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Itinerant-Electron Ferromagnetism in $R\,Rh_6B_4$ (R = Y,Lu,La,Eu^{3+})

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X-ray, magnetization, and Mössbauer studies of new hexagonal compounds RRh_6B_4 (R = rare earth) were performed. YRh_6B_4 and $LuRh_6B_4$ exhibit strongly enhanced itinerant paramagnetism. $LaRh_6B_4$ and $Eu^{3+}Rh_6B_4$ exhibit itinerant-electron ferromagnetism (T_c = 6 and 19 K) with large magnetic anisotropy and hysteresis [$H_c(EuRh_6B_4)$ = 2.1 kOe at 4.1 K]. All systems, when doped with 0.5 at.% Fe, show very high Curie points (100 to 300 K) and moments per Fe ion of up to $8\mu_B$.

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We prepared a new family of intermetallic compounds of the form RRh_6B_4, (R = Y, or any rare-earth element). They exhibit extremely unusual magnetic phenomena. $LaRh_6B_4$ and $EuRh_6B_4$ are anisotropic itinerant-electron ferromagnets[1] with Curie points at 6 and 19 K, respectively. YRh_6B_4 and $LuRh_6B_4$ are itinerant paramagnets with susceptibilities much higher than that of Pd metal. An addition of 0.5 at.% Fe to all systems induces ferromagnetic order up to very high temperatures (300 K in $LuRh_6B_4$).

Following the discovery of the unique properties of the RRh_4B_4 compounds by Matthias *et al.*[2] the R-Rh-B system has attracted great interest by many groups.[3] In an attempt to prepare $EuRh_4B_4$, we found this composition to crystallize in a new unknown hexagonal-type structure with some additional phases. For the composition $EuRh_6B_4$, the powdered x-ray pattern could be indexed with this hexagonal system without any extra lines. The elements were of a high-purity (99.9% R, 99.999% Rh and B) and were melted in an induction furnace. The new ternary RRh_6B_4 system is stable and well defined for all the rare-earth elements with $a \sim 5.65$ Å and $c \sim 17.1$ Å. The measured density is about 10.2 g/cm^3. The polycrystalline samples obtained from the melt contained relatively large single crystals which were separated for x-ray studies. The detailed structure is not yet clear. However, Mössbauer-effect studies (ME) of ^{151}Eu and ^{155}Gd indicated that these crystals contain a single rare-earth site. Some of the samples prepared were doped with 0.5 at.% Fe to allow ME studies of the ^{57}Fe probe. Samples, as obtained from the melt, and crushed fine powders, were studied by magnetic-susceptibility measurements at temperatures 1.6 to 300 K in fields of up to 17.5 kOe by a PAR Model No. 155 vibrating-sample magnetometer and up to 50 kOe in a PAR Model No. 156 magnetometer.[4] The samples containing ^{57}Fe, ^{151}Eu, and ^{155}Gd were also studied by the ME technique. We now proceed to discuss our results in what follows.

(I) $LaRh_6B_4$: The magnetic behavior of $LaRh_6B_4$ is shown in Figs. 1 and 2. The striking observation is the magnetic anisotropy of the as cast sample at low temperatures (inset of Fig. 1), where the sample was measured at different angles relative to the magnetic field direction. The later data presented in this paper is that of fine-powder samples. The second remarkable feature is the apparent tendency toward saturation (Fig. 2), but not reaching full saturation even at 1.6 K and 50 kOe, where the magnetic moment M_s is $0.09\mu_B$ per formula unit, a phenomenon typical to itinerant ferromagnetic compounds.[1,3] In order to estimate the ordering temperature of $LaRh_6B_4$ we used the conventional method in such cases and made the Arrott plots (inset of Fig. 2) from which $T_c \sim 6$ K is obtained. $LaRh_6B_4$ possesses a remanent moment and its coercive field is about 20 Oe at 1.6 K. At temperatures above 10 K the χ^{-1} vs T plot is linear and yields an effective moment per formula unit of $P_{eff} = 1.0\mu_B$ and $\theta = 9$ K. The large values of the ratio P_{eff}/M_s and the experimental ratio M_s/T_c are both consistent with itinerant-electron ferromagnetism[1] in $LaRh_6B_4$.

(II) $EuRh_6B_4$: The ^{151}Eu Mössbauer spectra show almost an identical pure quadrupole spectrum at 300, 4.1, and 1.5 K, and an isomeric shift of +1.6(1) mm/s relative to EuF_3. The isomer shift proves that the Eu ion is trivalent. For Eu^{3+} the magnetic hyperfine field is proportional to the local exchange field and to the local magnetic moment. The observed hyperfine field (10 ± 5 kOe) corresponds to a moment of less than $0.01\mu_B$. The magnetization measurements (Figs. 1 and 2) show that pure $EuRh_6B_4$ at 1.7 K and 50 kOe has a moment per formula unit of $0.5\mu_B$, large anisotropy, and a huge hysteresis loop (coercive field 2.1 kOe, Fig. 3). The magnetic moment, however, does not reach saturation even under these conditions. The remanent magnetization disappears at ~20 K (Fig. 1) while the T_c obtained from Arrott plot curves is 18 K. Well above T_c the inverse susceptibility versus T is linear and yields $P_{eff} = 4.2\mu_B$ and $\theta = -45$ K. This value of P_{eff} is much higher than that of trivalent Eu at those temperatures.

(III) YRh_6B_4, $LuRh_6B_4$, and $CeRh_6B_4$: All these

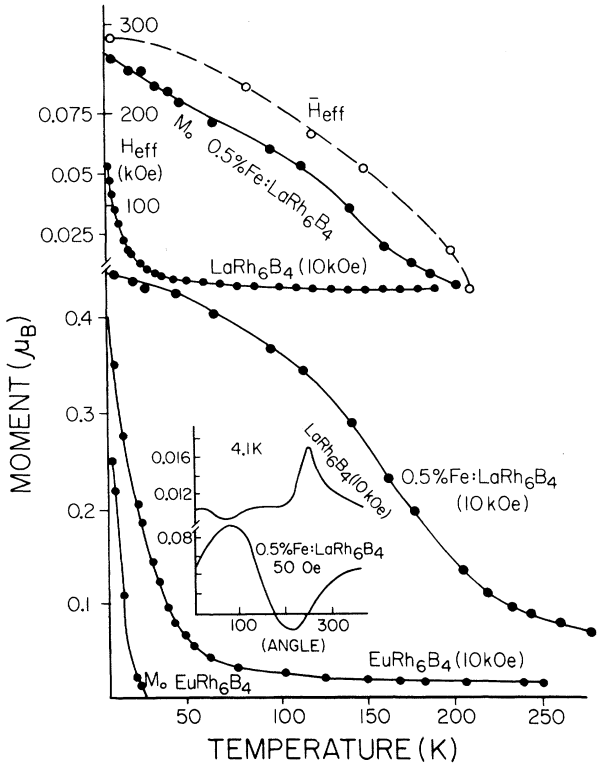

FIG. 1. Temperature dependence of the magnetic moments of RRh_6B_4 and the remanent magnetization M_0 of $EuRh_6B_4$ and of $LaRh_6B_4$ (with 0.5 at.% Fe). Also is shown the average Fe hyperfine field of the doped compound. The inset shows the magnetic anisotropy of pure and Fe-doped $LaRh_6B_4$.

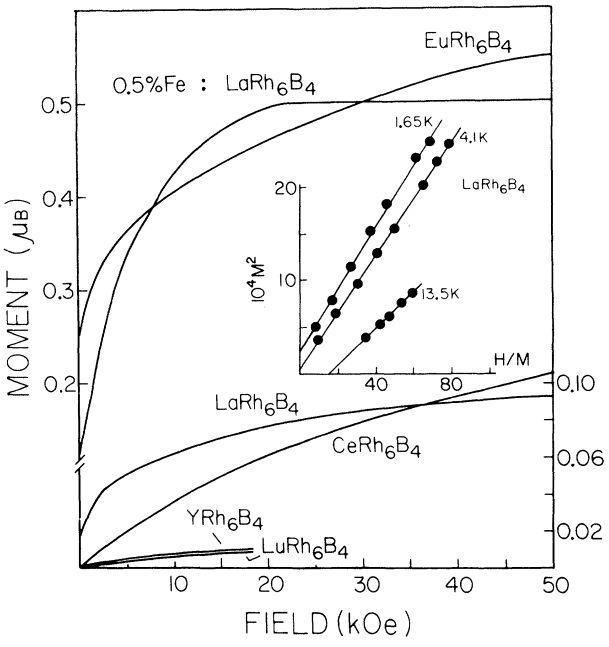

FIG. 2. Magnetization curves vs magnetic field at 1.65 K of RRh_6B_4 systems. The inset shows the Arrott plots of $LaRh_6B_4$. The units of M are electromagnetic units per mole and of H are oersteds.

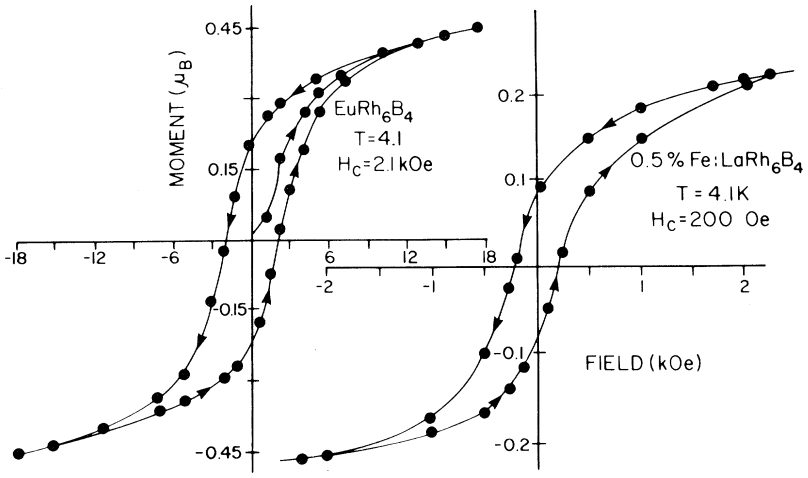

FIG. 3. Hysteresis curves of $R\mathrm{Rh}_6\mathrm{B}_4$ systems.

systems show strong paramagnetic behavior (Fig. 2). As for $CeRh_6B_4$, it is partly due to the Ce ion which is in a mixed-valence state.[5] However, the enhanced electron paramagnetism in YRh_6B_4 and $LuRh_6B_4$ [$\chi(4.1\ \mathrm{K}) = 24\times10^{-3}$ and 22×10^{-3} emu/mole, respectively] is huge in comparison to other known "enhanced paramagnets" as Pd metal or $TiBe_2$ (Ref. 6) where $\chi = 0.72\times10^{-3}$ and 8.6×10^{-3} emu/mole, respectively.

(IV) The 0.5 at.% Fe-doped systems ($R\mathrm{Rh}_{5.94}\mathrm{Fe}_{0.06}\mathrm{B}_4$): All systems $R\mathrm{Rh}_6\mathrm{B}_4$ when doped with 0.5 at.% Fe exhibit magnetic order up to relatively high temperatures (150, 220, 230, 285, and 300 K for R = Y, La, Ce, Eu, and Lu, respectively). This can be seen, for example, for $LaRh_6B_4$: Fe in Figs. 1, 2, and 4. In Fig. 1, we observe the temperature dependence of the remanent magnetization (M_0) and the Fe hyperfine field obtained from the Mössbauer studies (Fig. 4). We observe that both disappear at $T_c \sim 220$ K. Above 220 K a pure quadrupole Mössbauer spectrum is observed. In Fig. 2 one observes the field dependence of the magnetization. Unlike in pure $LaRh_6B_4$, the magnetization reaches saturation. The moment at 1.6 K in 50 kOe is $0.5\mu_B$, $0.4\mu_B$ more than in $LaRh_6B_4$, which means $7\mu_B$ per Fe ion. In 0.5 at.% ^{57}Fe in $EuRh_6B_4$ the moment rises by 0.46 μ_B ($8\mu_B$ per Fe ion). In Fig. 3 we observe the hysteresis loop of $LaRh_6B_4$:Fe at 4.1 K (H_c = 200 Oe). The Mössbauer spectra observed in Fig. 4 show, at 4.1 K, a superposition of two magnetic spectra with relative intensities of 2:1. At intermediate temperatures a distribution of hyperfine fields is observed. An alternative interpretation of the smeared spectra at the intermediate temperatures can be in terms of dynamical phenomena, slow spin relaxation rates of the Fe local

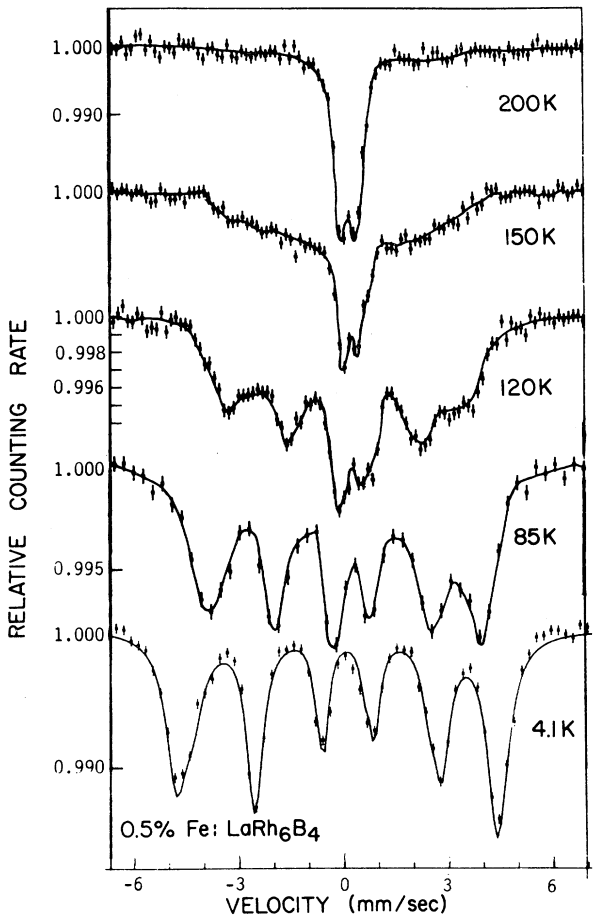

FIG. 4. Mössbauer spectra of ^{57}Fe in $LaRh_6B_4$ (with 0.5 at.% ^{57}Fe).

spin. Whatever the correct interpretation, it is evident from both the Mössbauer and remanent moment (Fig. 1) that the Fe ions are magnetically ordered up to 220 K.

The pure systems YRh_6B_4, $LuRh_6B_4$, and $CeRh_6B_4$ are strongly paramagnetic (Fig. 2) and the addition of 0.5% Fe induces magnetic order. All systems show magnetic anisotropy, hysteresis, and high moments per added Fe ion.

From our experimental results we can make the following conclusions:

(a) The phenomena observed are indicative of strong itinerant-electron paramagnetism in RRh_6B_4 (R = Y, Lu) and itinerant-electron ferromagnetism in $LaRh_6B_4$ and $EuRh_6B_4$.

(b) The addition of minute quantities of a paramagnetic ion (0.5 at.% Fe) has a huge enhancement effect on the magnetic properties of the RRh_6B_4 systems. These become itinerant ferromagnets with high Curie points, high anisotropy, large moments, and even display remanence. Seldom were observed such large changes in the magnetic behavior of a substance due to such a small amount of an added impurity.

(c) It is reasonable to speculate that the magnetism in $LaRh_6B_4$ and in $EuRh_6B_4$ resides on the Rh site and is due to 4d conduction-band polarization.[7]

(d) Mössbauer studies of ^{151}Eu in $EuRh_6B_4$ and also dilute ^{155}Gd in $EuRh_6B_4$ show very little magnetism at the rare-earth site, indicating weak coupling of the rare-earth element with the 4d conduction-band magnetism.

(e) It seems that the reported results now, and many more in our extended report to be published, must lead theoreticians to reexamine some of their accepted notions about itinerant-electron magnetism. It is also possible that this family of compounds, in particular YRh_6B_4 and $LuRh_6B_4$, may (because of their high density of states at the Fermi level) show at very low temperatures a phase transition to a superconducting state. On the other hand, they may become ferromagnetic in very high magnetic fields. This question is open for further research. Other interesting directions of research of these systems should be neutron diffraction studies, resistivity and magnetoresistance studies under pressure, and microscopic studies by Mössbauer and NMR spectroscopies at both B and Rh sites.

Early stages of this research started while one of us (I. F.) was staying in the Institute for Pure and Applied Physics Sciences, University of California San Diego, La Jolla, Cal. 92093. Part of this research by one of us (I. N.) was done at the Institut für Atom-und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin West 33, Germany.

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