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# Effects of rare-earth substitution in $\text{CeFe}_2$ : mixed-valence and magnetic properties

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**Abstract.** The lattice parameters and magnetic properties of  $\text{Ce}_{1-x}\text{R}_x\text{Fe}_2$  ( $\text{R} = \text{Ho}, \text{Er}$ ) have been investigated. The deviation of the lattice parameters from Vegard's law indicates that the Ce valence in both systems fluctuates with the concentration of the dopant R. This fluctuation is directly relevant to the degree of localization of Ce 4f electrons, and is independent of the atomic size of the dopant element. The observed metamagnetic transition of  $\text{Ce}_{1-x}\text{Er}_x\text{Fe}_2$  has been analysed from the description in the band picture. The Ce valence fluctuation from the mixed-valence state to the localized state increases the moments of the Ce and Fe ions, and the Curie temperature. The changes in the mixed-valence state also affect the properties of the Ce–Fe coupling.

## 1. Introduction

Cerium, the least expensive of all of the rare-earth elements, when present in a trivalent state, can give rise to rare-earth anisotropies and magnetostrictions much larger than those of other rare-earth elements, according to the single-ion crystalline-electric-field model. Unfortunately, it has been recognized [1, 2] that cerium-based compounds behave somewhat differently from other rare-earth materials, in that the 4f electrons cannot be regarded as entirely localized at the rare-earth site, and consequently their properties cannot be predicted either, by assuming a trivalent Ce ion. In fact,  $\text{CeFe}_2$ , a typical cerium-based compound, is a ferromagnet and its lattice parameter (0.73 nm), Curie temperature (233 K) and local Fe magnetic moment ( $1.15 \mu_{\text{B}}/\text{f.u.}$ ) [3, 4] are considerably lower than those predicted on the basis of a Ce trivalent ion. These anomalies were initially ascribed to the transfer of Ce 4f electrons to the conduction band [5]. However, recent theoretical studies [6, 7] and some experimental results [8, 9] emphasize the important role played by hybridization between 4f and 5d and/or 3d electrons in determining these physical parameters for  $\text{CeFe}_2$ .

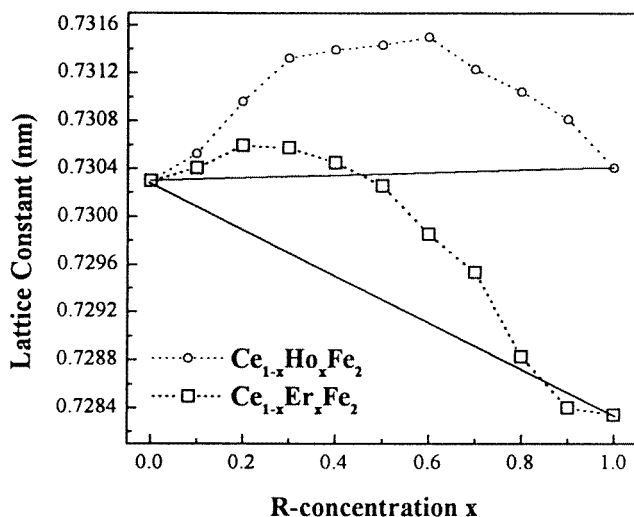
These parameters at the macroscopic level are mainly associated with 4f instabilities due to the effect of hybridization. In fact, it has been reported that cerium in  $\text{CeFe}_2$  is in a mixed-valence state (+3.29 valence) [10]. The pressure from either the external or the chemical factors generally has an influence on the hybridization between 4f and 3d electrons, which leads to a widening of the f level and the onset of the mixed-valence state. Therefore, the introduction of pressure will provide a useful tool for studying the mixed-valence behaviour and the related anomalous magnetic properties. The chemical pressure can be generated in a crystal lattice by the substitution of ions with larger (or smaller) ionic radii for the component ions to create a positive (or negative) internal pressure. It was initially observed that a very

small degree of Fe-site substitution (3%) with Al and Co gives rise to a low-temperature re-entrant spin-glass state and the disappearance of the ferromagnetic ordering [11]. Obviously, such a major change in the magnetic properties does not result from the pressure effect. On the other hand, in a previous publication [12] we have reported experimental results on the Ce-site substitution of the rare earth R (R = Tb, Dy)—with different atomic sizes from that of the  $\text{CeFe}_2$  parent. It has been clearly observed that a change occurred from the mixed-valence state in  $\text{CeFe}_2$  to the ‘nearly’ trivalent state in the substituted form. It is worth of noting that the lattice parameters of  $\text{RFe}_2$ , when R = Tb (0.7347 nm) [13], Dy (0.7325 nm) [14], Gd (0.7396 nm) [13], Y (0.7353 nm) [15], are all larger than those of  $\text{CeFe}_2$ , and consequently an internal positive pressure acts additionally on the Ce site. But what happens when there is a negative pressure acting on the Ce site?

In order to gain a deeper insight into the nature of the change of the mixed-valence state, we synthesized two serial pseudobinary compounds,  $\text{Ce}_{1-x}\text{Ho}_x\text{Fe}_2$  and  $\text{Ce}_{1-x}\text{Er}_x\text{Fe}_2$ , and measured their lattice parameters and magnetic properties. Considering the lattice constant of  $\text{CeFe}_2$  is essentially equal to that for  $\text{HoFe}_2$  (0.7304 nm) [13] and smaller than that for  $\text{ErFe}_2$  (0.7283 nm) [13], the presence of the internal pressure on the Ce site is different from the case of the positive pressure mentioned above.

## 2. Experiments

The samples of  $\text{Ce}_{1-x}\text{R}_x\text{Fe}_2$  (R = Ho, Er) with  $x$  from 0.0 to 1.0 were prepared by arc melting the appropriate amounts of Fe (purity better than 99.9 wt%) and the rare earth (99.95 wt%) under a purified argon atmosphere, and they were remelted several times to ensure good homogeneity. They were thermally treated under vacuum at 850 °C for one week. 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 calculated lattice constants was estimated to be  $\pm 0.0002$  nm.



**Figure 1.** The lattice parameter of  $\text{Ce}_{1-x}\text{R}_x\text{Fe}_2$  (R = Ho, Er) as a function of the concentration  $x$  of the dopant R. The accuracy is estimated to be  $\pm 0.0002$  nm. The full line represents the linear fit according to Vegard's law.

Magnetization isotherms were measured with an extracting-sample magnetometer at fields up to 60 kOe at 5 K. The saturation magnetization was deduced from  $M^2$  versus  $H/M$  plots. The Curie temperature was determined by plotting the magnetization versus temperature, measured using a vibrating-sample magnetometer in a magnetic field of 500 Oe, and extrapolating the steepest part of the curve to zero magnetization. The values are believed to be accurate to  $\pm 3$  K.

### 3. Results and discussion

The results from XRD measurements show that the cubic Laves ( $MgCu_2$ ) structure is maintained for  $Ce_{1-x}Ho_xFe_2$  and  $Ce_{1-x}Er_xFe_2$  throughout the alloy series. The lattice constants ( $a$ ) of both compounds are shown in figure 1 as functions of the dopant concentration  $x$ . We found that the composition dependences of the lattice constants each exhibit positive deviation from Vegard's law. Because the ionic radius of the localized Ce ions is larger than that of the delocalized Ce ions, the type of deviation can be regarded as a result of the transition tendency of the Ce valence to move from +3.29 towards +3 valence. This phenomenon has also been observed in the systems  $Ce_{1-x}R_xFe_2$  ( $R = Tb, Dy, Gd, Y$ ) [12, 16, 17] which are characterized by positive internal pressure. It is noteworthy that, although the internal pressure can be essentially negligible or negative in the present systems, the same positive deviation can still be observed as in the case of the positive internal pressure. This implies that the change of the mixed-valence state is independent of the ionic radius of the dopant elements and of the characteristics of the internal pressure introduced by the alloying method.

Figure 2 shows the magnetization isotherms of  $Ce_{1-x}Ho_xFe_2$  and  $Ce_{1-x}Er_xFe_2$  at 5 K measured with an extracting-sample magnetometer at fields up to 60 kOe. A rapid increase of the magnetization for  $Ce_{1-x}Er_xFe_2$  is observed well within the concentration range  $0.4 \leq x \leq 0.6$ . The critical field of the metamagnetic transition (MT) increases with increasing dopant concentration  $x$ . A similar phenomenon has been observed for the systems  $Ce_{1-x}Tb_xFe_2$  and  $Ce_{1-x}Dy_xFe_2$ . In general, the MT is closely correlated with the electronic structure. A sharp peak in the density-of-states (DOS) curve of the Ce 4f band exists above the Fermi level, as shown by the band calculation [7]. From the description in the band picture, it is considered that a partial substitution of Er for Ce in  $CeFe_2$  shifts the 4f DOS peak to a position close to the Fermi level. The sharp peak of the DOS close to the Fermi level was considered as being responsible for the MT transition. However, it is surprising that a MT has not been observed in the  $Ce_{1-x}Ho_xFe_2$  system (figure 2). In fact, no MT occurs in the range of applied magnetic fields up to 60 kOe in the compounds  $Ce_{1-x}R_xFe_2$  when  $R = Pr, Nd, Gd, Y$ . It is possible that these substitutions do not have a sufficiently strong effect to cause a large shift in the peak of the DOS.

The saturation magnetization  $\mu_s$  of  $Ce_{1-x}R_xFe_2$  ( $R = Er, Ho$ ) as a function of the dopant concentration  $x$  at 5 K is shown in figure 3. It is found that the magnetic moments of both systems increase with increasing  $x$ . If we suppose that the magnetism of  $Ce_{1-x}R_xFe_2$  can be regarded as the simple average of those of two isostructural  $MgCu_2$  phases, namely,  $CeFe_2$  and  $RFe_2$ , the theoretical total magnetic moments of the systems investigated, as functions of the dopant concentration  $x$ , can be expressed in a linear form as follows:

$$\mu_s = x\mu_{RFe_2} - (1 - x)\mu_{CeFe_2} \quad (1)$$

where the saturation magnetizations of  $ErFe_2$ ,  $HoFe_2$  and  $CeFe_2$  were found from the present measurement to be 5.40, 5.95 and 2.32  $\mu_B/f.u.$ , respectively. The theoretical saturation magnetizations  $\mu_s$  calculated from equation (1) for both systems are also shown as functions of  $x$  in figure 3 as two straight lines. It is found that the experimental values are in good

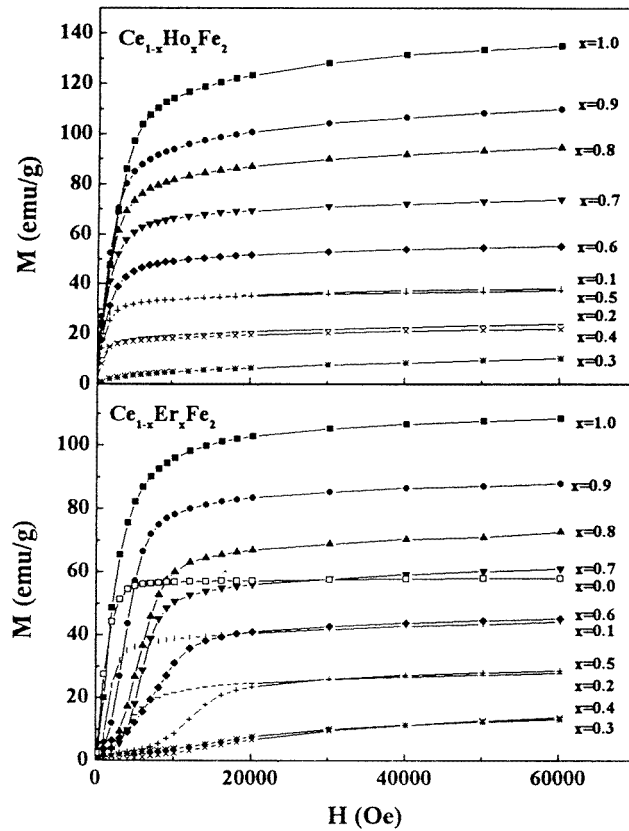
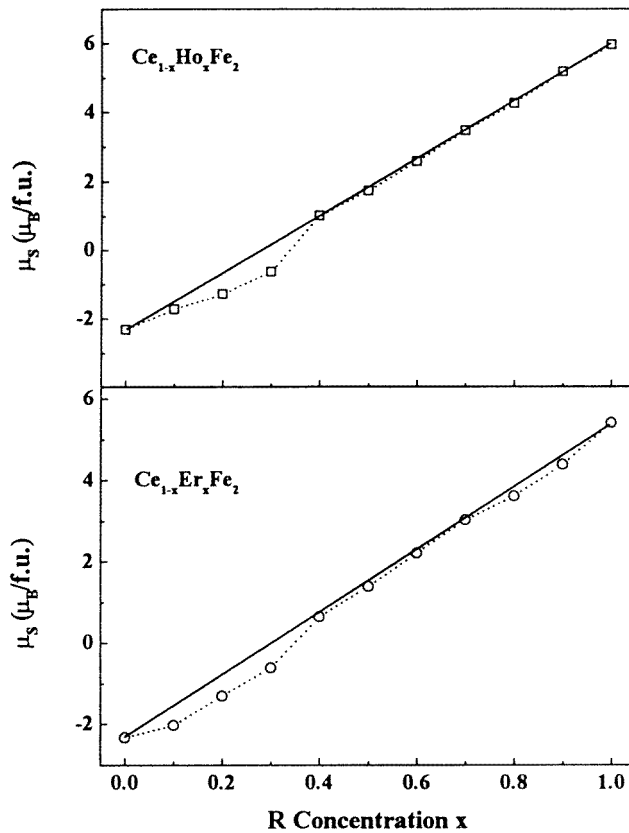


Figure 2. Magnetization isotherms for  $Ce_{1-x}R_xFe_2$  ( $R = Ho, Er$ ) at 5 K.

agreement with the theoretical ones at high dopant concentrations of  $x > 0.4$ . However, the measured data for the two systems exhibit substantial deviations from the theoretical values in the high-Ce-concentration range.

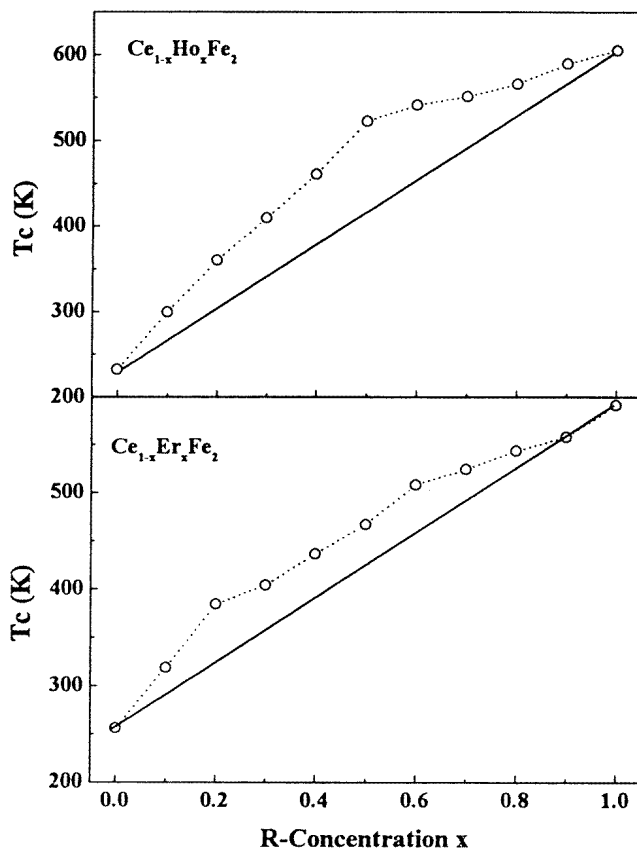
Considering the change in Ce valence on the basis of the lattice parameter data, the change in the degree of localization of Ce 4f electrons will cause changes of the magnetic moments of both the Ce sublattice and the Fe sublattice. In general, the Ho (Er) moment can be regarded as constant, because the 4f electrons are positioned within the ion cores and also the hybridization with the conduction band electronic state is negligible. The moments of Ce and Fe sublattices increase with the enhancement of the degree of localization of the Ce 4f electron states and the decrease of the hybridization between the Ce 4f and Fe 3d electrons. The moments of the Ce ion with +3 valence and Fe in normal  $RFe_2$  are  $2.54 \mu_B$  and  $1.77 \mu_B$ , respectively. However, it has been reported [4], 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. In the mixed-valence state, the moment of Ce decreases more rapidly than the Fe moment, and consequently the change of the Ce moment is more sensitive to the degree of 4f-3d hybridization. Therefore it is reasonable that the increasing magnitude of the Ce moment can become larger than that of Fe with increasing degree of localization of the Ce 4f electron, when the Er and Ho ions are introduced. The different increments of the Ce and Fe moments, even if they couple in an



**Figure 3.** The saturation magnetic moments as functions of the concentration of R,  $x$ , for  $Ce_{1-x}R_xFe_2$  ( $R = Ho, Er$ ) at the same temperature, 5 K. The full lines result from the assumption that the total saturation magnetic moment is the average of the contributions of  $CeFe_2$  and  $RFe_2$ .

antiparallel fashion with each other, causes the magnetizations for the  $Ce_{1-x}R_xFe_2$  ( $R = Ho, Er$ ) systems to deviate negatively from the lines, as in the interpolations mentioned above. Of course, in the low-Ce-concentration range, the magnetization contribution from the change of the Ce valence is too small to cause an observable deviation. In the high-Ce-concentration range, however, this contribution to the magnetization can clearly be observed, and confirms the conclusion.

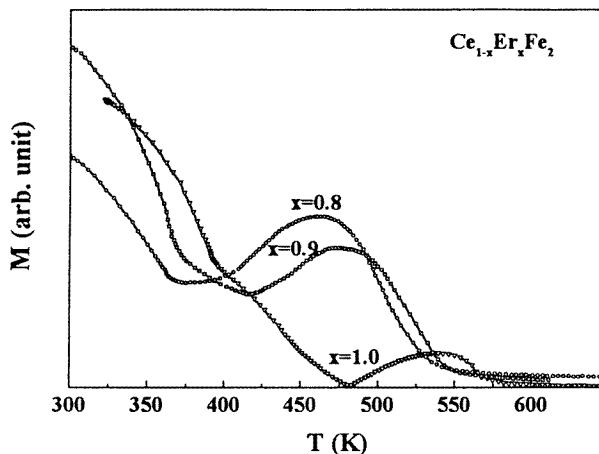
Another effect on magnetic properties arising from the change of the mixed-valence state is also observed directly from the dependence on the Ce concentration of the Curie temperature  $T_c$  of  $Ce_{1-x}R_{1-x}Fe_2$  ( $R = Er, Ho$ ). Figure 4 shows this influence on  $T_c$ . The dependence of  $T_c$  for  $Ce_{1-x}Ho_xFe_2$  on  $x$  can be basically divided into two fields bounded by  $x = 0.5$ . Within the two fields, different rates of change of  $T_c$  occur: when  $x > 0.5$ ,  $T_c$  decreases slowly from the value at  $x = 1.0$ , by about 80 K, from 605 K for  $HoFe_2$  to 523 K for  $Ce_{0.5}Ho_{0.5}Fe_2$ . However, it decreases rapidly by about 190 K from 523 K for  $Ce_{0.5}Ho_{0.5}Fe_2$  to 233 K for  $CeFe_2$ .  $T_c$  for the  $Ce_{1-x}Er_xFe_2$  system shows a broadly similar tendency, except that the boundary between the two fields lies at  $x \sim 0.6$ . It is also noteworthy that the concentration dependences of  $T_c$  and the lattice parameters show quite similar behaviours. This indicates that they have the same origin—that is, the change in the degree of localization of the Ce 4f electronic state.



**Figure 4.** The dependence on the concentration of R of the Curie temperature for the  $Ce_{1-x}R_xFe_2$  ( $R = Ho, Er$ ) compounds. The error is smaller than 5 K.

The contribution to the Curie temperature of the rare-earth–iron intermetallic compounds is thought to result mainly from the exchange interaction between Fe 3d electrons. Therefore the change of the mixed-valence state in the systems investigated enhances the degree of Fe–Fe coupling.

In addition to causing the changes in the Curie temperature and the magnitudes of the Ce and Fe moments, the mixed-valence state is also relevant to the properties of the coupling between Ce 4f and Fe 3d electrons. The parallel coupling between the rare-earth spin and the Fe moments for the light rare-earth compounds leads to ferromagnetism. However, for  $CeFe_2$  the experimental and theoretical results indicate that the Ce 4f moment couples ferrimagnetically with the Fe moment. It is the 3d–4f hybridization that causes this exception. The substitutions of Er and Ho ions for Ce decrease the degree of hybridization and drive the Ce into changing towards the normal state. The direction of the coupling should change gradually to agree with the ferromagnetic coupling rule for the normal light-rare-earth–iron-based compounds. Therefore, a non-collinear alignment between rare earths and Fe moments could occur to some extent. Figure 5 shows the temperature dependence of the magnetization for  $Ce_{1-x}Er_xFe_2$  ( $x \geq 0.8$ ).  $ErFe_2$  is the only compound of the  $RFe_2$  type to show a compensation temperature for the magnetic moment. The temperature measured in our experiment is 468 K and is in agreement with that reported previously [13]. The compensation temperature for  $Ce_{1-x}Er_xFe_2$



**Figure 5.** The temperature dependence of the magnetization of  $Ce_{1-x}Er_xFe_2$  ( $x \geq 0.8$ ). The applied magnetic field is 500 Oe.

decreases with increasing Ce concentration. The  $M-T$  curve for  $ErFe_2$  exhibits a region of rapid change near the compensation temperature. When Ce ions are substituted into the compound, however, the curve near the compensation temperature changes smoothly and the magnetic moment does not vanish at this temperature. This confirms the non-linear relationship between the Ce and Fe moments. This non-linear relationship may be relevant to the characteristics of magnetic couplings, which also depend on the density of states at the Fermi level [18].

In conclusion, the substitutions of Ho and Er for Ce in  $Ce_{1-x}R_xFe_2$  indicate that the atomic radius of the substituting elements does not affect the characteristics of the Ce valence fluctuation, which is governed only by the change of electronic structure of the pseudobinary systems investigated. The Ce valence fluctuation from the mixed-valence state to the localized state increases the moments of both the Ce and the Fe ions, and enhances the degree of Fe-Fe coupling; consequently, the Curie temperature increases. The change of the mixed-valence state also affects the properties of the Ce-Fe coupling.

### Acknowledgment

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