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On the instability of ferromagnetism in $CeFe_2$: effects of alloying with Al, Mn, Y and U

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Abstract. Results are reported for the magnetic transitions in quasi-binary $CeFe_2$ alloys with substitutions of Al or Mn on the Fe sites and substitutions of Y or U on the Ce sites. The transitions have been studied by magnetic susceptibility and electrical resistance measurements, and comparisons are made with previous work involving alloying with a number of other transition metals, especially Co and Ru. The role of 4f–3d hybridisation indicated by theory is emphasised in the discussion, as are the variety of magnetic phase diagrams possible and the possible influence of changes in the effective valency of cerium.

1. Introduction

In a recent communication (Roy and Coles 1987) we have discussed the instability of ferromagnetism in $CeFe_2$ for small substitutions of Al on Fe sites. The main aim of that work was to shed further light on the various unusual behaviours of $CeFe_2$ (Atzmony and Dariel 1976, Deportes *et al* 1981) and its pseudo-binaries $Ce(Fe_{1-x}Co_x)_2$ (Rastogi and Murani 1987) and $Ce(Fe_{1-x}Al_x)_2$ (Franceschini and da Cunha 1985). We suggested the presence of competing ferro- and antiferromagnetic interactions for very small substitutions of Al, giving rise to a low-temperature re-entrant spin-glass-like phase, and then the total disappearance of long-range ferromagnetic order somewhere between 3.5 and 8%Al substitution, true order being replaced by a spin-glass-like phase. We proposed a magnetic phase diagram that was qualitatively similar to that of the isostructural system $Y(Fe_{1-x}Al_x)_2$ for $x < 0.25$ (Hilscher *et al* 1982). The much earlier change in $Ce(Fe_{1-x}Al_x)_2$ indicates the fragility of ferromagnetic order in the system.

Since then we have undertaken a major study of the magnetic and structural properties of $CeFe_2$ and its pseudo-binaries, replacing Fe with Co, Ru, Rh, Pd, Re, Os, Ir, Pt etc (Roy and Coles 1988, 1989). The picture emerging from this effort convinces us that the magnetic phase diagram of $Ce(Fe_{1-x}Al_x)_2$ for $x \leqslant 0.1$ is more complicated as well as more interesting than we had thought earlier (Roy and Coles 1987), and we decided to reinvestigate this system. There has also been some recent interesting work on the behaviour of the Ce valence in CeT_2 compounds (where T = Co, Ni, Fe and $Fe_{1-x}Mn_x$) (Croft *et al* 1987). In the light of this work, together with the interesting magnetic properties of $Ce(Fe_{1-x}Co_x)_2$, we have decided to investigate the magnetic properties of $Ce(Fe_{1-x}Mn_x)_2$ as well. Since we now have a strong suspicion that the electronic character of Ce is playing a quite important role in the magnetic properties of

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$CeFe_2$ and its pseudo-binaries, to throw some light on this we have prepared a few quasi-binary alloys of Ce (Fe, Al)$_2$, replacing some of the Ce with Y or U. In the following sections we describe first the experimental methods, then the susceptibility and resistivity data for each system. Finally, the results are discussed in the light of various pieces of theoretical work, and conclusions are drawn.

2. Experimental details

The alloys were prepared by arc melting from metals of at least nominal 99.99% purity and suction chill casting into copper moulds to produce rods of square cross section. The annealing procedure is quite important in these systems. The alloys reported in our previous study of the Ce(Fe, Al)$_2$ system (Roy and Coles 1987) were homogenised *in vacuo* at 600 °C for seven days. Our metallographic investigation revealed a small amount of second phase; also preliminary measurements at room temperature indicated the presence of some magnetic impurity. A similar presence of magnetic impurity has been reported by other workers (Franceschini and da Cunha 1985). From our work with $CeFe_2$ pseudo-binaries we have found that the heat treatment 600 °C for two days → 700 °C for five days → 800 °C for two days → 850 °C for one day improves the quality of the samples appreciably, hence we followed the same procedure for the alloys of the present investigation. The amount of second phase in $Ce(Fe_{0.9}Al_{0.1})_2$ is larger (about 5%) than in the other alloys in this series and it is to be remembered that $Ce(Fe_{1-x}Al_x)_2$ has a solubility limit around $x = 0.12$ (Franceschini and da Cunha 1975). In the $Ce(Fe_{1-x}Mn_x)_2$ system—although according to the published works (Croft *et al* 1987) the solid solubility limit is $x = 0.4$—we find an appreciable amount (10%) of the second phase in alloys with $x > 0.2$. Regarding the Y- and U-substituted quasi-binary alloys, we are quite satisfied about their phase constitution from our metallographic studies. The magnetic behaviour of these alloys (discussed later on in this work) also indicates that the various intended substitutions at the Ce site are actually taking place.

AC susceptibility measurements were performed with a driving frequency of 320 Hz and a driving field of 0.7 G parallel to the axis of the samples. A standard DC four-probe method, with computerised on-line data collection, has been used for resistivity measurements.

3. Results

3.1. AC susceptibility

3.1.1. $Ce(Fe_{1-x}Al_x)_2$; $x = 0.04, 0.05, 0.06, 0.07, 0.08$ and 0.1. There are two primary reasons for measuring AC susceptibility (χ) in these systems:

(i) to make a careful comparison with $Ce(Fe_{1-x}Co_x)_2$ with $0.1 \leqslant x \leqslant 0.2$ (Rastogi and Murani 1987) and $Ce(Fe_{1-x}Ru_x)_2$ with $0.04 \leqslant x \leqslant 0.08$ (Roy and Coles 1988) systems, especially in the light of the suggestion of a ferro–antiferromagnetic transition in those systems;

(ii) to find the critical composition where the straightforward long-range ferromagnetism breaks down.

We have also remade an $x = 0.08$ alloy for this new batch and given it identical heat

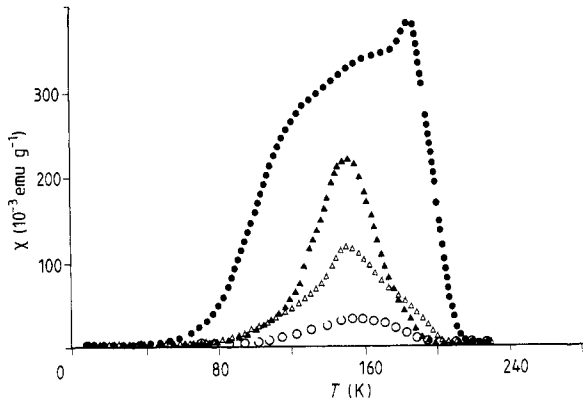

Figure 1. The AC susceptibility, χ of $Ce(Fe_{1-x}Al_x)_2$ alloys as a function of temperature, T: ●, $x = 0.04$; ▲, $x = 0.05$; ▽, $x = 0.06$; ○, $x = 0.07$.

treatment. We present the AC-susceptibility results in figures 1 and 2. The highlight of the result for $x = 0.04$ is that the ferromagnetic transition (at T_C) is followed by another lower-temperature magnetic transition (at T_F). A similar low-temperature transition has also been observed for $x = 0.035$ (Roy and Coles 1987). In our earlier study (Roy and Coles 1987) we suggested this second transition (which is marked by a sharp drop in susceptibility) to be re-entrant spin-glass-like (Coles *et al* 1978, Nieuwenhuys *et al* 1979). However, the behaviour of other $CeFe_2$ pseudo-binaries, for instance Co and Ru, with similar concentrations made us think more carefully on this subject. We present the AC susceptibility results for $Ce(Fe_{0.95}Ru_{0.05})_2$ (details will be published later) and $Ce(Fe_{0.96}Al_{0.04})_2$ in figure 3 for comparison. We note that there is a marked difference between the character of the lower-temperature transitions; it seems to be very sharp, with almost vanishing low-temperature magnetic response in the case of 5% Ru, whereas it is much less sharp and shows gradually diminishing magnetic response in the case of 4% Al. The alloy with 3.5% Al (Roy and Coles 1987) showed an even greater contrast with the sharp transition of the alloy with 5% Ru. We shall discuss this topic further later in this paper. For $x = 0.05$, T_C and T_F seem to be very close to each other, and, on cooling, the rise in susceptibility at T_C is almost immediately followed by the drop at T_F, giving rise to a sharp peak-like behaviour in the susceptibility. Susceptibility results for $x > 0.05$ suggest that there is no simple long-range ferromagnetic order in these alloys and we now believe that the present system is more interesting than re-entrant spin-glass systems, and cannot be characterised on the basis simply of the AC susceptibility.

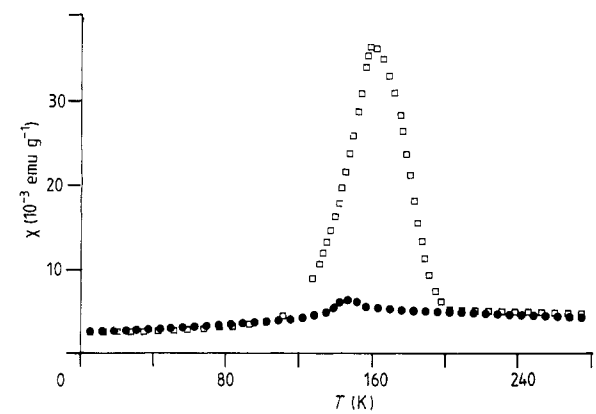

Figure 2. The AC susceptibility, χ, of $Ce(Fe_{1-x}Al_x)_2$ alloys as a function of temperature, T: □, $x = 0.08$; ●, $x = 0.1$.

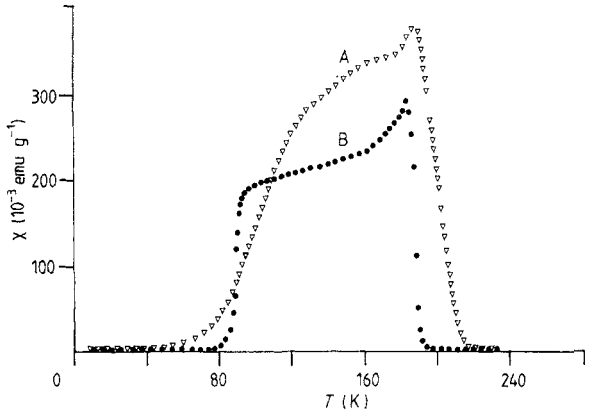

Figure 3. A comparison of the AC susceptibility, χ, of (A) $Ce(Fe_{0.96}Al_{0.04})_2$ with that of (B) $Ce(Fe_{0.95}Ru_{0.05})_2$.

Nishihara *et al* (1987) have recently reported magnetic measurements on $Ce(Fe_{0.95}Al_{0.05})_2$ that are very reminiscent of the behaviour of $Ce(Fe_{1-x}Co_x)_2$ with $0.2 \geqslant x \geqslant 0.1$ (Rastogi and Murani 1987) and $Ce(Fe_{1-x}Ru_x)_2$ with $0.08 \geqslant x \geqslant 0.04$ (Roy and Coles, 1988, 1989), in contrast to the susceptibility peak we have observed in our present study. Nishihara *et al* (1987) also reported the results of preliminary neutron measurements indicating the presence of magnetic scattering caused by antiferromagnetism at low temperature in $Ce(Fe_{0.95}Al_{0.05})_2$. It is to be remembered here that Nishihara and co-workers performed their measurements in fairly high magnetic field (5 kG), while our measurements were performed in a much smaller field (0.7 G). This difference in measuring field can be quite important, since the present system shows magnetic instability in presence of magnetic field (Nishihara *et al* 1987, Franceschini and da Cunha 1985). In figure 4 we present the AC susceptibility (χ) of two 5% Al alloys, one heat treated at 600 °C for two days, the other having undergone the general heat treatment discussed earlier. The marked difference in behaviour between the two alloys emphasises the sensitivity of this system to the metallurgy and heat treatment. As x increases, the magnitude of the susceptibility peak goes on decreasing. In figure 5 we plot $\log_{10}\chi_{peak}$ against x. The sharp drop in susceptibility peak magnitude around $x = 0.05$ also supports the idea of the disappearance of long-range ferromagnetic order in these systems.

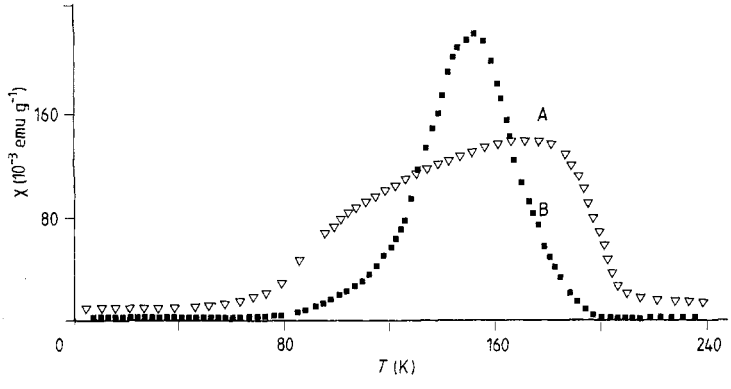

Figure 4. The AC susceptibility of $Ce(Fe_{0.95}Al_{0.05})_2$: A, heat treated at 600 °C for two days; B, given general heat treatment (as discussed in the text).

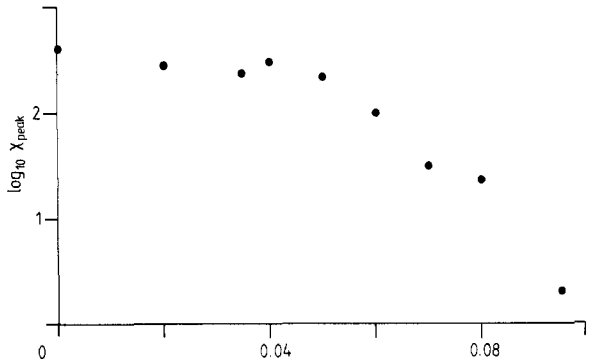

Figure 5. A plot of $\log_{10} \chi_{peak}$ against Al concentration (x) for $Ce(Fe_{1-x}Al_x)_2$; $0.02 < x < 0.1$.

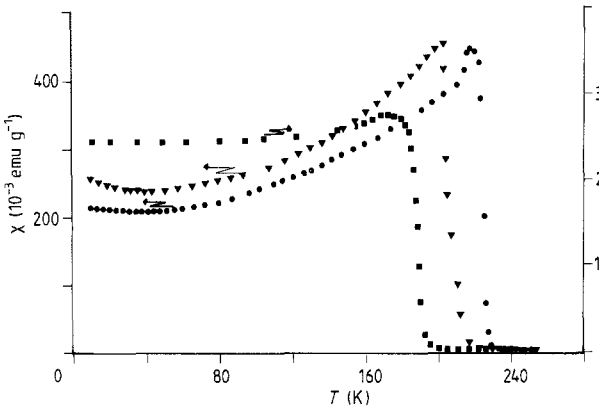

Figure 6. The AC susceptibility, χ, as a function of temperature, T, of $Ce(Fe_{1-x}Mn_x)_2$: ●, $x = 0.05$; ▼, $x = 0.1$; ■, $x = 0.2$.

3.1.2. $Ce(Fe_{1-x}Mn_x)_2$; $x = 0.05, 0.1, 0.15, 0.2$ and 0.25. AC susceptibility results (figure 6) for these alloys do not show the dramatic behaviour of the $Ce(Fe, Al)_2$ systems; instead T_C goes on decreasing gradually with increase in Mn concentration. The behaviour of $x = 0.15$ and 0.25 (not shown in figure 6) is very similar to that of $x = 0.2$, the value of T_C being slightly greater and lesser respectively than that for $x = 0.2$. We find the small upturn in susceptibility at low temperature in $x = 0.05$ and $x = 0.1$ rather puzzling. It might be due to small amount of undissolved Mn in the system but our metallographic analysis shows that the amount of second phase (if any) is certainly less than 5%, at least for $x < 0.15$.

3.1.3. $(Ce_{1-z}Y_z)(Fe_{0.965}Al_{0.035})_2$; $z = 0.05, 0.1$ and 0.15. AC susceptibility results for these compounds are shown in figure 7. With the increase in Y concentration T_C moves up in temperature but T_F is suppressed; for $z = 0.15$ there is no low-temperature anomaly at all. The fact that with $z = 0.1$ it was found that T_C reached 235 K (which is of same magnitude as the T_C of pure $CeFe_2$) and went up further (to 252 K) for $z = 0.15$ shows these compounds are really quasi-binaries, i.e. Y is replacing Ce. Complete substitution up to $Y(Fe_{0.965}Al_{0.035})_2$ can possibly be achieved. In the case of $(Ce_{1-z}Y_z)Fe_2$ it was possible to obtain a solid solution across the whole range and T_C showed a linear increase from $CeFe_2$ to YFe_2 (Buschow and van Staple 1971). Similar work on quasi-binaries to study the influence of rare-earth atoms on the order of Fe atoms has been reported by Steiner (1979) for the series (R, Y)(Fe, X)$_2$, where R = Gd, Dy and Ho and X = Al or Co.

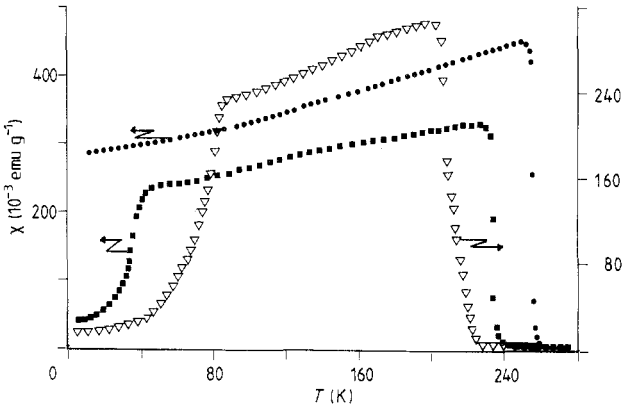

Figure 7. The AC susceptibility, χ, as a function of temperature, T, of $(Ce_{1-z}Y_z)(Fe_{0.965}Al_{0.035})_2$: ▽, $z = 0.05$; ■, $z = 0.1$; ●, $z = 0.15$.

3.1.4. $(Ce_{1-z}Y_z)(Fe_{0.95}Al_{0.05})_2$; $z = 0.05$ *and* 0.15. AC susceptibility results for these compounds (figure 8) show that the substitution of Y as before elevates T_C and suppresses T_F, and 15% Y totally erased the low-temperature anomaly.

3.1.5. $(Ce_{0.85}U_{0.15})(Fe_{0.95}Al_{0.05})_2$ *and* $(Ce_{0.85}U_{0.15})(Fe_{0.965}Al_{0.035})_2$. Substitution of U on the Ce site elevates T_C while suppressing T_F (figure 9) but in neither of the alloys could the low-temperature anomaly be erased totally.

3.2. Resistivity

3.2.1. $Ce(Fe_{1-x}Al_x)_2$; $x = 0.04, 0.05, 0.06, 0.07, 0.08$. The resistivity results for these alloys are shown in figure 10. The resistivity (ρ) for $x = 0.07$ has been reported earlier by Takeuchi and da Cunha (1985) but we shall repeat this here for the sake of uniformity in our discussion. The alloys are quite brittle and full of microcracks; hence we are not very confident about the absolute values of their resistivities. To overcome this problem we have normalised the resistivity with respect to that at 270 K.

For $x = 0.04$ the resistivity–temperature curve shows a distinct knee at a temperature that tallies well with the value for T_C found from susceptibility measurements, followed by an anomaly in the form of a local minimum at lower temperature. This low-temperature anomaly clearly has some relationship with the observed low-temperature

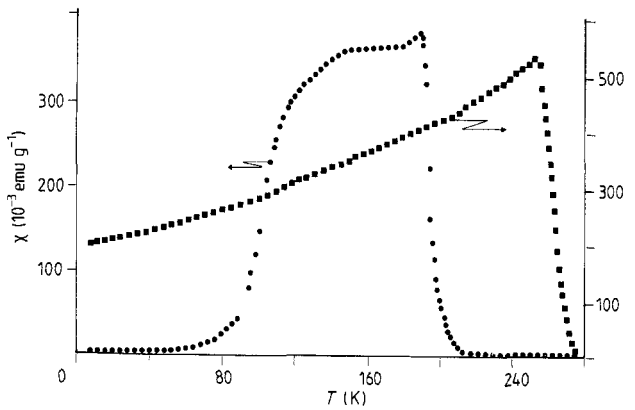

Figure 8. The AC susceptibility, χ, as a function of temperature, T, of $(Ce_{1-z}Y_z)(Fe_{0.95}Al_{0.05})_2$: ●, $z = 0.05$; ■, $z = 0.15$.

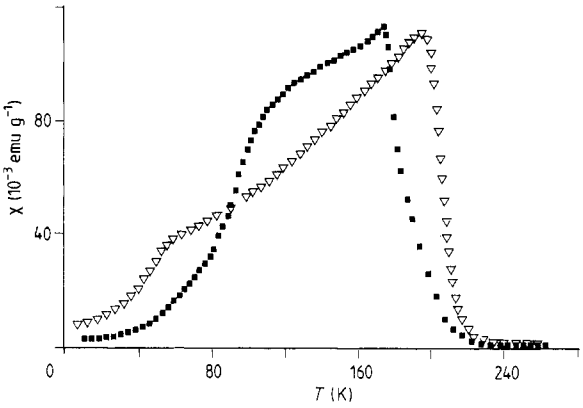

Figure 9. The AC susceptibility, χ, as a function of temperature, T, of $(Ce_{0.85}U_{0.15})(Fe_{1-x}Al_x)_2$: ▽, $x = 0.035$; ■, $x = 0.05$.

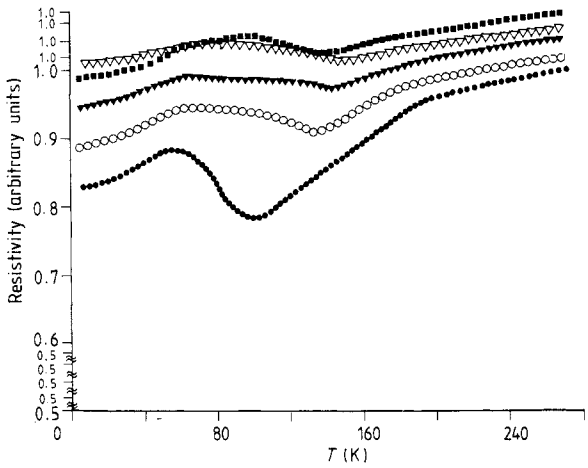

Figure 10. The normalised resistivity $(\rho(T)/\rho(280\,K))$ as a function of temperature, T, of $Ce(Fe_{1-x}Al_x)_2$: ●, $x = 0.04$; ○, $x = 0.05$; ▼, $x = 0.06$; ▽, $x = 0.07$; ■, $x = 0.08$.

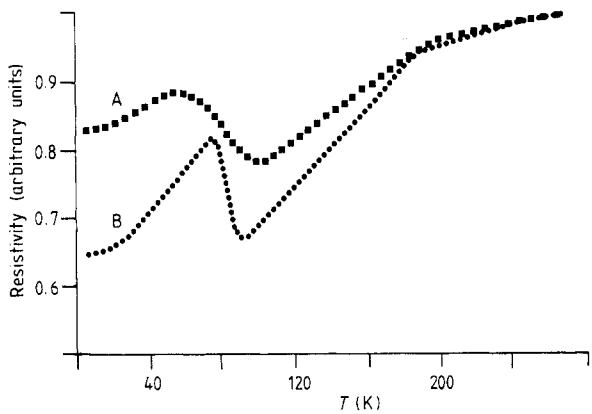

Figure 11. A comparison of the resistivity as a function of temperature, T, of (A) $Ce(Fe_{0.96}Al_{0.04})_2$ and (B) $Ce(Fe_{0.95}Ru_{0.05})_2$.

magnetic anomaly. For comparison, we present the results for $CeFe_2$ with 5% Ru (details will be published elsewhere) in figure 11. The observed anomalies for $x = 0.04$ seem to be less sharp than for 5% Ru, and this is in accordance with the susceptibility behaviour. Takeuchi and da Cunha (1985) and Rastogi *et al* (1988) observed a similar broad

resistivity anomaly in 3.5% Al. The susceptibility and resistivity anomalies in the alloy with 5% Ru are now clearly associated with a first-order transition from ferro- to antiferromagnetism and a similar conclusion has been reached for $Ce(Fe_{1-x}Co_x)_2$ with $0.1 \leqslant x \leqslant 0.2$ (Rastogi *et al* 1988). The sharp rise in resistivity at the ferro- to antiferromagnetic transition can be compared with the similar sharp behaviour at the antiferro–ferromagnetic transition of pure Dy.

At the onset of the antiferromagnetic type of ordering, a magnetic periodicity differing from the ionic-lattice periodicity is introduced (Coles 1958, Mackintosh 1962, Bellau and Coles 1963, Elliot and Wedgewood 1963). This magnetic periodicity introduces into k-space planes of energy discontinuity defining magnetic superzones which destroy a part of the Fermi surface and alter the resistivity quite drastically. Thus the sharp rise in resistivity discussed above can be related to the appearance of magnetic superzones at the ferro–antiferromagnetic transition temperature. In contrast, the resistivity transition in $Ce(Fe, Al)_2$ with 3.5% Al (Takeuchi and da Cunha 1985, Rastogi *et al* 1988) and 4% Al appears to be too gradual to be associated with the appearance of the magnetic super-zones in a first-order ferro–antiferromagnetic transition. For $x = 0.05$ the knee (which is the indication of the para–ferromagnetic transition) in the ρ–T plot is almost smeared out and, at the same time, the low-temperature anomaly becomes much broader. With further increase in Al concentration the knee disappears altogether and the low temperature anomalies are too broad to be explained simply by the onset of magnetic super-zones at a para–antiferromagnetic transition as in Dy (Elliot and Wedgewood 1963) for local moments or in Cr (Akiba and Mitusi 1972) for itinerant antiferromagnetism.

3.2.2. $(Ce_{1-z}Y_z)(Fe_{0.965}Al_{0.035})_2$; $z = 0.05$, 0.1 and 0.15. The resistivity results for these alloys are shown in figure 12. Within the resolution of our apparatus we could not observe any resistivity anomaly for $z \geqslant 0.1$, although the susceptibility results showed signs of the anomaly for $z = 0.1$. Similar results were observed in $Ce(Fe_{0.98}Al_{0.02})_2$ (Takeuchi and da Cunha 1985) where no resistivity anomaly was observed at or around the temperature of the magnetic anomaly.

3.2.3. $(Ce_{1-z}Y_z)(Fe_{0.95}Al_{0.05})_2$; $z = 0.05$ and 0.15. Y substitution in $Ce(Fe_{0.95}Al_{0.05})_2$ made the knee in the ρ–T curve (figure 13) prominent and at the same time raised its

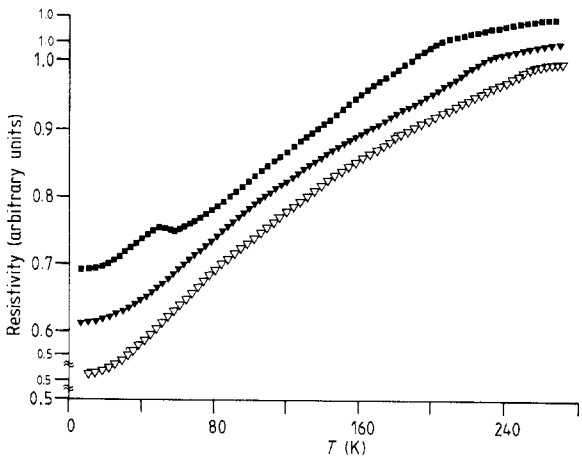

Figure 12. The normalised resistivity ($\rho(T)/\rho(270\,K)$) as a function of temperature, T, of $(Ce_{1-z}Y_z)(Fe_{0.965}Al_{0.035})_2$: ■, $z = 0.05$; ▼, $z = 0.1$; ▽, $z = 0.15$.

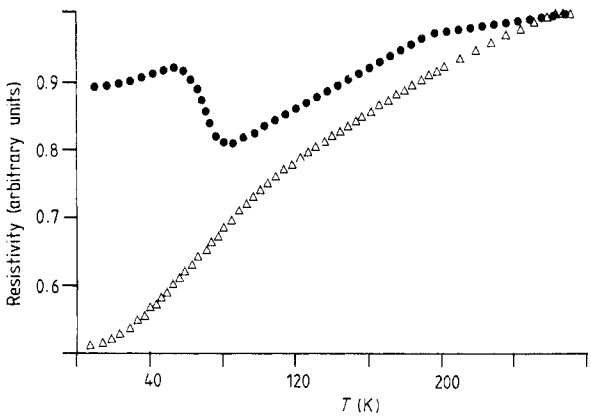

Figure 13. The normalised resistivity ($\rho(T)/\rho(270\,K)$) as a function of temperature, T, of $(Ce_{1-z}Y_z)(Fe_{0.95}Al_{0.05})_2$: ●, $z = 0.05$; △, $z = 0.15$.

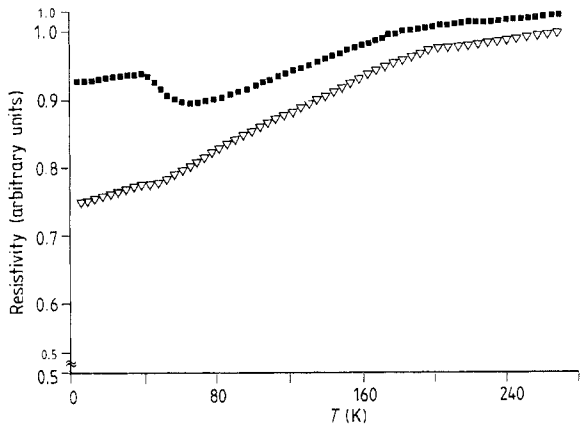

Figure 14. The normalised resistivity ($\rho(T)/\rho(270\,K)$) as a function of temperature, T, of $(Ce_{0.85}U_{0.15})(Fe_{1-x}Al_x)_2$: ■, $x = 0.035$; ▽, $x = 0.05$.

temperature. On the other hand, the low-temperature anomaly became diffuse (in comparison with that for $z = 0$) and decreased in temperature for $z = 0.05$ and totally disappeared for $z = 0.15$).

3.2.4. $(Ce_{0.85}U_{0.15})(Fe_{0.965}Al_{0.035})_2$ and $(Ce_{0.85}U_{0.15})(Fe_{0.95}Al_{0.05})_2$. 15% U substitution in $Ce(Fe_{0.965}Al_{0.035})_2$ raised the knee temperature (T_C) and at the same time almost erased the low-temperature anomaly. On the other hand, in the case of $Ce(Fe_{0.95}Al_{0.05})_2$, 15% U substitution decreased T_F and slightly changed the nature of the accompanying anomaly; compare figure 14 and figure 10.

4. Discussion and conclusion

The most important questions now to be considered are the cause of the low-temperature anomaly observed in $CeFe_2$ with Al substitution and the nature of the low-temperature ground state in these pseudo-binaries. We have now seen that Mn substitution does not give rise to similar anomalies. Also Ni (Rastogi and Murani 1987), Rh, Pd and Pt (Roy and Coles 1989) substitution showed simple dilution effects. These results, along with the fact that the observed anomalies can be drastically affected by substitution of U and

Y at the Ce site, show that these anomalies are not caused simply by the effects of disorder on the Fe sublattice.

In comparison with other rare-earth RM_2 (M = Fe, Co, Ni) Laves-phase intermetallic compounds, CeM_2 compounds have anomalously small lattice constants. Moreover, the lattice constant, instead of decreasing monotonically from $CeFe_2$ to $CeNi_2$ (as for the other RM_2 compounds), shows an anomalous minimum at $CeCo_2$. The same behaviour has been observed in the UM_2 series. Also it has been observed that the electronic specific heat of $CeFe_2$ is quite high ($\gamma = 53$ mJ mol^{-1} K^{-2}), which is of same magnitude as that of UFe_2 ($\gamma = 55$ mJ mol^{-1} K^{-2}) and there is a marked similarity in the resistivity behaviour of these two compounds—both exhibiting a negative curvature of $\rho(T)$ and almost the same T^2 coefficient (the magnon scattering term) (Rastogi *et al* 1988). In this sense the behaviour of CeM_2 compounds is more like that of the UM_2 compounds rather than that of the RM_2 ones. In recent theoretical work, Eriksson *et al* (1988) have discussed these aspects of CeM_2 within the framework of itinerant electron theory. The most important suggestion of this work is that the 4f electrons in CeM_2 are itinerant in nature and hybridise with the 3d electrons giving rise to the various anomalies. The same authors also suggest that the total spin moment of $CeFe_2$ is comprised of antiferromagnetically coupled moments of 1.43 μ_B per Fe atom and 0.7 μ_B per Ce atom. The calculated Fe moment is almost entirely of 3d character, whereas for Ce it is an almost equal mixture of 4f (0.4 μ_B) and 5d (0.3 μ_B) contributions. It was observed that the 4f orbital moment is almost totally quenched due to itinerancy, even when spin–orbit coupling is included in the calculation.

In a theoretical analysis in 1977, Moriya and Usami discussed the various magnetic phase transitions possible in itinerant-electron systems and the possibility of the co-existence of ferro- and antiferromagnetism. They considered an interesting itinerant-electron system without magnetic anisotropy (which has however been considered in a later work by Isoda (1984)) and expressed its free energy as a function of the uniform and staggered components of magnetisation, M_0 and M_Q respectively, retaining up to the fourth-order term. The coefficients of the terms of various orders can, in principle, be calculated for different systems if their electronic band structure is known. The possible equilibrium states, which Moriya and Usami (1977) obtained by minimising the free-energy expression, are really rich in variety. Among them, the possibility of para–antiferro–ferromagnetic transitions has already obtained experimental support for $(Hf_{1-x}Ta_x)Fe_2$ (Nishihara and Yamaguchi 1983) and $(Zr_{1-x}Nb_x)Fe_2$ (Yamada *et al* 1984) hexagonal Laves-phase compounds. In the present context of $CeFe_2$ pseudo-binaries we find two particular phase diagrams to be the most relevant, one yielding para–ferro–antiferromagnetic transitions and the other consisting of para–ferro–antiferromagnetic transitions via an intermediate regime of co-existing ferro- and antiferromagnetism.

From looking carefully at our experimental results we can suggest that $Ce(Fe_{0.95}Ru_{0.05})_2$ probably belongs to the first category, as does $Ce(Fe_{1-x}Co_x)_2$ with $0.1 < x < 0.2$ (Rastogi and Murani 1987, Rastogi *et al* 1988). In those cases both the susceptibility and resistivity transitions are quite sharp, indicating a first-order ferro–antiferromagnetic transition. In comparison, the low-temperature magnetic transition in $Ce(Fe_{1-x}Al_x)_2$ with $0.035 < x < 0.05$ seems to be significantly broader, and it appears that the ferro–antiferromagnetic transition is taking place rather gradually, perhaps via a regime of coexistence or superposition, in which canting of spins in opposite directions introduces an antiferromagnetic character. Also, it has been observed in the work by Moriya and Usami (1977) that the transition temperatures are quite sensitive to applied magnetic field, and that they shift with field towards lower temperatures. This might be

the cause of the apparent dissimilarity of our results in the case of $Ce(Fe_{0.95}Al_{0.05})_2$ from those of Nishihara *et al* (1987). As we mentioned earlier, T_C and T_F for this alloy almost coincided, producing a sharp susceptibility peak. The measuring field of 5 kG (in comparison to our value of 0.7 G) used by Nishihara *et al* (1987) probably shifted T_C and T_F away from each other and hence led to the apparent difference. It may also be noted in the Moriya–Usami work that the extent of the intermediate co-existent regime narrows down in the presence of an external magnetic field; hence one might expect a sharper transition to antiferromagnetism. The resistivity and susceptibility behaviours for alloys with $x > 0.05$ (along with those for $x < 0.05$) indicate that these alloys are not simple spin glasses and there are possibilities of antiferromagnetic correlations in these alloys. It is to be noted however that 5% Al substitution in YMn_2 (Motoya 1986) did break down the long-range magnetic order, giving rise to spin-glass ordering.

In the light of the various interesting (but at the same time complicated) behaviours of $Ce(Fe_{1-x}Al_x)_2$ with $x \leqslant 0.1$, we hesitate to present a definite magnetic phase diagram and believe other experiments (specific heat, Mössbauer spectroscopy, neutron measurements etc) are required to identify the precise nature of the various magnetic phases. In any case, whatever the nature of the observed low-temperature phase, be it spin glass, canted, antiferromagnetic or some sort of admixture, long-range ferromagnetic order does not seem to be present for $x > 0.05$.

We have now seen that the magnetic behaviour of $Ce(Fe_{1-x}Al_x)_2$ with $x \leqslant 0.1$ can be easily modified by substituting in small amounts of Y and U at the cerium site. Similar behaviour has also been observed in the $Ce(Fe_{1-x}Co_x)_2$ system (Rastogi *et al* (1988), and unpublished work by S B Roy). This again emphasises the role of the electronic structure in the magnetic properties of these compounds. It is clear that an important role for 3d–4f hybridisation will make alloying substitutions on either site of $CeFe_2$ important, and their effects sensitive to the nature of the alloying element. Although, as we pointed out earlier, $CeFe_2$ seems to be much closer to UFe_2 than to the other RFe_2s, the observed magnetic behaviour is probably some special characteristic of the Ce compounds. This is apparent here in that U, although less appreciably than Y, helped to suppress the anomalous behaviour of $Ce(Fe, Al)_2$. Also it is to be remembered that various levels of substitution with Al, Co, Re (Hilscher 1982, Tomi *et al* 1987) etc in UFe_2 never gave rise to the anomalous behaviour we find in $CeFe_2$ pseudo-binaries.

Some recent L_{III} x-ray absorption studies (Croft *et al* 1987) show an interesting trend of Ce valence v in CeT_2 compounds (T = Fe, Co, Ni). As one approaches from the Ni side, v reaches a maximum value of 3.32 for $CeCo_2$ and starts to decrease again, the value for $CeFe_2$ being 3.29. The continual decrease is confirmed by studies on $Ce(Fe, Mn)_2$ alloys up to the solid solution limit (40% Mn). It is interesting to note that, while the Ce valence of $CeFe_2$ and $CeCo_2$ is in the so-called saturation regime $3.26 < v < 3.32$, for $CeNi_2$ and $Ce(Fe, Mn)_2$ pseudo-binaries it is in the intermediate regime with $3.13 < v < 3.25$. These features and the hybridisation of 3d–4f states in the $CeFe_2$ pseudo-binaries probably have a close relation with the various magnetic properties. In the light of interesting magnetic properties of $Ce(Fe, Co)_2$, where the ferromagnetism lost at low temperature with initial Co substitution was recovered again with increase in the Co concentration (>25% Co) (Rastogi and Murani 1987), it would be particularly interesting to see how the Ce valence behaves between $CeFe_2$ and $CeCo_2$.

In conclusion, we would suggest that the alloying effects on $CeFe_2$ of various elements and the possibility of various types of magnetic phase diagram in $CeFe_2$ pseudo-binaries are explained more naturally within an itinerant-electron model (Moriya and Usami 1977). Such a band magnetic approach is in accordance with the recent theoretical work

on $CeFe_2$ (Erikson *et al* 1988). We would also support the suggestion of an important role for 3d–4f hybridisation in $CeFe_2$ (Erikson *et al* 1988, Rastogi *et al* 1988), from which it follows naturally that the magnetic properties can be affected to various extents by alloying at both Ce and Fe sites, as we have actually observed.

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