Colossal Positive Magnetoresistance in a Doped Nearly Magnetic Semiconductor

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We report on a positive colossal magnetoresistance (MR) induced by metallization of FeSb$_2$, a nearly magnetic or "Kondo" semiconductor with 3$d$ ions. We discuss contribution of orbital MR and quantum interference to enhanced magnetic field response of electrical resistivity.

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There is at present considerable technological interest in the magnetoresistive effect that is central to the operation of devices in magnetic storage media and a wide variety of magnetic sensors. The desire to maximize this effect has raised interest in new materials and mechanisms associated with the large change in electrical resistance in magnetic fields. FeSb$_2$ is a narrow gap semiconductor whose magnetic properties strongly resemble nearly magnetic or "Kondo" insulator Fe$_x$Si. The ab initio LDA+$U$ electronic calculations found that the ground state of FeSb$_2$ is nearly ferromagnetic. Temperature induced paramagnetic moment for field applied parallel to $\hat{b}$ - axis coincides with increased conduction at high temperatures. Electrical transport measurements showed pronounced anisotropy, metallic conductivity above 40 K and activated below that temperature for current applied along $\hat{b}$ axis. The exact temperature of metal-semiconductor crossover was found to be very sensitive to small current misalignment, implying quasi - one dimensional nature of electronic transport.

Optical conductivity revealed anisotropic energy gap $E_g$ in the spectral range between 100 - 350 cm$^{-1}$ and negligible Drude weight of $\sigma(\omega)$ at low frequencies, i.e. a true insulating state. In addition, a full recovery of $\sigma(\omega)$ and no visible subspectrum of impurities.

The application of a magnetic field of 90 kOe induces up to 2.5 orders of magnitude change in the resistivity in Fe$_{1-x}$Co$_x$Sb$_2$ ($x = 0 - 0.4$) and 30% of MR at room temperature for $x = 0.1$ (Fig. 1). This is comparable to MR in the colossal magnetoresistive manganites. What could be the most likely cause of CMR in this system?

The mechanism could involve a presence of charge carriers from different parts of the Fermi surface that have different scattering times or a breakdown of the semiclassical transport theory and relation between conductivity and scattering time $\rho \sim 1/\tau^{10}$. Hall resistivity is shown as a nonlinear function of magnetic field in Fig. 2(b). The pronounced field dependence of Hall constant is reminiscent of anomalous Hall effect. When there are magnetic moments involved, the Hall resistivity can be written as:

$$\rho_{xy}(H) = R_0 H + R_s M(H)$$

where $R_0$ and $R_s$ are the normal and spontaneous Hall constants, and $M$ is the sample magnetization. Fitting $\rho_{xy}$ data by using the experimental values of $M(H)$ (Fig. 2(a)), we found that the anomalous Hall effect is unlikely cause of Hall resistivity nonlinearity. The nonlinearity of Hall resistivity in field and band structure calculations suggest that there are more than one band participating in the conduction (Fig. 3).

In what follows we discuss the case when there are more than one type of carrier participating in the conduction.
The Hall constant takes the general form\cite{12}:

\[
R_H = -\frac{1}{H} \sum \frac{\sigma_{xy}}{(\sum \sigma_{xx})^2} \quad \sigma_{xx}^i = \frac{q n_i \mu_i}{1 + \mu_i^2 H^2}, \quad \sigma_{xy}^i = \frac{q n_i \mu_i^2 H}{1 + \mu_i^2 H^2}
\]

where \( \sigma_{xx}^i \) and \( \sigma_{xy}^i \) are longitudinal and Hall conductivities of individual bands, \( \mu_i \) is the band mobility. A matrix formalism for the Hall effect in multicarrier semiconductor systems was devised and provided a closed form formula for two or three-carrier systems\cite{13,13}. The magnetoresistance within the same formalism for two-carrier system is:

\[
R_H = \rho_0 \frac{\alpha_2 + \beta_2 H^2}{1 + \beta_3 H^2}, \quad MR_D = \frac{\alpha D H^2}{1 + \beta D H^2}
\]

\[
\alpha_2 = f_1 \mu_1 + f_2 \mu_2, \quad \beta_2 = (f_1 \mu_2 + f_2 \mu_1) \mu_1 \mu_2
\]

\[
\beta_3 = \beta_D = (f_1 \mu_2 + f_2 \mu_1)^2, \quad \alpha_D = f_1 f_2 (\mu_1 - \mu_2)^2
\]

\[
MR_T = \frac{(\alpha_T + \gamma_T H^2) H^2}{1 + (\beta_T + \delta T H^2) H^2}
\]

where \( \rho_0 \) is the zero field resistivity, \( \mu_i \) is the mobility of \( i \)th carrier and \( f_i = |n_i \mu_i|/ \sum |n_i \mu_i| \) is the f factor, \( n_i \) is the carrier concentration, as defined in Ref. 13. The agreement with our experimental values of \( R_H \) was excellent as the solid lines shown in Fig. 3. FeSb\(_2\) can be described well by two-carrier model. Fe\(_{1-x}\)Co\(_x\)Sb\(_2\) is

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**FIG. 1**: (a) Electrical transport properties of Fe\(_{1-x}\)Co\(_x\)Sb\(_2\) dramatically change with small change in stoichiometry. The sample with \( x = 0.1 \) manifests lowest resistivity. With further Co substitution we see gradual increase in residual resistivity. (b) Temperature dependence of magnetoresistance \( MR = (\rho(90\text{kOe}) - \rho(0))/\rho(0) \) in doped Fe\(_{1-x}\)Co\(_x\)Sb\(_2\) semiconductor alloys for \( x = 0 - 0.4 \). CMR is observed for all \( x \). Resistivity isothersms of Fe\(_{0.9}\)Co\(_{0.1}\)Sb\(_2\) up to 350 kOe. Resistivity increases three orders of magnitude (103,100%) at 1.8K.

**FIG. 2**: Hall resistivity versus magnetic field. Solid lines are the fits when magnetization \( M \) is taken into account.
best described within three-carrier model since two carrier model cannot explain minima and maxima in $R_H$ (H). Co substitution in Fe$_{1-x}$Co$_x$Sb$_2$ fills energy bands that are not involved in thermal excitation of carriers across the gap in FeSb$_2$. $R_H$ shows excellent agreement with the three-carrier model for all $x$, selected data are shown for clarity. Solids lines are fits to the multicarrier model.

FIG. 3: (a) Hall constant $R_H = \rho_{xy}/H$ of FeSb$_2$ is well described by a two-carrier model. (b)-(d) For Fe$_{1-x}$Co$_x$Sb$_2$ ($0.1 \leq x \leq 0.4$) the fits of two-carrier model to experimental data are rather unsatisfactory since it cannot account for maxima and minima in $R_H$(H). Co substitution in Fe$_{1-x}$Co$_x$Sb$_2$ fills energy bands that are not involved in thermal excitation of carriers across the gap in FeSb$_2$. $R_H$ shows excellent agreement with the three-carrier model for all $x$, selected data are shown for clarity. Solids lines are fits to the multicarrier model.

FIG. 4: Magnetoresistance calculated according to multicarrier model for Fe$_{1-x}$Co$_x$Sb$_2$ in 90 kOe shown in the low plot as linked symbols, compared to the observed MR shown as the scattered symbols.

The fitting parameters are listed in Table I. As we can see, the contribution of Coulomb interaction to MR is of the order of several percent and the weak localization is dominant. Two inequalities justify our quasi 1D model: 1) the fitting parameters satisfy the criterion for the interference correction to be of a 1D character: $b < L_f$ and 2) in a field of 9T, the magnetic length $L_B$ is about 6nm, therefore $b < L_B$ is satisfied, otherwise the system should behave as three dimensional. The calculated MR agrees well with the observed MR. At $T = 1.8$ K, the calculated MR in an $H = 90$ kOe field is about 34,300% for Fe$_{0.9}$Co$_{0.1}$Sb$_2$, as compared to the observed value of 36,088%. The value is derived using a measured carrier concentration $n = 8.5 \times 10^{19}$ cm$^{-3}$ and a residual resistivity $\rho_0 = 1.0 \times 10^{-5}$ $\Omega$cm of Fe$_{0.9}$Co$_{0.1}$Sb$_2$, and $L_f \approx 240L_B$. The width of the quasi 1D channel $b$ is of the order of the unit cell. Quasi 1D localization effects are observed in pure FeSb$_2$ at 100K (Fig. 5(b)). It implies that the electronic transport is dominated by the singular corrections at the density of states at unusually high temperatures, apparently without usual cutoff by quantum interference effects.
TABLE I: Parameters of the fits to quantum correction of magnetoresistance. $\alpha F$ is the proportional parameter in the Coulomb interaction contribution. $L_f$ is the phase coherence length, $b$ is the 1D conduction channel width and $c$ is the coefficient of classical quadratic term.

| $x$ | $\alpha F$ | $L_f$(nm) | $b$(nm) | $c$ |
|-----|------------|-----------|---------|-----|
| 0   | $1.2 \times 10^{-9}$ | 162       | 1.6     | 0.001 |
| 0.1 | $6.2 \times 10^{-7}$ | 1463      | 0.2     | 0.055 |
| 0.2 | $5.1 \times 10^{-9}$ | 534       | 2.8     | 0.004 |
| 0.3 | $7.3 \times 10^{-9}$ | 188       | 4.0     | 0.002 |
| 0.4 | $9.9 \times 10^{-9}$ | 128       | 5.1     | 0.001 |

thermal effects, probably due to high spin orbit scattering rate $1/\tau_s$.\(^{21}\) Similar situation has been observed in Ta$_4$Te$_4$Si at 15K\(^{22}\) and Si nanowires at 27K\(^{23}\).

In conclusion, we have shown CMR effect in doped nearly magnetic semiconductor FeSb$_2$. Application of magnetic fields up to 350 kOe results in 103,100% increase in the resistivity at 1.8 K and 124% increase at room temperature. Our results suggest contribution of multiple electronic bands to electrical conduction. Quantum interference arising from Coulomb interactions and weak localization in the presence of strong spin-orbit scattering is the dominant mechanism of CMR.

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