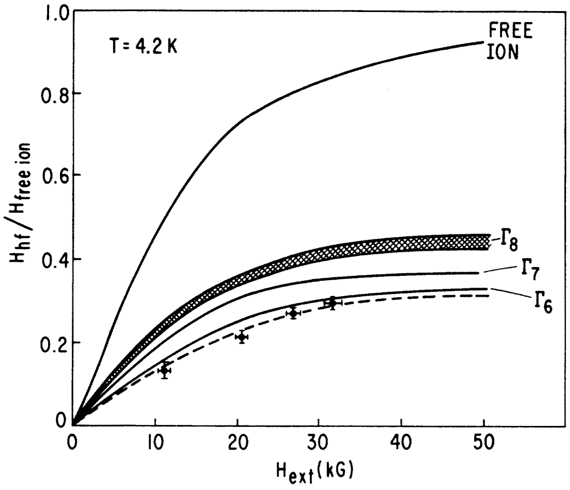

FIG. 4. Dependences of the hyperfine field on external field for various assumed crystal-field states are shown by the solid lines. Data obtained for ErH_2 are shown by the dots.

The data obtained from the spectra of Fig. 3 are shown by the solid points in Fig. 4. The results strongly indicate that the ground state is a well-isolated Γ_6 doublet. The small discrepancy seen may be due either to (i) a small exchange field which will, in effect, shift the abscissa of the figure, or (ii) a negative contribution to the hyperfine field arising from conduction-electron polarization, which will merely change the value of H_{sat} in Eq. (2). It should be noted that no admixtures of other crystal-field levels can cause H_{ext} to lie *below* the Γ_6 curve. The first possibility seems unlikely since at 4.2 K we have a reduced temperature of $T/T_c = 1.75$ where one ordinarily expects exchange effects to be negligible. We have assumed that the conduction-electron mechanism is predominant, and the dashed line in Fig. 4 shows Eq. (2) with a value of $H_{sat} = 2500$ kOe. This corresponds to a negative contribution of -200 kOe to the hyperfine field from this effect. Such a value is comparable, for example, to the value arising from polarization by the local ions in the metal[8] of +190 kOe, the change of sign reflecting the fact that Eu is in the first half-shell where the spin S

causing the exchange-induced polarization is oppositely aligned to the total angular momentum J, while Er is in the second half-shell where S is parallel to J. It is also interesting to note that the saturation value obtained by applied field in the paramagnetic state is equal to that obtained in the ordered state. Since the ordered state is probably antiferromagnetic, while saturation in the paramagnetic state corresponds to ferromagnetic alignment, one would anticipate that contributions to the hyperfine field arising from conduction-electron polarization due to neighboring ions would be different for the two cases. The similarity of the two hyperfine fields indicates that such effects are small.

In a more qualitative sense, the general form of the spectra of Fig. 3 shows that the ground state is a well-isolated doublet. As mentioned above, the presence of a Γ_8 component in the ground state can lead to severe line broadenings. In addition, the anisotropy of the Γ_8 state can result in the moment not being fully aligned along the external field, which will be seen as nonzero intensities in the transitions corresponding to $\Delta I_z = 0, \pm 2$. Both of these effects were observed previously in some Yb systems,[6,7] but are not seen here. As a result we may conclude not only that the ground state is a doublet, but also that the crystal-field splitting is sufficiently large that the excited $\Gamma_8^{(1)}$ level (see Fig. 1) is not significantly admixed by the external fields used here. Detailed considerations of this kind allow us to place a lower bound of ~150 K on the separation between the ground state and the first excited state.

Another estimate for crystal-field splitting can be obtained from the published susceptibility,[9] shown in Fig. 5. The dashed line shows the free-ion behavior in the absence of crystal-field and magnetic exchange effects, and is clearly a poor representation of the data. We have calculated the susceptibility including crystal-field effects in a manner previously described,[10] and including exchange effects in a molecular-field approximation. The solid curve shown in Fig. 5 corresponds to $W = 2.5$ and $x = -0.85$. From Fig. 1, this gives a Γ_6 ground state and a $\Gamma_6 - \Gamma_8^{(1)}$ splitting of roughly 125 K. While this is in satisfying agreement with the above estimate, neither approach should be considered to do more than give an estimate of the absolute magnitude of the crystal-field interactions. What is clear from this estimate, however, is that the crystal-field splittings are rather large for this conducting Er system.

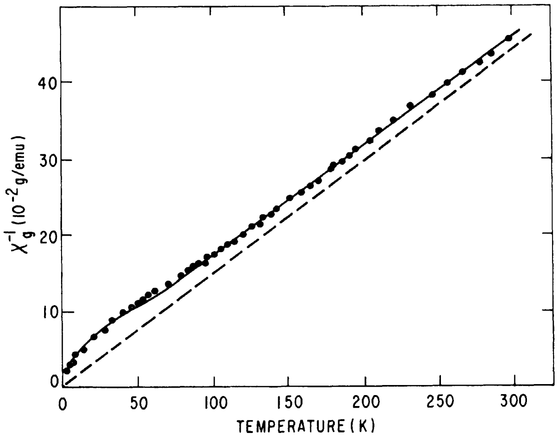

FIG. 5. Magnetic susceptibility for ErH_2. The data are from Ref. 9, the dashed line shows free-ion behavior, and the solid line is calculated including crystal-field and molecular-field effects.

In addition to the compound ErH_2, we have also investigated Er as a solute in YH_2. This was obtained by preparing a sample of 2000-ppm Ho in YH_2, irradiating to produce ^{166}Ho, and studying the hyperfine spectra of the resulting source material. Data are shown in Fig. 6. In this case, the severe dilution with a nonmagnetic species reduces the spin-spin relaxation time sufficiently that one sees a spectrum corresponding to the slow-relaxation limit of a Γ_7 ground state.[11] This is in agreement with the work of Stöhr and Cashion,[4] but is in disagreement with the Γ_6 ground state found above for ErH_2. The most likely explanation of this is that one has in these materials $x \approx -0.5$ (see Fig. 1), which is near the point where Γ_6 and Γ_7 cross one another. The change from a Γ_6 to a Γ_7 ground state then represents only a

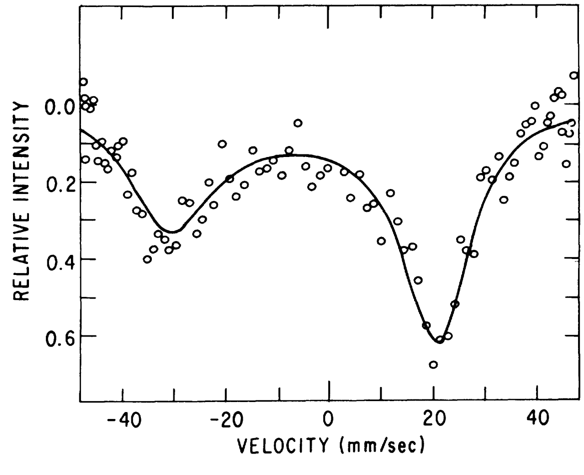

FIG. 6. Hyperfine spectrum for a source of 2000-ppm Ho in YH_2 with an ErH_2 absorber at 4.2 K.

TABLE I. Crystal-field ground state anticipated on the basis of a first-nearest-neighbor point-charge model for the rare-earth dihydrides. Both hydridic and protonic hydrogen are considered, and the known experimental results are shown.

	Calculated			
	Hydridic hydrogen	Protonic hydrogen	Experimental	Reference
CeH_2	Γ_7	Γ_8	Γ_7	12
PrH_2	Γ_1 $(x<0.52)$ Γ_5 $(x>0.52)$	Γ_3 $(x<0.85)$ Γ_1 $(x>0.85)$	Γ_5	12, 13
NdH_2	$\Gamma_8^{(2)}$	Γ_6	$\Gamma_8^{(1)}$ or $\Gamma_8^{(2)}$	12, 14, 15
PmH_2	Γ_1	Γ_5 $(x<-0.81)$ Γ_3 $(x>-0.81)$		
SmH_2	Γ_8	Γ_7		
TbH_2	Γ_2 $(x<0.81)$ Γ_3 $(x>0.81)$	$\Gamma_5^{(1)}$ $(x<0.58)$ Γ_1 $(x>0.58)$	Γ_1, Γ_2, or Γ_3	4
DyH_2	Γ_7 $(x<0.58)$ $\Gamma_8^{(1)}$ $(x>0.58)$	$\Gamma_8^{(3)}$ $(x<0.83)$ Γ_6 $(x>0.83)$	Γ_7	4
HoH_2	$\Gamma_5^{(2)}$ $(x<-0.54)$ $\Gamma_3^{(2)}$ $(x>-0.54)$	Γ_1 $(x<-0.46)$ $\Gamma_5^{(1)}$ $(x>-0.46)$		
ErH_2	Γ_6 $(x<-0.46)$ Γ_7 $(x>-0.46)$	$\Gamma_8^{(3)}$	Γ_6	Present work
TmH_2	Γ_2 $(x<0.81)$ Γ_3 $(x>0.81)$	$\Gamma_5^{(1)}$ $(x<0.58)$ Γ_1 $(x>0.58)$		

small change in the ratio of fourth-order to sixth-order cyrstal-field parameters obtained as one goes from ErH_2 to a dilute substitutional solid solution of Er in YH_2.

By way of summary, we present in Table I the anticipated crystal-field ground states on the basis of a nearest-neighbor point-charge calculation for all the rare-earth dihydrides, assuming both hydridic and protonic hydrogen. From the experimental results, it is clearly seen that hydrogen has to be hydridic (negatively charged) in order to understand the several results.

CONCLUSIONS

An investigation has been made of the crystal-field and magnetic properties of ErH_2. The material is found to undergo a magnetic transition at 2.4 ± 0.1 K. The crystal-field ground state is found to be a Γ_6 Kramers doublet, in agreement with that anticipated for a hydridic model.

ACKNOWLEDGMENT

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