Weak ferromagnetism in Fe$_{1-x}$Co$_x$Sb$_2$

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Weak ferromagnetism in Fe$_{1-x}$Co$_x$Sb$_2$ is studied by magnetization and Mössbauer measurements. A small spontaneous magnetic moment of the order of $\sim 10^{-3} \mu_B$ appears along the $b$ axis for $0.2 \leq x \leq 0.4$. Based on a structural analysis, we argue against extrinsic sources of weak ferromagnetism. We discuss our results in the framework of the nearly magnetic electronic structure of the parent compound FeSb$_2$.

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I. INTRODUCTION

FeSi and FeSb$_2$ are semiconductors that show a crossover from a nonmagnetic semiconducting ground state with a narrow gap to a thermally induced paramagnetic metal with enhanced susceptibility.1,2 The magnetic properties of FeSi have instigated considerable theoretical interest, starting with the narrow-band model of Jaccarino et al.3 Further models include a nearly ferromagnetic semiconductor model of Takahashi and Moriya4 in which the state was sustained by thermally induced spin fluctuations found in neutron scattering experiments.5,6 Moreover, the nearly ferromagnetic semiconductor picture was supported by local density approximation plus on-site Coulomb repulsion correction (LDA+U) band structure calculations by Mattheiss and Hamann7 and Anisimov et al.8 At the same time, Aeppli and Fisk9 pointed out that the magnetic properties of FeSi are analogous to the physics of Kondo insulators, albeit with a reduced on-site Coulomb repulsion $U$. The basis of their argument was a model, ruled out by Jaccarino in his original work, of the narrow gap and high density of states. Experiments of Mandrus et al.10 and Park et al.11 confirmed the validity of the model of Aeppli and Fisk.

A search for new model systems, where the applicability of the Kondo insulator framework to 3d transition metals can be investigated, led to the synthesis of large single crystals of FeSb$_2$. Furthermore, a crossover was discovered similar to the one in FeSi for the magnetic and electrical transport properties.2,12 Subsequent alloying studies have shown heavy-fermion metallic state induced in FeSb$_{2−x}$Sn$_x$ just as in FeSi$_{1−x}$Al$_x$.13,14 In both materials the optical conductivity revealed unconventional charge gap formation. That is, a complete recovery of spectral weight in FeSi and FeSb$_2$ occurs over an energy range of few eV, suggesting contributions of larger energy scales.15,16 This is in sharp contrast to metal-insulator transitions in band insulators where thermal excitations of charge carriers through the gap redistribute just above the gap.

One of the key predictions of the LDA+U approach was the close proximity of FeSi to a ferromagnetic state.17 In analogy to FeSi, recent ab initio calculations predicted the nearly ferromagnetic nature of the FeSb$_2$ ground state.18 In FeSi the ferromagnetic state has been induced by lattice expansion in FeSi$_{1−x}$Ge$_x$, (Ref. 19) or by carrier insertion in Fe$_{1−x}$Co$_x$Si (Ref. 20). In contrast, FeSb$_2$ has not yet been tuned to a ferromagnetic state by any external parameters. In this work, we demonstrate the presence of weak ferromagnetism (WFM) in Fe$_{1−x}$Co$_x$Sb$_2$ $(0.2 \leq x \leq 0.45)$. The origins of the WFM are discussed. Extensive structural analysis shows no evidence of extrinsic impurity-induced WFM. We argue that instead the WFM is a consequence of the nearly ferromagnetic electronic structure of the parent compound FeSb$_2$.

II. EXPERIMENT

The Fe$_{1−x}$Co$_x$Sb$_2$ single crystals were grown from excess Sb flux.2 Powder x-ray diffraction (XRD) patterns of the ground samples were taken with Cu $K\alpha$ radiation $(\lambda = 1.5418 \text{ Å})$ using a Rigaku Miniflex x-ray diffractometer. The lattice parameters were obtained using Rietica software.21 High-resolution XRD patterns were taken at the beamline X7A of the National Synchrotron Light Source at the Brookhaven National Laboratory using a monochromatic-synchrotron x-ray and gas-proportional position-sensitive detector. Rietveld refinements were performed using GSAS.22 A JEOL JSM-6500 scanning electron microscope (SEM) with resolution of 1.5 nm was used for verifying the Co concentrations and investigating the microstructure. Single crystals were oriented using a Laue camera. Magnetization measurements were performed in a Quantum Design MPMS XL 5 instrument. The iron-57 Mössbauer spectra, at temperatures ranging from 2.8 to 295 K, were measured on a constant-acceleration spectrometer that utilized a rhodium matrix cobalt-57 source. The instrument was calibrated at 295 K with $\alpha$-iron powder. The isomer shifts reported herein are relative to $\alpha$-iron at 295 K. The thickness of the absorber was 23 and 72 mg/cm$^2$ for FeSb$_2$ and Fe$_{0.75}$Co$_{0.25}$Sb$_2$, respectively. The sample temperature in the Janis SV-300 cryostat was controlled with a Lakeshore 330 temperature controller and a silicon diode mounted on the copper sample holder. The accuracy of the sample temperature is better than $\pm 1\%$.
The powder x-ray patterns show that the Fe$_{1-x}$Co$_x$Sb$_2$ (0.2 $\leq x \leq 0.45$) samples crystallize in the $P_{nnm}$ structure without any additional crystalline peaks introduced by Co alloying. The effect of Co substitution on the Fe site is to expand the unit cell volume as compared to FeSb$_2$. This expansion is anisotropic and results from a contraction in the basal $a$-$b$ plane and an expansion along the $c$ axis upon substitution of Fe by Co.

III. MAGNETIC PROPERTIES

At low temperature, the parent compound FeSb$_2$ is a narrow-gap semiconductor with a rather small and temperature-independent magnetic susceptibility. Similar to FeSi, above 100 K there is a temperature-induced paramagnetic susceptibility and an enhanced electronic conduction. The magnetic susceptibility can be described by both a thermally induced Pauli susceptibility and a low to high spin transition. FeSb$_2$ above 100 K shows little anisotropy with the magnetic field applied along the different crystallographic axes. As shown in Fig. 1, the temperature dependence of the susceptibility indicates Pauli paramagnetism at high temperature. A clear ferromagnetic transition at $T_C$=6 K for a field of 1 kOe applied along any of the three crystallographic axes is illustrated in the inset to Fig. 1. These observations are in agreement with ferromagnetic long-range order of the small magnetic moments below $T=5$ K.

The ferromagnetic nature of the transition is supported by the hysteresis loop measured at $T=1.8$ K and displayed in Fig. 2. For field strength varying between $-6$ and 6 kOe applied along the $b$ axis, hysteresis loops are observed for 0.20 $\leq x \leq 0.45$. The width of the hysteresis loop grows initially with increasing $x$ from $x=0.20$, peaks at $x=0.25$, and becomes progressively smaller upon further Co substitution. Hysteresis loops are absent for fields applied along the $c$ axis and are observed only for $x=0.25$ for fields applied along the $a$ axis. By extrapolating the magnetization of Fe$_{0.75}$Co$_{0.25}$Sb$_2$ to $H=0$, a lower limit of the saturation magnetization along the $b$ axis of $M_s=0.0005\mu_B$/f.u. or $5 \times 10^{-4}\mu_B$/Fe, where f.u. refers to the FeSb$_2$ formula unit, is obtained.

The Mössbauer spectra of FeSb$_2$ single crystals exhibit a doublet at $T=295$ and 4.2 K. No impurity, and in particular no impurity with a large hyperfine field, is observed in the Mössbauer spectra. Furthermore, the Mössbauer spectral parameters for FeSb$_2$ obtained herein are in excellent agreement with the previously reported parameters (see Table 1).

For Fe$_{0.75}$Co$_{0.25}$Sb$_2$, the Mössbauer spectra, shown in Fig. 3, exhibit a doublet for temperatures ranging from 295 K to 2.8 K. Again no impurity contribution is observed. The spectral parameters, obtained at $T=295$ K and 4 K, are close to those observed in FeSb$_2$. The isomer shift observed in Fe$_{0.75}$Co$_{0.25}$Sb$_2$ is ca. 0.01 mm/s smaller than in FeSb$_2$. This indicates a somewhat larger $s$-electron density at the $^{57}$Fe nucleus.

The variation of the quadrupole splitting from 295 to 4.2 K is larger in FeSb$_2$ than in Fe$_{0.75}$Co$_{0.25}$Sb$_2$. This strong temperature dependence of the quadrupole splitting in FeSb$_2$ is consistent with a scenario of electron delocalization appearing with increasing temperature, with a gap $\Delta E$ of 380 K. As illustrated in Fig. 4, a fit of the Fe$_{0.75}$Co$_{0.25}$Sb$_2$ quadrupole splitting as a function of temperature with the delocalization model described in Ref. 25 yields a somewhat larger gap energy $E_g=(480\pm50)$ K than that observed in FeSb$_2$. The difference between the hyperfine parameters in FeSb$_2$, and Fe$_{0.75}$Co$_{0.25}$Sb$_2$ indicates that there is indeed a modification of the FeSb$_2$ structure and that no phase segregation is present. The Mössbauer spectra show that the investigated phase is (Fe,Co)Sb$_2$ and not Fe$_{1-x}$Co$_x$Sb$_2$ since the hyperfine parameters are significantly different. Furthermore, no iron-bearing impurity is observed in Fe$_{0.75}$Co$_{0.25}$Sb$_2$.

The $T=2.8$ K spectrum of Fe$_{0.75}$Co$_{0.25}$Sb$_2$ is a doublet, which is somewhat surprising. Our interpretation is that either the iron experiences no magnetic hyperfine field
or that the hyperfine field is below the detection limit. If the small broadening of ca. 0.047(6) mm/s of the 2.8 K spectrum, when compared to the 4.2 K spectrum, was associated with a magnetic hyperfine field, it would correspond to a 1.5+/−0.2 kOe hyperfine field. With a linewidth constrained to 0.29 mm/s, a fit of this spectrum, with both a quadrupole interaction and a hyperfine field, yields a field of 2.8+/

IV. INTRINSIC OR EXTRINSIC MAGNETISM

Given the small value of the saturated moment, it is possible that WFM originates from extrinsic sources, such as artifacts of the measurement process or the presence of a small amount of ferromagnetic impurity—e.g., elemental Fe. The former can be excluded based on the lack of sample dependence, both in magnetization and in heat capacity data. Below we discuss the possibility of undetected second phases as extrinsic sources of the WFM.

No hysteresis loops are observed for temperatures above $T_C=(6−7)$ K for $x=(0.2−0.4)$ (example shown in Fig. 5).

| $T$ (K) | $\delta$ (mm/s)$^a$ | $\Delta E_Q$ (mm/s) | $\Gamma$ (mm/s) | $\delta$ (mm/s)$^a$ | $\Delta E_Q$ (mm/s) | $\Gamma$ (mm/s) |
|---------|---------------------|---------------------|----------------|---------------------|---------------------|----------------|
| 296$^b$ | 0.433(2)            | 1.343(2)            | 0.264(5)       | 0.450(6)            | 1.286(6)            |
| 295     | 0.483(2)            | 1.394(2)            | 0.265(2)       | 0.449(1)            | 1.275(2)            | 0.262(3)       |
| 240     | 0.509(2)            | 1.422(2)            | 0.267(2)       | 0.291(2)            | 1.545(2)            | 0.280(3)       |
| 190     | 0.538(2)            | 1.449(2)            | 0.273(2)       | 0.267(2)            | 1.602(2)            | 0.273(3)       |
| 90      | 0.559(2)            | 1.364(2)            | 0.284(2)       | 0.284(2)            | 1.574(2)            | 0.270(4)       |
| 50      | 0.569(2)            | 1.474(3)            | 0.290(4)       | 0.290(4)            | 1.574(2)            | 0.270(4)       |

$^a$Relative to $\alpha$-iron at 295 K.
$^b$The isomer shift reference in Ref. 26 is sodium nitroprusside, which has a $−0.26$ mm/s isomer shift relative to $\alpha$-iron at room temperature.
No known Fe-Sb, Co-Sb, Fe-Co, Fe-O, or Co-O phase shows a ferromagnetic transition in this temperature range. FeCo alloys have large hyperfine fields \(200–400\) kOe that would have been detected by Mössbauer measurement. We can calculate the x-ray patterns expected in the presence of bulk crystalline Fe impurities by superimposing the strongest peak of 0.3% elemental Fe to the measured patterns. No overlap between the calculated and measured Fe\(_{0.75}\)Co\(_{0.25}\)Sb\(_2\) x-ray patterns was observed. Any other unknown Fe-O, Fe-Co-O, Co-O, Fe-Co, Fe-Sb-Co, etc., phase with the same atomic ratio in the mixture would have been detected by Mössbauer measurement. We can calculate the x-ray patterns expected in the presence of bulk crystalline Fe impurities by superimposing the strongest peak of 0.3% elemental Fe to the measured patterns. No overlap between the calculated and measured Fe\(_{0.75}\)Co\(_{0.25}\)Sb\(_2\) x-ray patterns was observed (Fig. 6). Any other unknown Fe-O, Fe-Co-O, Co-O, Fe-Co, Fe-Sb-Co, etc., phase with the same atomic ratio in the mixture would have been detected and refined by synchrotron powder x-ray diffraction because its contribution to the scattering mixture would be higher than that of Fe. Though \(M_{LL}\) observed in magnetic hysteresis loops could be caused by Fe impurities of the order of the synchrotron powder x-ray diffraction detection limit, the absence of hysteresis loops above 6 K strongly argues against such a scenario.

Another possibility is that magnetism in Fe\(_{1-x}\)Co\(_x\)Sb\(_2\) is caused by magnetic nanoparticles. Mössbauer measurement shows no evidence of iron bearing nanoparticles (either FeCo or Fe oxide). Such nanoparticles would have a paramagnetic spectrum with different isomer shift and quadrupole splitting at room temperature, which would be detected with a 0.3% limit. Below the nanoparticle blocking temperature the field would be large, typically 500 kOe for typical oxides. Solid evidence against nanoparticles or bulk extrinsic phases comes from energy dispersive SEM measurements. Among the samples grown from several different batches for \(x=0.25\), the uncertainty in Co concentration is \(\Delta x=0.04\). SEM data taken with resolution down to 1.5 nm exclude the presence of either bulk secondary phases or embedded nanoparticles. This is because high-resolution SEM images of several randomly chosen polished crystals and crystalline surfaces show no trace of nanosize inclusions, clusters, or inhomogeneities (example shown in Fig. 7). The images were taken in the “composition” mode with a solid-state detector consisting of paired \(p-n\) junctions. This type of detector is very sensitive to back scattered electrons which in turn are sensitive to local variations in atomic number. If nano crystallites of Fe or other elements were present, they would have been visible as bright dots in the high-magnification image.

Taken in conjunction, our results argue against extrinsic sources of WFM in Fe\(_{1-x}\)Co\(_x\)Sb\(_2\). Recent muon spin relax-
ation measurements indicate that the WFM state is spread throughout the full sample volume for Fe$_{0.7}$Co$_{0.3}$Sb$_2$, further supporting our results.

V. DISCUSSION AND CONCLUSIONS

Examples of intrinsic WFM states in narrow-band materials are abundant in nature. Besides numerous oxide compounds, many intermetallic systems also exhibit intrinsic weak ferromagnetism, such as YbRhSb, MnS, and Yb$_{0.8}$Y$_{0.2}$InCu$_2$. Magnetism in FeSb$_2$ in analogy to FeSi has been predicted by LDA+U calculations. Besides the use of an external magnetic field, one interesting possibility would be to induce the ferromagnetic state by lattice expansion and band narrowing, as in FeSi$_{1-x}$Ge$_x$. Unfortunately, isoelectronic lattice expansion is limited to rather small values of $x$ in FeSb$_{2-x}$Bi$_x$. Our preliminary data show that the ferromagnetic state is not reached for $x=0.016$. As in Fe$_{1-x}$Co$_x$Si, a ferromagnetic state is induced with Co substitution in FeSb$_2$. In both alloy systems the critical temperature $T_C$ exhibits a characteristic peak as a function of Co concentration. Whereas metallicity simultaneously appears with ferromagnetism in Fe$_{1-x}$Co$_x$Si at $x=0.05$ in Fe$_{1-x}$Co$_x$Sb$_2$ alloys transport and spin gap vanish at $x=0.1$ and $x=0.2$, respectively.

What could be the mechanism of the WFM in Fe$_{1-x}$Co$_x$Sb$_2$ alloys? Knowing that there is an inversion symmetry at the Fe site in the Pmmn space group of FeSb$_2$, we can exclude the presence of a Dzyaloshinskii-Moriya (DM) type of interaction. This is in contrast to doped FeSi where the DM interaction is believed to be responsible for the WFM. A canted antiferromagnetism can be excluded based on the observed field dependence of the transition temperature. That is, the ferromagnetic tail at low temperature is insensitive to variation of the applied field. However, it is possible to ascribe the low magnetic moment in Co-doped FeSb$_2$ to the partial ordering of Co$^{3+}$ ions. This scenario is in agreement with a detailed analysis of the magnetic and thermodynamic properties of Fe$_{1-x}$Co$_x$Sb$_2$.

Besides the obvious lattice expansion, the effect of the Co insertion is to introduce extra carriers in the system. The carriers cause a closing of the gap by $x=0.1$. Thus, the WFM appearance could be a consequence of carrier-induced metallicity. This claim is further supported by discarding another well-known scenario for the WFM induction. More precisely, one can imagine that the WFM is induced by an "inverted metal-insulator" scenario. In this scenario, magnetic order exists only in the metallic phase. Furthermore, the metallicity is a direct consequence of transition to the ferromagnetic state where a bulk moment of $\sim 1\mu_B$ develops out of a small gap semiconductor with small susceptibility. However, in Fe$_{1-x}$Co$_x$Sb$_2$ for $x=0.2$–$0.45$ a small ordered moment is induced. Therefore, the presence of the small moment excludes the "inverted metal-insulator" scenario and leaves as the only possibility that the WFM arises as a consequence of carrier-induced metallicity.

In conclusion, detailed structural and magnetic measurements argue against extrinsic sources of WFM in Co-substituted FeSb$_2$. The ordered moment below the WFM transition for Fe$_{0.75}$Co$_{0.25}$Sb$_2$ is $M \sim (0.5–10) \times 10^{-3}\mu_B$/Fe. As opposed to FeSi where the metallic state is caused by band narrowing of nearly ferromagnetic parent electronic structure, weak ferromagnetism in Fe$_{1-x}$Co$_x$Sb$_2$ could be a consequence of a carrier-induced metallic state. In order to fully understand the magnetic structure, magnitude of moments, and mechanism of magnetic ordering, further neutron scattering and/or nuclear magnetic resonance measurements are envisaged.

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