Magnetic properties of $Fe_{1-x}Co_xSi$ alloys

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The solid solution between nonmagnetic narrow-gap semiconductor FeSi and diamagnetic semimetal CoSi gives rise to interesting metallic alloys with long-range helical magnetic ordering, for a wide range of intermediate concentrations. We report various magnetic properties of these alloys, including low-temperature reentrant spin-glass like behavior and an inverted magnetic hysteresis loop. The role of Dzyaloshinski-Moriya interaction in the magnetic response of these non-centro-symmetric alloys is discussed.

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The narrow-gap semiconductor FeSi has drawn the attention of condensed-matter physicists repeatedly since the late 1930.[1] The revival of strong interest[2] in FeSi during the last decade is mainly due to its similarities with those of narrow-gap rare-earth intermetallics popularly known as ''Kondo insulators''.[3] This comparison gives rise to the possibility of the study of complex many-body phenomena associated with Kondo-lattice systems. Doping with Al in FeSi leads to a heavy fermion metal through a metal-insulator transition with strong similarities to that for Si:P (Ref. 4) with the exception of a strongly renormalized effective carrier mass. The $Fe_{1-x}Co_xSi$ alloys are also remarkable in that they are magnetic for almost all of the intermediate concentration regime,[5–7] while the end compounds FeSi and CoSi are nonmagnetic, the latter being a diamagnetic semimetal.[8] The recent discovery of unusual positive magnetoresistance[7] in these supposedly helimagnetic $Fe_{1-x}Co_xSi$ alloys[6] along with the suggestion of the interplay of quantum coherence effects at relatively high temperature are quite exciting. The unusual square-root field-temperature dependence of electrical conductivity and the positive nature of the magnetoresistance are correlated to square-root singularity in the density of states probably associated with ''enhanced electron-electron interactions'' in a disordered ferromagnet with low carrier concentration.[7] These results suggest a possible microscopic mechanism of magnetoresistance that could lead to the development of magnetic materials of technological importance.[9] In light of these findings, we became motivated to closely scrutinize the magnetic properties of $Fe_{1-x}Co_xSi$ alloys, especially in the low-field and low-temperature regimes. There exist already some hints of unusual low-field magnetic properties of $Fe_{1-x}Co_xSi$ alloys in the form of an almost singular behavior in magnetization and a cusplike minimum in magnetoresistance near $H=0$ (Ref. 7). In this paper we report results of high-resolution magnetization measurements in $Fe_{1-x}Co_xSi$ alloys highlighting (i) low-temperature low-field reentrant spin-glass-like behavior and (ii) thermomagnetic history effects including an ''inverted hysteresis loop'' with negative remanence. The observation of this latter effect (which was so far considered to be limited to thin-film types of magnetic materials[10,11]) in relatively simple alloys such as the present (Fe, Co)Si is interesting. We shall argue that the occurrence of Dzyaloshinski-Moriya interaction in the present non-centro-symmetric cubic $B20$ $Fe_{1-x}Co_xSi$ alloys[6] plays an important role for the observed magnetic properties.

The polycrystalline samples of $Fe_{1-x}Co_xSi$, $x=0.1$, 0.15, 0.35, 0.45, and 0.65 were prepared by argon arc melting from high-purity starting materials. The samples were annealed for 90 h in vacuum at 900 °C to improve the homogeneity. Magnetization measurements were performed using a commercial superconducting quantum interference device magnetometer (Quantum Design, MPMS-5). A scan length of 4 cm with 32 data points in each scan was used for the measurements. However, all the important results were checked by varying the scan length from 2 to 8 cm, to rule out any possible role of the small field inhomogeneity of the superconducting magnet (which is actually scan-length dependent) in the observed magnetic properties. Also before the start of each experimental cycle the sample chamber is heated to 200 K and flushed with helium; this is to get rid of any oxygen leaking into the sample chamber over a period of time.

In Fig. 1(a) we plot magnetization (M) and inverse dc susceptibility (χ^{-1}) versus temperature (T) for $Fe_{1-x}Co_xSi$ with $x=0.15$ and 0.35. Estimated Curie temperatures (T_C) agree well with those reported in the literature.[7] In Figs. 1(b) and 1(c) we plot M vs field (H) plots for these alloys at various T both below and above T_C. Data also exist for $x=0.1$ and 0.45 but are not shown here for the sake of clarity and conciseness. The almost singular behavior in $M(H)$ near $H=0$ for $T<T_C$ as reported in Ref. 7 is quite evident in Figs. 1(b) and 1(c). We shall now concentrate on the low-H magnetic response of these alloys. In Fig. 2 we present M vs T plots for the $x=0.35$ alloy obtained both in the zero-field-cooled (ZFC) and field-cooled (FC) modes in various applied H. We observe two distinct features for $H\leqslant 500$ Oe, namely, (i) a peak in $M_{ZFC}(T)$ and a sharp change in slope in $M_{FC}(T)$ at a temperature $T_P(<T_C)$, and (ii) a distinct thermomagnetic irreversibility (TMI), i.e., $M_{ZFC}\neq M_{FC}$ for $T\leqslant T_P$. The same qualitative features have also been observed for $x=0.1$, 0.15, and 0.45. Both these features, which disappear with $H>500$ Oe, have not been reported so far (to our knowledge) for these (Fe,Co)Si alloys.

The low-T low-H magnetic response described above has an appreciable resemblance to the reentrant spin glasses.[12,13] To investigate more in this regard we have studied the H dependence of magnetization in detail in two different T-regimes: (i) $T<T_P$, and (ii) $T_P<T<T_C$. In Fig. 3 we plot M vs H for the $x=0.35$ alloy at 4.5 K highlighting the following striking features:

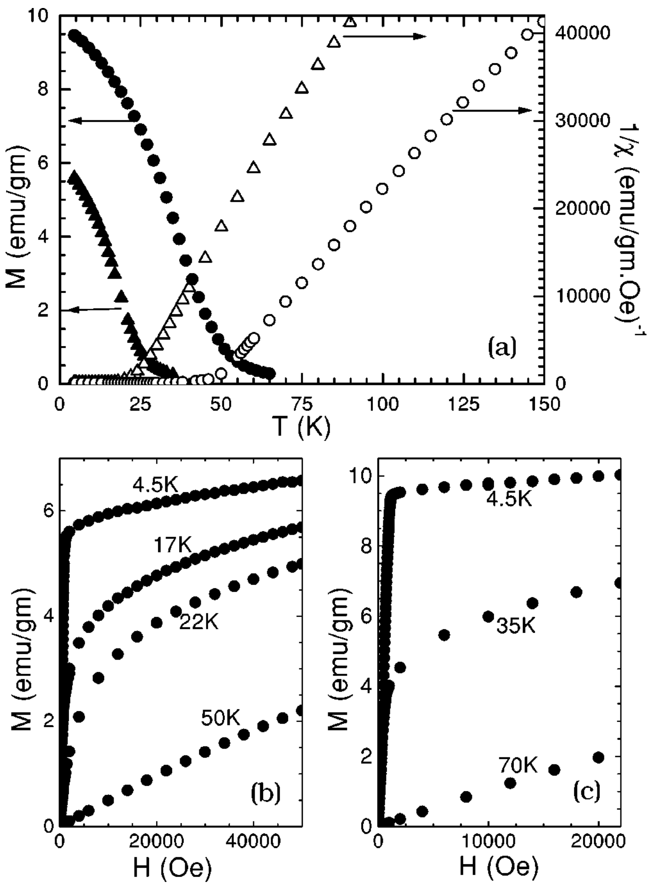

FIG. 1. (a) M and (χ^{-1}) vs T plots, and (b) and (c) M vs H plots for $(Fe_{1-x}Co_x)Si$, $x=0.15$ and 0.35. In (a) M is obtained with a field of 2 kOe and χ^{-1} from magnetization obtained with $H=200$ Oe.

1. There is a distinct bulge in the virgin M-H curve obtained after zero-field cooling the sample from $T>T_C$. This feature takes the virgin M-H curve in a limited H regime outside the field descending (ascending) M-H curve obtained after field cycling to 50 kOe (-50 kOe).

2. In the field cycling process if the maximum field of excursion H_{max} goes beyond the technical saturation point H_{sat} (≈ 1 kOe at $T=4.5$ K), the M-H curve takes the shape of an inverted hysteresis loop, i.e., the descending field leg of the M-H curve lies below that of the ascending field leg with positive coercivity and negative remanence (see the lower inset of Fig. 3).[14]

3. If H_{max} is limited to $H \ll H_{sat}$, M remains perfectly reversible. However, as H_{max} enters the H regime where the virgin M-H curve starts showing nonlinear behavior in the form of a bulge, a small but distinct positive hysteresis is observed (see the upper inset of Fig. 3). This hysteresis disappears as H approaches $H=0$ in the descending field cycle and M merges with the virgin M-H curve. With $H_{max}>H_{sat}$ this positive hysteresis changes sign giving rise to an "inverted hysteresis loop" in the low-field regime ($H<H_{sat}$) while the M-H curve remains perfectly reversible (within our experimental resolution) in the high-field regime ($H>H_{sat}$).

In the T regime $T_P<T<T_C$ the bulge in the virgin M-H curve and the associated positive hysteresis are not observed. However, inverted hysteresis loop behavior continues to exist at $H<H_{sat}$) even for $T>T_P$. And as before, the M-H curves remain reversible for $H>H_{sat}$. All these features of the M-H curve are also observed in $x=0.1$, 0.15, and 0.45 alloys in the same qualitative manner.

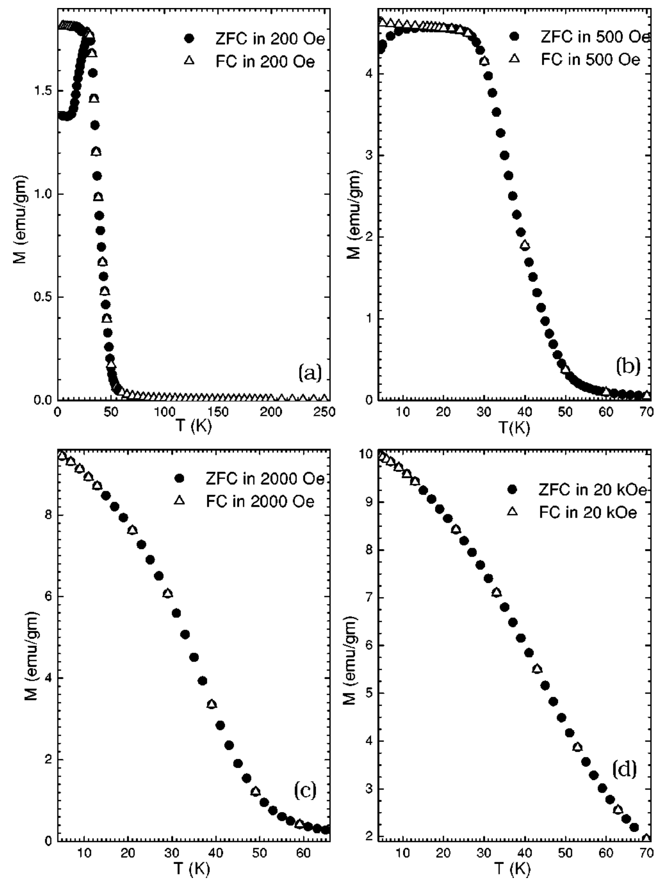

FIG. 2. M vs T plots for $(Fe_{0.65}Co_{0.35})Si$ obtained both in the ZFC and FC modes with $H=200$ Oe, 500 Oe, 2 kOe, and 20 kOe.

The observed peak in $M_{ZFC}(T)$ and TMI in M-T plots in Fig. 2 with $H \leqslant 500$ Oe can naively be interpreted in terms of the hindrance of domains' motion in a ferromagnetic system.[15] However, even if the various anomalous aspects of the M-H curves described above are ignored, the estimated coercivity field $|H_C|$ of the order of 15 Oe in our $x=0.35$ alloy at $T=4.5$ K rules out such a simple explanation in our measurements with applied H of 500 Oe which is much larger than $|H_C|$. Moreover the distinct change in slope in $M_{FC}(T)$ cannot be associated with any domain-related phenomena. These results suggest that there exists probably a reentrant spin-glass-like magnetic phase[13] for $T<T_P$ in these alloys. This low-T phase appears to be quite fragile and can easily be erased with moderate applied magnetic field. It is interesting to note here that the anomalous bulge in the virgin M-H curve is observed below T_P only, and it is quite clear from the above arguments that it is not associated with any domain-related phenomenon either. We suggest that this nonlinear behavior in the virgin M-H curve probably represents a field-induced transition from a low-H magnetic state to a high-H one. The bulge in the virgin M-H curve has been

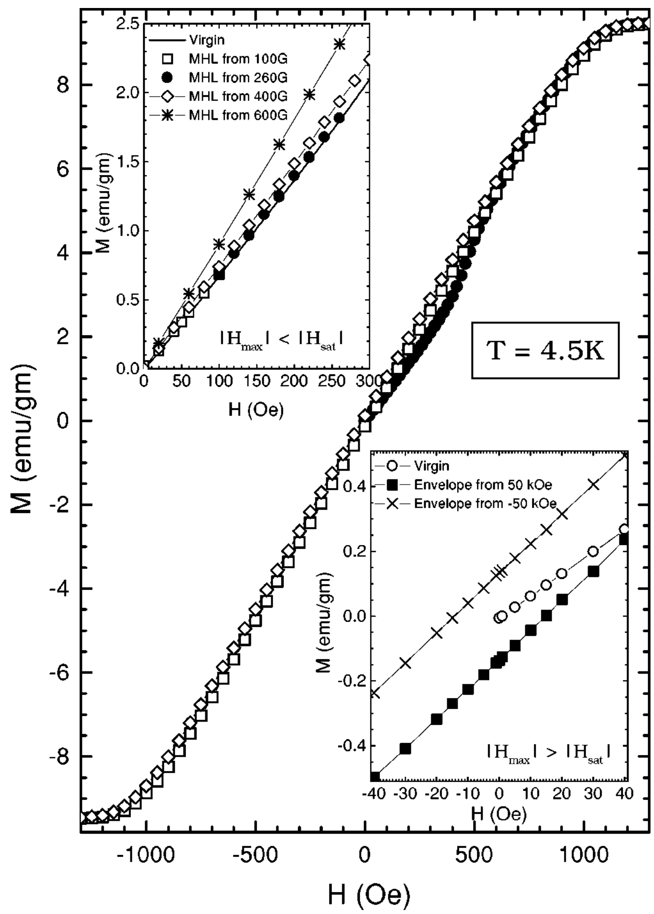

FIG. 3. M vs H for $(Fe_{0.65}Co_{0.35})Si$ at $T=4.5$ K highlighting various anomalous features of the M-H curve: (i) Below H_{sat} the M-H loop is inverted in nature, i.e, the ascending field M-H curve (diamonds) is lying above the descending field M-H curve (squares). This gives rise to a negative remanence which is highlighted in the lower inset. Above H_{sat} the M-H curve is reversible. (ii) In certain H regimes the virgin M-H curve (circles) is lying outside the envelope curves. Minor hysteresis loops (MHL) drawn from the nonlinear regime of the virgin curve (but the maximum field of excursion H_{max} being lower than H_{sat}) show positive hysteresis but merge with the virgin curve again before reaching $H=0$. MHL drawn from the low field linear regime of the virgin curve are perfectly reversible (see the upper inset).

reported earlier for (Fe,Co)Si in passing,[5,7] and in the absence of a detailed magnetization study it was attributed to domain-related effects in a ferromagnet.[5] A similar anomalous behavior of the virgin M-H curve in $CeFe_2$-based pseudobinary alloys has been associated recently with the first-order nature of a field induced metamagnetic transition.[16]

One might question now how to rationalize the magnetic properties of (Fe,Co)Si within the framework already developed for these alloys. Small-angle neutron-scattering measurements[6] have suggested the magnetic ordering in (Fe,Co)Si alloys to be of long period helimagnetic in nature. A model to explain such long period helimagnetic order can be based on a competition between a Dzyaloshinski-Moriya (DM) interaction and a Heisenberg-type exchange interaction.[5,6] The non-centro-symmetric cubic $B20$ structure of (Fe,Co)Si alloys supports the existence of DM interaction. Can this competition between these two types of interactions in (Fe,Co)Si alloys give rise to a reentrant spin-glass-like behavior? DM interaction apparently plays an important role in metallic spin glasses and reentrant spin glasses.[13] In this context the occurrence of a reentrant spin-glass-like phase in (Fe,Co)Si alloys is not entirely unexpected, especially with the presence of inherent disorder in the (Fe,Co) sublattice. In fact hints of repartition of the magnetic moments in the helix due to alloying effects exist in early neutron studies.[6] Satellites due to both clockwise and counterclockwise helices were observed in neutron measurements in zero-field-cooled samples. After excursion to a high H, the single clockwise helix was stabilized to the field direction with no satellites observed in any other direction.[6] On reduction of H to zero the helix does not come back to a specific eqnilibrium direction. This is in contrast to the case of isostructural ordered compound MnSi where also the helix follows the field, but comes back to the $\langle 111 \rangle$ direction in low H (Ref. 6). It was argued that the disorder in the (Fe,Co) sublattice caused local fluctuations of the coefficient of D-M interaction to produce two kinds of domains consisting of either a clockwise or counterclockwise helix in the zero-field-cooled state. The local fluctuation of magnetization might play the role of a pinning effect for the magnetic impurity preventing the propagation vector from pointing to the equilibrium direction.[6]

The observed ''inverted hysteresis loop,'' however, does not find a simple explanation within the above framework. Such ''inverted hysteresis loops'' have been observed in recent years in specific exchange-coupled multilayers such as Co/Pt/Gd/Pt and epitaxial Fe films on $W(001)$ (Refs. 10 and 11). In such materials their thin-film structure apparently plays an important role and hence it is considered that the ''inverted hysteresis loop'' is probably a phenomenon limited to thin-film type of magnetic materials. However, there is a very recent report of ''inverted hysteresis loops'' in a bulk magnetic material comprising cyanide-bridged multimetal complexes.[17] The observed ''inverted hysteresis loop'' in this bulk material is explained by ''the competition between the sublattice magnetization rotation due to the spin-flip transition and the trapping effect due to the uniaxial magnetic anisotropy.[17]'' While there exists a signature as discussed above of spin-flip transition in the present (Fe,Co)Si alloys and also the suggestion that D-M interaction can cause a trapping effect for domains especially if spins are canted within the domains,[13] it is a bit premature to apply the similar picture here. More experimental information, especially the microscopic kind, such as neutron-scattering measurements, is required to form even a qualitative model to explain the ''inverted hysteresis loop'' in the present system.

We note in Figs. 1(b) and 1(c) that while the technical saturation point is reached in the M-H curves below T_C for $x=0.15$ and 0.35 alloys at fairly low fields ($H_{sat}\approx 1$ kOe), M actually continues to increase beyond H_{sat} even up to the highest field of our measurement, i.e., 50 kOe. This two-stage magnetization process indicates that after the initial low-H alignment, the local spins, which are probably canted, line up slowly with a further increase in H beyond H_{sat}. We can actually make a reasonable fit of the M-H curve in the regime $H_{sat}<H<50$ kOe to a $H^{1/2}$ behavior. Similar behavior has also been observed for $x=0.1$ and 0.45 alloys. Manyala *et al.*[7] have earlier reported that magnetoresistance in some of these alloys also varied as $H^{1/2}$ in the H regime beyond technical saturation. This clearly indicates that the behavior of these alloys is quite different from a conventional ferromagnet even in the high-H regime.

In conclusion, our present dc-magnetization measurements in conjunction with the results of earlier neutron studies[6] suggest that there exists a low-T low-H magnetic state in (Fe, Co)Si alloys which resembles a lot of the reentrant spin glasses. With the increase in T and H, it transforms to a presently recognized high-H high-T helical FM state. Careful neutron measurements in various (H,T) regimes with different thermomagnetic historics will be useful to settle this issue. The high-T high-H magnetic state of these alloys has magnetic-field dependence in the form of $M \propto H^{1/2}$. Also, the magnetization response is reversible above the field for technical saturation H_{sat}, and produces a narrow ''inverted hysteresis loop'' below H_{sat}. A proper understanding of these magnetic responses and their possible correlation to technologically promising magnetotransport[7,9] will help in the search for newer magnetic materials tunable for practical use.

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