

Entropy change at the ferromagnetic–antiferromagnetic transition in the intermetallic compound $\text{Ce}(\text{Fe}_{0.8}\text{Co}_{0.2})_2$

Xianfeng Zhang and Naushad Ali*

Department of Physics and Molecular Science Programs, Southern Illinois University, Carbondale, IL 62901 (USA)

Abstract

The intermetallic compounds $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$ show two magnetic transitions (for $x < 0.3$), one occurring at T_c due to paramagnetic–ferromagnetic (PM-FM) transition, and the other arising at T_N lower than T_c , supposedly a ferromagnetic–antiferromagnetic (FM-AFM) transition. We present the results of magnetization measurements around T_N under various magnetic fields for $\text{Ce}(\text{Fe}_{0.8}\text{Co}_{0.2})_2$. The field dependence of the transition temperature T_N has been established. The entropy change at the transition is calculated and the result shows a linear region in the entropy change versus T_N . An explanation for this linear behavior has been proposed in terms of electronic band structure. The calculated coefficient difference of electronic specific heat between the FM and AFM states agrees well with the value measured by others.

1. Introduction

Recently, considerable interest has been drawn to the Lave phase pseudobinary intermetallic compound $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$. Magnetization and susceptibility measurements as a function of temperature [1–3] have shown two magnetic transitions in this system. With decreasing temperature, the first transition appears at T_c from the paramagnetic (PM) to the ferromagnetic (FM) state, and the second transition occurs at T_N , below T_c . Thermal expansion studies [2] indicate that the second transition is first order. The nature of this transition has been determined by neutron diffraction [4,5] to be a ferromagnetic to antiferromagnetic (AFM) transition. The results of Mössbauer effect measurements have shown that the average hyperfine field has a smooth temperature dependence across T_N , suggesting no dramatic change in the magnitude of the Fe moment at the second transition. Similar phase diagrams for $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$, established by different research groups [1,2], show that a small substitution of Fe by Co can lead to a substantial shift in both T_c and T_N .

The suggestion has been made [6–8] that hybridization of the 4f electrons in Ce with the 3d band in Fe is responsible for the magnetic behavior of CeFe_2 and $\text{Ce}(\text{Fe}_{1-x}\text{M}_x)_2$ compounds where M is a 3d transition metal. A number of electronic specific heat studies have been carried out on CeFe_2 and $\text{Ce}(\text{Fe}_{1-x}\text{M}_x)_2$. Rastogi *et al.* [9] reported that the electronic specific

heat coefficient (γ) for CeFe_2 is about $53 \text{ mJ K}^{-2} \text{ mol}^{-1}$, and the value for paramagnetic CeCo_2 as reported by Sa *et al.* [10] is $21 \text{ mJ K}^{-2} \text{ mol}^{-1}$, being much smaller than that of CeFe_2 . The results by Wada *et al.* [11] give $48 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $25 \text{ mJ K}^{-2} \text{ mol}^{-1}$ for CeFe_2 and CeCo_2 , respectively. They also measured the electronic specific heat coefficient as a function of Co concentration for $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$. The measured large γ -value for CeFe_2 is believed to result from the hybridization of the Ce 4f electrons with the Fe 3d band. Band structure calculations [6–8,12] also suggest a strong relationship between magnetic behavior and electronic band structure for CeFe_2 and $\text{Ce}(\text{Fe}_{1-x}\text{Co}_x)_2$.

In this paper, we present magnetization measurements around T_N with various applied magnetic fields for $\text{Ce}(\text{Fe}_{0.8}\text{Co}_{0.2})_2$. Based on the experimental results, the field dependence of the transition temperature T_N has been established, and the determination of the entropy change at the FM-AFM transition is carried out. The result of the entropy change suggests that the electronic entropy change represents the main portion of the total entropy change at the FM-AFM transition, and that the electronic band structure may have a change across the transition.

2. Experimental details

Polycrystalline samples were prepared by arc melting as described previously [2]. The analysis of X-ray powder diffraction studies showed that the samples are in single

*Author to whom correspondence should be addressed.

phase. A SQUID magnetometer (Quantum Design, California, USA) was used for dc magnetization measurements. The ratio of the length to the diameter of the sample is about 5. The samples were oriented longitudinally in the magnetic field. Typically, the sample was zero-field cooled and the data were collected as the sample warmed from about 5 K to a temperature well above the T_N . To investigate the magnetic field dependence of T_N , the magnetization was measured as a function of temperature for several applied constant magnetic fields.

3. Results and discussion

Figure 1 shows the phase diagram for the system $Ce(Fe_{1-x}Co_x)_2$. The first transition temperature, T_c , decreases continuously as the cobalt concentration increases for $x \leq 0.40$. Meanwhile, the second transition temperature, T_N , increases first with increasing x and then decreases after a maximum at 15% Co. For the Co concentration higher than 30%, no second transition has been observed down to the temperature of 4.2 K. The second transition is weak for 3% Co and can not be seen for Co concentrations of 1% and 2% down to the temperature of 5 K. In Fig. 2 we plotted several curves of the magnetization as a function of temperature under different applied magnetic fields for the system $Ce(Fe_{0.8}Co_{0.2})_2$. The magnetization value is a constant in the low temperature region. When the temperature reaches the transition temperature T_N , an abrupt rise in magnetization occurs from the antiferromagnetic phase to the ferromagnetic phase. The magnitudes of the magnetization in different applied magnetic fields do not vary remarkably, but the effect of the magnetic field on T_N is significant. Fig. 3 is a plot of T_N versus the applied magnetic field. As shown in this figure, T_N

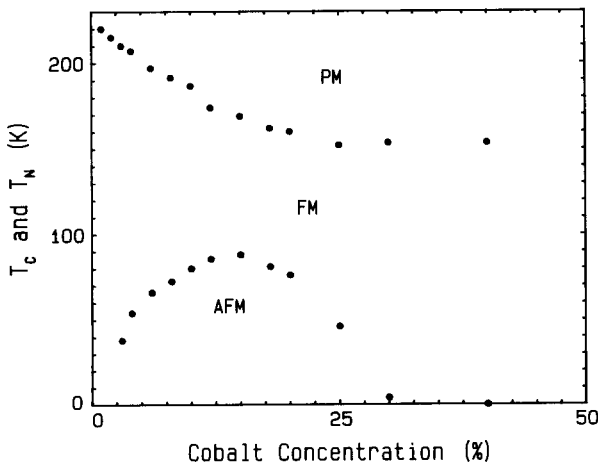


Fig. 1. Magnetic phase diagram of the $Ce(Fe_{1-x}Co_x)_2$ system. T_c and T_N are plotted against cobalt concentration (x).

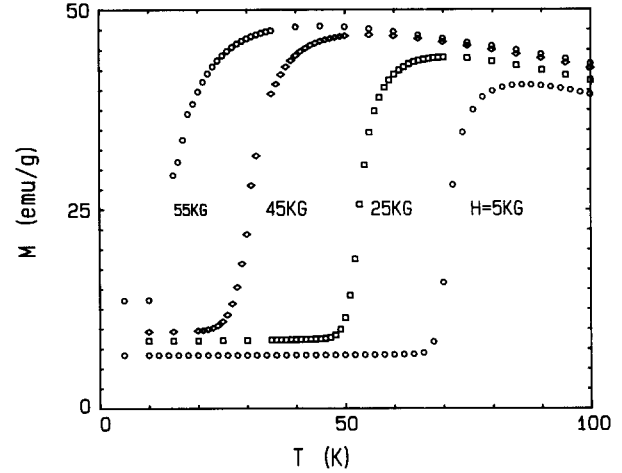


Fig. 2. Magnetizations (M) versus temperature (T) around T_N under various constant applied magnetic fields for the sample $Ce(Fe_{0.8}Co_{0.2})_2$.

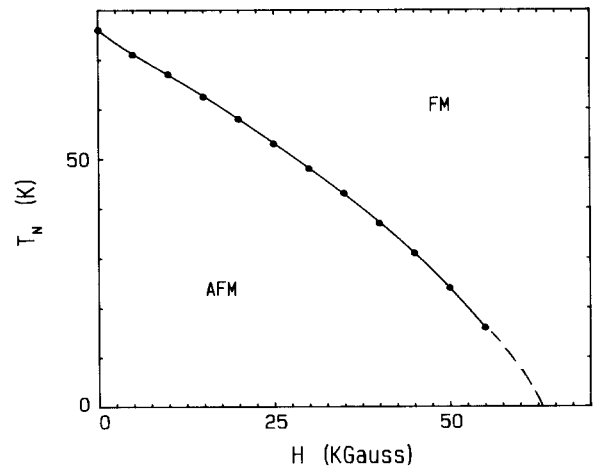


Fig. 3. Magnetic field (H) dependence of the transition (AFM-FM) temperature T_N for $Ce(Fe_{0.8}Co_{0.2})_2$.

decreases with increase in the applied magnetic field, from 76 K at 0.1 kG to 16 K at 55 kG. The solid line in Fig. 3 is a polynomial fit.

With the above experimental results in hand, the entropy change associated with the FM-AFM transition can be calculated by means of the thermodynamic relationship

$$\Delta S_T = -\Delta M(\partial H_c/\partial T)_{T_N} \quad (1)$$

where ΔS_T is the total entropy change, consisting of the lattice entropy change and electronic entropy change across the transition, ΔM is the magnetization change between the antiferromagnetic state and the ferromagnetic state at T_N , and $(\partial H_c/\partial T)_{T_N}$ is the derivative of the field dependence curve of the transition temperature T_N , which can be calculated by using the polynomial fit of the data in Fig. 2. The resulting entropy change as a function of T_N , shown in Fig. 4,

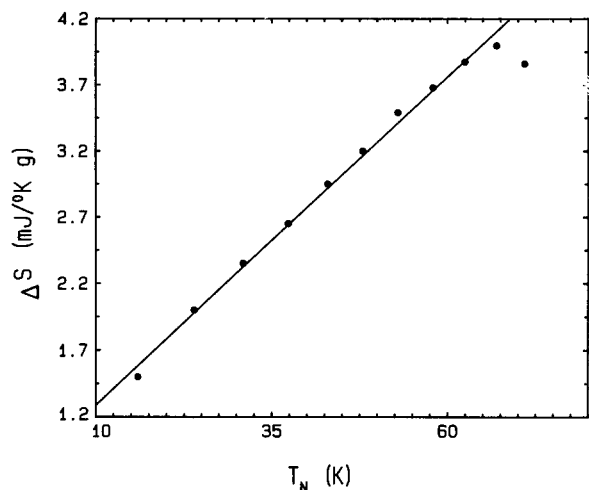


Fig. 4. Entropy change (ΔS) as a function of T_N for the compound $Ce(Fe_{0.8}Co_{0.2})_2$; here T_N is dependent on the applied magnetic field.

increases with T_N linearly. The linearity of the entropy change with T_N suggests the electronic entropy change is involved in the FM-AFM transition in our system.

For the electronic entropy, we can write

$$S_E = \int (C/T) dT = \gamma T \quad (2)$$

where we have used the linear term for the electronic specific heat, $C = \gamma T$.

Since γ is proportional to the density of the electronic states at the Fermi surface, S_E is strongly influenced by the electronic band structure. At the FM-AFM transition, the electronic entropy change would be

$$\Delta S_E = (\gamma_{FM} - \gamma_{AFM})T_N \quad (3)$$

where γ_{FM} and γ_{AFM} are the electronic specific heat coefficients for the FM and AFM states, respectively.

Equation (3) can describe very well the entropy change behavior shown in Fig. 4. Thus, it is not unreasonable to assume that total entropy change at the FM-AFM transition for the system here is mainly contributed by electronic entropy. The slope obtained from Fig. 4 is $10 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The value of $\gamma_{FM} - \gamma_{AFM}$ by Wada *et al.* [11] is $13 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The two values are in good agreement. All the results above indicate that the FM-AFM transition of the $Ce(Fe_{1-x}Co_x)_2$ compound is associated with the electronic band structure change. The positive value of S_E means that the FM state has a larger γ value than the AFM state, or, the electronic state density in the FM state is higher than that in the AFM state.

Across the FM-AFM transition, the significant change in the system is the magnetic structure which would give rise to a periodic potential change. The periodicity in the AFM state is twice that of the FM state in terms of magnetic structure. In simple band theory,

the doubling of the potential periodicity would lead to an additional energy gap in the electronic band structure, thereby reducing the electronic state density at the Fermi surface. This is supported for FeRh by the band calculations [12] in which the development of the AFM state introduces a new energy gap in the band structure. In the case of $Ce(Fe_{1-x}Co_x)_2$, there has been no report on band structure calculations for the AFM state. However, a rapid rise in the electric resistivity just below T_N for $Ce(Fe_{1-x}Co_x)_2$ [2,9] suggests the formation of a new energy gap in the AFM state.

Associated with the FM to AFM transition there is a distortion of the cubic Laves phase symmetry in the FM state to rhombohedral symmetry in the AFM state. This has been observed in a neutron diffraction study by Kennedy *et al.* [5]. The thermal expansion study [2] showed the discontinuity in sample volume at T_N .

4. Conclusions

The magnetization measurements around T_N have been performed in order to establish the magnetic field dependence of the transition temperature T_N for $Ce(Fe_{0.8}Co_{0.2})_2$ compound. The total entropy change at the FM-AFM transition has been calculated based on the experimental results. The linear behavior of the entropy change versus T_N suggests that the primary contribution to the total entropy change at the transition T_N comes from electronic entropy, and an electronic band structure change at T_N is associated with the FM-AFM transition. The FM state has a higher electronic state density at the Fermi level than the AFM state. This reduction in state density may result from the doubling of the periodicity of the magnetic structure in the AFM state. The increase in resistivity [2,9] at T_N in going from the FM to AFM state is most likely due to the formation of a superzone gap and hence is evidence for the reduction in the state density at the Fermi energy below T_N . A band structure calculation for the AFM state of $Ce(Fe_{1-x}Co_x)_2$ would be very useful in understanding this system.

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