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Weak ferromagnetism in $Fe_{1-x}Co_xSb_2$

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Weak ferromagnetism in $Fe_{1-x}Co_xSb_2$ is studied by magnetization and Mössbauer measurements. A small spontaneous magnetic moment of the order of $\sim 10^{-3}\mu_B$ appears along the $\hat{b}$ 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 Moriya[4] 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 Hamann[7] and Anisimov *et al.*[8] At the same time, Aeppli and Fisk[9] 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 $Fe_{1-x}Co_xSi$ (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 $Fe_{1-x}Co_xSb_2$ $(0.2 \leq x \leq 0.45)$. 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 $Fe_{1-x}Co_xSb_2$ 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 ($\lambda = 1.5418$ 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) microprobe 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 α-iron powder. The isomer shifts reported herein are relative to α-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 ±1%.

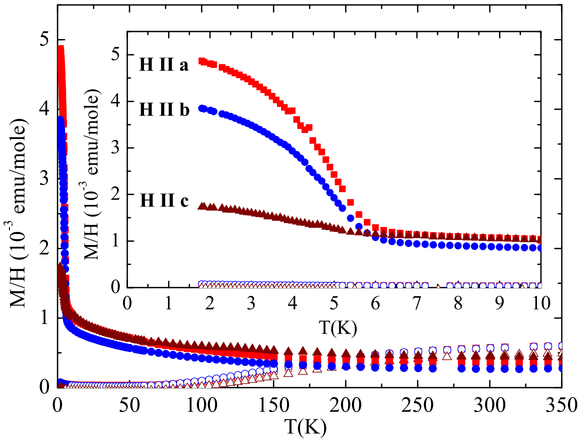

FIG. 1. (Color online) Magnetic susceptibility M/H of $FeSb_2$ (open symbols) and $Fe_{0.75}Co_{0.25}Sb_2$ (solid symbols) for a 1-kOe field applied along all three principal crystalline axes.

The powder x-ray patterns show that the $Fe_{1-x}Co_xSb_2$ ($0.2 \leq x \leq 0.45$) samples crystallize in the *Pnnm* 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.[23]

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.[2] 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.[2,12,24] In the temperature (T) range from 1.7 to 150 K the $Fe_{0.75}Co_{0.25}Sb_2$ magnetic susceptibility is larger than that of $FeSb_2$. For T above 6 K, it 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.[23] 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 $\hat{b}$ 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 $\hat{c}$ axis and are observed only for $x = 0.25$ for fields applied along the $\hat{a}$ 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 $\hat{b}$ axis of $M_{LL} = 0.0005\mu_B$/f.u. or $5 \times 10^{-4}\mu_B$/Fe, where f.u. refers to the $FeSb_2$ formula unit, is obtained.

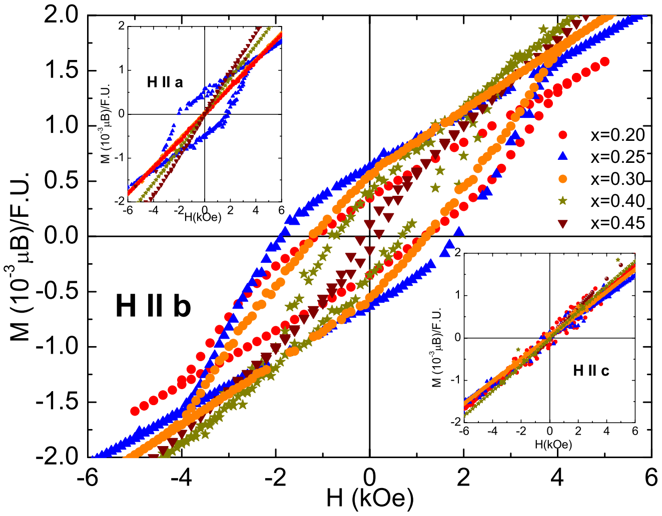

FIG. 2. (Color online) Hysteresis loops for $Fe_{1-x}Co_xSb_2$ in the ferromagnetic state ($x = 0.2 - 0.45$) at $T = 1.8$ K. Magnetization does not saturate; it continues to increase with applied magnetic field, similar to bulk itinerant ferromagnets with 3*d* ions.

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 I).[25,26] For $Fe_{0.75}Co_{0.25}Sb_2$, the Mössbauer spectra, shown in Fig. 3, exhibit a doublet for temperatures ranging from $T = 295$ 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 ΔE of 380 K.[25,27] 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 $E_g = (480 \pm 50)$ 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 $FeSb_2 + CoSb_2$ since the hyperfine parameters are significantly different. Furthermore, no iron-bearing impurity is observed in $Fe_{0.75}Co_{0.25}Sb_2$.

Apparently, 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

TABLE I. The hyperfine parameters for $FeSb_2$ and $Fe_{0.75}Co_{0.25}Sb_2$.

	$Fe_{0.75}Co_{0.25}Sb_2$			$FeSb_2$		
T (K)	δ (mm/s)[a]	ΔE_Q (mm/s)	Γ (mm/s)	δ (mm/s)[a]	ΔE_Q (mm/s)	Γ (mm/s)
296[b]				0.450(6)	1.286(6)	
295	0.433(2)	1.343(2)	0.264(5)	0.449(1)	1.275(2)	0.262(3)
240	0.483(2)	1.394(2)	0.265(2)			
190	0.509(2)	1.422(2)	0.267(2)			
140	0.538(2)	1.449(2)	0.273(2)			
90	0.455(2)	1.364(2)	0.284(2)			
50	0.569(2)	1.474(3)	0.290(4)			
6.4[b]				0.572(6)	1.575(6)	
4.2	0.560(2)	1.483(2)	0.291(2)	0.572(1)	1.573(3)	0.270(4)
2.8	0.558(2)	1.483(3)	0.338(4)			

[a] Relative to α-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 α-iron at room temperature.

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+/−1.2 kOe. Taking the usual proportionality of ca. 150 kOe/μ_B, these values can be used to estimate an upper limit of about $M_{UL}=0.01\mu_B$ for the magnetic moment on Fe.

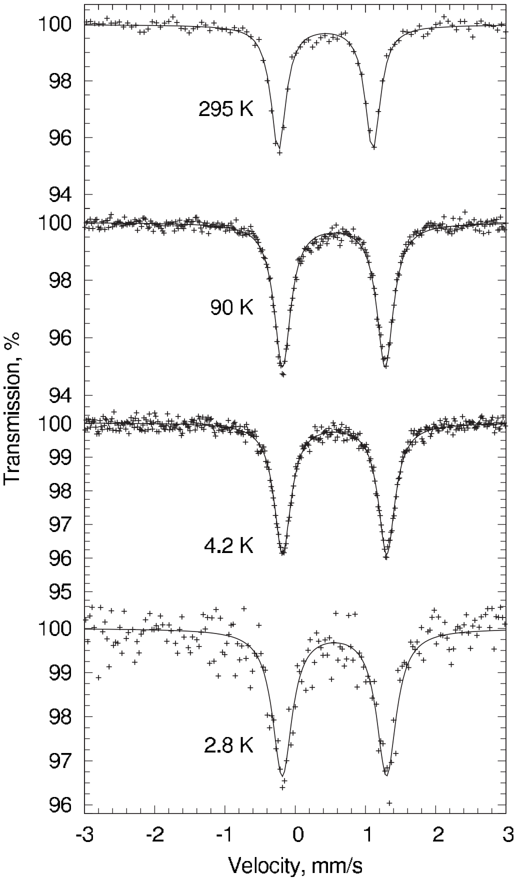

FIG. 3. The ^{57}Fe Mössbauer spectra of $Fe_{0.75}Co_{0.25}Sb_2$ at the indicated temperatures. The solid line is a fit to a doublet, using the parameters indicated in Table I.

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.[23] 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).

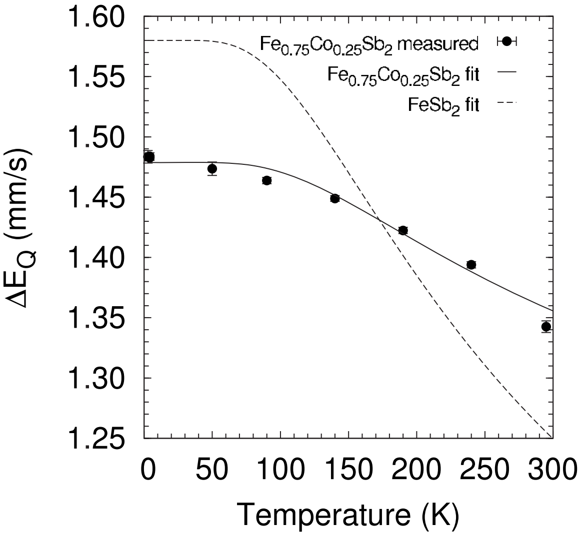

FIG. 4. Fit of the $Fe_{0.75}Co_{0.25}Sb_2$ quadrupole splitting as a function of temperature with the delocalization model.

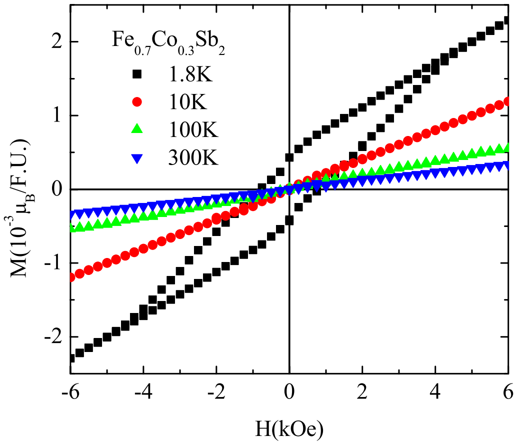

FIG. 5. (Color online) Magnetic hysteresis for the $Fe_{0.7}Co_{0.3}Sb_2$ sample. It is important to note the absence of hysteresis loops above the ferromagnetic transition of $FeSb_2$. Data were taken on a crystal from independently grown batch.

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 (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 $Fe_{1-x}Co_xSb_2$ 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.

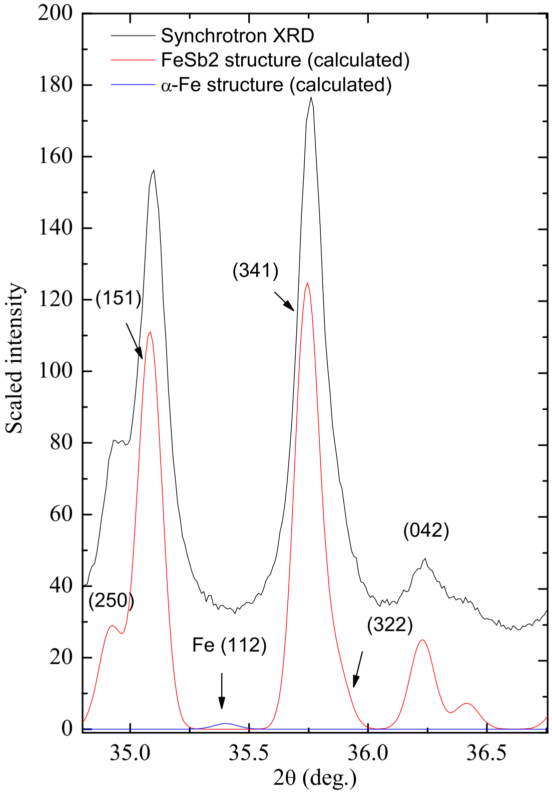

FIG. 6. (Color online) Observed (black) and calculated (red) synchrotron powder x-ray diffraction patterns of $Fe_{0.75}Co_{0.25}Sb_2$. Calculated pattern includes 0.3% of a superimposed α-Fe impurity. If present, the impurity would have caused detectable deviation of the observed pattern since there is no peak overlap.

Taken in conjunction, our results argue against extrinsic sources of WFM in $Fe_{1-x}Co_xSb_2$. Recent muon spin relax-

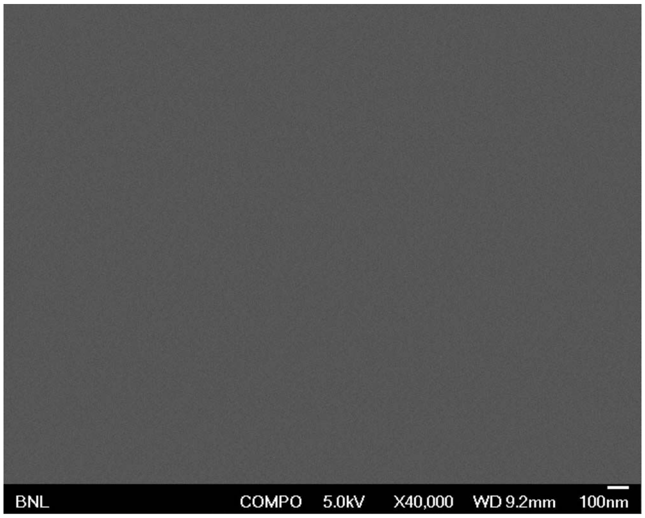

FIG. 7. Typical scanning electron microscope image of $Fe_{0.75}Co_{0.25}Sb_2$. SEM images on randomly chosen surface did not detect secondary phases or randomly distributed nanoparticles.

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.[28]

V. DISCUSSION AND CONCLUSIONS

Examples of intrinsic WFM states in narrow-band materials are abundant in nature.[29] Besides numerous oxide compounds, many intermetallic systems also exhibit intrinsic weak ferromagnetism, such as YbRhSb,[30] MnS,[31] and $Yb_{0.8}Y_{0.2}InCu_4$.[32] Magnetism in $FeSb_2$ in analogy to FeSi has been predicted by LDA+U calculations.[18] 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 $FeSi_{1-x}Ge_x$.[19,33] 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 $Fe_{1-x}Co_xSi$, 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.[23,24] Whereas metallicity simultaneously appears with ferromagnetism in $Fe_{1-x}Co_xSi$ at $x=0.05$,[20] in $Fe_{1-x}Co_xSb_2$ alloys transport and spin gap vanish at $x=0.1$ and $x=0.2$, respectively.[23]

What could be the mechanism of the WFM in $Fe_{1-x}Co_xSb_2$ alloys? Knowing that there is an inversion symmetry at the Fe site in the *Pnnm* 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.[33,34] 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^{2+} ions. This scenario is in agreement with a detailed analysis of the magnetic and thermodynamic properties of $Fe_{1-x}Co_xSb_2$.[23]

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 $x=0.1$.[23] 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.[17,34] 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.[17,34] However, in $Fe_{1-x}Co_xSb_2$ 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 $M\sim(0.5-10)\times10^{-3}\mu_B/\text{Fe}$. As opposed to FeSi where the metallic state is caused by band narrowing of nearly ferromagnetic parent electronic structure, weak ferromagnetism in $Fe_{1-x}Co_xSb_2$ 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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