Low-temperature specific heat of Laves phase Ce(Fe$_{1-x}$Co$_x$)$_2$

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Abstract. We have studied the low-temperature specific heat of the pseudo-binary Ce(Fe$_{1-x}$Co$_x$)$_2$ system, which shows a double transition from a ferromagnetic to anti-ferromagnetic state for $0.04 < x < 0.3$. The electronic specific heat coefficient γ is large in the ferromagnetic state, while it is reduced in the antiferromagnetic state. The results are discussed on the basis of the band structure.

1. Introduction

The instability of ferromagnetism in the cubic Laves phase compound with Ce and Fe is one of the current topics of considerable interest. CeFe$_2$ is a ferromagnet with a magnetic moment of 1.15 μ_B per Fe atom and $T_C = 230$ K [1]. The substitution of Fe by a small amount of impurity, such as Al, Co and Ru, destabilizes the ferromagnetism and leads to a second transition to an antiferromagnetic state at a temperature T_0 lower than T_C [2–5]. Figure 1 shows the magnetic phase diagram of Ce(Fe$_{1-x}$Co$_x$)$_2$ established by
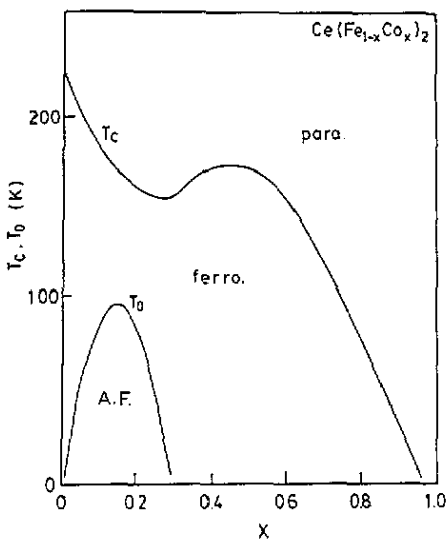
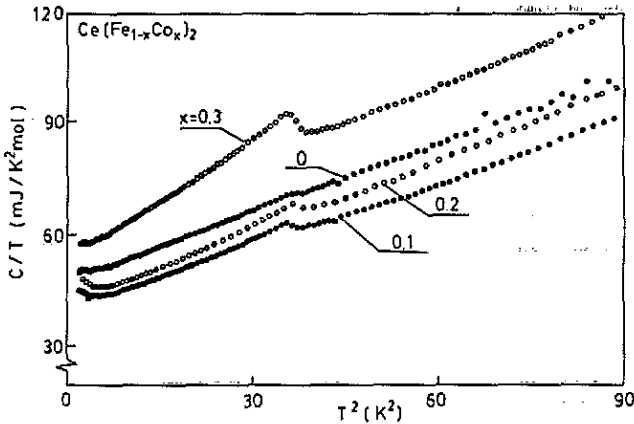**Figure 1.** Magnetic phase diagram of Ce(Fe$_{1-x}$Co$_x$)$_2$ reported by Rastogi and Murani [3].

Figure 2. Low-temperature specific heats for $Ce(Fe_{1-x}Co_x)_2$ with $0 \leq x \leq 0.3$ plotted in the form C/T versus T^2.

Rastogi and Murani [3]. The compounds with $0.04 < x < 0.3$ show a double transition and ferromagnetism is replaced by antiferromagnetism below T_0. Long-range anti-ferromagnetic order was confirmed by Kennedy and co-workers [5, 6] using neutron diffraction measurements. They proposed a magnetic structure, in which the Fe moments within a (111) plane are parallel and those between adjacent planes antiparallel. On the other hand, the results of Mössbauer effect studies have revealed that the average hyperfine field shows a smooth temperature dependence across T_0 [7], suggesting no dramatic change in the magnitude of the Fe moment at T_0.

Beyond $x = 0.3$, ferromagnetism is stabilized down to the lowest temperature. The Curie temperature shows a broad maximum at around $x = 0.5$ and decreases with increasing x, falling to zero at around $x = 0.9$.

Rastogi *et al* [8] have reported that the electronic specific heat coefficient γ for $CeFe_2$ is about 53 mJ K^{-2} mol^{-1} [8], which is about four times that of isostructural YFe_2. The large γ-value of $CeFe_2$ is considered to result from strong hybridization of the Ce 4f band with the 3d band. On the other hand, the γ-value of paramagnetic $CeCo_2$ has been reported to be 21 mJ K^{-2} mol^{-1} by Sá *et al* [9], being much smaller than that of $CeFe_2$.

In order to investigate the effect of a change in the magnetic state on the electronic specific heat, we have studied the low-temperature specific heat of $Ce(Fe_{1-x}Co_x)_2$ in the whole range of concentration x. In this paper, we report our results and discuss them on the basis of the band structures of this system.

2. Experimental procedure

All the samples except $CeCo_2$ were prepared from 99.9% pure metals by argon arc melting followed by annealing at 850 °C in an evacuated quartz tube for a week. $CeCo_2$ was prepared by a levitation technique using Ce and Co from a different source. X-ray analysis has shown that all the samples have a single phase of C15 Laves phase structure. The lattice parameter of the pseudo-binary compounds obeys Vegard's law, being in agreement with a previous report by Longworth and Harris [10].
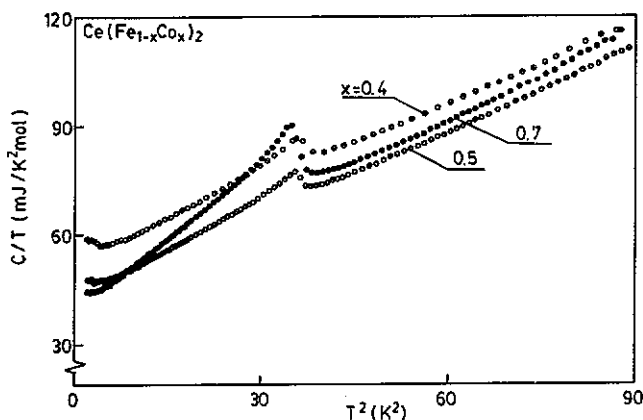
Figure 3. Low-temperature specific heats for Ce(Fe$_{1-x}$Co$_x$)$_2$ with $0.4 \leqslant x \leqslant 0.7$.

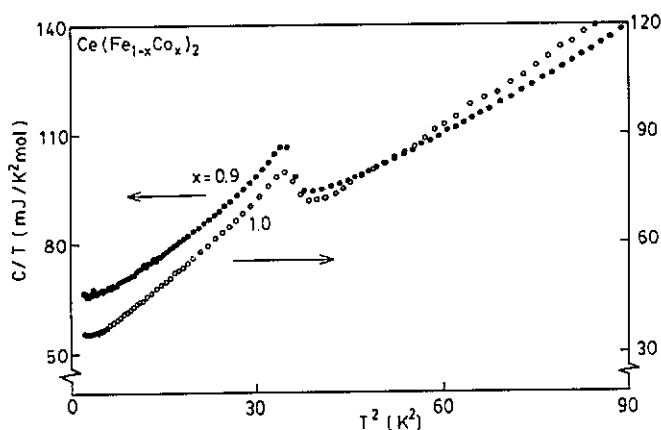**Figure 4.** Low-temperature specific heats for Ce(Fe$_{1-x}$Co$_x$)$_2$ with $x = 0.9$ and 1.

The low-temperature specific heat was measured by a conventional heat pulse method in an adiabatic cell. The sample was cooled to 1.4 K using a mechanical heat switch. The measurements were done between 1.4 and 9.5 K. Button-shaped bulk samples of 3–8 g were used.

3. Results

Figures 2–4 show the C/T versus T^2 plots for Ce(Fe$_{1-x}$Co$_x$)$_2$. A specific heat anomaly is observed at around 6 K for all samples. No systematic concentration dependence of the magnitude of the anomaly is found. A similar anomaly has often been observed for other Ce compounds, Ce(Co$_{1-x}$Ni$_x$)$_2$ [9], CeRu$_2$ [11], Ce(Pd$_{1-x}$Rh$_x$)$_3$ [12] and CeRu$_2$Si$_2$ [13] at the same temperature, and this is probably due to a transition of an impurity phase, such as Ce oxide. Above this transition temperature, the C/T-values show a nearly linear T^2 dependence. By subtracting the extrapolated line of the linear part from the total
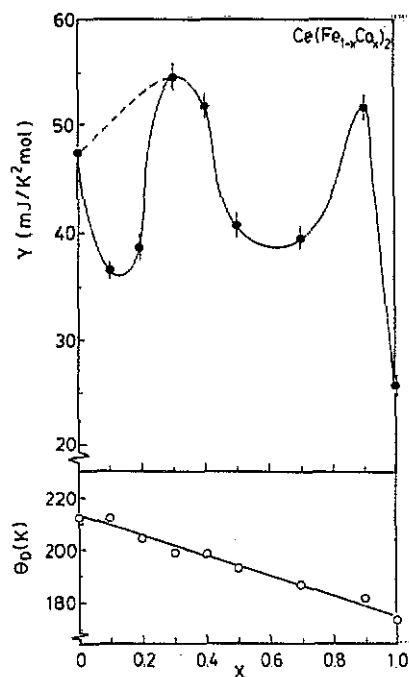
Figure 5. Concentration dependence of the electronic specific heat coefficient γ, and the Debye temperature Θ_D for $Ce(Fe_{1-x}Co_x)_2$. The full curves are to guide the eye. The broken curve is the tentative concentration dependence of γ for a hypothetical ferromagnetic state below $x \leqslant 0.3$.

specific heat, we estimated the entropy S associated with the impurity specific heat as 35 mJ K^{-1} mol^{-1} for $x = 0.5$. Using the relation $S = cR\ln 2 = 5763c$ mJ K^{-1} mol^{-1} for the ground-state doublet with $J = \frac{5}{2}$ in a cubic crystal field [11], where c is the concentration of the impurity per mole and R the gas constant, we obtain a c-value of only 0.6% for $Ce(Fe_{0.5}Co_{0.5})_2$. This is consistent with the fact that no foreign phase other than the C15 structure was detected by x-ray analysis for our samples. Since the amount of impurity phase is negligibly small, we adopted the linear part of the C/T versus T^2 plots above 6 K to estimate the γ-value and the Debye temperature Θ_D, for $Ce(Fe_{1-x}Co_x)_2$. The concentration dependence of γ and Θ_D is shown in figure 5. The γ-values for $CeFe_2$ and $CeCo_2$ are about 48 mJ K^{-2} mol^{-1} and 25 mJ K^{-2} mol^{-1}, respectively, which are comparable with those of the previous reports, 53 mJ K^{-2} mol^{-1} and 21 mJ K^{-2} mol^{-1} [8, 9]. With x increasing from 0, the γ-value first decreases and then rapidly increases beyond $x = 0.1$, showing a maximum at around $x = 0.3$. Beyond $x = 0.3$, it decreases with increase in x again, but strong enhancement of the γ-value is observed at around $x = 0.9$. This concentration dependence of the γ-value is discussed in the following section.

4. Discussion

First, we discuss the γ-value for $CeCo_2$ and $CeFe_2$. Recently, the band calculations for CeM_2 ($M \equiv Fe$, Co and Ni) compounds have been carried out by Eriksson *et al* [14] and suggest the itinerant character of Ce 4f electrons in these compounds. They have reported that the calculated γ-value γ_{cal} for $CeCo_2$ is 14.7 mJ K^{-2} mol^{-1}. The observed value γ_{ob} of 25 mJ K^{-2} mol^{-1} is, therefore, 1.7 times larger than γ_{cal}. Similar enhancement

of the γ-value is also observed for paramagnetic CeRu$_2$ ($\gamma_{ob}/\gamma_{cal} = 1.6$ [11, 15]) and is reasonably ascribed to the electron–phonon interaction. On the other hand, γ_{ob} for CeFe$_2$ is 48 mJ K^{-2} mol^{-1}, which is fairly large compared with other rare-earth RM$_2$ compounds. Rastogi *et al* [8] have suggested that the Ce 4f states near the Fermi level are strongly hybridized with the 3d band, resulting in a high density $D(E_F)$ of states at the Fermi level and hence a large γ-value for CeFe$_2$ [8]. The strong hybridization of 4f–3d bands is supported by the band calculations of Eriksson *et al* [14]. The calculated density of states for paramagnetic CeFe$_2$ gives a much larger γ_{cal} than that for CeCo$_2$. Although γ_{cal} for ferromagnetic CeFe$_2$, which has not been reported, is probably somewhat smaller than the paramagnetic value by analogy with the band calculations for UFe$_2$ [16], we expect that γ_{ob} for CeFe$_2$ is explained by considering γ_{cal} and assuming a similar enhancement of γ by the electron–phonon interaction as in the case of CeCo$_2$.

Next, we discuss the concentration dependence of γ_{ob} for Ce(Fe$_{1-x}$Co$_x$)$_2$. As seen in figure 5, γ_{ob} first decreases and then increases, reaching a maximum value when x is increased from 0 to 0.3. It should be noted that the antiferromagnetic state is realized in the ground state for $0.04 < x < 0.3$. Our results suggest that γ for the antiferromagnetic state is smaller than that for the ferromagnetic state. The difference between the γ-values of the two magnetic states will be discussed later. Therefore, if we had only the ferromagnetic state for $x \leqslant 0.3$, we would be able to draw the broken line tentatively in figure 5, which shows a maximum at around $x = 0.3$. These results suggest that $D(E_F)$ has a maximum in ferromagnetic Ce(Fe$_{1-x}$Co$_x$)$_2$ with increasing x. According to the recent band calculation by Khowash [17], the Fermi level of ferromagnetic CeFe$_2$ is located just below the sharp peak of both the majority and the minority band. In the framework of a rigid-band model, the substitution of Fe by Co increases the number of 3d electrons, which occupy both the majority and the minority bands, provided that the exchange splitting decreases monotonically with increasing electron concentration. This is supported by the Mössbauer study of the present system, in which the hyperfine field decreases linearly with increasing x in the ferromagnetic region [10]. Therefore, one would expect an increase in $D(E_F)$, until the Fermi level shifts to the sharp peak in the majority or minority band in the ferromagnetic state. This will correspond to a maximum of $D(E_F)$ for Ce(Fe$_{1-x}$Co$_x$)$_2$ and will be followed by a decrease in $D(E_F)$ on further increasing the number of 3d electrons.

A very large γ-value is also observed at around $x = 0.9$, which is the critical concentration for ferromagnetism. Similar behaviour is observed for Y(Fe$_{1-x}$Co$_x$)$_2$ near the same concentration range [18]. This large γ-value is ascribed to spin fluctuations, which usually play a dominant role in the enhancement of γ around the critical concentration for itinerant electron ferromagnetism.

Finally, we discuss the substantial reduction in the γ-value of the antiferromagnetic compounds. Similar results have been reported for the ordered FeRh alloy [19], which also shows a double magnetic transition. In simple band theory, the formation of an antiferromagnetic state gives rise to a new energy gap due to the doubling of the unit cell, which leads to a lower value of $D(E_F)$ than that for a ferromagnetic or paramagnetic state. This is supported for FeRh by the band calculations [20]. In the case of CeFe$_2$, there has been no report on the band calculation for the antiferromagnetic state. However, a rapid rise in the electrical resistivity just below T_0 for Ce(Fe$_{1-x}$Co$_x$)$_2$ with $x = 0.1$ and 0.15 [8] suggests the formation of a new energy gap in the antiferromagnetic state. Therefore, we expect that the small γ-value in the antiferromagnetic state is the result of the appearance of magnetic superzones, as in FeRh.

In conclusion, the large γ-value for $CeFe_2$, the maximum of concentration dependence of γ in the ferromagnetic region and the significant reduction in γ in the antiferromagnetic region are observed for $Ce(Fe_{1-x}Co_x)_2$. We have shown that these characteristics can be explained by the band structure. In order to clarify our interpretation, further band calculations for antiferromagnetic $CeFe_2$ and the ordered $Ce(Fe_{1-x}Co_x)_2$ are strongly desired.

Acknowledgments

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