Mössbauer Study of Some 2–17 Lanthanide–Iron Compounds*

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We have studied the iron-rich, rare-earth–iron intermetallic compounds RFe17 (R = Pr, Gd, Tm, Lu), using the Mössbauer effect in 57Fe. The measured average hyperfine field \( H(T/T_c) \) acting on the \( ^{57}\text{Fe} \) nuclei is a unique, monotonically decreasing function of \( T/T_c \) with no observed irregularity at temperatures corresponding to a suspected ferromagnetic–antiferromagnetic phase transition in these compounds. The onset of paramagnetism occurs at temperatures close to the upper transition points measured by Strnat et al., namely at \( T_e = 282^\circ, 472^\circ, 271^\circ, \) and \( 263^\circ \text{K } \) for \( \text{PrFe}_{17}, \text{GdFe}_{17}, \text{TmFe}_{17}, \) and \( \text{LuFe}_{17} \), respectively. Low-temperature \( (\approx 90^\circ \text{K}) \) spectra indicate the presence of at least four magnetically nonequivalent Fe sublattices, while for \( T>T_e \) broadened 2-line absorption spectra typical of \( ^{57}\text{Fe} \) at noncubic sites in paramagnetic material are observed.

In recent investigations 1–3 of the magnetic properties of iron-rich lanthanide–iron compounds (stoichiometry 4 R2Fe17, where \( R \) denotes a rare earth) an ordered, possibly antiferromagnetic phase has been postulated to exist at temperatures above the magnetic Curie point for \( R = \text{Ce, Pr, Nd, Gd, Tm, and Lu} \). Low-field ac permeability 1,2 or neutron diffraction 3 measurements have indicated the presence of two transition temperatures in these materials, the lower transition temperature \( T_{CL} \) being identified 1–4 with the disappearance of ferro- or ferrimagnetic order. The significance of the upper transition temperature \( T_{CD} \) is unclear. Strnat et al. 1 tentatively suggested that an antiferromagnetic phase might be present for \( T_{CL} < T < T_{CD} \).

We have used the Mössbauer effect in \( ^{57}\text{Fe} \) to examine the magnetic behavior of \( \text{PrFe}_{17}, \text{GdFe}_{17}, \text{TmFe}_{17}, \) and \( \text{LuFe}_{17} \). In particular, we wished to test whether impurity effects could be a possible explanation for the appearance of two transition temperatures in the latter three compounds. (One could interpret \( T_{CL} \) as the order–disorder transition of the material proper, and ascribe the small permeability peak observed at \( T_{CD} \) to the presence of a ferromagnetic impurity.) The alloys used had been prepared for previous investigations. Preparation and analysis are described in the Refs. 1, 2, and 5.

Our Mössbauer measurements indicate that \( \text{GdFe}_{17}, \text{TmFe}_{17}, \) and \( \text{LuFe}_{17} \) become paramagnetic at temperatures \( T_e \) close to the previously determined 1 upper transition points \( T_{CD} \) (see Table I). Since the Mössbauer spectra correspond to the main phase, we may conclude that \( T_{CD} \) is a bulk property and cannot be associated with impurity effects. The newer permeability measurements 3 confirm this: The most likely contaminants are pure iron or other R–Fe compounds. None of these have their Curie point, or any known transition, near \( T_{CD} \). Moreover, we find that the hyperfine field and spectral shape are continuous with no unusual anomaly near \( T_{CL} \). This fact is rather difficult to reconcile with the postulated ferromagnetic–antiferromagnetic transition at \( T_{CL} \), though we feel that the possibility of such a transition is perhaps not completely ruled out by our data.

\( \text{PrFe}_{17} \) becomes paramagnetic at \( T_e = 282^\circ \text{K} \), and the antiferromagnetic phase postulated by Weik et al. 3 for \( T>T_{CL} \) was not observed. Strnat et al. 1 also observed only one transition temperature (denoted arbitrarily \( T_{CD} \) in Table I) for this compound, and their value agrees well with our Mössbauer results.

In Fig. 1 we present typical low-temperature Mössbauer absorption spectra of \( \text{PrFe}_{17} \) and \( \text{GdFe}_{17} \). Spectra of \( \text{TmFe}_{17} \) and \( \text{LuFe}_{17} \) in the ordered phase are similar. The spectra in Fig. 1 are complex, and at least four different component subspectra can be discerned. Such complexity is to be expected in view of the rather complicated crystal structure 1,3,4 of the \( R_2\text{Fe}_{17} \) compounds, there being four crystallographically nonequivalent Fe sites per unit cell. We have attempted a computer analysis of the \( \text{PrFe}_{17} \) spectrum, assuming four nonequivalent collinear Fe sublattices, but have been unsuccessful in obtaining a convincing fit to the experimental data. It seems that the actual magnetic structure is more complex.

In Fig. 2 we plot the temperature dependence of the approximate average hyperfine field \( H \) as a function of \( T/T_e \). For \( T/T_e \geq 0.6 \) the component subspectra are not resolved. At lower values of \( T/T_e \) we have plotted the weighted average hyperfine field. We stress that for the \( \text{Gd, Tm, and Lu} \) compounds our disordering temperature \( T_e \), corresponding to the onset of paramagnetism, is close to the temperature \( T_{CD} \) reported in Refs. 1 and 2. It is also interesting, that within the accuracy of our measurements, the hyperfine field \( H(T/T_e) \) appears to be a unique function of \( T/T_e \) for all four compounds studied.

Above \( T_e \), the four compounds have 2-line absorption

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Table I. Comparison of "Curie" temperatures of some R$_2$Fe$_{17}$ compounds (R is a rare earth). The temperature $T_{CL}$ corresponds to the disappearance of "ferromagnetism" (Refs. 1-3). At $T_{CU}$ a secondary peak in the permeability is obtained (Refs. 1 and 2), or neutron diffraction (Ref. 3) indicates the persistence of magnetic order. We have used $T_e$ to denote the onset of paramagnetism, as determined from the Mössbauer effect.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{CL}$</th>
<th>$T_{CU}$</th>
<th>$T_{CL}$</th>
<th>$T_{CU}$</th>
<th>$T_{CL}$</th>
<th>$T_{CU}$</th>
<th>$T_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>2$Fe$</em>{17}$</td>
<td>93</td>
<td>411</td>
<td>91</td>
<td>403</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Pr$<em>2$Fe$</em>{17}$</td>
<td>283</td>
<td>none</td>
<td>287</td>
<td>none</td>
<td>280</td>
<td>&gt;570</td>
<td>282±1</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{17}$</td>
<td>327</td>
<td>none</td>
<td>327</td>
<td>none</td>
<td>326</td>
<td>&gt;570</td>
<td>472±3</td>
</tr>
<tr>
<td>Gd$<em>2$Fe$</em>{17}$</td>
<td>460</td>
<td>472</td>
<td>460</td>
<td>~473</td>
<td>...</td>
<td>...</td>
<td>271±3</td>
</tr>
<tr>
<td>Tm$<em>2$Fe$</em>{17}$</td>
<td>232</td>
<td>277</td>
<td>248</td>
<td>282</td>
<td>...</td>
<td>...</td>
<td>263±2</td>
</tr>
<tr>
<td>Lu$<em>2$Fe$</em>{17}$</td>
<td>238</td>
<td>265</td>
<td>235</td>
<td>268</td>
<td>...</td>
<td>...</td>
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</tr>
</tbody>
</table>

spectra typical of $^{57}$Fe in a paramagnetic material. In view of the noncubic symmetry at the various iron sites, a quadrupole splitting is to be expected, average values being 0.62±0.05 mm/sec, 0.59±0.05 mm/sec, 0.58±0.05 mm/sec, and 0.58±0.05 mm/sec for Pr$_2$Fe$_{17}$, Gd$_2$Fe$_{17}$, Tm$_2$Fe$_{17}$, and Lu$_2$Fe$_{17}$, respectively. At room temperature these compounds have isomer shifts close to that of Fe metal, the measured values being $-0.01\pm0.03$ mm/sec, $-0.19\pm0.05$ mm/sec, $-0.07\pm0.02$ mm/sec, and $-0.10\pm0.03$ mm/sec, respectively, relative to Fe metal at room temperature.

We have also undertaken macroscopic magnetic moment measurements on a powder sample of Lu$_2$Fe$_{17}$, using a vibrating sample magnetometer. Measurements in a field of 500 G showed a rapid drop of the magnetic moment.

![Mössbauer absorption spectra of Pr$_2$Fe$_{17}$ and Gd$_2$Fe$_{17}$ at 92° and 86°K, respectively.](image1.png)

![Hyperfine field $H(T/T_e)$ for Pr$_2$Fe$_{17}$, Gd$_2$Fe$_{17}$, Tm$_2$Fe$_{17}$, and Lu$_2$Fe$_{17}$. At low temperatures, where more than one subpeak can be resolved, we have plotted the weighted average hyperfine field.](image2.png)
moment in the vicinity of $T_{CL}$ and a small peak at $T_{CU}$ in accordance with the ac permeability data. The latter peak vanished upon repeating the measurement in a field of 5 kG. We may speculate that $T_{CL}$ represents a drastic change of the crystal anisotropy while the ferromagnetic order persists up to $T_{CU}$. Our data does not support the notion that magnetic order in some $R_2Fe_17$ compounds exists even above $\sim 500$K. More work will be necessary before the magnetic behavior of these substances is fully understood.

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4 The intermetallic phases $RF_2$ of the structure type $Th_2Zn_17$ had been reported to be deficient in Fe for $R = Ce$ through Sm, but the single-phase composition is now believed to be $R_2Fe_17$ for the entire Lanthanide series. Johnson et al., [Acta Cryst. B24, 274 (1968)] have undertaken an x-ray refinement of the phase previously thought to be $PrFe_7$. They found it has the composition $PrFe_7$.

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Numerical Solution of the Behavior of Helical Spin Structures in Applied Magnetic Fields

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The behavior of helical spin structures and the phase transitions they exhibit in applied magnetic fields are studied theoretically.1 Approximate solutions have been developed in the cases of high and low fields.2 We have obtained a numerical solution valid for the case of the planar helix with an arbitrary number of interplanar exchange interactions, an arbitrary form of in-plane anisotropy, and an external magnetic field applied in the plane. We calculated the phase diagram for the case of two interplanar exchange constants and no anisotropy in order to compare with the previous theory and found different behavior in the intermediate field region. As a new result in the case of an in-plane anisotropy the angle dependence of the transition fields has been obtained.


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Speculations on Magnetic Charge

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