# Crossover in magnetic properties of FeSi

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The magnetization of high quality iron monosilicide single crystals has been studied in a wide temperature and magnetic-field range. These data are analyzed by taking into account strong Hubbard correlations between $e_g$ and $t_{2g}$ states of Fe and the formation of spin polarons in the cubic FeSi matrix at low temperatures ($T<100$ K). These heavy particles are transformed into ferromagnetic microregions at $T_c\approx 15$ K, which result in the appearance of the low-temperature anomalies in transport and thermodynamic properties of this compound. The suppression of the many-body resonance at $E_F$ occurs in FeSi at high temperatures, thus leading to the crossover in magnetic properties of FeSi. The transition to the temperature induced magnetic moments causes a dramatic increase of the magnetic susceptibility at temperatures $T>100$ K.

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Interest in iron monosilicide FeSi dates back to the end of 1930s when Foex[1] had discovered that the magnetic susceptibility of this compound increased with temperature above 200 K. These results were later confirmed by Benoit,[2] who observed the broad susceptibility maximum $\chi(T)$ near 540 K (see, for example, the inset in Fig. 1) and then $\chi(T)$ dependence was analyzed in detail in Ref. 3, where a simplified semiconductor two-band model with a gap $E_g\sim 0.1$ eV was proposed to describe $\chi(T)$ and specific-heat anomalies. Additionally a Curie-Weiss-type behavior was established from the $\chi(T)$ measurements in FeSi at high temperatures 700–1500 K (Ref. 4) (see the inset in Fig. 1, interval Ia) with the Curie constant corresponding to the localized moment of about $2\mu_B$ per Fe atom. The absence of the long-range magnetic order has been verified by neutron diffraction,[5] $^{29}$Si NMR, and $^{57}$Fe Mössbauer[6] experiments.

A theoretical model of the unconventional magnetic behavior of FeSi has been proposed in the framework of the general self-consistent renormalization theory of spin fluctuations.[7] This approach[7,8] has been quite successful in explaining the temperature induced local magnetic moments formed in FeSi at temperatures above 100 K (inset in Fig. 1, interval Ib). Moreover, inelastic neutron-scattering experiments[9] have confirmed the presence of thermally induced spin fluctuations in FeSi. At the same time, no alternative was worked out in addition to the localized moments description of the $\chi(T)$ behavior in FeSi at $T>100$ K[3] up to now.

In contrast to the explanation of the magnetic properties at intermediate and high temperatures $T>100$ K, the origin of the low-temperature magnetic anomalies in iron monosilicide (inset in Fig. 1, intervals II-III) still remains a controversial issue. At present there are only a few rather diverging approaches applicable for the interpretation of both the low-

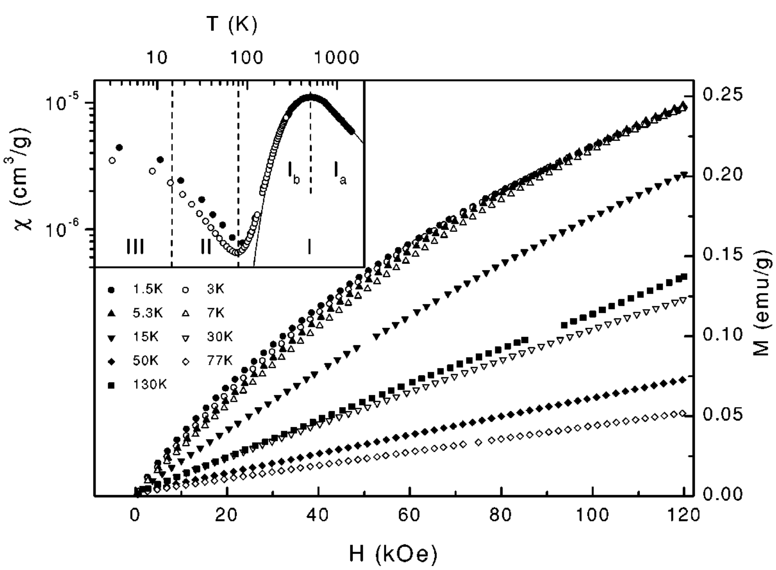


FIG. 1. Magnetization $M(H,T_0)$ vs magnetic field at different temperatures $T_0$ between 1.5 and 300 K. The inset shows susceptibility vs temperature dependence of FeSi obtained in Ref. 4 (●) and in this study (○) at $H=10$ kOe.

 

temperature ($T<70$ K) ‘‘Curie-Weiss-like tail’’ of the magnetic susceptibility[3,4,10–20] (inset in Fig. 1, interval II) and the absence of the magnetization saturation $M(H,T=4.2$ K) in fields up to 200 kOe.[21] Among these approaches the most commonly used one is the description based on the idea that local fluctuations in the relative concentrations of Fe and Si in the FeSi structure play very important role in this compound,[3] together with some residual imperfections in the crystal such as lattice defects, impurities, off-stoichiometry.[4] From this point of view the low-temperature Curie-like $\chi(T)$ behavior can be attributed to the presence of paramagnetic impurity moments[3,4,10–15,17–19] which are rather unusual for the B20 cubic lattice of iron monosilicide. Moreover, a very weak ferromagnetic response has been detected at helium temperatures even for very high quality FeSi single crystals[12–15,17,18] and it was attributed to the presence of the uncompensated iron in these samples. Despite the aforementioned ‘‘impurity problem’’ it is, however, believed[12–14] that ‘‘...the low-temperature properties can, even if impurity influenced or *because* they are impurity influenced, play an important role in clarifying the physical characteristics of FeSi.’’[14]

Another approach to the interpretation of the low-temperature $\chi(T)$ behavior has been proposed in the framework of a disordered conductor model[16] where the susceptibility $\chi=\chi_0(1-\eta\sqrt{T})$ is derived from the analysis of the density of states anomalies caused by the electron-electron interactions. At the same time, the results of Arushanov *et al.*[15] show that the contribution to the magnetic susceptibility from the single-occupied Anderson-localized states in the FeSi samples is negligible. Using all these models it is difficult to explain the observation that the presence of impurities and their random distribution in the iron monosilicide matrix do not depend dramatically on the technique[12] used to synthesize these samples (see also the inset of Fig. 1, intervals II-III).

Recently, detailed transport and thermoelectric measurements[20,22] have been carried out in combination with a preliminary magnetization study on high quality single crystals of FeSi. It was shown that strong Hubbard correlations in iron monosilicide at low temperatures ($T<100$ K) can be considered as the mechanism responsible for the appearance of the numerous anomalies in transport and thermodynamics properties of FeSi. Moreover, the formation of heavy quasiparticles—spin polarons with effective masses $m_p\sim 100m_0$—occurs below liquid-nitrogen temperatures resulting from a strong polarization of the Fe magnetic moments located in the nearest environment of the charge carriers in the upper Hubbard band. The presence of these heavy fermions in the cubic FeSi matrix may be interpreted in terms of a strong renormalization of the density of states (DOS) and the transition to the narrow-band transport.[20,22] The DOS renormalization effects lead to the magnetic susceptibility increase in FeSi at temperatures $T<70$ K, which arises due to the Pauli paramagnetic contribution from the charge carriers in the narrow conduction band (many body resonance) at Fermi level $E_F$.

To verify this approach, it is important to carry out a detailed study of magnetic characteristics of this unusual compound. In this paper we present magnetization measurements carried out in a broad temperature (1.5–300 K) and magnetic field (up to 120 kOe) range on high quality single crystals of FeSi. The samples are the same as the ones used in our previous studies.[20,22] The magnetization $M(H,T)$ was measured along different directions in the [111] plane using the Oxford Instruments magnetometer VSM12/V.

A typical family of the experimental $M(H,T_0)$ curves obtained in several magnetic-field scans for one of the FeSi samples is given in Fig. 1. These isothermal field dependencies of magnetization were measured by first increasing and then decreasing $H$. The $M(H)$ curves are completely reversible except of a small magnetic-fields region $H\leqslant 3$ kOe, where only a very weak ferromagnetic response has been detected below $T_c\approx 15$ K.[22] It should be mentioned here that in these experiments the magnetic-field directions $H\perp(111)$ have been used to minimize possible ferromagnetic contributions[22] at liquid-helium temperatures.

The $M(H)$ isothermal dependencies do not demonstrate any trend to a saturation in the fields up to 120 kOe (Fig. 1), in agreement with the results of Motokawa *et al.*[21] for $T=4.2$ K. In Fig. 2 the temperature dependencies of the magnetic susceptibility $\chi(T)=M(H_0,T)/H_0$, obtained from the magnetization measurements at fixed magnetic fields $H_0$, are presented in a double logarithmic plot. As found previously, $\chi$ decreases from 300 K down to liquid nitrogen and then rises again at lower temperatures.

To analyze the magnetization behavior (Figs. 1 and 2), we focus first on the so-called low-temperature Curie-Weiss-like tail (interval II). It is well known from the general self-consistent renormalization theory of spin fluctuations[7] that in the case of itinerant magnetic metals or nearly ferromagnetic semiconductors the Curie-Weiss-type susceptibility dependence does not correspond to any sort of an analytical solution. Moreover, such approximations of the $\chi(T)$ behavior in the itinerant electron magnetic systems are usually valid only in a narrow range of microscopic parameters.[7] The conclusions formulated in Ref. 7 can be used to analyze the data given in Figs. 1 and 2. From the $M(H,T)$ data (Fig. 2), which include also an empty cell correction for every temperature and magnetic-field scan, it is easy to come to the conclusion that the $\chi(T)$ behavior cannot be described by the Curie-Weiss law $\chi^{-1}\sim T$. Instead, the form $\chi^{-1}\sim T^{-\alpha}$ represents the susceptibility data quite well with the exponents varying from $\alpha=0.89$ at low $H_0$ values ($H_0\leqslant 20$ kOe) to $\alpha=1.04$ at high magnetic fields $H>100$ kOe (see fits in Fig. 2). Moreover, the tendency to saturation of the susceptibility $\chi(T)=M(T)/H$ is clearly seen below 10 K, especially for magnetic fields $H>20$ kOe (Fig. 2), contrary to any low-field approximation based on the Brillouin-like dependence. The problems with the previously discussed impurity based models used for the $\chi(T)$ interpretations in FeSi become more evident when the Brillouin-type double logarithmic plot of magnetization is applied (Fig. 3). Indeed, at low temperatures the magnetization data (Figs. 1 and 2) can be fitted by the dependence $M\sim(H/T)^{\alpha}$ with $\alpha<1$, where the exponent $\alpha$ is temperature dependent (see the upper inset in Fig.

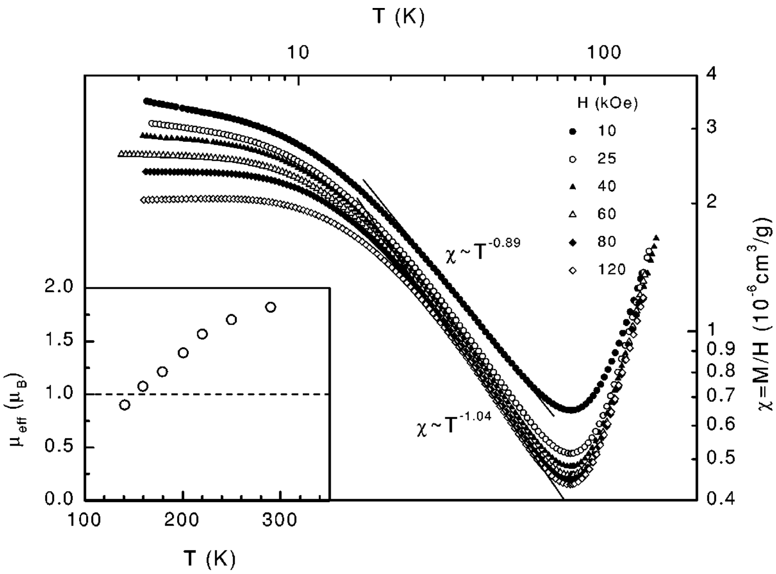


FIG. 2. Susceptibility $\chi = M/H$ vs temperature in double logarithmic plot in different magnetic fields $H \leqslant 120$ kOe. The inset shows the result of the effective magnetic moment $\mu_{eff}(T)$ estimation in the frameworks of Eqs. (1) and (2) (see text) at temperatures above 100 K.

3). Thus any kind of impurity models fails to shed the light on the origin of the low-temperature $\chi(T)$ increase in iron monosilicide.

It is worth noting here that, opposite to the situation at low temperatures, the Brillouin-type behavior ($\alpha = 1$) can be certainly used to analyze the data at intermediate and high temperatures $T > 70$ K (Figs. 1–3). According to the classification proposed in Refs. 20 and 22–23 for FeSi, the interval $T > 70$ K (I) corresponds to the intrinsic conduction region. In this temperature range one can obtain a linear $M \sim H/T$ dependence (see, for example, the curve for $T = 130$ K in Fig. 3). Then, taking into account that the ground state of FeSi is nonmagnetic ($S = 0$) and that the system is thermally excited to $S = 1$ state with increasing temperature[22] (see also a simplified view of the band scheme of FeSi in the Fermi level vicinity, lower inset in Fig. 3), it is easy to estimate the changes in $\chi(T)$ in the intrinsic conduction region of iron monosilicide,

$$\chi(T) = \frac{Ng^2\mu_B^2}{k_BT}\,\frac{2}{3+\exp(E_g/k_BT)} \tag{1}$$

($k_B$: Boltzmann constant; $g$: $g$ factor) and variation in magnitude of the effective magnetic moment on Fe sites $\mu_{eff}(T)$. As a result, the analysis in the framework of a simple relation,

$$M = \frac{n_0\exp(-E_g/2k_BT)\,\mu_{eff}^2(T)}{3k_BT}H, \tag{2}$$

makes it possible to reveal the $\mu_{eff}(T)$ variation between $2\mu_B$ at room temperature and $\mu_{eff} \approx \mu_B$ at temperatures slightly above 100 K (inset in Fig. 2). It should be mentioned here that $\mu_{eff} \approx \mu_B$ coincides with the value typical for a delocalized electron with $s = 1/2$ and $g \approx 2$. This transformation of the charge carriers characteristics may be interpreted in terms of a *crossover* in magnetic properties of FeSi from thermally induced magnetic moments behavior to a narrow-band spin polaron transport through the intragap states (manybody resonance at $E_F$, lower inset in Fig. 3).

In Ref. 20 the DOS renormalization effects in FeSi have been estimated in the approximation of the low-temperature

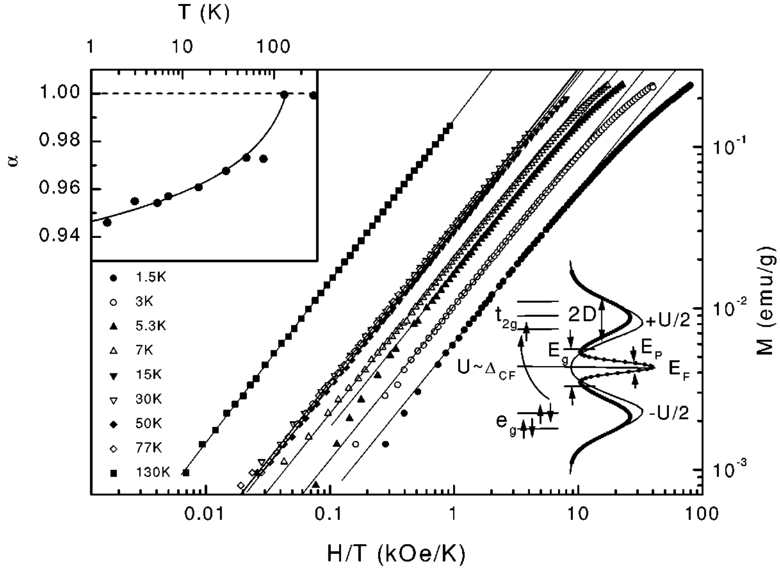


FIG. 3. A Brillouin-type magnetization $M$ vs $H/T$ ratio is shown in double logarithmic plot at different temperatures between 1.5 and 130 K. In the upper inset a temperature variation of an exponent $\alpha$ ($\alpha$ is the slope of the double logarithmic $M$ vs $H/T$ presentation) is shown. In the lower inset a simplified view of the FeSi band structure is given (see text).

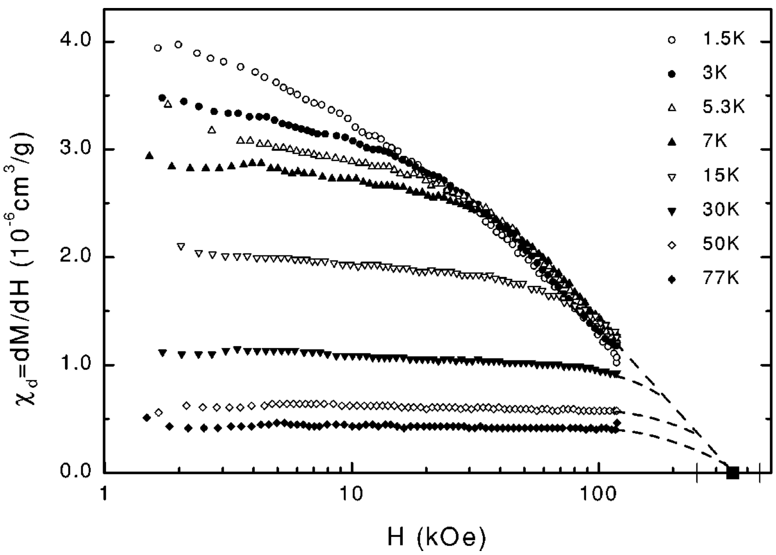


FIG. 4. Differential susceptibility $\chi_d = dM/dH$ vs magnetic field at different temperatures between 1.5 and 77 K. The saturation field $H_{ex} \approx 350 \pm 100$ kOe is marked (see text).

Pauli-like paramagnetic contribution from the charge carriers in the narrow conduction band of the width $E_p \approx 6$ meV at $E_F$. A dramatic DOS transformation is predicted for the fully frustrated Hubbard model at half filling from the metallic side $U < U_c \approx 3D$ of a Mott-Hubbard type metal-insulator transition[24] ($U$ is an on-site Coulomb interaction, $D$ is the band half-width). The transition from intrinsic conduction through the iron $3d$ states to the spin polaron transport at low temperatures can be considered as a crossover between two different regimes of a metallic-type behavior in FeSi. Besides that, essential changes have been detected from detailed Hall and Seebeck coefficients data[22] within the low-temperature "spin polaron phase" in FeSi. As a result, the appearance of a ferromagnetic contribution was found below $T_c \approx 15$ K from these studies and also from the low-field magnetization measurements along the (111) axis.[22] Additional features, such as hysteresis and "memory effects," together with a long-time relaxation behavior, allowed us to conclude in favor of the formation of ferromagnetic microregions (<10 Å in size) in the nearest environment of the charge carriers in the upper ($t_{2g}$, inset in Fig. 3) Hubbard band.[22]

At the same time, it is natural to expect that fast spin fluctuations between $e_g$ and $t_{2g}$ states which are responsible for the manybody resonance formation in FeSi are suppressed by a sufficiently high magnetic field. To verify this assumption the magnetization data of Figs. 1 and 2 were analyzed by a numerical differentiation procedure, where the susceptibility $\chi_d(H,T) = dM(H,T_0)/dH$ was deduced from the $M(H,T_0)$ dependencies. The results of these calculations are shown in Figs. 4 and 5. A universal behavior is clearly seen in the family of the $\chi_d(H,T)$ curves, when all $\chi_d(H)$ dependencies converge to the lowest temperature $\chi_d(H)$ curve (Fig. 4). From this point of view there is no qualitative difference between the susceptibility behavior at $T < T_c \approx 15$ K and $T > T_c$ although the transition from "the heavy fermions" to ferromagnetic microregions possibly occurs at $T_c$. In this situation it is natural to interpret the results,[22] where a uniform activation energy $E_p \approx 6$ meV has been detected both for spin polaron transport ($E_p$ is a so-called spin polaron well) and for reversal of magnetization in the small ferromagnetic domains, in terms of a universal nature of these paramagnetic and ferromagnetic particles with a

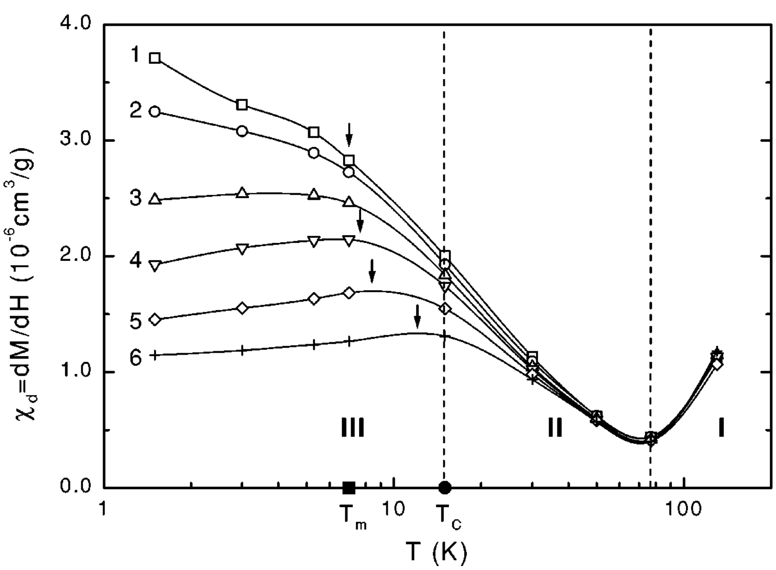


FIG. 5. Differential susceptibility $\chi_d = dM/dH$ vs temperature in different magnetic fields: 1: $H = 4$ kOe; 2: 10 kOe; 3: 30 kOe; 4: 50 kOe; 5: 80 kOe; 6: 115 kOe. The arrows correspond to the magnetic-phase transitions in FeSi at $T_m$ and $T_c$ (Ref. 22).

magnetic phase transition at $T_c$ in the microregions. Moreover, to support the picture it is necessary to point out a good agreement in the exchange magnetic field value in these ferromagnetic domains $H_{ex} \leqslant 500$ kOe as estimated from anomalous Hall coefficient study in Ref. 22, and the magnetic moments saturation field $H_s \approx 350 \pm 100$ kOe, which can be deduced from our results (Fig. 4).

The suppression of the spin fluctuations' amplitude and, as a consequence, the susceptibility decrease in FeSi at high magnetic fields is in a good agreement with the data presented in Fig. 5, where the family of $\chi_d(T,H_0)$ temperature dependencies is given. Indeed, the magnetic susceptibility increase at low temperatures $T<30$ K is strongly reduced in fields about 120 kOe both in paramagnetic ($T>T_c \approx 15$ K, interval II in Fig. 5) and ferromagnetic ($T<T_c$, range III) regimes. Moreover, additional features (marked by arrows in Fig. 5) in these $\chi_d(T,H_0)$ curves can be well established and possibly attributed to the ferromagnetic ($T_c \approx 15$ K) and mictomagnetic ($T_m \approx 7$ K, Ref. 22) transitions inside and between short-range ($<10$ Å) spin polarons in the FeSi matrix. A detailed study of the iron monosilicide magnetic phase diagram at low temperatures is in progress now and will be the subject of the future publications.

In summary, the magnetization of high quality iron monosilicide single crystals has been studied in a wide temperature and magnetic-field range. The data were analyzed in terms of strong Hubbard correlations between $e_g$ and $t_{2g}$ states of Fe and the formation of spin polarons in cubic FeSi matrix at low temperatures ($T<100$ K). The transition from the heavy fermion regime to ferromagnetic microregions formation at $T_c \approx 15$ K may explain numerous low-temperature anomalies, which are observed in transport and thermodynamic properties of this compound. The exchange magnetic field in these ferromagnetic domains $H_{ex} \approx 350 \pm 100$ kOe may be estimated from our magnetization measurements, which is comparable with the value $H_{ex} \leqslant 500$ kOe obtained from the anomalous Hall coefficient data. At temperatures high enough ($T>100$ K) to destroy the many-body resonance at $E_F$ the transition to the temperature induced magnetic moments behavior [thermal excitation between $e_g$ and $t_{2g}$ states of Fe, $\mu_{eff}(\mathrm{Fe}) \approx 2\mu_B$] occurs, leading to a dramatic increase of the magnetic susceptibility. Due to that, at intermediate and high temperatures both the transport and magnetic properties of FeSi may be reasonably well interpreted in terms of an electronic structure which consists of two narrow ($2D \approx 210$ meV) and rather localized Fe $3d$ bands in the vicinity of the Fermi level.

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