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Low-temperature magnetic and thermodynamic properties of $Fe_{1-x}Co_xSi$

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Abstract

We report measurements of the low-field AC magnetic susceptibility $\chi'(T,f)$ and of the specific heat $C_p(T)$ for polycrystalline samples of $Fe_{1-x}Co_xSi$ with $0 \leqslant x \leqslant 0.03$ at low temperatures. For $x \geqslant 0.01$, the $\chi'(T)$ curves show maxima indicative of a spin-glass-type freezing of magnetic moments below 1 K. The small values of T_f/x and the $T_f(f)$ variations both suggest a weak magnetic interaction. The specific heat $C_p(T)$ contains a term γT which raises with increasing x from 2.1 T mJ mol^{-1} K^{-1} for FeSi to 7.6 T mJ mol^{-1} K^{-1} for $Fe_{0.97}Co_{0.03}Si$.

Keywords: $Fe_{1-x}Co_xSi$; Narrow-gap semiconductors; Specific heat; Magnetic susceptibility; Thermodynamic properties

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FeSi is a cubic narrow-gap semiconductor that has been claimed to share common features with a class of rare-earth compounds known as hybridization-gap semiconductors or Kondo insulators [1]. The magnetic susceptibility $\chi(T)$ of FeSi shows a maximum at about 500 K and an activated behaviour below that temperature corresponding to a narrow gap in the excitation spectrum. No magnetic order or spin-glass freezing occurs in this material, at least down to 0.04 K [2]. At very low temperatures, the electrical conductivity of FeSi is very low but metallic in character. Its isostructural counterpart CoSi is a diamagnetic semimetal with a temperature-independent susceptibility. Here we report the results of our investigation of some low-temperature thermodynamic and magnetic properties of Co-doped FeSi. $Fe_{1-x}Co_xSi$ forms disordered solid solutions with the *B*20 structure at all x. This system exhibits two critical concentrations $x_1 = 0.05$ and $x_2 = 0.8$ for the on-set of a long-period helimagnetic order, tentatively attributed to a Dzyaloshinsky–Moria spin–orbit-type coupling which can occur in the non-centrosymmetric *B*20 structure [3].

Polycrystalline samples of $Fe_{1-x}Co_xSi$ with Co concentrations in the range $0 \leqslant x \leqslant 0.03$ were prepared by melting together appropriate quantities of constituents in an RF furnace. The low-frequency and low-field AC magnetic susceptibility $\chi'(T,f)$ was measured by a conventional mutual inductance technique at various frequencies in the range between 18 and 630 Hz and with an excitation field amplitude of 0.1 Oe. The specific heat $C_p(T)$ was measured using a relaxation-type method.

In Fig. 1, we show the magnetic susceptibility $\chi'(T)$ for the samples with $x = 0.01$, 0.02 and 0.03

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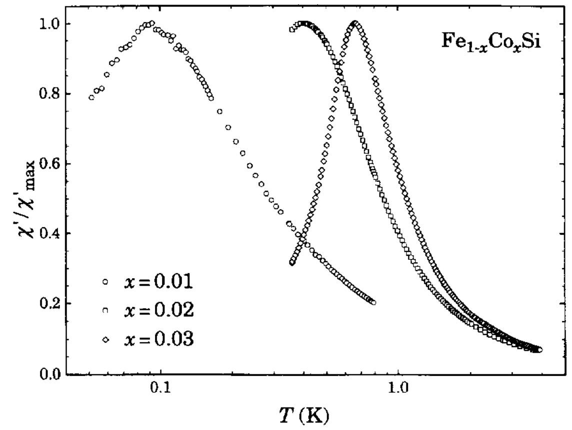

Fig. 1. Temperature variation of the AC susceptibility $\chi'(T)$ for the $Fe_{1-x}Co_xSi$ samples with $x \geqslant 0.01$, below 4 K.

between 0.05 and 4 K. For the nominally pure sample, the $\chi'(T)$ curve follows a Curie–Weiss-type law with a paramagnetic Curie temperature $\Theta = -0.036$ K and a very low value of the Curie constant. Well-defined maxima in the χ' versus T plots appear at 0.09, 0.40 and 0.67 K for the alloys containing 1, 2 and 3 at% of Cobalt, respectively, suggestive of a spin-glass-type freezing of magnetic moments, presumably related with the Co substitutions.

Above the respective temperatures T_f, at which the maxima in $\chi'(T)$ occur, the χ' versus T variations can be well fitted using a Curie–Weiss-type law. The value of the Curie constant, calculated per one Cobalt atom, increases with increasing Co concentration. For the samples with $x = 0.02$ and 0.03, Θ is positive and of the order of T_f, indicating predominantly ferromagnetic interactions. On the contrary, for $Fe_{0.99}Co_{0.01}Si$, Θ is negative and of much smaller absolute value than the corresponding T_f, indicating a trend towards weak antiferromagnetic coupling between magnetic moments. This sign change of the interaction may be related with a decrease of the characteristic length k_F^{-1} of the RKKY-type interaction with increasing carrier concentration. Here k_F is the Fermi wave vector. Measurements of the electrical resistivity $\rho(T)$ on the same samples as those investigated here show that Co-doping on the at% level enhances the low-temperature electrical conductivity by orders of magnitude [4].

We note surprisingly small values of T_f/x, which fall between 9 and 22 K. Typical metallic spin glasses are characterized by much higher values of T_f/x, e.g., $T_f/x \approx 10^3$ K for $Au_{1-x}Fe_x$ [5]. T_f/x values that are comparable to our results for $Fe_{1-x}Co_xSi$ have previously been reported for the spin-glass systems $La_{1-x}Gd_xAl_2$, $Y_{1-x}Gd_xAl_2$ and $La_{1-x}Gd_xB_6$, all with a weak exchange interaction between Gd moments, mediated by itinerant electrons [6].

We have also measured $\chi'(T)$ curves near T_f for several excitation frequencies f in the range between 18 and 630 Hz. The χ' versus T maxima shift to higher temperatures with increasing frequency. Fitting the $T_f(f)$ data with a Vogel–Fulcher-type relation.

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B(T_f - T_0)}\right) \tag{1}$$

and choosing $\tau_0 = 1 \times 10^{-13}$ s [7], leads to values of T_0 that are substantially lower than the measured T_f-values, indicating that the relaxation behaviour is close to an Arrhenius type. Arrhenius-type relaxations are characteristic of metallic spin glasses with a strongly reduced RKKY interaction and of insulating spin glasses with low concentrations of magnetic moments [7]. This is compatible with our evaluation of the very small values of T_f/x.

The complete set of the $C_p(T)$ data for all our samples of $Fe_{1-x}Co_xSi$ in the temperature range between 0.06 and 30 K is shown in Fig. 2. The same data, in the form of C_p/T versus T^2, are plotted in Fig. 3. First, we note a broad maximum in C_p/T of nominally pure FeSi centered at approximately 8.5 K, indicating a large excess specific heat $C_{ex}(T)$. The FeSi results between 1.5 and 30 K are very well fitted by the sum of contributions of the common low-temperature electronic and lattice excitations and a Schottky anomaly resulting from excitations within a two-level system with a single interlevel energy Δ, i.e.,

$$C_p = \gamma T + \beta T^3 + \delta T^5 + a\frac{x^2 e^x}{(1 + e^x)^2}, \tag{2}$$

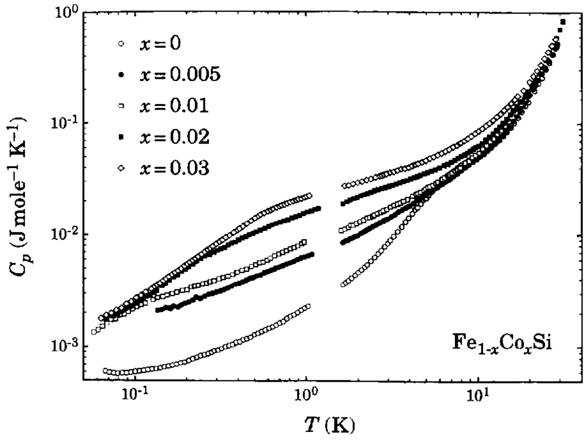

Fig. 2. Specific heat C_p of $Fe_{1-x}Co_xSi$ as a function of temperature between 0.06 and 30 K.

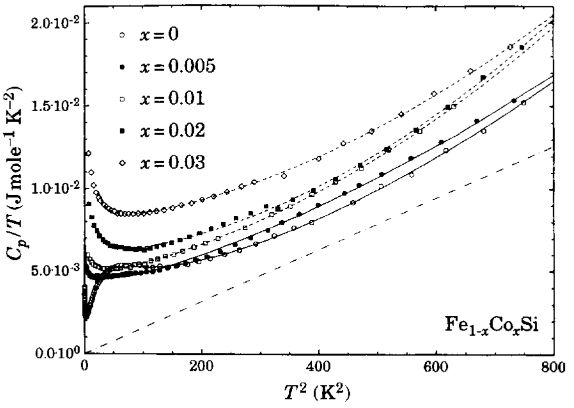

Fig. 3. C_p/T versus T^2 of $Fe_{1-x}Co_xSi$. The solid and broken lines indicate the fits of Eqs. (2) and (3) to the C_p data for the samples with $x \leqslant 0.005$ and $x \geqslant 0.01$, respectively (see text). The dashed–dotted line indicates the Debye contribution of acoustic lattice excitations.

where $x = \Delta/(k_B T)$. This fit is shown as the solid line in Fig. 3. The Schottky anomaly is characterized by a level separation $\Delta \approx 2$ meV and an entropy release of 0.029 R at 30 K. This Schottky anomaly is distinctly smaller for the sample with $x = 0.005$ and it cannot be identified in the $C_p(T)$ data for the samples with $x \geqslant 0.01$ (see Fig. 3).

For analyzing the $C_p(T)$ data of $Fe_{1-x}Co_xSi$ with $0.01 \leqslant x \leqslant 0.03$ above 5 K, we recall that our $\chi'(T)$ results indicate that these samples undergo a spin-glass-type freezing at low temperatures. Therefore, we assume that the main contributions to C_p are from electronic, lattice and high-temperature spin-glass excitations, i.e.,

$$C_p = \gamma T + \beta T^3 + \delta T^5 + A T^{-2}. \qquad (3)$$

The fits of the $C_p(T)$ data using Eq. (3) are shown as the broken lines in Fig. 3. The fitting parameters are given in Table 1. In Fig. 3, we also show the expected acoustic phonon contribution for FeSi, characterized by a Debye temperature of $\Theta_D = 313.5$ K [2]. For $x \geqslant 0.01$, the magnetic contributions $C_m(T)$ to the total measured specific heat $C_p(T)$ obtained by subtracting off the estimates of the electronic and lattice terms exhibit broad maxima at temperatures which are distinctly higher than the respective freezing temperatures T_f. This is consistent with our conjecture of a spin-glass-type freezing of magnetic moments in these materials [5]. We also note that the magnetic entropy ΔS_m, obtained from the magnetic specific heat C_m via

$$\Delta S_m(T) = \int_{T_0}^{T} \frac{C_m}{T'}\, dT', \qquad (4)$$

saturates at 30 K reaching $\approx 0.20R$ per mole Co. The freezing at T_f removes only about $\frac{1}{4}$ of ΔS_m, implying a considerable short-range order above T_f. This again is a common feature of spin glasses [5].

Table 1
Parameters of the fits of Eqs. (2) and (3) to $C_p(T)$ of $Fe_{1-x}Co_xSi$ (see text)

x	γ $\left(\frac{\text{mJ}}{\text{g at K}^2}\right)$	β $\left(\frac{\mu\text{J}}{\text{g at K}^4}\right)$	δ $\left(\frac{\text{nJ}}{\text{g at K}^6}\right)$	A $\left(\frac{\text{JK}}{\text{g at}}\right)$
0	2.2	9.7	9.9	
0.005	3.4	10.7	7.7	
0.01	4.5	7.6	14.3	0.07
0.02	5.7	4.3	17.4	0.20
0.03	7.6	5.5	13.2	0.24

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