The magnetic field dependence of the electronic specific heat of $Ce(Fe_{1-x}Co_x)_2$

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Abstract. The magnetic field dependence of the specific heat was examined for CeFe$_2$ and Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$. The former compound is a simple ferromagnet, while the latter shows an antiferromagnetic-to-ferromagnetic (AF-to-F) transition with increasing temperature and undergoes a metamagnetic transition at around 6 T at low temperatures. The results indicate that the electronic specific heat coefficient, γ, is larger in the F state than in the AF state. These results suggest the importance of the electronic specific heat as regards the entropy change associated with the AF-to-F transition. In the F state, a decrease of γ with increasing field was observed for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ as well as for CeFe$_2$. The origin of this behaviour is also discussed.

1. Introduction

The Laves phase compound CeFe$_2$ is a ferromagnet with $T_C = 230$ K. The substitution of Co for Fe destabilizes ferromagnetism and an antiferromagnetic state appears at low temperatures for $0.04 < x < 0.3$ below T_0 which is lower than T_C [1]. In this concentration range, the system undergoes an antiferromagnetic-to-ferromagnetic (AF-to-F) transition with increasing temperature. On further substituting Co for Fe, an F state reappears in the ground state. Previously, we have measured the specific heat of Ce(Fe$_{1-x}$Co$_x$)$_2$ at low temperatures and evaluated the electronic specific heat coefficient, γ, in both the F and AF states [2]. The results are shown in figure 1, in which a complicated concentration dependence of γ is observed. Noting that the compounds with $x = 0.1$ and 0.2 are antiferromagnetic, it is likely that the γ-value in the F state (γ_F) is larger than that in the AF state (γ_{AF}). This is explained by a simple band theory, which predicts a decrease in the density of states (DOS) at E_F in the AF state due to the formation of a new energy gap. In reference [3], we pointed out the importance of the difference between γ_F and γ_{AF} in the AF-to-F transition. The difference in γ contributes to an entropy change at T_0. This is the electronic entropy change expressed as $(\gamma_F - \gamma_{AF})T_0$. The total entropy change at T_0 was evaluated as 1.2 J K^{-1} mol^{-1} for $x = 0.1$ from specific heat measurements. On the other hand, we have $\gamma_{AF} = 36.6$ mJ K^{-2} mol^{-1} from figure 1. Although a γ_F for $x = 0.1$ is not obtained from the experiments, we can roughly estimate $\gamma_F \sim 50$ mJ K^{-2} mol^{-1} from the values for $x = 0$ (47.5 mJ K^{-2} mol^{-1}) and $x = 0.3$ (54.6 mJ K^{-2} mol^{-1}). On putting these values and $T_0 = 80.8$ K into the above expression, the electronic entropy change is evaluated as 1.1 J K^{-1} mol^{-1}, which is comparable to the total entropy change. In reference [3], we also discussed a relation between T_0 and the metamagnetic transition field, H_0. Assuming $C_F(T) - C_{AF}(T) = (\gamma_F - \gamma_{AF})T$, where $C_F(T)$ and $C_{AF}(T)$ represent

the specific heat in the F state and the AF state, respectively, we obtained a simple relation, $H_0 = (\gamma_F - \gamma_{AF})T_0^2/2\,\Delta M$, where ΔM is the difference in magnetization between the two states at H_0. Putting the above parameters into this equation, we have $H_0 = 3.9$ T, which compares favourably with the experimental value of 5.6 T. Moreover, a T^2-dependence of H_0 was derived near T_0, which is in accordance with the observations. These results are strongly indicative that the electronic specific heat plays an important role in the AF-to-F transition in $Ce(Fe_{1-x}Co_x)_2$.
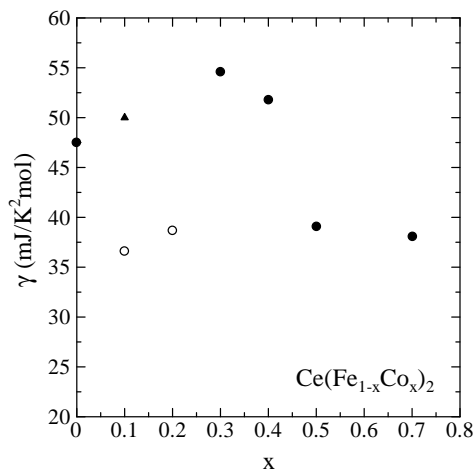

Figure 1. The concentration dependence of the electronic specific heat coefficient, γ, of $Ce(Fe_{1-x}Co_x)_2$ [2]. Closed and open circles represent the ferromagnetic and antiferromagnetic compounds, respectively. A closed triangle indicates the γ-value of $Ce(Fe_{0.9}Co_{0.1})_2$ in the hypothetical ferromagnetic state, which was estimated in the present study (see the text).

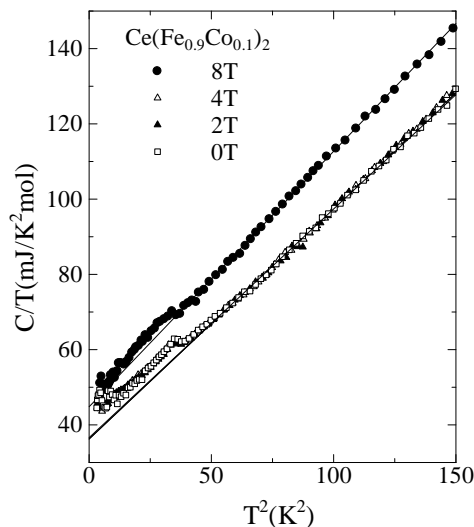**Figure 2.** The specific heat of $Ce(Fe_{0.9}Co_{0.1})_2$ in fields of 0, 2, 4 and 8 T plotted in the form of C/T versus T^2. The solid lines are the results of a least-squares fitting of the data to $C/T = \gamma + \beta T^2$.

Since the AF-to-F transition is induced by a magnetic field of 6 T for $x = 0.1$, γ_F and γ_{AF} can be directly measured for the same sample from the specific heat measurements under magnetic fields. In this paper, we report the magnetic field dependence of γ for $Ce(Fe_{0.9}Co_{0.1})_2$. For comparison, measurements on ferromagnetic $CeFe_2$ were also carried out.

2. Experiments

The samples were prepared by argon arc melting. For $x = 0.1$, we used the same sample as was used for the specific heat measurements made previously [3]. A $CeFe_2$ sample was newly prepared and was annealed at 850 °C for one week in an evacuated quartz tube. No phase other than C15 was detected by x-ray diffraction. The specific heat was measured by a conventional heat pulse method from 1.4 to 15 K under a magnetic field up to 14 T by using a superconducting magnet. A calibrated carbon-glass thermometer was used for the temperature measurements. The magnetization for $x = 0.1$ was measured by using a SQUID from 5 to 30 K.
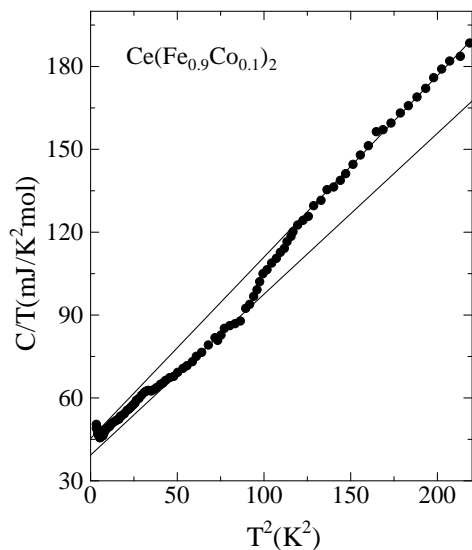
Figure 3. A C/T versus T^2 plot for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ at 6 T. The two lines are the results of a least-squares fitting in lower-temperature region (50 K^2 < T^2 < 90 K^2) and in the higher-temperature region (130 K^2 < T^2 < 220 K^2).
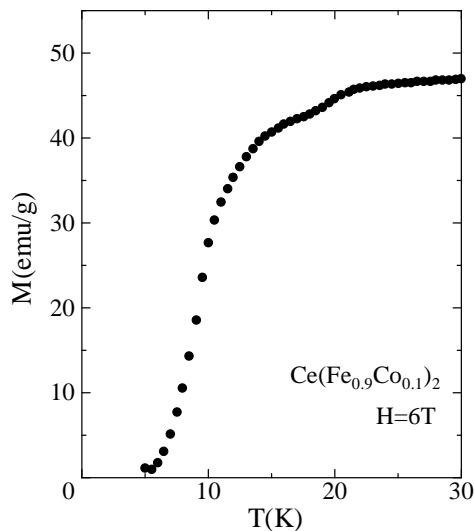
Figure 4. The magnetization versus temperature curve of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ at 6 T.

3. Results

Figure 2 shows the temperature dependence of the specific heat of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ in fields of 0, 2, 4 and 8 T plotted in the form of C/T versus T^2. The compound is antiferromagnetic below 4 T, while it is ferromagnetic at 8 T in this temperature range. Each of the C/T versus T^2 curves above 7 K is well approximated by the straight line $C/T = \gamma + \beta T^2$. A small anomaly at 6.5 K is not intrinsic but is due to an impurity phase, as referred to previously [3]. The amount of this impurity phase is quite small (less than 0.6%). The C/T versus T^2 plots lie on the same line for 0–4 T, while the plot for 8 T shows a considerable shift with a larger γ-value. These results provide direct evidence that $\gamma_{AF} < \gamma_F$ in Ce(Fe$_{1-x}$Co$_x$)$_2$. The slope of the plot, β, is slightly larger for the F state than for the AF state. The C/T versus T^2 plot for an intermediate field of 6 T is shown in figure 3. Interestingly, the points seem to lie in a straight line for 50 K^2 < T^2 < 90 K^2, while they deviate above $T^2 = 90$ K^2 and eventually lie on another straight line for $T^2 > 150$ K^2. This behaviour is understandable, if the system undergoes an AF-to-F transition at around 10 K. To confirm this, we measured the magnetization versus temperature curve of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ at 6 T. The result is shown in figure 4, in which the magnetization rapidly increases at around 10 K, indicating the AF-to-F transition. Therefore, the nonlinear behaviour of the C/T versus T^2 curve at 6 T is ascribed to the change of a magnetic state.

Figure 5 shows the C/T versus T^2 plots of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ in the F state above 8 T. In contrast to the plots for the AF state, we observed a definite shift of the straight line towards a smaller value of C/T with increasing magnetic field from 8 T to 14 T. These results indicate that γ_F decreases with increasing field for the F state. In order to study the magnetic field dependence of γ_F over a wide field range, we measured the specific heat of ferromagnetic CeFe$_2$ in fields of 0–14 T. The results at 0, 8 and 14 T are displayed in
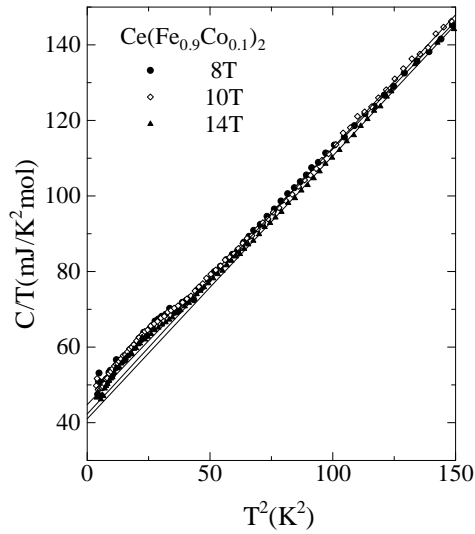
Figure 5. C/T versus T^2 plots for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ for fields of 8–14 T. The solid lines are the results of least-squares fitting of the data to a straight line.
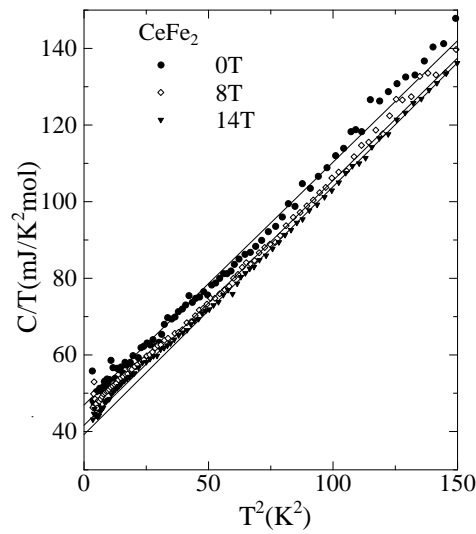
Figure 6. C/T versus T^2 plots for CeFe$_2$ for fields of 0, 8 and 14 T. The solid lines are the results of least-squares fitting of the data to a straight line.

figure 6. Similarly to the case for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ in the F state, the C/T versus T^2 curve depends on the magnetic field and γ_F decreases as the magnetic field is increased.

The magnetic field dependence of γ for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ and CeFe$_2$ is shown in figure 7. Two values of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ at 6 T were evaluated from the low-temperature region (50 K$^2 < T^2 < 90$ K^2) and from the high-temperature region (130 K$^2 < T^2 < 220$ K^2), respectively. The γ-value of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ is nearly field independent for the AF state. It is suddenly raised by the onset of the F state, and this is followed by a decrease with increasing field. On the other hand, the γ-value of CeFe$_2$ decreases remarkably, from 47 mJ K^{-2} mol^{-1} to 39 mJ K^{-2} mol^{-1}, as the magnetic field is increased from 0 to 14 T. The Debye temperature, Θ_D, was also evaluated from β, and is shown in figure 8 as a function of the magnetic field for $x = 0.1$ and CeFe$_2$. It is found that Θ_D for $x = 0.1$ is smaller for the F state than for the AF state, while no field dependence of Θ_D is observed for CeFe$_2$.

4. Discussion

As shown in figure 7, the present study confirmed that the γ-value is larger for the F state than for the AF state for $x = 0.1$. Several systems are known to show the AF-to-F transition with increasing temperature, such as FeRh [4], Mn$_3$GaC [5] and La$_{1-x}$Y$_x$Mn$_2$Ge$_2$ [6]. The hypothesis that $\gamma_F > \gamma_{AF}$ was first proposed for FeRh [7]. Baranov and Khlopkin examined the specific heat under a magnetic field for (Fe$_{0.965}$Ni$_{0.035}$)$_{49}$Rh$_{51}$ [8], where a small amount of Ni is substituted for Fe to reduce the metamagnetic transition field. They found that γ_F is twice as large as γ_{AF} for this alloy. These results are in qualitative agreement with those obtained from the band calculations [9, 10]. It was also pointed out that the electronic specific heat gives a dominant contribution to the entropy change at T_0 in FeRh [7]. In this sense, Ce(Fe$_{1-x}$Co$_x$)$_2$ and FeRh are in the same category of AF-to-F transition systems. To confirm our interpretation, band calculations for both the F states and hypothetical AF
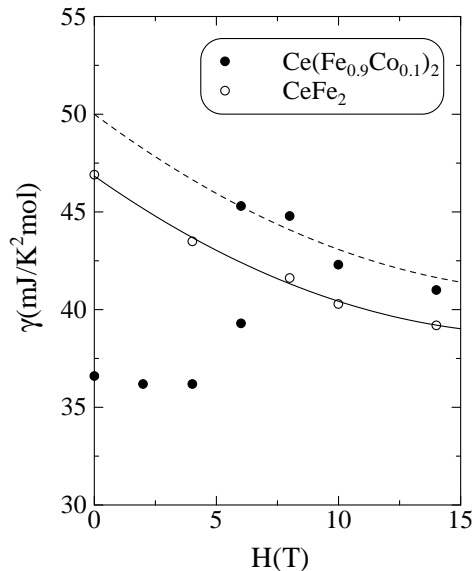
Figure 7. The magnetic field dependence of γ for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ and CeFe$_2$. The solid line is a curve connecting the points for CeFe$_2$ smoothly. The dashed line was obtained by shifting the solid line by 3 mJ K^{-2} mol^{-1} to extrapolate the γ_F-value of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ to $H \to 0$.
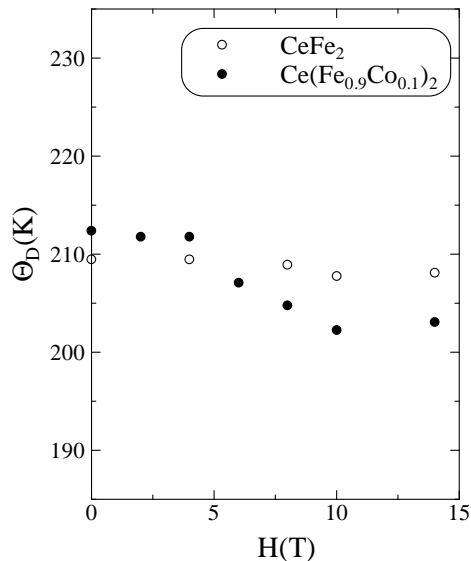
Figure 8. The magnetic field dependence of the Debye temperature, Θ_D, for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ and CeFe$_2$.

states of CeFe$_2$ are strongly desired.

Unexpectedly, remarkable field effects on γ were observed in the F state for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ and CeFe$_2$. So far, a large field dependence of γ has been reported only for weakly or nearly ferromagnetic metals. We define the reduction factor of γ per unit field, r, as $r = (\gamma(0) - \gamma(H))/\gamma(0)H$. For example, the r-factor of nearly ferromagnetic LuCo$_2$ is 1% T^{-1} [11]. Our results revealed that $r = 1.2\%$ T^{-1} for CeFe$_2$, which is comparable to the value for LuCo$_2$. A possible origin of the large r for CeFe$_2$ is the suppression of spin fluctuations by the magnetic field. The γ-value for CeFe$_2$ at 0 T is quite large (48 mJ K^{-2} mol^{-1}) compared with the values for other Laves phase compounds of rare-earth elements and Fe [12]. This is attributable to spin fluctuations, as pointed out by Gratz *et al* [13]. Furthermore, the coefficient of the T^2-dependence of the electrical resistivity of CeFe$_2$ is ten times as large as that of YFe$_2$ [13]. These facts strongly suggest that the thermal properties at low temperatures are dominated by spin fluctuations in CeFe$_2$. It is expected that spin fluctuations are quenched by applying a magnetic field. Therefore, the enhancement of γ is reduced with increasing field. This interpretation can be supported by the fact that no field dependence of γ was observed for the AF state with $x = 0.1$, because antiferromagnetic fluctuations are not suppressed by a static field.

Finally, we now complement the discussion on the importance of the electronic specific heat in the AF-to-F transition given in reference [3] and summarized in section 1 of the present paper. As described there, the γ-value for the F state of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ is required for quantitative discussion. Since γ_F for $x = 0.1$ is field dependent, the value at $H = 0$ T has to be estimated. We assume that γ_F for Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ shows a similar field dependence to that for CeFe$_2$. Shifting the γ_F versus x curve of CeFe$_2$ by 3 mJ K^{-2} mol^{-1}, we obtain

the dashed line in figure 7, which enables us to extrapolate the γ_F versus H curve of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ to $H = 0$ T. The estimated value of γ in the hypothetical ferromagnetic state for $x = 0.1$ at 0 T is 50 mJ K^{-2} mol^{-1}. This indicates the validity of our previous estimation of it from the concentration dependence of γ, although it was estimated rather roughly. Another fact found here is that the Debye temperature of Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ also depends on the magnetic state, as shown in figure 8. This result suggests that there is some contribution from the lattice entropy at T_0, which was neglected in our previous discussion. However, the correct estimation of the lattice entropy change at T_0 is quite difficult, because the lattice specific heat cannot be described by a simple Debye model with a constant value of Θ_D. As described in reference [3], we could not find any significant difference in the lattice specific heat between CeFe$_2$ and Ce(Fe$_{0.9}$Co$_{0.1}$)$_2$ below and above T_0. It is likely that the contribution of the lattice entropy change at T_0 is small, if it exists at all, and that the entropy change is dominated by the electronic entropy change in this system.

Acknowledgments

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