

Anomalous magnetic properties of cerium ions in the compounds $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ (R = Tb, Dy)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 2797

(<http://iopscience.iop.org/0953-8984/10/12/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 12:47

Please note that [terms and conditions apply](#).

Anomalous magnetic properties of cerium ions in the compounds $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ ($\text{R} = \text{Tb}, \text{Dy}$)

C C Tang[†], W S Zhan[†], D F Chen[†], Y X Li[‡], J Du[†], B G Shen[†] and G H Wu[†]

[†] State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

[‡] Hebei University of Technology, Tianjin 300130, People's Republic of China

Received 8 September 1997, in final form 15 January 1998

Abstract. The lattice parameters and spontaneous magnetizations of the pseudobinary compounds $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ ($\text{R} = \text{Tb}, \text{Dy}$) are reported. The analysis of these results revealed the mutability of the Ce 4f ferromagnetism. The change of the degree of delocalization of the Ce 4f electron is used to analyse the changes of the lattice parameter and the spontaneous magnetic moment. A metamagnetic phase transition can be observed for each of the systems investigated, $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$, when the Ce concentration x is about 0.5. The critical phase field increases with the Ce concentration, and the itinerant-electron model has been applied to analyse the tendency towards change of the critical phase field with x .

1. Introduction

It became apparent that the magnetism of the cerium ion is a very special case among those of the rare-earth ions when a series of rare-earth–transition metal compounds and alloys, with different rare earths but the same transition metal, were investigated. The dubious procedure usually adopted is to regard the cerium ion as tetravalent and nonmagnetic. However, for the Laves phase compound CeFe_2 the existence of magnetism of the cerium 4f electron has been confirmed, indicating the formation of a 4f band and a hybridization of this band with the 3d band [1]. The fragility of the ferromagnetic order in CeFe_2 has also been reported for very small degrees of substitution of Al—in such a case, a low-temperature re-entrant spin-glass-like phase occurs and the long-range ferromagnetic order disappears [2]. These anomalies are uniquely associated with the mixed-valence behaviour of the cerium ion. We have to take into account the strong mixing of the 4f electrons with their own conduction electron band and the hybridization of the 4f electrons with the electrons of the ligand atoms. Hybridization effects may lead to a delocalization of the 4f electrons, and to a certain extent a description of the magnetism of cerium 4f states in terms of itinerant electrons can be applied [3].

It had been reported that the valence of the cerium ion in CeFe_2 is 3.29 [4]. It has not been clarified how 4f electrons immigrate into and emigrate out of the 4f sub-shell, although the effect of hybridization between Ce 4f electrons and the conduction band could play an important part. One of the most interesting phenomena is that indicated by previous studies of the pseudobinary compound $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ ($\text{R} = \text{Y}$ [5], Gd [6], Dy [7]): substitution at the rare-earth sublattice causes a drastic valence fluctuation from a delocalized to a localized

state. Considering these substitution effects, we have a strong suspicion that the magnetism of the Ce ion in CeFe_2 is ferromagnetism or ferrimagnetism in the usual conception.

In this paper, we have studied the structural parameters and the magnetic properties of $\text{Ce}_x\text{Tb}_{1-x}\text{Fe}_2$ and $\text{Ce}_x\text{Dy}_{1-x}\text{Fe}_2$. A metamagnetic phase transition is observed at a Ce concentration x of around 0.5 for both samples, and the corresponding analysis is presented.

2. Experiment

The ingots of $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ ($\text{R} = \text{Tb, Dy}$) were prepared by arc melting the appropriate amounts of Fe (purity better than 99.9 wt%) and rare earth (99.95 wt%) under a purified argon atmosphere. The as-cast ingots were wrapped in tantalum foils and vacuum annealed for a week at 850 °C in sealed quartz capsules.

The x-ray diffraction (XRD) measurements on the powder samples were performed using Cu $K\alpha$ radiation to check the phase purity and to determine the crystallographic parameters by least-squares fitting to the x-ray pattern. The accuracy of the lattice parameters is estimated to be $\pm 0.002 \text{ \AA}$.

An extracting-sample magnetometer was used to measure the magnetization at the different temperatures, and all of the samples for which measurements were made were pulverized to an average particle size of about 10 μm . The spontaneous magnetization (M_s) at 1.5 K was obtained by fitting the experimental $M(H)$ versus H data using the law of approach to saturation:

$$M(H) = M_s(1 - a/H - b/H^2 - c/H^3 - \dots) + \chi_p H \quad (1)$$

where a , b and c are fitting parameters, and χ_p is the parallel (paramagnetic) susceptibility. The method for determining the spontaneous magnetization is only suitable for the situation in which the applied magnetic field is sufficient to saturate the sample.

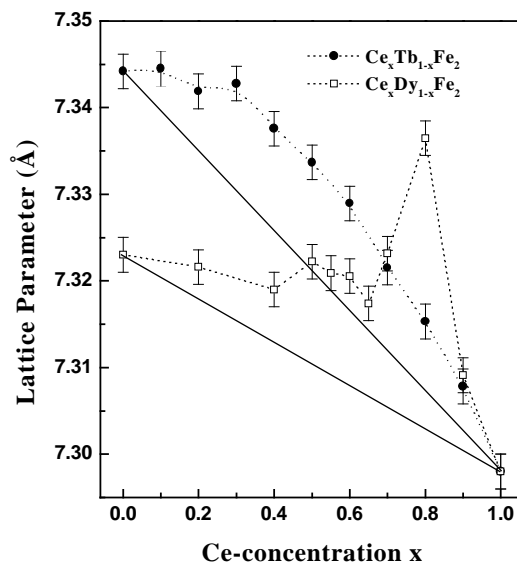


Figure 1. The dependence on the Ce concentration of the lattice parameters for $\text{Ce}_x\text{Tb}_{1-x}\text{Fe}_2$ and $\text{Ce}_x\text{Dy}_{1-x}\text{Fe}_2$. The accuracy is estimated to be $\pm 0.002 \text{ \AA}$. The solid lines represent Vegard's law behaviour. The dotted lines are guides to the eye.

3. Results and discussion

3.1. Valence change

The results from the XRD measurements show that the cubic Laves ($MgCu_2$) structure is maintained for $Ce_xTb_{1-x}Fe_2$ and $Ce_xDy_{1-x}Fe_2$ throughout the alloy series. The lattice parameters of both compounds as a function of the Ce concentration x are shown in figure 1. We find that they both exhibit positive deviation from Vegard's law. A similar dependence of the lattice parameter on x has already been reported for other $Ce_xR_{1-x}Fe_2$ ($R = Gd, Y$) systems (an exceptionally large lattice parameter was observed, but only near $x = 0.8$, for $Ce_xDy_{1-x}Fe_2$; this is attributed to the fluctuation of the local Ce valence, and an anomalous increase of the anisotropic magnetostriction can be observed at this point—see reference [7]). On the basis of the same consideration as in [5], the positive deviation of the lattice parameter due to the substitution of R for Ce can be regarded as a result of the tendency of Ce towards trivalency, because the localized Ce ions contribute an additional volume to the total. Therefore the Ce valence in $Ce_xR_{1-x}Fe_2$ should change from local +3 to intermediate +3.29 valence. With the increasing of the concentration of the heavy rare-earth element R, Ce 4f electrons first drift rapidly towards localized states, and the maximum value of this drift occurs at about $x = 0.4$ (Tb) and $x = 0.8$ (Dy); further increase of the concentration of R does not lead to a decrease of the degree of delocalization of Ce 4f electrons. Our studies [7] indicate that the pure Ce^{3+} is still not achieved, even for $Ce_{0.8}Dy_{0.2}Fe_2$ for which the largest lattice parameter is observed.

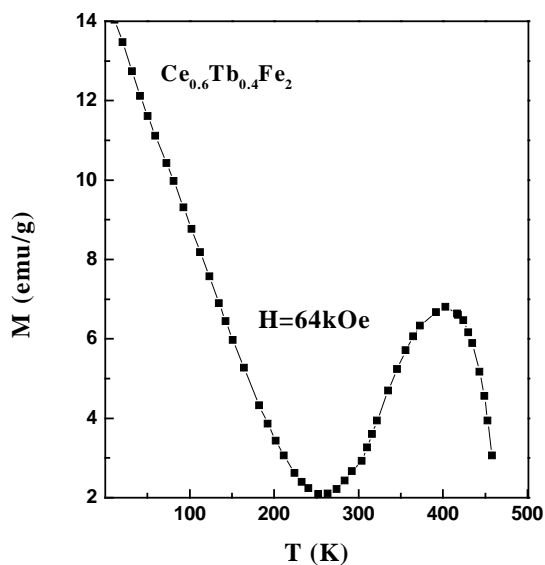


Figure 2. The temperature dependence of the magnetization of $Ce_{0.6}Tb_{0.4}Fe_2$ in a field of 64 kOe.

3.2. Spontaneous magnetization

The spontaneous magnetizations of $TbFe_2$, $DyFe_2$ and $CeFe_2$ were found by measurement to be $5.03 \mu_B/f.u.$, $5.77 \mu_B/f.u.$ and $2.32 \mu_B/f.u.$, respectively. Their Curie temperatures were

found by measurement to be 693 K, 630 K and 233 K, respectively. These values are close to the previously reported ones [8–10]. The antiparallel coupling between the rare-earth spin moment and the Fe moment for the heavy rare-earth compounds leads to ferrimagnetism, while the parallel coupling for the light rare-earth compounds leads to ferromagnetism. However, for CeFe_2 the experimental [10] and theoretical results [2] indicate that the Ce 4f moment couples ferrimagnetically with the Fe moment. The exception has been attributed to the 3d-4f hybridization. It has been reported, on the basis of a polarized neutron study of CeFe_2 , that the Ce and Fe moments are $-0.14 \mu_B/\text{atom}$ and $1.17 \mu_B/\text{atom}$, respectively. With the increasing of the Ce concentration x , the R-sublattice moment will decrease. At a certain concentration, the R-sublattice moment becomes higher than the Fe-sublattice moment at 1.5 K. However, because the R-sublattice moment decreases more rapidly as a function of temperature than the Fe-sublattice moment does, they will be equal at a certain temperature. Therefore a compensation temperature should be observed in the high-field magnetization curves versus temperature. Indeed, this phenomenon can be observed for both $\text{Ce}_x\text{Dy}_{1-x}\text{Fe}_2$ and $\text{Ce}_x\text{Tb}_{1-x}\text{Fe}_2$ at a Ce concentration x of about 0.6 (see figure 2).

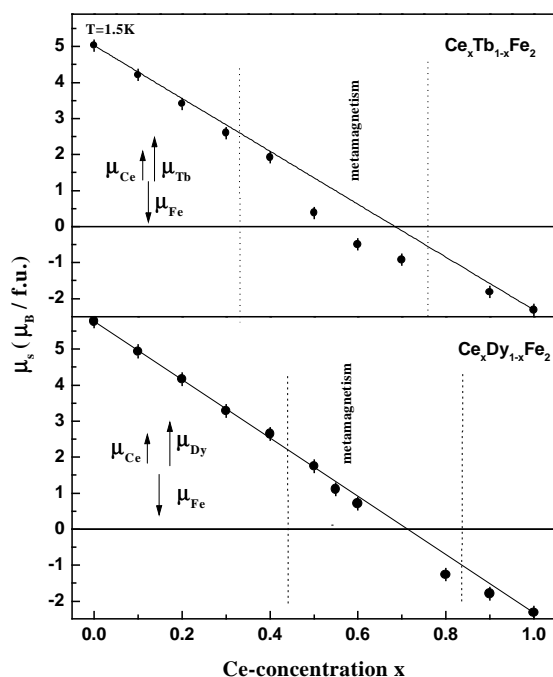


Figure 3. The spontaneous magnetic moments as functions of the concentration of Ce, x , for $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ ($\text{R} = \text{Tb}, \text{Dy}$) at the same temperature, 1.5 K. The solid circles represent the spontaneous magnetic moment obtained by the law of approach to saturation. The solid lines result from the assumption that the total spontaneous magnetic moment is the sum of the contributions of CeFe_2 and RFe_2 . For each compound, a metamagnetic phase transition is observed in the area between the two dotted lines.

If we suppose that the magnetism of $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ can be regarded as the simple addition of those of two isostructural MgCu_2 systems, namely, CeFe_2 and RFe_2 ($\text{R} = \text{Tb}, \text{Dy}$), the theoretical total magnetic moments of the systems investigated, as functions of the concentration of Ce, x , can be expressed as follows:

$$\mu_s = (1 - x)\mu_{\text{RFe}_2} - \mu_{\text{CeFe}_2}. \quad (2)$$

The results calculated for both systems are shown in figure 3. In this figure we also give the dependence on the Ce concentration of the spontaneous magnetic moments measured at 1.5 K for both systems. It is found that the theoretical values are in good agreement with the observed ones at the low Ce concentrations of $x < 0.5$ for $R = Dy$ and $x < 0.4$ for $R = Tb$. However, the two curves exhibit a great degree of deviation in the high-Ce-concentration range. Within this range, the dependence on the Ce concentration of the absolute value of the magnetic moment at 1.5 K can be basically divided into two fields bounded by the net zero magnetic moment, which occurs at $x = 0.68$ for $R = Tb$ and $x = 0.71$ for $R = Dy$ at the same temperature. That is, the negative deviation occurs on the left and the positive deviation occurs on the right.

Considering the change in Ce valence on the basis of the measurements of the lattice parameter, the change of the degree of localization of Ce 4f electrons will cause changes of the magnetic moments of both the Ce sublattice and the Fe sublattice. The Dy (Tb) moment is constant because Dy (Tb) 4f electrons are positioned within the ion cores and also hybridization with the conduction band electron state is negligible. The full realization of the dependence on the Ce concentration of the magnetizations for $Ce_xR_{1-x}Fe_2$ can be very complicated if we accept the conclusion that the change of magnetic moment can be regarded as a change of the degree of delocalization of Ce 4f electrons, which will affect the Fe-sublattice moment. In the range of the lower Ce concentrations, the magnetic moments of the Ce and Fe sublattices increase with the decreasing degree of delocalization of the Ce 4f electrons. Because of the antiparallel alignment of the Ce and Fe moments, the total magnetic moment will be almost constant.

In general, the Ce-based intermetallic compounds can be characterized as local-magnetic-moment γ -Ce-like and Pauli paramagnetic α -Ce-like in terms of their magnetic properties [11]. The experiments described in [12, 13] indicate that high pressure can lead to the passage from a γ -Ce-like to an α -Ce-like phase for elemental Ce in dilute alloys and in some intermetallic compounds. The alloying method using volume-mismatch substitution has been successfully applied to stabilize the high-pressure phase of Ce-based compounds at ambient pressure [14], and intermediate-valence behaviour has been observed. In spite of the deficiency of the information on the Ce-ion properties as regards the conditions that must be met for lattice expansion to occur, we can deduce that the spin fluctuation is related to the volume mismatch caused by the substitution of a rare earth with a larger atomic radius (Tb, Dy) for Ce.

It is also worth noticing that the dependences on the concentration of R of the lattice parameters of the two systems show quite different behaviours. The magnetic moments, however, exhibit similar trends of change. In fact the exchange integrals of Fe and of Ce(4f) depend on the type of R ion in the rare-earth-iron intermetallic compounds. It has been reported [8, 9, 15, 16] that the local Fe moment exhibits different values for different choices of R. Distance changes may also affect the 3d-4f hybridization, or even the 3d-5d overlap. However, the variation of the Fe moment with R in the isostructural compounds is small and the role of the molecular field due to R can be neglected.

3.3. Metamagnetism

Another interesting phenomenon is the occurrence of a metamagnetic phase transition in the moderate-concentration ranges for both systems. Figure 4 shows the magnetization isotherms at 1.5 K measured with the extracting-sample magnetometer at fields up to 60 kOe on the free-powder samples of $Ce(Tb, Dy)Fe_2$. A rapid increase of the magnetization is observed well within the concentration ranges $0.4 \leq x \leq 0.7$ for $Ce_xTb_{1-x}Fe_2$ and $0.5 \leq$

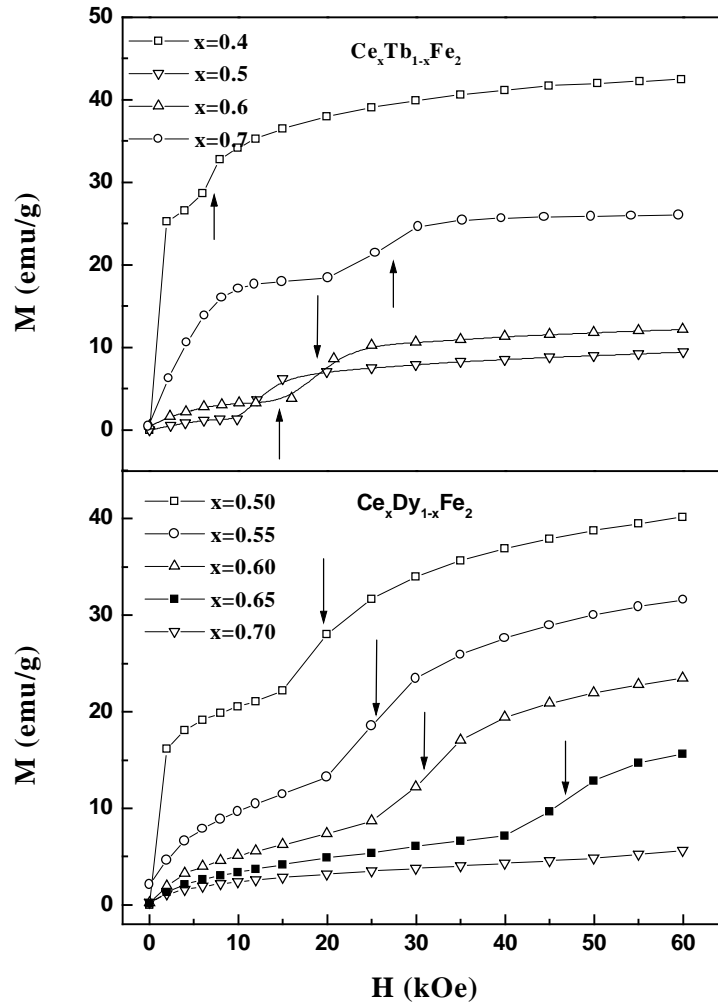


Figure 4. Magnetization isotherms at 1.5 K for $Ce_xR_{1-x}Fe_2$ ($R = Tb, Dy$). The arrows point to the critical phase fields.

$x < 0.7$ for $Ce_xDy_{1-x}Fe_2$. Before the occurrence of this transition, the field dependences of the magnetizations of all of the samples exhibit ferromagnetic (ferrimagnetic) behaviour. This suggests a ferromagnetic environment for Ce ions. The increase of the magnetization is about 10 emu g^{-1} . The critical magnetic fields of both systems increase with the Ce concentration (see figure 5).

These behaviours are similar to the itinerant-electron metamagnetism (IEM) observed for Co in $ThCo_5$ and Ni in Y_2Ni_{16} [17]. The metamagnetism was predicted theoretically by Wohlfarth and Rhodes [18] for a paramagnetic compound close to the Stoner criterion and with a strong positive curvature of the density of states at the Fermi level. For $Ce_xR_{1-x}Fe_2$ it appears, on the basis of the above-mentioned analysis, that the Stoner criterion for the onset of ferromagnetism of cerium 4f electrons can almost be satisfied in this system. Therefore we will discuss this metamagnetism on the basis of IEM theory.

According to Shimizu [19], in the presence of an applied field H , the free energy of an

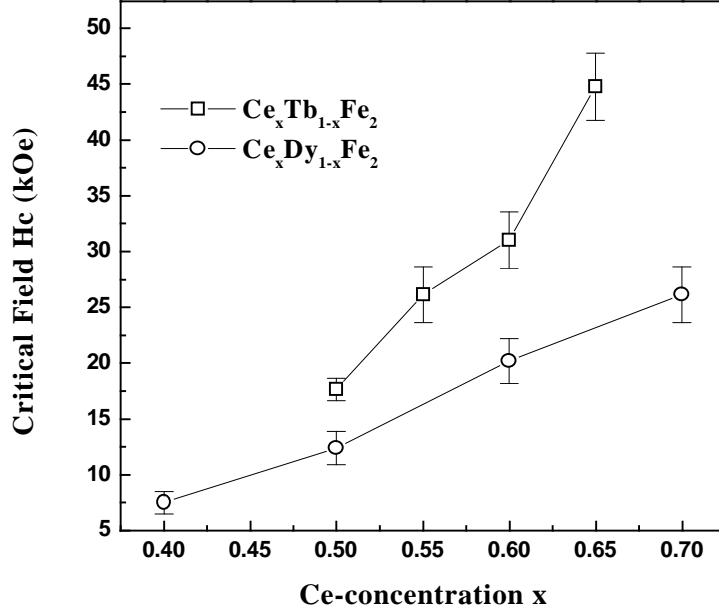


Figure 5. The critical phase field (H_c) versus the concentration of Ce, x , at a temperature of 1.5 K. H_c is determined as the point of the magnetization curves with the steepest gradient. The lines are guides to the eye.

itinerant-electron system can be expressed as

$$F(M_{Ce}) = F_0 + \frac{1}{2}AM_{Ce}^2 + \frac{1}{4}BM_{Ce}^4 + \frac{1}{6}CM_{Ce}^6 + \dots - M_{Ce}(H + H_M) \quad (3)$$

where F_0 is a constant independent of the magnetization M_{Ce} of Ce ion and H_M is the molecular field acting on the Ce 4f band. For the systems investigated, $Ce_xR_{1-x}Fe_2$, the latter can be expressed as follows:

$$H_M = 2n_{Fe,Ce}\mu_{Fe} + (1-x)n_{R,Ce}\mu_R + xn_{Ce,Ce}\mu_{Ce} \quad (4)$$

where $n_{Fe,Ce}$, $n_{Ce,Ce}$ and $n_{R,Ce}$ are the molecular-field constants for the Fe, Ce and R sublattices, respectively. In general, the Ce–Ce and R–Ce interactions are relatively small and can be regarded as negligible. The final two terms of equation (4) are absent.

In equilibrium, $\partial F(M_{Ce})/\partial M_{Ce} = 0$, and we obtain the equation

$$AM_{Ce} + BM_{Ce}^3 + CM_{Ce}^5 + \dots = H + H_M. \quad (5)$$

Then the magnetization of the Ce ion can be expressed as

$$M_{Ce} = A^{-1}(H + H_M) - A^{-4}B(H + H_M)^3 + \dots \quad (6)$$

Therefore the critical phase field, H_{crit} , should be the sum of the critical magnetic field H_c and the molecular field H_M acting on the Ce 4f band:

$$H_c = H_{crit} - H_M. \quad (7)$$

H_{crit} is determined by the electronic structure of Ce 4f near the Fermi level and is relevant to the coefficients A , B , C , ... If we assume that the density of states at the Fermi level exhibits no appreciable variation upon the substitution of R for Ce, the observed critical transition field H_c only changes with H_M . The Fe moment μ_{Fe} decreases with the increase

of the Ce concentration and H_M decreases correspondingly. This can be used to interpret the tendency towards change of the observed critical field H_c with the Ce concentration.

The above discussion is only a first approach to explaining the observed behaviour of the critical phase field. The difference of the coupling constants $n_{\text{Ce-Ce}}$ and $n_{\text{Ce-R}}$, if the R ions are considered, can explain these differences between the Tb and Dy systems. In addition, the metamagnetic phase transition cannot be observed when the field H_M increases substantially enough to depress H_{crit} with the decrease of the Ce concentration. However, with the increase of the Ce concentration, the enhancement of the degree of localization will decrease the local magnetic moment of the Fe sublattice and thus reduce H_M . Therefore the transitions cannot be observed under magnetic fields of up to 60 kOe, which is the highest value used in our experiment. Experiments on these samples using pulsed strong magnetic fields should be carried out.

4. Conclusion

The theory of the formation of the Ce 4f band has been applied in order to analyse the magnetic properties of CeFe_2 . To some extent, the assumption of the Ce 4f electrons being itinerant can be made, in order to explain the spontaneous magnetic moment, lattice parameter and low Curie temperature of CeFe_2 . In this paper, it seems evident that the tendency towards change of the lattice parameter and spontaneous magnetization of $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$ (R = Tb, Dy) can be interpreted according to this theory. The decrease of the degree of delocalization of the Ce 4f electrons, which results from the substitution of a heavy rare earth for Ce, plays an important part in the valence fluctuation and change in spin of the pseudobinary compounds. The change undergone by the Ce 4f electron in intermetallic compounds cannot be simply attributed to the change of the 4f occupation number, and must also—and even more importantly—be seen as a consequence of the nature of the electronic structure and the 4f-electron-conduction band hybridization.

A metamagnetic phase transition can be observed for each of the systems investigated, $\text{Ce}_x\text{R}_{1-x}\text{Fe}_2$, at moderate Ce concentration, x . The occurrence of the transition further indicates the fragility of the Ce 4f ferromagnetism. The tendency towards change of the critical phase field with x can be roughly analysed within the itinerant-electron model. Further studies, including ones involving the variation of the magnetic properties of $(\text{Ce}, \text{R})\text{Fe}_2$ under high pressure and a pulsed high magnetic field, are in progress.

Acknowledgment

This work was supported by the National Natural Science Foundation of China.

References

- [1] Eriksson O, Nordstrom L, Brooks M S S and Johansson B 1988 *Phys. Rev. Lett.* **60** 2523
- [2] Roy S B and Coles B R 1987 *J. Phys. F: Met. Phys.* **17** L215
- [3] Johansson B, Eriksson O, Nordstrom L, Severin L and Brooks M S S 1991 *Physica B* **172** 101
- [4] Croft M, Neifield T, Qi B, Liang G, Perez I, Gunapala S, Lu F, Shaheen S A, Spencer E G, Stoffel N and de Boer M 1987 *5th Int. Conf. on Valence Fluctuations* ed S K Malik and L C Gupta (New York: Plenum) pp 217
- [5] Cunha S F, Guimaraes A P and Livi F P 1980 *J. Phys. Chem. Solids* **41** 761
- [6] Miskinis E T, Narsimhan K S V, Wallace W E and Craig R S 1975 *J. Solid State Chem.* **13** 311
- [7] Tang C C, Chen D F, Li Y X, Wu G H, Jia K C and Zhan W S 1997 *J. Appl. Phys.* **82** 4424
- [8] Barbara B, Giraud J P, Laforest J, Lemaire R, Siaud E and Schweizer J 1977 *Physica B* **86-88** 155

- [9] Bara J J, Pedziwiatr A T, Zarek W, Konopka D and Gacek U 1982 *J. Magn. Magn. Mater.* **27** 159
- [10] Kennedy S J, Brown P J and Coles B R 1993 *J. Phys.: Condens. Matter* **5** 5169
- [11] Croft M, Weaver J, Peterman D and Franciosi A 1965 *Phys. Rev. Lett.* **46** 1104
- [12] Jayaraman A 1965 *Phys. Rev. A* **137** 179
- [13] Jayaraman A 1979 *Handbook on the Physics and Chemistry of Rare Earths* ed K A Gschneidner Jr and L Eyring (Amsterdam: North-Holland) p 580
- [14] Lawrence J M, Riseborough P S and Parks R D 1981 *Rep. Prog. Phys.* **44** 1
- [15] Givord D, Gregory A R and Schweizer J 1980 *J. Magn. Magn. Mater.* **15-18** 293
- [16] Fuess H, Givord D, Gregory A R and Schweizer J 1979 *J. Appl. Phys.* **50** 2000
- [17] Gignoux D, Givord F, Lemaire R and Tasset F 1983 *J. Less-Common Met.* **94** 1
- [18] Wohlfarth E P and Rhodes P 1962 *Phil. Mag.* **7** 1817
- [19] Shimizu M 1981 *Rep. Prog. Phys.* **44** 329