PHYSICAL REVIEW B VOLUME 55, NUMBER 22 1 JUNE 1997-II

^{57}Fe Mössbauer investigations on $(Er,Pr)_2(Fe,Al)_{17}$ compounds and their nitrides

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(Received 4 September 1996; revised manuscript received 6 January 1997)

^{57}Fe Mössbauer studies have been carried out on $(Er_{1-x}Pr_x)_2Fe_{17}$ compounds [$x=0$, 0.4, 0.6, 1.0], $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$ [$x=0,1,2,3,5,6,8,10$] and their nitrides, both in the ferromagnetic and in the paramagnetic phases. Individual hyperfine parameters corresponding to the four crystallographically inequivalent Fe sites have been obtained by analyzing the Mössbauer spectra. The easy magnetization direction, which lies in the basal plane for $(Er_{1-x}P_x)_2Fe_{17}$ compounds, changes to the axial direction at 18 K, on nitrogenation, which may be due to the increase in the rare-earth sublattice anisotropy. There is an increase in the hyperfine fields at all Fe sites on nitrogenation and the maximum increase in the weighted average hyperfine field is about 40 kOe, which is explained on the basis of $3d$ band narrowing. The isomer shifts are also found to increase with increasing nitrogen content, which may be due to the reduction in the s-electron density at the nucleus as a result of lattice expansion and the chemical effect. Mössbauer studies carried out on $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$ compounds show that there is a decrease in the hyperfine fields at various Fe sites with an increase of Al concentration. This may be due to the reduction in the Fe magnetic moment as well as the magnetic dilution, as a consequence of Al substitution. The isomer shift is found to increase with an increase in Al concentration, which is due to the reduction in the s-electron density at the nucleus, owing to the charge transfer from Al to Fe. In both series of compounds, the weighted average hyperfine fields follow a T^2 behavior, which is indicative of the role of single-particle excitations in reducing the $3d$ sublattice magnetization with an increase in temperature. [S0163-1829(97)02722-7]

I. INTRODUCTION

Recently, we have investigated the magnetic and electrical properties of $(Er_{1-x}P_x)_2Fe_{17}$ and their nitrides.[1,2] It has been found that there is an increase in the magnetization and Curie temperature on nitrogenation. It has also been observed there is a spin reorientation transition at low temperatures in the nitrides of these compounds. To investigate the effect of substitution of a nonmagnetic element such as Al for Fe, we have chosen a composition, viz. $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$ and studied the structural, magnetic, and electrical properties.[3,4] It has been found that there is a reduction in the magnetization with an increase in Al concentration. In order to find out the individual hyperfine parameters, their temperature dependences, and the changes on nitrogenation and Al substitution, we have carried out ^{57}Fe Mössbauer studies on the above-mentioned series of compounds and the results are presented in this paper.

II. EXPERIMENTAL DETAILS

The method of preparation of the parent compounds as well as their nitrides has been reported earlier.[1] The spectra were recorded using a CMTE Mössbauer spectrometer in the constant acceleration mode. The γ-ray source was 20 mCi ^{57}Co embedded in Rh matrix. The spectrometer was calibrated with α-Fe at room temperature. The Mössbauer absorbers were prepared by smearing approximately 30 mg of the powdered sample over an area of 1.5×0.8 cm^2. The temperature variation studies were carried out in the range 18–500 K. In the temperature range 18–300 K, the spectra were recorded with the help of a closed-cycle helium refrigerator, which is interfaced with the Mössbauer spectrometer.[5] The sample chamber was filled with helium gas at a pressure of 1 atm. The temperature of the sample was monitored using a carbon glass resistor as temperature sensor. At high temperatures, the spectra were recorded with the help of an oven assembly fitted with beryllium windows. The sample chamber was evacuated continuously to a vacuum of 10^{-5} torr to prevent the oxidation of the sample. The samples were mixed with boron nitride powder to make isotropic absorbers and sandwiched between two beryllium foils. A chromel-alumel thermocouple was used to measure the sample temperature.

III. RESULTS

Figure 1 shows the Mössbauer spectra recorded at various temperatures for Er_2Fe_{17}. Similar spectra have been obtained for the compounds with $x=0.4$, 0.6, and 1.0 and their nitrides. Figure 2 shows the spectra recorded for $(Er_{0.5}Pr_{0.5})_2Fe_{16}Al$, at various temperatures. Similar spectra have been obtained for compounds containing other Al concentrations as well as their nitrides.

IV. ANALYSIS OF THE SPECTRA

The analysis of these spectra has been performed using the PCMOS least-squares fitting program, taking into account the following factors. R_2Fe_{17} compounds crystallize in two related crystal structures according to whether the rare earth is lighter or heavier. The compounds containing light rare earths crystallize in the rhombohedral Th_2Zn_{17} structure, whereas, those containing heavy rare earths crystallize in the hexagonal Th_2Ni_{17} structure. There are four crystallographically inequivalent sites for Fe in both the unit cells and there-

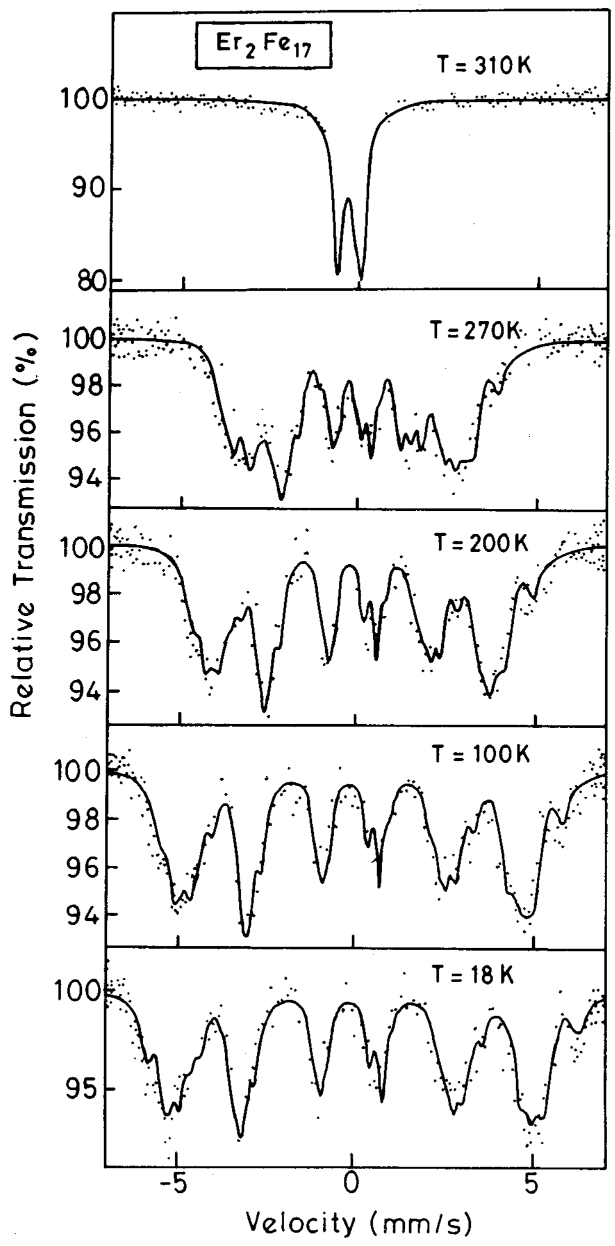

FIG. 1. Mössbauer spectra of Er_2Fe_{17} at various temperatures.

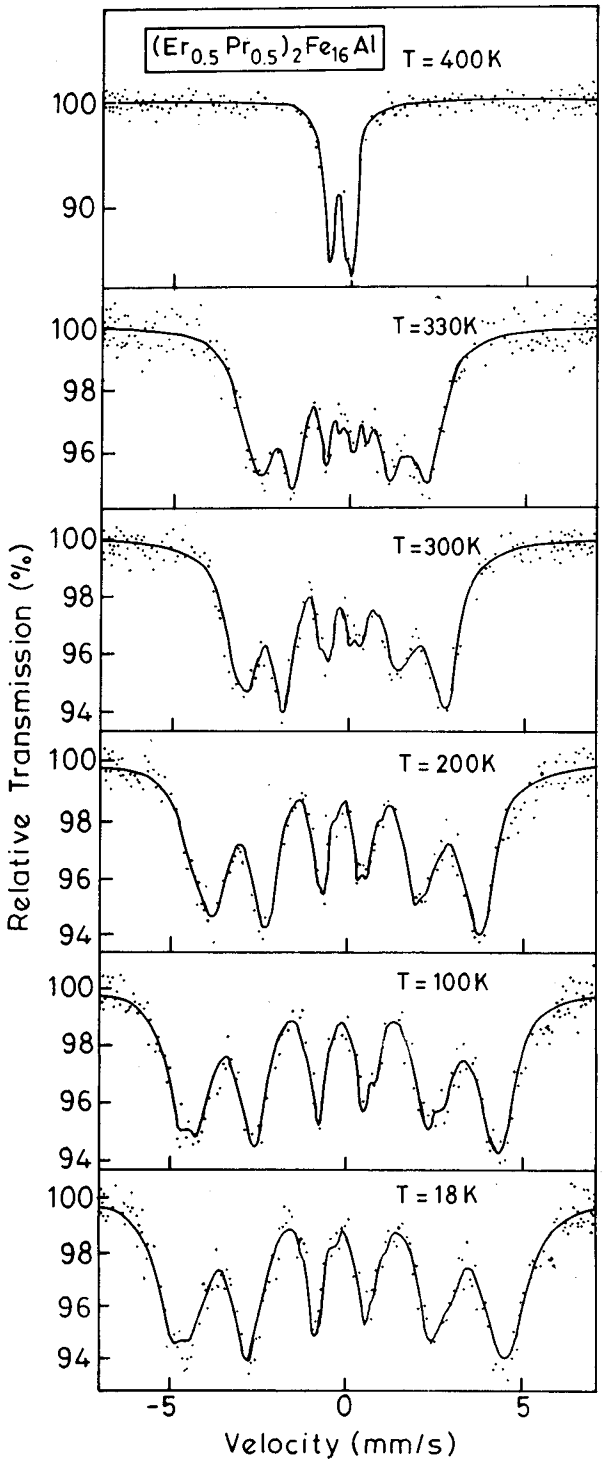

FIG. 2. Mössbauer spectra of $(Er_{0.5}Pr_{0.5})_2Fe_{16}Al$ at various temperatures.

fore, the Mössbauer spectra of these compounds are quite complex. The different Fe sites in the rhombohedral and the hexagonal (given in brackets) unit cells are designated as $6c(4f)$, $9d(6g)$, $18f(12j)$, and $18h(12k)$. Out of these four sites, at the $6c(4f)$ site, the angle between the hyperfine field and the electric-field-gradient tensor is zero. For the other three sites, this angle is zero, only if the total anisotropy is uniaxial. Therefore, there will be a total of four spectra with the relative intensities 6(4):9(6):18(12):18(12), if the total anisotropy is uniaxial. On the other hand, if the total anisotropy is planar, for the latter three Fe sites, the angle between the hyperfine field and the electric-field gradient will be nonzero and therefore, these three Fe sites will split into two magnetically inequivalent sites. This would give rise to the splitting of the spectrum corresponding to each of these three sites into two, with an intensity ratio 2:1, thereby resulting in a total number of seven subspectra with the intensity ratio 6(4):6(4):3(2):12(8):6(4):12(8):6(4). In addition, there will be traces of α-Fe, for which another sextet has to be incorporated to get a reliable fit.[6] In the fitting procedure adopted in the present study, since there are a large number of sextets, some constraints have to be adopted. As the sample is in the form of random powder, the intensities of the six absorption lines of each of the sextets were assumed to obey the 3:2:1 intensity relationship.[7] The isomer shifts for the magnetically inequivalent sites were constrained to be the same. One common linewidth was assumed for all the seven sextets. The recording time depends on the amount of

TABLE I. Magnetic hyperfine fields (in kOe) and the weighted average values at different Fe sites for the $(Er_{1-x}Pr_x)_2Fe_{17}N_y$ compounds with different values at 18 K. Maximum error: ±4 kOe.

		$(Er_{1-x}Pr_x)_2Fe_{17}N_y$ Hyperfine fields (kOe)				
x	y	$6c(4f)$	$9d(6g)$	$18f(12j)$	$18h(12k)$	Wt. avg.
0	0	373	328	317	295	318
	2.6	416	384	341	337	356
0.4	0	360	314	304	289	307
	2.7	398	365	337	333	347
0.6	0	361	313	308	284	307
	2.6	379	366	331	329	342
1.0	0	365	303	308	287	306
	2.8	378	353	334	328	340

Fe content in the sample. In the present case, the minimum recording time was around 15 h and the maximum around 50 h. The reliability of the fits have been given by the χ^2, whose maximum value in the present study was around 2, as reported in the case of similar compounds having complex spectra by Qi *et al.*[8]

The analysis of the spectra in the case of $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$ compounds have been performed by employing a slightly different method, as compared to the method used in the case of $(Er_{1-x}Pr_x)_2Fe_{17}N_y$ compounds. It has been reported by neutron-diffraction studies on several $R_2Fe_{17-x}Al_x$ compounds that Al does not occupy Fe sites randomly. On the other hand, there is a preferential occupancy of different Fe sites, depending on the Al content. Long *et al.*[9] have carried out neutron-diffraction studies on $Nd_2Fe_{17-x}Al_x$ compounds and found the site occupancies of Al in the lattice. It has also been reported that the site occupancy is independent of the type of rare earth.[10] Based on these facts, we have assumed the same site occupancies for Al in $(Er_{0.5}Pr_{0.5})_2Fe_{17-x}Al_x$ compounds as well. Using this, we have calculated the area under each individual spectrum corresponding to the different Fe sites and fitted the spectra.

V. DISCUSSION

$(Er_{1-x}Pr_x)_2Fe_{17}$ compounds with $x=0$ and 0.4 possess hexagonal Th_2Ni_{17} structure, whereas those with $x=0.6$ and 1, possess the rhombohedral Th_2Zn_{17} structure. The Curie temperatures of these compounds vary in the range 305–285 K.[1] Table I gives the hyperfine fields at various Fe sites at 18 K for all the compounds in this series. The hyperfine fields at various Fe sites follow the order $H_{hf}[6c(4f)] > H_{hf}[9d(6g)] > H_{hf}[18f(12j)] > H_{hf}[18h(12k)]$. The number of Fe near neighbors for $6c(4f)$, $9d(6g)$, $18f(12j)$, and $18h(12k)$ are 13, 10, 10, and 9, respectively. It is obvious that $6c(4f)$ site has the maximum hyperfine field, since it has the maximum number of Fe nearest neighbors, whereas, the $18h(12k)$ site has the minimum number of Fe neighbors and consequently the least hyperfine field. $9d(6g)$ and $18f(12j)$ sites have the same number of Fe neighbors, but the former has comparatively smaller Fe-Fe distances and hence a larger hyperfine field.[6] It can be seen from Table I that there is a reduction in the weighted average hyperfine field as the Pr content in the sample increases. This may be due to the following reason. The hyperfine field originates mainly from the Fermi contact term. This arises because of the imbalance in the spin-up and spin-down densities of states at the nucleus, as a result of the polarization of the core *s* electrons and the conduction electrons, by the magnetic *d* electrons. The reduction in the hyperfine field with increase in Pr content may be a consequence of the fact that Pr has less $4f$ electrons as compared with Er. Therefore, the $3d$-$4f$ coupling will become smaller as Pr content increases, which will give rise to a reduction in the Fermi contact term.[11]

In the case of the Mössbauer spectra at 18 K for $(Er_{1-x}Pr_x)_2Fe_{17}N_y$ compounds with $x \leqslant 0.8$, the spectra could be fitted to four sextets, implying that these nitrides possess axial anisotropy. Table I gives the magnetic hyperfine fields at various Fe sites for all the nitrides at 18 K. The spectra at higher temperatures have been fitted to seven sextets, which indicates that the anisotropy is planar. It can be seen that the hyperfine fields at the four sites vary in the same way as in the parent compounds, with the $6c(4f)$ site having the maximum and the $18h(12k)$ site having the minimum hyperfine fields. In the case of the nitrides too, the weighted average hyperfine fields decrease as Pr content increases, which may be due to the smaller contribution from the $3d$-$4f$ overlap to the Fermi contact term.

It can be seen from the Table I that there is an increase in the hyperfine fields at all Fe sites on nitrogenation. In particular, the increase is very pronounced in the case of $9d(6g)$ and $18h(12k)$ sites. The Fe-N distances are on the order of $d_{\text{Fe-N}}[18h(12k)] < d_{\text{Fe-N}}[18f(12j)] < d_{\text{Fe-N}}[9d(6g)] < d_{\text{Fe-N}}[6c(4f)]$.[12] There are two effects occurring in these compounds on nitrogenation. They are the magnetovolume effect and the chemical effect. The former will cause an increase in the magnetic moment as a result of lattice expansion and a consequent $3d$-band narrowing. The latter effect is due to the differences in the electronegativities of Fe and N and causes transfer of charges from the *s* and *p* bands of N to the $3d$ band of nearest Fe. This gives rise to a reduction in the magnetic moment. However, the latter effect is significant only at $18f(12j)$ and $18h(12k)$ sites, where the Fe-N distances are the least. But the magnetovolume effect is predominant at all sites and hence there is an increase in the magnetic moment at all sites. The increase in the hyperfine field is the smallest at the $6c(4f)$ site. This is

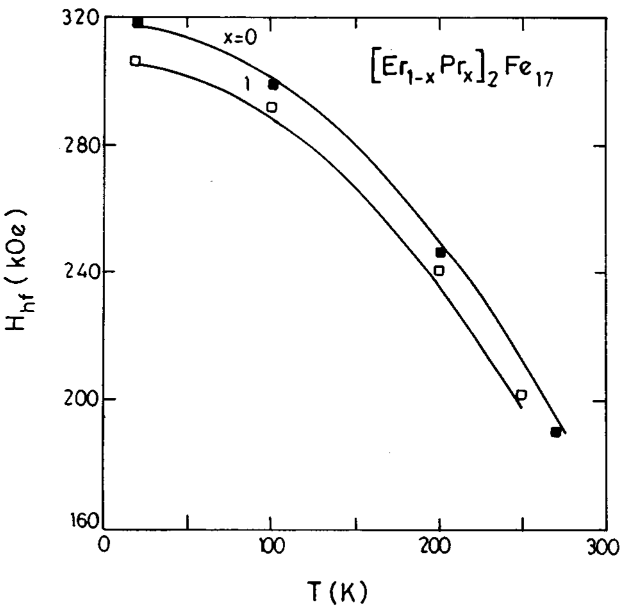

FIG. 3. Temperature variation of the weighted average hyperfine fields fitted to the equation $H_{\mathrm{hf}}(T)=H_{\mathrm{hf}}(0)\{1-b(T/T_C)^2\}$ for $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}$ compounds with $x=0$ and 1.0.

because the Fe-N distance is the largest at this site and therefore, the effect of N is correspondingly smaller. This is in accordance with the band-structure calculations carried out by Gu *et al.*[12] on similar $R_2\mathrm{Fe}_{17}$ compounds and their nitrides. It has been shown that the projected density of states for the $6c(4f)$ site in the nitride is almost identical to that of the parent compound, which explains the very small increase in the hyperfine field. The differences in the amounts of increase in the hyperfine fields at various Fe sites is due to the differences in the configuration of nearest-neighbor N atoms for the various sites. A similar increase has been observed in the case of $\mathrm{Nd}_2\mathrm{Fe}_{17}\mathrm{N}_y$ compounds.[13]

The increase in the hyperfine field implies that there is an increase in the Fe magnetic moment. The increase is due to the magnetovolume effect present in $R_2\mathrm{Fe}_{17}$ compounds. Iron-rich compounds are classified as weak ferromagnets as, both the spin-up and spin-down subbands are unsaturated. Because of this reason, the densities of states at the Fermi level are large and according to Coehoorn,[14] the volume dependence on the magnetic moment is also high. Nitrogenation of these compounds is followed by lattice expansion and as a consequence of this, the Fe-Fe distance increases and hence the $3d$ band gets narrowed. Heine[15] has calculated that in transition-metal-rich compounds, the width of the $3d$ band is inversely proportional to the fifth power of the lattice parameter. The narrowing of the $3d$ band results in more localization of the $3d$ electrons and a concomitant moment enhancement. Dong, Yang, and Yang[16] have observed that there is an increase in the magnetic moment in $R\mathrm{TiFe}_{11}$ compounds on nitrogenation, which is also attributed to the band narrowing effect.

Figure 3 shows the temperature variation of the weighted average hyperfine field for the $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}$ compounds fitted to the equation

$$H_{\mathrm{hf}}(T)=H_{\mathrm{hf}}(0)\left\{1-b\left(\frac{T}{T_C}\right)^2\right\}. \tag{1}$$

TABLE II. Isomer shifts (in mm/s) at various Fe sites in the $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$ compounds at 18 K. (Isomer shifts are calculated with respect to that of α-Fe at room temperature.) Maximum error: ±0.03 mm/s.

		$(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$ Isomer shifts (mm/s)			
x	y	$6c(4f)$	$9d(6g)$	$18f(12j)$	$18h(12k)$
0	0	0.30	−0.04	0.12	0.10
	2.6	0.32	0.12	0.23	0.32
0.4	0	0.30	−0.03	0.11	0.09
	2.7	0.35	0.12	0.23	0.32
0.6	0	0.29	−0.03	0.11	0.10
	2.6	0.34	0.13	0.23	0.33
1.0	0	0.28	−0.05	0.11	0.08
	2.8	0.34	0.07	0.19	0.29

The value of the hyperfine field at 18 K was taken as $H_{\mathrm{hf}}(0)$. It can be seen from the figure that the temperature variation of the hyperfine field follows this function very well up to temperatures close to the Curie temperature with a typical value of b approximately equal to 0.5. Since there is a proportionality between the hyperfine fields and the $3d$ magnetic moments, it is reasonable to assume that the $3d$ magnetization also follows such a power-law behavior. Blandain[17] has studied the temperature variation of magnetization of $3d$ elements and found that the magnetization decreases with temperature obeying a T^2 behavior, which has been attributed to the single-particle excitations. Therefore, the T^2 dependence of the hyperfine fields in the present series of compounds suggests that single-particle excitations may be responsible for suppressing the $3d$ sublattice magnetization, with increase in temperature. The temperature variations of the hyperfine fields in $\mathrm{Y}_2\mathrm{Fe}_{17}$, $\mathrm{Nd}_2\mathrm{Fe}_{17}$, and $\mathrm{Dy}_2\mathrm{Fe}_{17}$ are also found[18] to follow Eq. (1) with a value of $b=0.5$.

The change in the easy magnetization direction at 18 K, from the basal plane to the c axis, on nitrogenation for these compounds with $x\leqslant 0.8$ implies that there is an increase in the total anisotropy on nitrogenation. The increase may be due to the increase in the R sublattice anisotropy, since there has been no reports on the changes in the Fe sublattice anisotropy on nitrogenation. The first-order anisotropy constant for the R sublattice could be written as[19]

$$K_1(R)=(-3/2)\alpha_J\langle r_{4f}^2\rangle\langle 3J_z^2-J(J+1)\rangle A_2^o, \tag{2}$$

where α_J is the Stevens factor, r_{4f} is the radius of the $4f$ orbital, J and J_z are the total and z component of the angular

TABLE III. Volume coefficients of the isomer shifts $(\Delta\delta_{\mathrm{av}}/\Delta\ \ln V)$ for $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$ compounds at 18 K.

	$(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$
x	$\Delta\delta_{\mathrm{av}}/\Delta\ \ln V$
0	1.99
0.4	2.05
0.6	2.13
1.0	1.68

TABLE IV. Quadrupole splittings (in mm/s) at various Fe sites in $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}$ compounds and their nitrides (given in brackets) with different x values at 18 K. Maximum error: ±0.04 mm/s.

	$(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$ Quadrupole splittings (mm/s)						
x	$6c$ $(4f)$	$9d_1$ $(6g_1)$	$9d_2$ $(6g_2)$	$18f_1$ $(12j_1)$	$18f_2$ $(12j_2)$	$18h_1$ $(12k_1)$	$18h_2$ $(12k_2)$
0	0.08	0.37	−0.39	0.06	0.65	−0.20	0.40
	(−0.39)	(0.35)	(0.35)	(−0.37)	(−0.37)	(0.34)	(0.34)
0.4	−0.06	0.37	−0.25	0.08	0.23	−0.02	0.44
	(0.14)	(0.39)	(0.39)	(−0.24)	(−0.24)	(0.51)	(0.51)
0.6	0.01	0.10	−0.37	−0.03	0.48	−0.04	−0.81
	(0.02)	(0.42)	(0.42)	(−0.17)	(−0.17)	(0.55)	(0.55)
1.0	0.03	0.62	−0.31	0.09	0.47	−0.20	0.44
	(0.37)	(−0.06)	(−0.20)	(0.30)	(0.67)	(−0.32)	(0.16)

momentum, and A_2^o is the second order crystal-field parameter. The angle brackets give the expectation values of the corresponding quantities. The unit cell of $R_2\mathrm{Fe}_{17}\mathrm{N}_y$ structure consists of R atoms, which have three nitrogen neighbors in the c plane. As a consequence of this, there will be an excess charge density in the c plane on nitrogenation, which increases the A_2^o values, without changing its sign and hence an increase in the value of $K_1(R)$.[20] In this condition, the R sublattice anisotropy dominates the planar anisotropy of the Fe sublattice, resulting in a resultant axial anisotropy. However, this occurs only at low temperatures. At high temperatures, the Fe sublattice anisotropy predominates and the sign of the total anisotropy constant changes, resulting in a spin reorientation, as has been observed[1] in the case of $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}\mathrm{N}_y$ compounds with $x \leqslant 0.8$. A similar increase in the R sublattice anisotropy and the consequent spin-reorientation transitions have been observed in other $R_2\mathrm{Fe}_{17}$ (R=Er,Tm) compounds on nitrogenation.[6] In the case of the nitride with $x=1$, the increase in the R sublattice anisotropy may not be strong enough to counter the Fe sublattice anisotropy and therefore, the net anisotropy is planar even at the lowest temperature.

Table II shows the variation of the isomer shifts for the $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}$ compounds and their nitrides. There is an increase in the isomer shift on nitrogenation for all Fe sites in these compounds. The increase is more pronounced in the case of $9d(6g)$, $18f(12j)$, and $18h(12k)$ sites. The increase in the isomer shift is due to the chemical effect and increase in the unit-cell volume upon the nitrogenation. The increase in the unit-cell volume will give rise to an increase in the Wigner-Seitz cell volume and hence a reduction in the s-electron density, which in turn increases the isomer shift. Fe atoms at the $6c(4f)$ site have no N near neighbors, which may be the reason for the smaller increase in the isomer shift, on nitrogenation at that site. Though the $9d(6g)$ site also does not possess any N near neighbors, the increase in the Wigner-Seitz cell volume is larger and this accounts for the increase in the isomer shift at this site. The Fe atoms at $18f(12j)$ and $18h(12k)$ sites have one N near-neighbor

TABLE V. Magnetic hyperfine fields (in kOe) and the weighted average values at different Fe sites for the $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x\mathrm{N}_y$ compounds with different x values at 18 K. Maximum error: ±4 kOe.

		$(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x\mathrm{N}_y$ Hyperfine fields (kOe)				
x	y	$6c$	$9d$	$18f$	$18h$	Wt. avg.
0	0	362	316	309	285	308
	2.7	390	363	337	330	345
1	0	308	295	270	268	285
	2.3	345	346	296	298	322
2	0	304	259	247	242	263
	1.9	335	307	263	269	294
3	0	275	242	219	219	239
	1.3	322	264	254	239	271
5	0	224	204	181	174	194
6	0	219	172	167	131	173
8	0	191	151	146	108	143
10	0	—	131	103	97	115

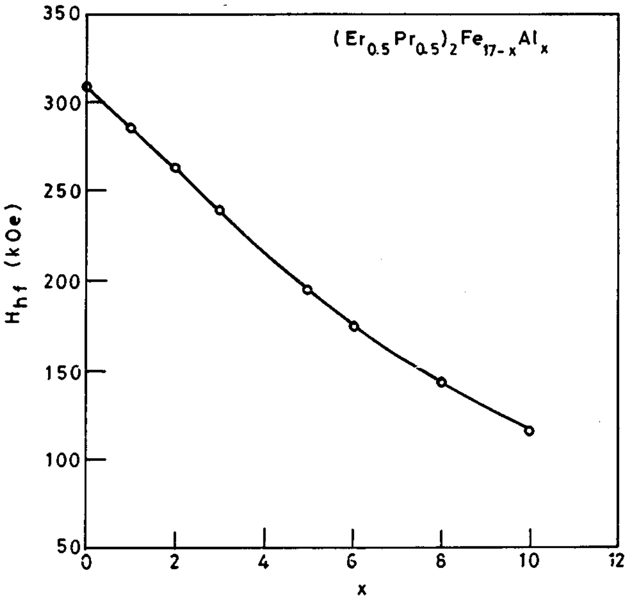

FIG. 4. Variation of the weighted average hyperfine field as a function of Al concentration in $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ at 18 K.

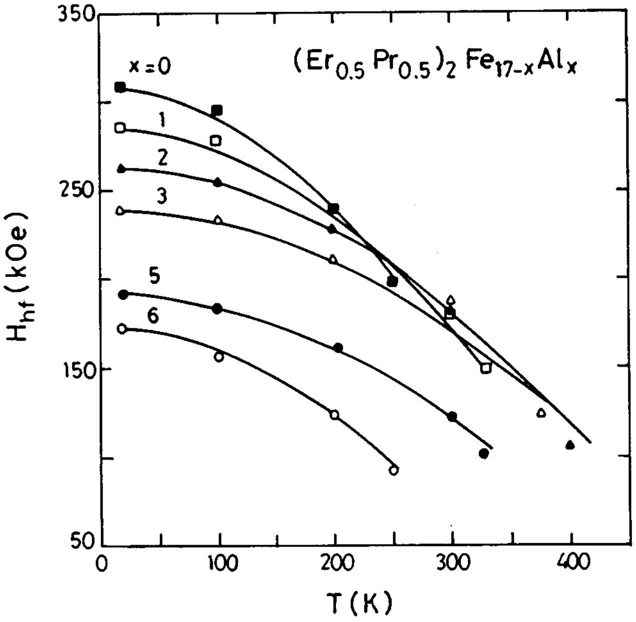

FIG. 5. Temperature variation of the weighted average hyperfine fields fitted to the equation $H_{\mathrm{hf}}(T)=H_{\mathrm{hf}}(0)\{1-b(T/T_C)^2\}$ for $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ compounds.

each. But the larger increase observed in the latter site is as a result of the combined effect of N near neighbors and the Wigner-Seitz cell expansion. The nominal increase in the isomer shift at the $18f(12j)$ site is due to the proximity of N. From the isomer shifts at various sites, we have calculated the weighted average isomer shift and obtained the volume coefficient $\Delta\delta/\Delta \ln V$ for all the compounds and is given in Table III. The value of 1.7 obtained for $\mathrm{Pr}_2\mathrm{Fe}_{17}\mathrm{N}_y$ in the present case is in close agreement with the value of 1.68 reported by Long *et al.*[21]

Table IV shows the quadrupole splittings observed at various Fe sites for the $(\mathrm{Er}_{1-x}\mathrm{Pr}_x)_2\mathrm{Fe}_{17}$ compounds as well as for their nitrides at 18 K. There is a change in the magnitude as well as the sign of the quadrupole splitting at various sites for these compounds. It is of particular interest to note that the sign of the quadrupole splittings at the $18f(12j)$ and $18h(12k)$ sites for the compounds with $x\leq 0.8$ change on nitrogenation, whereas it remains unchanged for the compound with $x=1.0$. This may be due to the fact that the easy magnetization direction changes from c plane to c axis in compounds with $x\leq 0.8$ on nitrogenation, whereas it remains in the c plane in the case of the nitride with $x=1.0$. Similar changes in the quadrupole splittings have been reported in $(\mathrm{Sm,Pr})_2\mathrm{Fe}_{17}$ compounds and their nitrides.[11]

Table V shows the hyperfine fields for various Fe sites for the $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ compounds and their nitrides at 18 K. It can be seen that there is a gradual decrease in the hyperfine fields at all Fe sites as well as the weighted average hyperfine fields, with an increase in Al concentration. This may be due to the reduction in the Fe magnetic moment as a result of the charge transfer from the valence band of Al to the $3d$ band of Fe. In addition, there will be magnetic dilution effect on Al substitution. Figure 4 shows the variation of the weighted average hyperfine field as a function of Al concentration. On nitrogenation, there is an increase in the weighted average hyperfine fields in these compounds as well, as shown in Table V. This increase is due to the effect of $3d$ band narrowing.

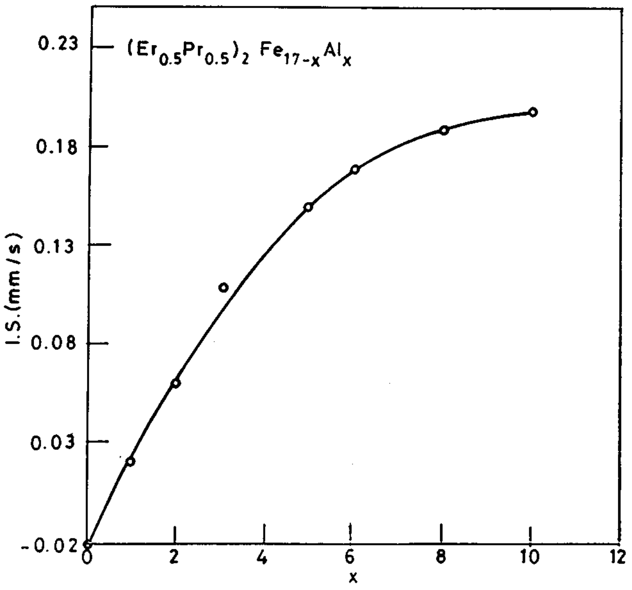

FIG. 6. Weighted average isomer shifts in $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ compounds at 18 K, as a function of Al concentration.

Figure 5 shows the weighted average hyperfine fields of $(\mathrm{Er}_{0.5}\mathrm{Pr}_{0.5})_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ compounds fitted to Eq. (1). In these compounds too, the hyperfine fields follow a T^2 behavior, which may be indicative of the role of single-particle excitations in suppressing the magnetism at high temperatures.

Figure 6 shows the variation of the weighted average isomer shifts as a function of Al concentration at 18 K. There is an increase in the isomer shifts with increase in Al concentration, which may be due to the reduction in the s-electron density at the nucleus. This is because of the intratomic $3d$-$4s$ charge transfer in Fe, as a consequence of the chemical effect, on Al substitution. A similar increase in the isomer shifts has been reported in $\mathrm{Nd}_2\mathrm{Fe}_{17-x}\mathrm{Al}_x$ compounds.[9]

ACKNOWLEDGMENT

K.G.S. is grateful to the Indian Institute of Technology, Madras, for financial support.

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