Interesting magnetic properties of $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ alloys

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(March 22, 2022)

Abstract

Solid solution between nonmagnetic narrow gap semiconductor FeSi and diamagnetic semi-metal CoSi gives rise to interesting metallic alloys with long-range helical magnetic ordering, for a wide range of intermediate concentration. We report various interesting magnetic properties of these alloys, including low temperature re-entrant spin-glass like behaviour and a novel inverted magnetic hysteresis loop. Role of Dzyaloshinski-Moriya interaction in the magnetic response of these non-centrosymmetric alloys is discussed.
The narrow-gap semiconductor FeSi has drawn attention of condensed matter physicists repeatedly since late nineteen thirties. The revival of strong interest in FeSi during last decade is mainly due to its similarities with those of narrow gap rare-earth intermetallics popularly known as ”Kondo insulators " in 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 with that for Si:P (Ref.4) with the exception of a strongly renormalized effective carrier mass. The Fe\textsubscript{1−x}Co\textsubscript{x}Si alloys are also remarkable in that they are magnetic for almost all the intermediate concentration regime, while the end compounds FeSi and CoSi are nonmagnetic, the latter being a diamagnetic semi-metal. The recent discovery of unusual positive magnetoresistance in these supposedly helimagnetic Fe\textsubscript{1−x}Co\textsubscript{x}Si alloys along with the suggestion of the interplay of quantum coherence effect 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. These results suggest a possible new microscopic mechanism of magnetoresistance that could lead to the development of new type of magnetic materials of technological importance. In the light of these unusual findings, we became motivated for a closer scrutiny of the magnetic properties of Fe\textsubscript{1−x}Co\textsubscript{x}Si alloys, especially in the low field and low temperature regime. There exist already some hints of unusual low field magnetic properties of Fe\textsubscript{1−x}Co\textsubscript{x}Si alloys in the form of an almost singular behaviour in magnetization and cusp-like minimum in magnetoresistance near H = 0 (Ref. 7). In this communication we report results of high resolution magnetization measurements in Fe\textsubscript{1−x}Co\textsubscript{x}Si alloys highlighting (i) low temperature low field re-entrant spin-glass like behaviour (ii) interesting thermomagnetic history effects including a novel ”inverted hysteresis loop” with negative remanence. The observation of this latter effect (which was so far considered to be limited to thin-film type of magnetic materials) in relatively simple alloys like the present (Fe,Co)Si, is definitely interesting.
We shall argue that the occurrence of Dzyaloshinski-Moriya interaction in the present non-centrosymmetric cubic B20 Fe$_{1-x}$Co$_x$Si alloys is playing an important role for the observed magnetic properties.

The polycrystalline samples of Fe$_{1-x}$Co$_x$Si; 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 hours in vacuum at 900°C for improving the homogeneity. Magnetization measurements were performed using a commercial SQUID-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 ($\chi^{-1}$) versus temperature (T) for Fe$_{1-x}$Co$_x$Si with x = 0.15 and 0.35. Estimated Curie temperatures ($T_C$) agree well with those reported in the literature. In Fig.1(b)-(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 not shown here for the sake of clarity and conciseness. The almost singular behaviour in M(H) near H = 0 for T < $T_C$ as reported in Ref. 7 is quite evident in Fig. 1(b)-(c). We shall now concentrate in the low H magnetic response of these alloys. In fig.2 we present M vs T plots for x = 0.35 alloy obtained both in the zero field cooled (ZFC) and field cooled (FC) mode in various applied H. We observe two distinct features for H $\leq$ 500 Oe, namely (1) a peak in $M_{ZFC}(T)$ and a sharp change in slope in $M_{FC}(T)$ at a temperature $T_P$ (< $T_C$). (2) a distinct thermomagnetic irreversibility (TMI) i.e. $M_{ZFC} \neq M_{FC}$ for T $\leq$ $T_P$. 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 appreciable resemblance with the re-entrant spin-glasses\textsuperscript{12,13}. To investigate more in this regard we have studied the H dependence of magnetization in details in two different T-regimes: (1) T < T_P, and (2) T_P < T < T_C. In Fig.3 we plot M vs H for x = 0.35 alloy at 4.5K highlighting the following striking features:

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}(\approx 1 kOe at T = 4.5K), 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)\textsuperscript{14}.

3. If H_{max} is limited to H << H_{sat}, M remains perfectly reversible. However, as H_{max} enters the H-regime where the virgin M-H curve starts showing the non-linear behaviour 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 behaviour 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.

The observed peak in $M_{ZFC}(T)$ and TMI in M-T plots in Fig.2 with $H \leq 500$ Oe can naively be interpreted in terms of the hindrance of domains’ motion in a ferromagnetic system. 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 exist probably a re-entrant spin-glass like magnetic phase 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 non-linear behaviour 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 reported earlier for (Fe,Co)Si in passing, and in the absence of a detailed magnetization study it was attributed to domain related effects in a ferromagnet. A similar anomalous behaviour 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.

The question now arises how to rationalise the interesting magnetic properties of (Fe,Co)Si within the framework already developed for these alloys. Small angle neutron scattering measurements 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. The non-centrosymmetric 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 re-entrant spin-glass like behaviour? DM interaction apparently plays an important role in metallic spin-glasses and
re-entrant spin-glasses. In this context the occurrence of a re-entrant 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. Satellites due to both clockwise and counterclockwise helixes 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. On reduction of H to zero the helix does not come back to a specific equilibrium direction. This is in contrast to the case of isostructural ordered compound MnSi where also the helix follows the field but comes back to $<111>$ direction in low H (Ref. 6). It was argued that the disorder in (Fe,Co) sublattice caused a local fluctuations of the co-efficient 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 a role of pinning effect of the magnetic impurity preventing the propagation vector from pointing to the equilibrium direction.

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) (Ref. 10 and 11). In such materials their thin film structure apparently play an important role and hence it is considered that "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 loop" in a bulk magnetic material comprising of cyanide-bridged multi metal complexes. 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". While there exists 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 trapping effect for domains especially if spins are canted within the domains, it is a bit premature to import the similar
picture here. More experimental information, especially the microscopic ones like neutron scattering, is required to form even a qualitative model to explain the "inverted hysteresis loop" in the present system.

We note in Figs.1 (b)-(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 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 $H^{1/2}$ behaviour. Similar behaviour has also been observed for $x = 0.1$ and 0.45 alloys. Manyala et al. 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 behaviour 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, suggest that there exists a low-T low-H magnetic state in (Fe, Co)Si alloys which resembles a lot of the re-entrant 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 history will be useful to settle this issue. The high-T high-H magnetic state of these alloys has an unusual 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 the technologically promising magnetotransport will help in the search for newer magnetic materials tunable for practical use.
I. ACKNOWLEDGEMENT

We would like to acknowledge Dr. K. J. Singh for the help in sample preparation and Dr. P. Chaddah for useful discussion.
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associated with our magnetometer, we have measured the M-H loop of a ferromagnetic
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FIGURES

FIG. 1. (a) M and $(\chi^{-1})$ vs T plots, (b) and (c) M vs H plots for $(\text{Fe}_{1-x}\text{Co}_x)\text{Si}$, $x = 0.15$ and 0.35. In Fig. 1 (a) M is obtained with a field of 2 kOe and $\chi^{-1}$ from magnetization obtained with $H = 200$ Oe.

FIG. 2. M vs T plots for $(\text{Fe}_{0.65}\text{Co}_{0.35})\text{Si}$ obtained both in the ZFC and FC mode with $H = 200$ Oe, 500 Oe, 2 kOe and 20 kOe.

FIG. 3. M vs H for $(\text{Fe}_{0.65}\text{Co}_{0.35})\text{Si}$ at $T = 4.5$ K highlighting various anomalous features of the M-H curve. (i) Below $H_{\text{sat}}$ the M-H loop is inverted in nature i.e the ascending field M-H curve (diamond) is lying above the descending field M-H curve (square). This gives rise to a negative remanance which is highlighted in the lower inset. Above $H_{\text{sat}}$ the M-H curve is reversible. (ii) In certain H regime the virgin M-H curve (circle) is lying outside the envelope curves. Minor hysteresis loops (MHL) drawn from the non-linear regime of the virgin curve (but the maximum field of excursion $H_{\text{max}}$ being lower than $H_{\text{sat}}$) show positive hysteresis but merge with the virgin curve again before reaching $H = 0$. MHL’s drawn from the low field linear regime of the virgin curve are perfectly reversible (see the upper inset).
\[ |H_{\text{max}}| < |H_{\text{sat}}| \]

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\[ T = 4.5K \]