

## Magnetic behavior of $\text{CeFe}_2$ : Effects of Ru, Rh, and Pd substitutions

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Results are presented for the effects of substitution of Ru, Rh, and Pd for Fe in  $\text{CeFe}_2$ . For Ru and Pd the Curie temperature is lowered for up to 10% substitution without change in magnetic character. Ru substitutions produce (for 4% to 8%) the low-temperature loss of ferromagnetism observed for around 10% Co. At larger Ru substitutions no ferromagnetic regime is found but resistivity, susceptibility, and magnetization results suggest the presence of magnetic freezing which has some antiferromagnetic and some spin-glass features. These results are discussed in terms of the effects that might be produced by  $4f$ -conduction-band hybridization, its modification by alloying and theories of the types of phase diagram that can be produced in itinerant-electron systems with competing interactions.

### I. INTRODUCTION

$A\text{Fe}_2$  Laves-phase compounds, where  $A = \text{Sc, Ti, Hf, Nb, Zr, Y, U}$  and various rare earths  $M$ , have been a subject of intensive experimental and theoretical studies in recent years because of the interesting relationship between magnetism and crystal structure in these compounds. Various types of magnetic order appear depending on the element at the  $A$  site. In the hexagonal ( $C14$ ) Laves-phase structure,  $\text{ScFe}_2$  exhibits ferromagnetism,<sup>1,2</sup>  $\text{TiFe}_2$  antiferromagnetism,<sup>3</sup> and  $\text{NbFe}_2$  (at and around its stoichiometric composition) various interesting ferromagnetic and antiferromagnetic behavior.<sup>4</sup> On the other hand, the cubic ( $C15$ ) Laves-phase iron compounds with U and rare-earth elements are well known for their interesting magnetic and magnetostrictive properties.<sup>5,6</sup>

The alloying effects in the  $C14$  compounds have revealed exotic magnetic transitions between ferromagnetism and antiferromagnetism as a function of composition and temperature in  $(\text{Hf}_{1-x}\text{Ta}_x)\text{Fe}_2$  (Ref. 7) and a possibility of the coexistence of ferromagnetism and antiferromagnetism in  $(\text{Sc}_{1-x}\text{Ti}_x)\text{Fe}_2$  (Ref. 8) and  $(\text{Zr}_{1-x}\text{Nb}_x)\text{Fe}_2$ .<sup>9</sup> Similar studies of alloying in  $C15$  compounds have, so far, been mainly in relation to the interesting magnetostrictive properties of the heavy rare earths,<sup>6</sup> but interesting magnetic behavior (spin glass and reentrant spin glass, etc.) is also found in  $C15$  compounds.<sup>10</sup>

A significant feature of the  $A\text{Co}_2$  compounds, where  $A$  is not magnetic is that, unlike the corresponding  $A\text{Fe}_2$  compounds, they never show magnetic order, and a lot of work has been done on  $A\text{Co}_2$ - $A\text{Fe}_2$  systems to study the ways in which magnetic order sets in. In the course of such work on  $\text{CeCo}_2$ - $\text{CeFe}_2$  (a system made particularly interesting by the superconductivity of  $\text{CeCo}_2$  and low Curie temperature and low ordered moment of  $\text{CeFe}_2$ ) Rastogi and Murani<sup>11</sup> discovered a range of compositions around 10% Co substitution for Fe, showing a dramatic loss of magnetic response at low temperatures. It was later shown by neutron-scattering measurements that the

loss of magnetic response was due to a ferromagnetic-to-antiferromagnetic transition accompanied by a rhombohedral lattice distortion,<sup>12</sup> although at Co substitutions greater than 20%, normal ferromagnetic character reappears. It has since become clear that anomalous behavior can be induced in  $\text{CeFe}_2$  by small substitutions of other elements on the Fe site. For Al additions, 2% to 3.5% substitutions showed a spin-canting<sup>13</sup> or reentrant spin-glass-like<sup>14</sup> behavior and 4% to 5% substitutions probably lead to antiferromagnetic-type transitions.<sup>15,16</sup> All these results suggest that the ferromagnetism in  $\text{CeFe}_2$  is very close to some type of instability. In order to shed more light on this matter we have undertaken the study of the effects of alloying in  $\text{CeFe}_2$  of various  $4d$  and  $5d$  elements. Here we shall present some of the results, namely the effects of Ru, Rh, and Pd substitutions in  $\text{CeFe}_2$ . A preliminary report of this work has been presented at the 32nd Annual Conference of Magnetism and Magnetic Materials.<sup>17</sup> We hope to show that the various interesting behavior of  $\text{CeFe}_2$  pseudobinaries can be rationalized in terms of theories of itinerant magnetism when the possibility of and evidence for variations in  $4f$  hybridization with  $d$  electrons are taken into account.

### II. EXPERIMENT

The alloys were prepared by argon arc melting from metals of at least nominal 99.99% purity and suction chill casting into copper molds<sup>18</sup> to produce square cross-section rods. The first few alloys of the series were homogenized *in vacuo* for seven days at 600°C. Preliminary measurements at room temperature revealed a trace of magnetic impurities in all the samples. Due to the peritectic reactions during the solidification process, one expects to find in the as-cast structure cores of  $\text{Ce}_2\text{Fe}_{17}$  with perhaps some iron-solid solution at their center, surrounded by shells of  $\text{CeFe}_2$  and eutectic material. Normally the first-formed solids should disappear with adequate heat treatment, but in practice there is almost always some trace of second phase in the annealed

samples. The presence of a second phase in the form of magnetic impurities was reported in  $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$  (Ref. 13) and  $\text{Ce}(\text{Fe}_{1-x}\text{Ni}_x)_2$  (Ref. 19). Questions may now arise about the role of the second phases and their effect on the sought-after Laves phase. This was considered by Harris and Longworth,<sup>19</sup> and they argued that since previous work on the cubic rare-earth transition metal Laves phase indicated that this phase generally had a range of homogeneity on the transition-metal-rich side of stoichiometry, it is unlikely, therefore, that the Laves phase in pseudobinary iron alloys is iron deficient. We ourselves have prepared a few samples of  $\text{CeFe}_2$  varying the stoichiometric composition both towards the Fe-rich and Ce-rich side and found little change in the magnetic properties. (It should be remembered, however, that there were indications in  $\text{UCo}_2$  that at the ideal composition some degree of occupation of U sites by Co atoms took place.<sup>20</sup>) With various heat treatment we have found that the sequence of annealing at 600°C for two days, 700°C for five days, 800°C for two days, and 850°C for one day improved the quality of the  $\text{CeFe}_2$  samples a great deal. All the samples were subjected to careful metallographic analysis to investigate the possible presence of a second phase. In the Ru series a small amount of second phase (certainly less than 5%) was found in almost all the samples, and this was considered to be negligible for the purpose of our present study. In the Rh and Pd series a marked increase in the amount of second phase was observed with 10% substitution (more in the case of Pd), and 15% alloys are certainly not single-phase alloys. It should be noted here that in the  $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$  system, it was not possible to get a single-phase alloy for  $x > 0.12$  (Ref. 13). We have made x-ray diffraction measurements on some of the  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  alloys, and they all show the C15 Laves-phase structure of the parent compound  $\text{CeFe}_2$ . A plot of our lattice constant (only accurate to  $\pm 0.005$ ) versus concentration of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  is shown in Fig. 1. ac susceptibility measurements were performed with a driving frequency of 300 Hz and a driving field of 0.7 Oe parallel to the long axis of samples. A standard four-probe dc method with

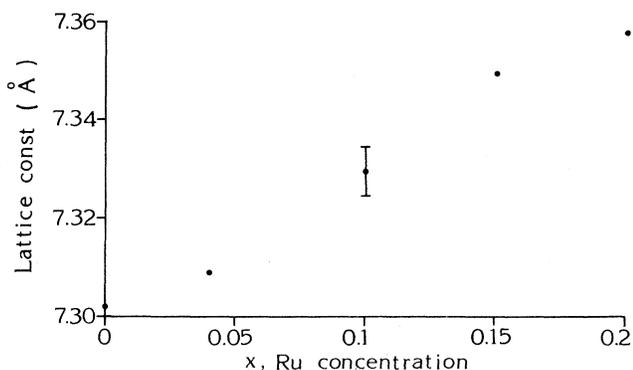


FIG. 1. Plot of lattice constant vs Ru concentration ( $x$ ) of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x < 0.2$ .

computerized on-line data collection was employed for the resistivity measurements. To support some of the ac susceptibility results, dc magnetization measurements using an extraction magnetometer and a vibrating sample magnetometer were performed on a few samples.

### III. RESULTS AND DISCUSSION

#### A. ac susceptibility ( $\chi$ )

##### 1. $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$ , $x = 0, 0.01$ and $0.03$

We present the ac susceptibility ( $\chi$ ) versus temperature ( $T$ ) for these alloys in Fig. 2. In fact ac susceptibility results for  $x = 0$  along with  $x = 0.02, 0.04,$  and  $0.06$  were presented earlier in a preliminary report of this work<sup>17</sup> but are reproduced here for the sake of comparison. We estimate the Curie temperature ( $T_C$ ) from the point of inflexion in the region of sharp rise of  $\chi$  against  $T$ . Our  $T_C$  in  $\text{CeFe}_2$  is 235 K which tallies well with published results.<sup>5</sup>  $T_C$  decreases with increase in  $x$  and a change in the  $\chi(T)$  slope appears at a lower temperature ( $T_F$ ) in  $x = 0.03$ . This change in slope also appeared in  $x = 0.02$  (Ref. 17) (at a temperature lower than that at  $x = 0.03$ ) and is very similar to that observed in other pseudobinaries of  $\text{CeFe}_2$ , e.g., those with 2% Al (Ref. 14) and 4% Co (Ref. 11). Similar behavior has also been observed in the  $\text{Y}(\text{Fe}_{1-x}\text{Al}_x)_2$  system.<sup>10</sup> This characteristic of  $\chi$  versus  $T$  has sometimes been linked with reentrant spin-glass phenomenon as observed in  $\text{AuFe}$  and other reentrant spin glasses,<sup>21-23</sup> but here a spin canting, prefiguring the antiferromagnetism found at higher Ru concentrations, seems more likely. An alternative explanation of the low-temperature anomaly could be put forward in terms of a well-defined onset of contributions to anisotropy that make the motion of domain walls difficult. Miyazaki *et al.*<sup>24</sup> used such a domain wall pinning model to explain a similar low-temperature magnetic anomaly in Fe-Ni and Fe-Ni-Mn alloys, but the  $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$  results<sup>11</sup> suggest a more fundamental origin.

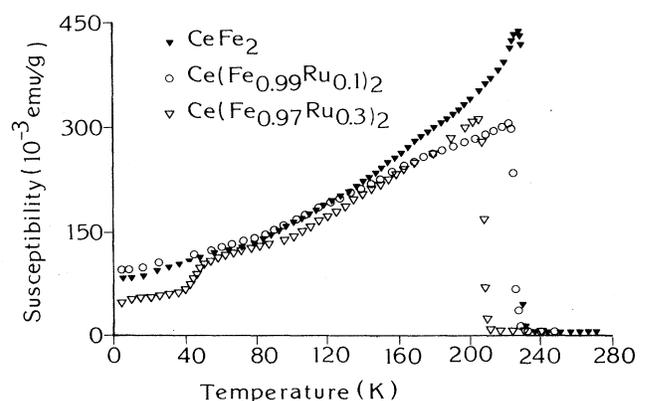


FIG. 2. ac susceptibility vs temperature of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0, 0.01,$  and  $0.03$ .

### 2. $Ce(Fe_{1-x}Ru_x)_2$ , $x = 0.05, 0.07, \text{ and } 0.08$

$\chi$  versus  $T$  plots for these samples are shown in Fig. 3. Note that the change in slope of  $\chi$  at the low-temperature anomaly  $T_F$  has become very dramatic, while  $T_C$  decreases steadily with  $x$ . This dramatic drop in susceptibility  $\chi$  in fact had already appeared at  $x = 0.04$ .<sup>16</sup> As we go from  $x = 0.04$  to  $x = 0.08$ ,  $T_C$  and  $T_F$  approach each other, and for  $x = 0.08$  the behavior becomes particularly interesting. In this sample  $T_C$  and  $T_F$  apparently are so near that the susceptibility drops dramatically at  $T_F$  almost immediately after the sharp rise at  $T_C$  (see Fig. 3).

$Ce(Fe_{0.9}Co_{0.1})_2$  was the first of the  $CeFe_2$  pseudobinaries to show this anomalous behavior,<sup>11</sup> but it has now been observed in various  $CeFe_2$  pseudobinaries with 4% Al and 3% Ir and Os (Ref. 25). It suggests that a drastic canting or even a ferromagnetic-to-antiferromagnetic transition is taking place at  $T_F$ . It is to be noted that for Ru substitutions the drop in susceptibility is more drastic than that of  $CeFe_2$  with 3.5% Al (Ref. 14), and the idea of a reentrant spinglass (suggested as a possible explanation for  $CeFe_2$  with 3.5% Al) is unlikely to hold good here.

### 3. $Ce(Fe_{1-x}Ru_x)_2$ , $x = 0.09, 0.1, 0.12, \text{ and } 0.15$

The behavior of these samples is altogether different from that of the earlier ones. Here the  $\chi$  versus  $T$  plot (Fig. 4) shows a maximum which shifts slightly towards lower temperatures with increase in  $x$ . Such behavior has been observed in  $CeFe_2$  with 8% Al (Ref. 14). While other workers described similar behavior in  $CeFe_2$  with 7% and 10% Al in terms of a spin-canting phase,<sup>13</sup> we originally referred to it as a spin-glass-like.<sup>14</sup> We have since extended our work<sup>16</sup> in the  $Ce(Fe_{1-x}Al_x)_2$  system and now think these systems are too complicated to be described simply as spin-glass-like and that the results of ac susceptibility alone cannot be definitive. It is interesting to note that the behavior of  $(Rh_{1-x}Ir_x)Fe$  (Ref. 26) is

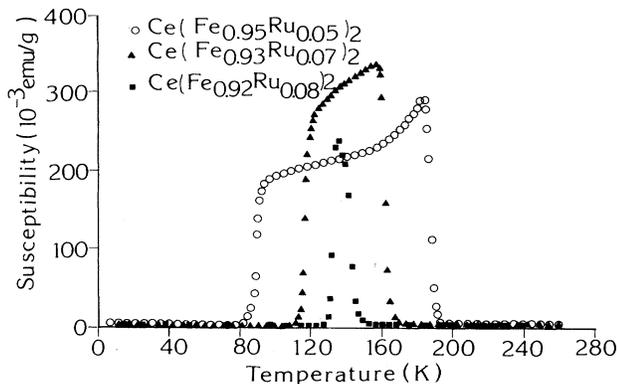


FIG. 3. ac susceptibility vs temperature of  $Ce(Fe_{1-x}Ru_x)_2$  with  $x = 0.05, 0.07, \text{ and } 0.08$ .

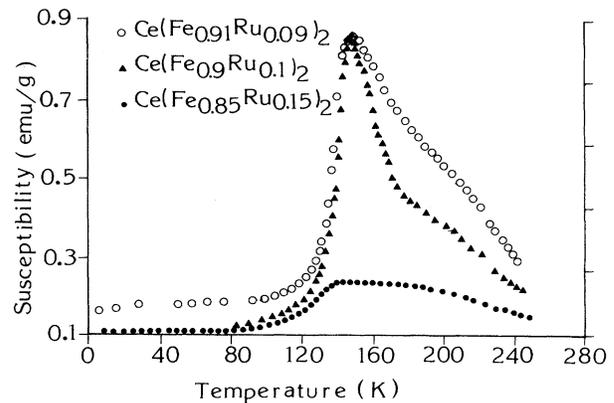


FIG. 4. ac susceptibility vs temperature of  $Ce(Fe_{1-x}Ru_x)_2$  with  $x = 0.09, 0.1, \text{ and } 0.15$  (units are  $10^{-3}$  emu/g).

closely similar to that of our present system. In  $(Rh_{1-x}Ir_x)Fe$  also, with increase in Ir concentration,  $T_C$  and  $T_N$  approach each other, and for  $x = 0.121$  the behavior is very similar to that of  $Ce(Fe_{1-x}Ru_x)_2$  with  $x = 0.09-0.15$ .

The drastic loss of ferromagnetic response at  $x = 0.09$  is brought out in Fig. 5 where we plot  $\ln_{10}\chi_{(\text{peak})}$  against Ru concentration ( $x$ ), where  $\chi_{(\text{peak})}$  is the maximum value of susceptibility for various  $x$ . All these results suggest that whatever may be the magnetic ground state of the alloys  $x > 0.09$ , be it antiferromagnetic, spin glass, or some sort of admixture, no trace of true long-range ferromagnetic character remains.

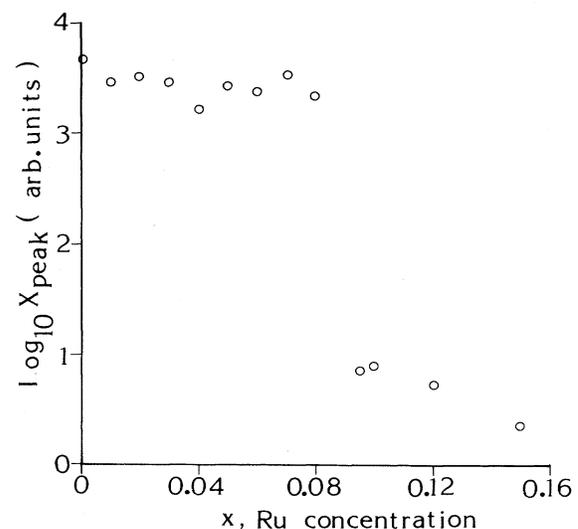


FIG. 5. Plot of  $\log_{10}\chi_{\text{peak}}$  vs Ru concentration ( $x$ ) of  $Ce(Fe_{1-x}Ru_x)_2$  with  $x < 0.15$ , where  $\chi_{\text{peak}}$  is the maximum susceptibility in individual alloys multiplied by  $10^4$ .

#### 4. $\text{Ce}(\text{Fe}_{1-x}\text{Rh}_x)_2$ , $x = 0.02, 0.04, \text{ and } 0.1$

$\chi$  versus  $T$  plots (Fig. 6) for these alloys show simple dilution effects, in contrast to the dramatic behavior of the  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  system. As indicated earlier, solid solubility in this system probably ceases above about 10% Rh substitution. There is a small change in slope in the susceptibility-versus-temperature curve in the temperature region of 130–170 K in all the three alloys. This change in slope is similar to that observed in the pure  $\text{UFe}_2$  compound<sup>27,28</sup> but there it is nowhere near as dramatic.

#### 5. $\text{Ce}(\text{Fe}_{1-x}\text{Pd}_x)_2$ , $x = .05 \text{ and } 0.1$

The susceptibility behavior of  $\text{Ce}(\text{Fe}_{0.95}\text{Pd}_{0.05})_2$  is also shown in Fig. 6 and is similar to that of the Rh alloys; the decrease in  $T_C$  is even slower. The  $T_C$  of  $\text{Ce}(\text{Fe}_{0.9}\text{Pd}_{0.1})_2$  (not shown in Fig. 6) is almost the same as that of the 5% Pd alloy and along with the metallographic study suggests that the solid solubility limit of this system probably has already been reached by 10% Pd substitution.

### B. dc magnetization

We have performed dc magnetization measurements on  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0.04$  and  $0.06$  in a field of 300 Oe using an extraction magnetometer. The results are presented in Fig. 7, which shows that the magnetization drops sharply to a very small value at low temperatures. The transition temperature tallies well with  $T_F$  measured by the ac susceptibility.

We have also measured the dc magnetization of  $\text{Ce}(\text{Fe}_{0.9}\text{Ru}_{0.1})_2$  in a field of 500 Oe using a vibrating-sample magnetometer (VSM), in both zero-field-cooled (ZFC) and field-cooled (FC) condition (Fig. 8). Such ZFC and FC magnetization measurements have often been used for characterizing spin-glass systems. Though our measurement in  $\text{Ce}(\text{Fe}_{0.9}\text{Ru}_{0.1})_2$  shows a difference between ZFC and FC magnetization at temperatures somewhat below the maximum, the nature of it is not quite like that observed in the case of typical spin glasses.<sup>29</sup>

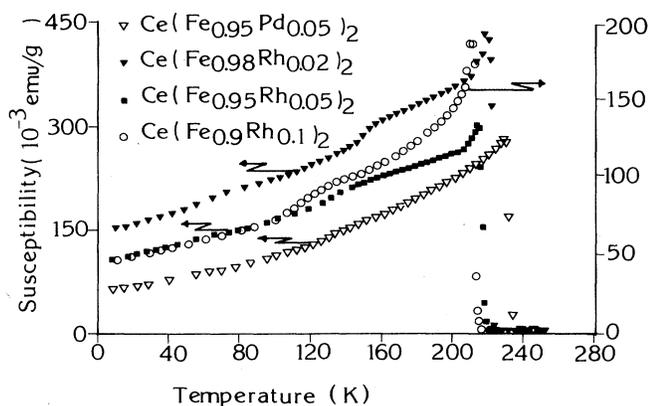


FIG. 6. ac susceptibility vs temperature of  $\text{Ce}(\text{Fe}_{0.95}\text{Pd}_{0.05})_2$  and  $\text{Ce}(\text{Fe}_{1-x}\text{Rh}_x)_2$  with  $x = 0.02, 0.04, \text{ and } 0.1$ .

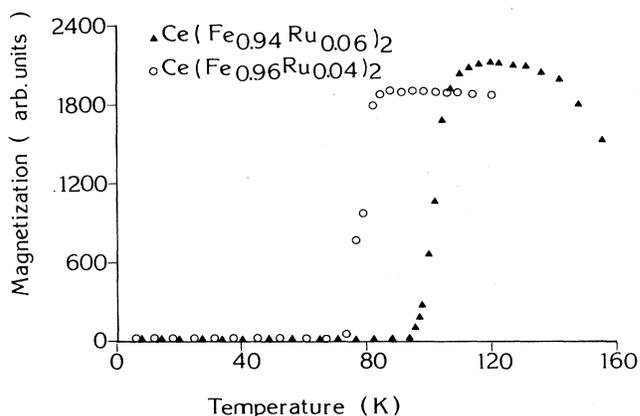


FIG. 7. Magnetization vs temperature of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0.04$  and  $0.06$ .

The peak temperature observed in the dc magnetization measurement is slightly lower than that observed in ac susceptibility measurement. It is to be remembered that the ac susceptibility measurement was performed in a field much smaller than that used in the dc magnetization measurement.

### C. Resistivity

We have measured the resistivity of the series of alloys  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $0.15 \geq x \geq 0$  in order to seek more insight into the interesting magnetic behavior of those alloys. We present these results in Figs. 9–11. The parent compound  $\text{CeFe}_2$  shows a distinct knee in the resistivity ( $\rho$ ) versus temperature ( $T$ ) plot at about 235 K which is indicative of its Curie temperature ( $T_C$ ), and the overall behavior matches quite well with earlier results on this compound.<sup>30</sup> It is to be noted here (as also pointed out by Rastogi *et al.*<sup>31</sup>) that the resistivity behavior of  $\text{CeFe}_2$  is anomalous in contrast with that of other  $M\text{Fe}_2$ ; with a

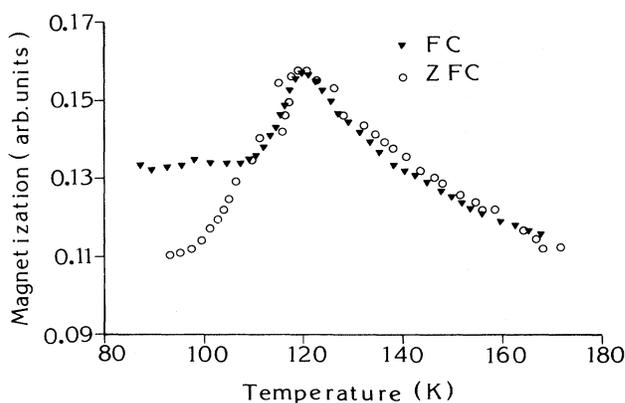


FIG. 8. Zero-field cooled (ZFC) and field-cooled (FC) magnetization of  $\text{Ce}(\text{Fe}_{0.9}\text{Ru}_{0.1})_2$ .

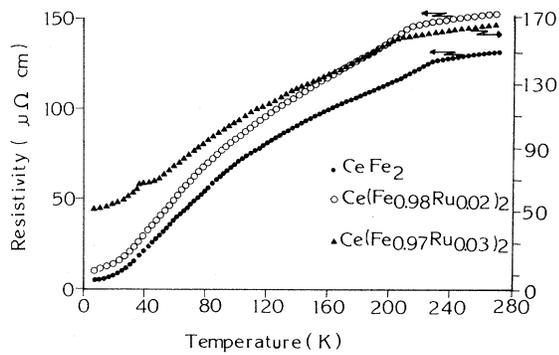


FIG. 9. Resistivity vs temperature of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0, 0.02,$  and  $0.03$ .

negative curvature in much of the temperature range below  $T_C$  in contrast to the positive curvature in all other  $M\text{Fe}_2$  compounds, where  $M$  is a rare earth. Also it has been shown by Rastogi *et al.*<sup>31</sup> that the coefficient  $A$  given by fitting the low-temperature results to  $\rho = AT^2$ , and presumably giving a measure of the magnon scattering, is ten times larger than in other  $M\text{Fe}_2$  compounds. The “knee” in the  $\rho$  versus  $T$  curve shifted towards lower temperature with  $x$ , in agreement with the susceptibility results. Within the resolution of our apparatus we could not detect any anomaly in the  $x = 0.02$  specimen in the low-temperature region where the  $\chi$  versus  $T$  plot showed a distinct change in slope, but a distinct anomaly did appear in  $x = 0.03$  at the same temperature where the susceptibility showed anomalous behavior. For  $x = 0.04$  this anomaly took the shape of a sharp local minimum. Similar relations between resistivity and susceptibility results have been observed in  $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$  (Ref. 30) and  $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$  (Ref. 31). It should be remembered here that in equiatomic  $\text{RhFe}$  a similar resistivity minimum appeared at the transition region from ferromagnetism to antiferromagnetism.<sup>32</sup> In the present sys-

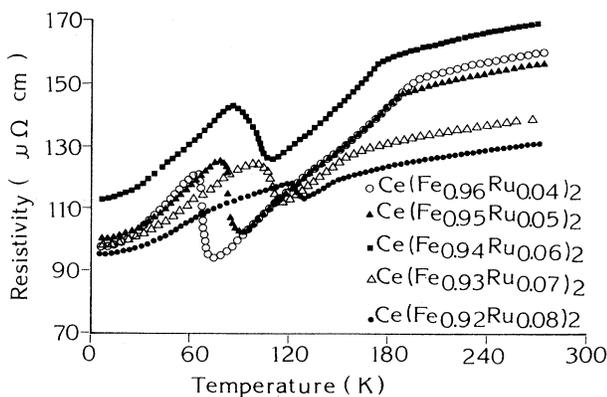


FIG. 10. Resistivity vs temperature of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0.04, 0.05, 0.06, 0.07,$  and  $0.08$ .

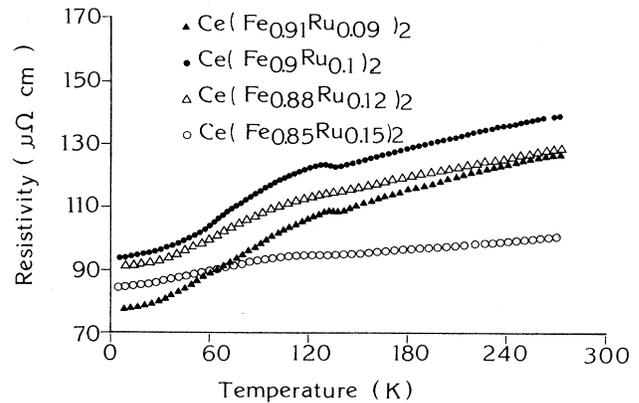


FIG. 11. Resistivity vs temperature of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x = 0.09, 0.1, 0.12,$  and  $0.15$ .

tem this resistivity minimum persisted until about  $x = 0.08$  and then started to fade away, having almost disappeared for  $x = 0.15$ . We denote the temperature where the susceptibility anomaly or resistivity minimum (or anomaly) appears as  $T_F$  in our subsequent discussion.

Because of the presence of microcracks in these brittle alloys the absolute values of their resistivities are very uncertain. The following general points can, however, be made with some confidence. The resistance ratio,  $R_{(4.2\text{ K})}/R_{(270\text{ K})}$  rises rapidly with initial Ru substitutions, reaching about 0.7 by  $x = 0.4$ , but thereafter at a much slower rate. The resistivity at room temperature probably increases slightly with initial additions of Ru and later decreases when the magnitude of maximum susceptibility has collapsed at around  $x = 0.09$ , and spin-disorder scattering at high temperature presumably decreases. This is also approximately the concentration above which a sharply defined resistivity anomaly is no longer found. (The depth of the minimum falls steadily with  $x$  from its value at  $x = 0.04$  where it is first clearly visible.) The weak minimum, with a more rounded maximum below it, found for  $x = 0.09$  and  $0.1$ , is rather like that seen in the itinerant antiferromagnet Cr at  $T_N$ .<sup>33</sup> This resistivity behavior can, we believe, be rationalized in terms of the models<sup>34,35</sup> used to discuss the resistivity behavior of rare-earth metals like dysprosium, with the significant difference that in Dy the order in temperature of the ferromagnetic and antiferromagnetic (helical) phases is reversed. As was earlier pointed out<sup>36</sup> while the same Brillouin-zone structure is appropriate for the conduction electrons in the paramagnetic and ferromagnetic conditions, the superzone boundaries that appear on antiferromagnetic ordering cause a remapping of the Fermi surface, reduce the effective freedom of the conduction electrons, and increase (for a given degree of magnetic order) the electrical resistivity. Thus in Dy the resistivity increases initially as antiferromagnetic order sets in and also, on raising the temperature, when the order changes from ferromagnetism to antiferromagnetism.<sup>37</sup> In the present alloys the initial onset of magnetic order is to fer-

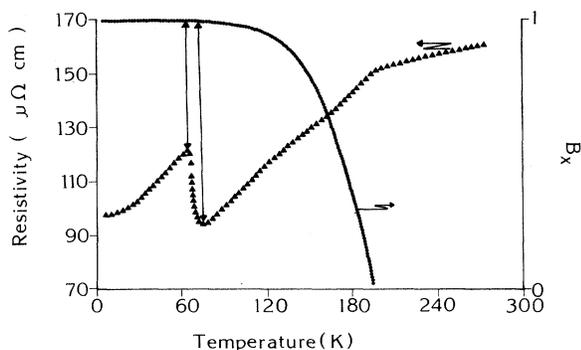


FIG. 12. The resistivity of  $\text{Ce}(\text{Fe}_{0.95}\text{Ru}_{0.05})_2$  together with a schematic sublattice magnetization (represented by a Brillouin-function-like order parameter  $B_x$ ) as a function of temperature which would explain the sharpness of resistivity anomaly when the alignments of the sublattice magnetizations change from parallel to antiparallel.

romagnetism, with a simple diminution of spin-disorder scattering at  $T_C$ , and it is only at the lower magnetic transition that superzone boundaries appear and increase the resistivity. This increase is fairly sharp when the degree of magnetic order is already well established by the time the transition is reached, but will be less so when the two transition temperatures are comparable. These two situations seem to be represented, respectively, by the behaviors of the  $x=0.05$  (Fig. 12) and the  $x=0.07$  (Fig. 13) alloys. In the latter,  $T_F$  lies in a temperature region where the sublattice magnetization is still increasing with decreasing temperature. A marked resistivity anomaly is still observed but it now extends over a temperature range in which significant changes in the degree of magnetic order are taking place. In this regard the case of  $\text{Ce}(\text{Fe}_{0.97}\text{Ru}_{0.03})_2$  is interesting in that although  $T_F$  is much lower than  $T_C$ , the resistivity anomaly is more like that found in higher Ru concentrations. We suggest that since the low-temperature antiferromagnetic character

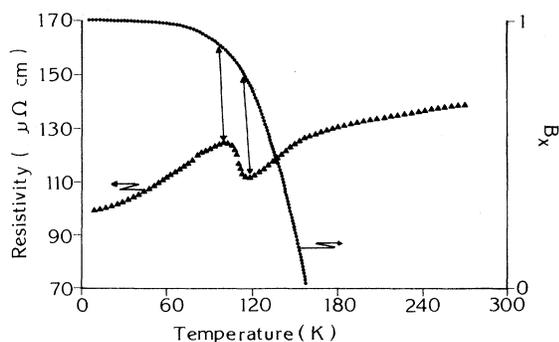


FIG. 13. The resistivity of  $\text{Ce}(\text{Fe}_{0.93}\text{Ru}_{0.07})_2$  together with a schematic sublattice magnetization (as in Fig. 14) which would explain the broadening of the resistivity anomaly.

has only just started to appear at  $x=0.03$  (but is fully developed at  $x=0.04$ ), a less sharp resistivity anomaly is to be expected in the former, where the susceptibility also suggests that the antiferromagnetism never becomes fully developed.

#### IV. DISCUSSION

The transition temperatures observed in the alloys with up to 15% substitution of Ru for Fe are shown in Fig. 14. This is only a tentative phase diagram, since it is not yet clear whether sharp boundaries separate (a) the dilute (canted-spin) regime, (b) the well-defined antiferromagnetic regime developing from ferromagnetism, and (c) the regime with >9% Ru where a less well-defined state of magnetic order exists. The loss of long-range ferromagnetism above  $x=0.08$  is very clear; but the resistivity behavior suggests that, while an appreciable correlation length for antiferromagnetism still exists at  $x=0.09$  and 0.1, this is gradually lost for further increase in  $x$ , itinerant antiferromagnetism probably being replaced by something more like Stoner spin-glass freezing found in Cu-Mn alloys at 55–65% Mn.<sup>38</sup> The field-cooling effects seen in the dc magnetization of the  $x=0.1$  alloy clearly suggest some spin-glass character. (At concentrations of Ru above 15% both the magnitude of the frozen magnetization and the freezing temperature should gradually fall to zero, since our preliminary results show that by 50% Ru substitution the susceptibility is very small and almost temperature independent, but in this range the actual behavior is obscured by small amounts of a magnetic impurity phase.) Without detailed neutron studies the distinction between a spin-glass state

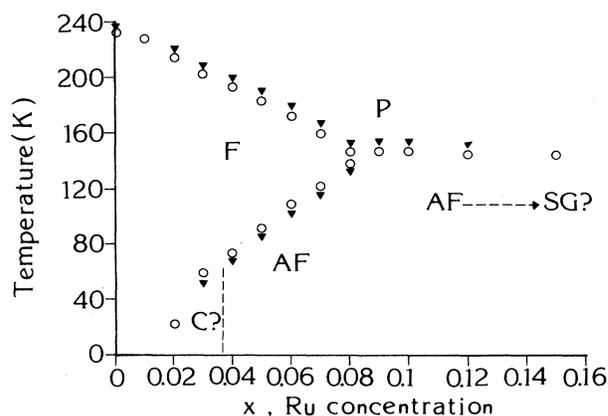


FIG. 14. Magnetic phase diagram of  $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$  with  $x < 0.15$ , where  $P$  stands for paramagnetism,  $F$  for ferromagnetism,  $AF$  for antiferromagnetism,  $C$  for canted magnetic structure, and  $SG$  for spin glass.  $\blacktriangledown$  denotes various transition temperatures obtained from resistivity measurements and  $\circ$  denotes transition temperatures obtained from ac susceptibility measurements.

and one with a periodicity of canting or antiferromagnetism (with a correlation length of many interatomic spacings) is not easily made. We would expect for  $0.04 \leq x \leq 0.1$  to find distinct, if broadened, antiferromagnetic Bragg peaks and a lattice distortion of the sort found in  $\text{Ce}(\text{Fe},\text{Co})_2$  (Ref. 12). (This has been confirmed recently in the 4% Ru alloy.<sup>39</sup>)

Other rare-earth-iron Laves-phase compounds show related distortions<sup>6</sup> connected with spin reorientation, although the spin reorientation observed in pure  $\text{CeFe}_2$ ,<sup>40</sup> which is indicative of some sort of anisotropic interactions, does not seem to produce a static lattice distortion.

The possibility of various types of phase diagrams for systems in which alloying introduces competing exchange interactions and competing anisotropies has been shown in various theoretical studies,<sup>41,42</sup> and competition of this sort can be shown to arise naturally when band-structure occupation [and consequently the structure of wave-vector-dependent susceptibility  $\chi(q)$ ] varies with composition in systems with itinerant electrons.<sup>43,44</sup> What makes alloys based on  $\text{CeFe}_2$  rather special is that an added source of variation in the wave-vector-dependent susceptibility  $\chi(q)$  is provided by the possibility of variations in the hybridization of the  $4f$  wave functions on the Ce atoms with the  $d$ -like Bloch states of the band ( $5d$  on Ce,  $3d$  on Fe). Such variations are strongly suggested by the anomalous lattice-spacing variation along the series  $\text{CeFe}_2$ - $\text{CeCo}_2$ - $\text{CeNi}_2$  (Ref. 45) and by recent  $L_{\text{III}}$  absorption spectroscopy measurements<sup>46,47</sup> on  $\text{CeT}_2$  compounds. The latter measurements have been interpreted in terms of effective valencies of Ce of about 3.3 (varying with  $T$ ), and even if the absolute numbers have little significance it is clear that a simple  $4f^0$  description, even in superconducting  $\text{CeCo}_2$ , must be abandoned.

It is gratifying that electronic structure calculations for  $\text{CeFe}_2$  (Ref. 45) show the itinerant character given to the  $4f$  electrons by  $f$ - $d$  hybridization, the existence of  $4f$  magnetization and a lattice-spacing anomaly at  $\text{CeCo}_2$ .

This itinerant character is not unlike that of dilute Anderson-Friedel alloys like  $\text{AuFe}$  or Anderson lattices like  $\text{Zn}_{13}\text{Mn}$ , where the transition-metal atoms are too far apart for  $d$ - $d$  overlap but  $d$ -conduction band hybridization is strong. With less extended  $4f$  functions such character is still present at closer Ce-Ce approaches.

Our observation that complex magnetic phase diagrams are not produced by substitutions for Fe of Rh, Pd, and Ni (Ref. 11) underlines the fact that simple disordering of the Fe sublattice cannot be responsible for those complexities, and the fact that all those elements come from the columns in the periodic table later than that of Fe suggests an important role for the  $d$ -band occupation; although the effect of Co and Ir then seems anomalous.

We would encourage further band-structure calculations and the measurement of other properties like specific heat and magnetostriction. In the recently held International Conference on Magnetism (Paris, 1988), we have become aware of magnetic and Mossbauer measurements on various  $\text{CeFe}_2$  pseudobinaries by a group from Tata Institute of Fundamental Research (TIFR), Bombay.<sup>48</sup> Their results where the compositions overlap agree, at least qualitatively, with those of ours.

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