Anisotropy and large magnetoresistance in narrow gap semiconductor FeSb$_2$

C. Petrovic, J. W. Kim, S. L. Bud’ko, A. I. Goldman and P. C. Canfield

Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

W. Choe and G. J. Miller

Ames Laboratory and Department of Chemistry, Ames, Iowa 50011

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A study of the anisotropy in magnetic, transport and magnetotransport properties of FeSb$_2$ has been made on large single crystals grown from Sb flux. Magnetic susceptibility of FeSb$_2$ shows diamagnetic to paramagnetic crossover around 100K. Electrical transport along two axes is semiconducting whereas the third axis exhibits a metal-semiconductor crossover at temperature T$_{crossover}$ which is sensitive to current alignment and ranges between 40 and 80K. In H=70kOe semiconducting transport is restored for T < 300K, resulting in large magnetoresistance $\rho(70kOe)/\rho(0) = 2200\%$ in the crossover temperature range.

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Small gap semiconductors are materials of choice not only as model electronic systems in materials physics but also in many applications. Semiconducting compounds often show many phenomena not seen in pure silicon, such as variety of optical effects, giant magnetoresistances, and ultimately they can be rather flexible in material design due to possibility for tuning their fundamental physical properties. Highly anisotropic semiconductors with directional bands and low dimensional conducting states can provide an important bridge between bulk and mesoscopic semiconducting materials. One such material is FeSb$_2$. It represents an interesting case of a semiconductor where a band of itinerant electron states originates in the $t_{2g}$ orbitals of the $e_g$ multiplet which overlap along c-axis of the crystal, distinguishing it from loengillate crystal structure from normal marcasites. Its magnetic susceptibility is a reminiscent of the one seen in another narrow gap semiconductor, FeSi, but with very small low temperature impurity tail in diamagnetic region. In this work we examine the anisotropic magnetic and electronic properties of FeSb$_2$, discuss the possible mechanism for these phenomena and suggest pathways for further theoretical and experimental work.

Synthesis of large single crystals of FeSb$_2$ has allowed us to study the anisotropy in its magnetic and electrical transport properties. The self flux method of crystal growth is particularly convenient for the growth of semiconducting compounds since it does not introduce any additional elements into the melt which could randomly fill band structure with impurity states. To this end, single crystals of FeSb$_2$ were grown from an initial composition of constituents Fe$_{0.08}$Sb$_{0.92}$. The constituent elements were placed in an alumina crucible and sealed in quartz ampoule. After initial heating to 1000°C, the melt was fast cooled to 800°C in 14h, then slow cooled to 650°C where excess Sb flux was removed via decanting. The crystals grew as silvery rods, their long axis parallel to b crystalline axis.

Room temperature (c.a. 300K) X-ray diffraction data of a single crystal of FeSb$_2$ were collected using a Bruker CCD-1000 diffractometer with Mo K$_{\alpha}$ radiation ($\lambda=0.71073\AA$). The structure solution was obtained by direct methods and refined by full-matrix least-squares refinement of $F^2$ using the SHELXTL 5.12 package. Powder X-ray diffraction spectra are taken with Cu K$_{\alpha}$ radiation in a Scintag diffractometer. Electrical contacts were made with Epotek H20E silver epoxy. Resistivity on oriented rectangularly cut single crystals was measured by LR 700 resistance bridge from 1.8 to 300K and in fields up to 70kOe. These measurements as well as magnetic measurements have been performed in H,T environment of Quantum Design MPMS-5 and MPMS-7 magnetometers. Magnetic susceptibility was measured by mounting oriented sample on disk whose background has been subtracted, in a typical field of 50kOe.

FeSb$_2$ crystallizes in marcasite structure similar to rutile (TiO$_2$), a structure observed primarily for oxides, for example VO$_2$. Basic construction units in both structures are TiO$_{6}$ (FeSb$_{6}$) octahedra that form edge sharing chains along c axis, sharing corners between chains. The tilt of octahedra in a-b plane orthogonal to chain direction distinguishes the marcasite structure from rutile.

Since phase purity and and questions of exact stoichiometry are important in semiconductor physics, we have performed a thorough structural analysis. A crystal with dimensions 0.25 $\times$ 0.19 $\times$ 0.13mm$^3$ was chosen for the data set collection. The space groups corresponding to the observed systematic extinctions are the orthorhombic groups $Pmn2_1$ and $Pm2_1$. We refined the structure in the $Pmn2_1$, the centrosymmetric space group of the two. Lowering symmetry from $Pmn2_1$ to $P2_1/n$ led to no meaningful decrease in R factor. Crystallographic data taken on single crystal of FeSb$_2$ are in accordance with previously reported, and it is consistent with orthorhombic marcasite structure with lattice constants $a=5.815(4)$, $b=6.517(5)$ and $c=3.190(2)$Å. Single
crystal X-ray diffraction measurement showed that site occupancy does not deviate from ideal FeSb$_2$ stoichiometry to within our 1% resolution limit. In addition to that, powder X-ray pattern taken on several randomly chosen samples grown under same conditions was consistent with FeSb$_2$ structure with no additional impurity phases present.

Fig. 1 shows magnetic susceptibility of FeSb$_2$ measured along a, b and c axis of the crystal. It is qualitatively similar to polycrystalline magnetic susceptibility obtained on crystals grown by a vapor transport technique. All three directions have similar temperature dependences but for H || c there is a shift of $\sim 1\times10^{-4}$ emu/mole. The polycrystalline magnetic susceptibility directly measured on different sample can be estimated by $\chi_{polyc} = \frac{1}{3}(\chi_a + \chi_b + \chi_c)$ and is shown in the inset of Fig. 1. It increases with increase of temperature from low temperature diamagnetic and temperature independent value of $-4\times10^{-5}$ emu/mole (close to core diamagnetism value of $-4.7\times10^{-5}$), passes through a region of diamagnetic to paramagnetic crossover and becomes paramagnetic at high temperatures. The crossover temperatures are $\sim 100$K for field applied along a and b axis and $\sim 125$K for field applied along c axis.

Whereas the anisotropy in $\chi(T)$ of FeSb$_2$ is relatively small, the anisotropy in the electrical resistivity $\rho(T)$ is dramatic (Fig. 2). For the current along either the a and c axis $\rho(T)$ is semiconducting over the whole temperature range. The resistivity increases by four orders of magnitude down to lowest measured temperature of 1.8K (Fig. 2(inset)). From arrenhius plots of $\rho(T)$ curves we can estimate gap values $\Delta \rho(a,c) \approx 300K$ (Fig. 3 inset), in accordance with previous results.

The b axis transport manifests a metallic behavior above $\sim 40$K, with resistivity ratio $\rho(300K)/\rho(40K)=6.3$ (extrapolation to T=0 of the high temperature b axis resistivity gives RR=98). Below 40K the b axis resistivity increases five orders of magnitude, to values comparable to a and c axis resistivity, and shows activated behavior only below $T_{\text{min}}$ (~40K for optimal current orientation) with activation energy of $\Delta \rho(b) \approx 250K$ (Fig. 3 inset). Application of 70kOe along a and c axis has small influence on resistivity ($\Delta \rho/\rho < 0.15$), but on the other hand crossover temperature region in b-axis resistivity disappears in this field.

It has been reported that $\rho_{ab} > \rho_c$. Contrary to expected, we observe that high conductivity axis is not c, but b axis. It should be noted though that the observed metallic conductivity in the b axis electrical transport as well as the $T_{\text{min}}$ are very sensitive to current misalignment. The effect of deliberate small misalignment in current path along b axis in ab plane is shown in Fig. 3. RR above $T_{\text{min}}$ for sample 1 can be changed by a factor of two and $T_{\text{min}}$ itself can be shifted 30K up in temperature.

As shown in Fig. 2, an applied field enhances b-axis resistivity near $T_{\text{min}}$ leading to a large magnetoresistance. The 70kOe magnetoresistance is temperature dependant, and it has a sharp maximum $\Delta \rho/\rho = 22$ in the crossover region (Fig. 4).

Magnetic isotherms (Fig. 4 inset) show $H^a$ dependence where $\alpha = 1.5 - 1.7$, a value smaller than $\alpha = 2$ expected for a simple one-carrier system with energy independent carrier relaxation time ($\Delta \rho(H)/\rho_0 = \mu^2 H^2$ where $\mu$ is the carrier mobility).

The marcasite-type FeSb$_2$ has been classified as a semimetal or narrow gap semiconductor, in which both valence and conduction band are derived from d-like states. We rationalize our observation of anisotropy in its physical properties within the framework of tem-
temperature induced transitions within the 3d multiplet.

In the orthorhombic marcasite structure Fe (cation) is surrounded by a deformed Sb (anion) octahedra. These octahedra then share edges along c-axis. The edge sharing octahedra form chains parallel to c axis causing overlap of $d_{xy}$ atomic orbitals. As opposed to normal marcasites with filled $d_{xy}$ orbitals and a c/a ratio between 0.73-0.75, loellingites with $d^2$ and $d^4$ cations have c/a ratio between 0.50-0.53 and empty $d_{xy}$ orbitals. Based on the scheme given by Goodenough, $t_{2g}$ orbitals are further split in two lower lying ($\Lambda$) orbitals associated with $d_{xz}$ and $d_{yz}$, and a higher lying ($\Xi$) orbital associated with $d_{xy}$ which create $\Xi$ orbital of itinerant electron states due to their overlap.

Starting at low temperatures, FeSb$_2$ is a diamagnetic semiconductor, as expected for $S=0$ low spin $d^2$ ground state ($t_{2g}$, $S=0$) where low energy $\Lambda$ orbitals are filled with electrons with opposite spin due to crystalline fields which are larger than Hund’s rule spin pairing energy. We performed analysis of the thermal excitation from ground state nonmagnetic ($S=0$) to paramagnetic excited ($S\neq 0$) state: it results in a change of magnetic susceptibility $\chi(T) = N g^2 \mu_B^2 J_{is}^2 \frac{2 f+1}{2 f+3} \exp(\Delta_\chi/k_B T)$, where $J=\frac{2 f+1}{2 f+3}$ and $\Delta_\chi$ is susceptibility gap. A fit to polycrystalline average of our data over the whole temperature range for fixed $g=2$ (Fig. 1 inset) describes well behavior of FeSb$_2$ and yields $\Delta_\chi \approx 546 K$, $S=0.59$ for spin value in Curie constant and $\chi_0=4 \times 10^{-5}$ (emu/mole).

One possible explanation for enhanced conductivity in paramagnetic state and its anisotropy is the population of the $\Xi$ band of itinerant states induced by thermal de-pairing on low energy $\Lambda$ orbitals. As the temperature is raised, some of 3d electrons are thermally excited to $\Xi$ band responsible for conduction, while electrons in localized $\Lambda$ or $e_g$ orbitals are responsible for temperature induced paramagnetic moment, as seen in magnetic susceptibility which shows significant enhancement above 100K. Delocalization in this scenario is connected with transition within $t_{2g}$ multiplet and it is possible that it occurs at lower temperatures than the transition to higher lying $e_g$ orbital which explains $T_{\text{min}}$ as low as 40K for current applied along b axis in diamagnetic state. We also note the difference between susceptibility ($\Delta_\chi$) and resistivity ($\Delta_\rho$) gaps, indicating that the gap relevant for conductivity is smaller than gap relevant for the susceptibility, an observation which is not in contradiction with above description. A possible difference between gaps in charge and spin excitation channels has been also observed in some samples of FeSi.

The magnetic susceptibility of FeSb$_2$ is reminiscent of $\chi(T)$ data seen in FeSi, albeit with diamagnetic susceptibility at low temperature and a much smaller tail below 5K. Apart from the "free-ion"-like model of localized electrons described above, the model of metallic paramagnetism by Jaccarino et al. has been invoked to apply magnetic susceptibility of FeSb$_2$ to the model of two narrow bands with rectangular and constant density of states of width $W$ separated by energy gap $E_g$ that did not produce meaningful fitting parameters. More refined analysis with a different band shape and photoemission spectroscopy measurements could offer a more definite statement about validity of narrow band Kondo insulator - like description of this material. Moreover, since the difference in $\Delta_\chi$ and $\Delta_\rho$ seen in FeSi was explained in the framework of metallic paramagnetism by invoking the existence of indirect (smaller) energy gap responsible for transport and direct (larger) gap of the same width for both spin and charge excitations, possible Kondo insulator - like features in FeSb$_2$ deserve further study.

The large magnetoresistance (MR) seen in FeSb$_2$ for
manganate perovskites. The spin disorder scattering mechanism of MR does not seem to be a viable mechanism in this material. One possible, but speculative, explanation of the large magnetoresistance phenomenon can be found in analogy with the extraordinary magnetoresistance (EMR) seen in non-magnetic semiconductors with embedded metallic inhomogeneities. 

Since the Ξ band of conducting states is highly directional in real space, (our measurement in Fig. 3 also is consistent with this interpretation), it can act as a region of metallic conductivity in a semiconducting environment, short-circuiting the most of applied current passing through it. In the simplest picture of isotropic conductivity, the single band carrier mobility is $\mu = R_H/\sigma$. By including scattering time $\tau$ through general relation $R_H = \omega_c / \tau B$, we obtain $\mu B \sim \omega_c / \tau$. Large positive magnetoresistance is then a consequence of the large mobility of the carriers in the itinerant Ξ band since even modest fields could enhance value of $\omega_c / \tau$. The steep rise of the Hall constant below 120K seen in Ref. 7 holds promise of reaching $\sim 2250\%$ at $T_{\min}$=40K for b axis resistivity. Taking $\rho(T_{\min}) \sim 50\mu\Omega cm$ from our measurement, we estimate $\mu(T_{\min}) \sim 2000 cm^2/Vs$, comparable to high mobility values found in antimony based materials with skutterudite structure. Hence, the condition $H > 1/\mu$ is satisfied for fields of the order of 50kOe. Strong magnetoresistance therefore is likely to have its origin in band effects, and the above description is further supported with Kohler’s rule $\Delta \rho / \rho_0$ and $H / \rho_0$ curves which fall on the single manifold (not shown) in the metallic region of b axis conductivity from 40K to 300K. Measurement of the Hall coefficient at low temperature would be useful to clarify this issue as well as further crystallographic studies and band structure calculations for elucidating the orientation of Ξ band. In addition, neutron scattering experiments could offer decisive information about thermally induced paramagnetism. Further study may explain physics contained in FeSb$_2$ in single-electron picture, but on the other hand it might turn into a playground for many body effects in 3d material with anisotropic crystal and possible electronic structure. Since narrow gap semiconductors are important ingredients in optoelectronic devices for both civilian and military use, further study and tuning of FeSb$_2$ properties deserves some attention.

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