# SUMMARY OF Ph.D. DISSERTATION

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Title

## Unusual Magnetic Properties and Correlated Electronic States in Cr- spinel and Mn- perovskite Related Sulfides


Abstract

The magnetic and electronic nature of Cr- spinel and Mn- perovskite related sulfides were surveyed as spin electronics material candidates. General knowledge on magneto- transport properties and crystal structures for Cr- spinel and Mn- perovskite related sulfides were mentioned with historical backgrounds in chap. 1. Experimental methods are described in chap. 2.

Mn substitution effects on magnetism and transport properties in $Fe_{1-x}Mn_xCr_2S_4$ ($x$ = 0.2, 0.5) were described in chap. 3. $FeCr_2S_4$ has a spin-glass like phase below 60 K (= $T_g$) and a ferrimagnetic phase in the temperature range 60-170 K ($T_c$ = 170 K). Upon substitution of Fe by Mn, $Fe_{1-x}Mn_xCr_2S_4$ ($x$ = 0.2, 0.5) exhibits a larger maximum negative magnetoresistance (MR) than $FeCr_2S_4$. These phenomena can be well explained on the basis of the magnetic polaron model. Magneto- transport properties of Cr 3*d* band filling controlled $CuCr_2S_4$ were described in chap. 4. $CuCr_2S_4$ shows a *p*- type metallic conductivity and ferromagnetism with $T_c$ of 375 K, and exhibits magnetic anomaly at 84 K (= $T_m$). The partial Ge-substitution in Cu site changes Cr 3*d* band filling and greatly reduces $T_c$ and slightly reduces $T_m$ for $CuCr_2S_4$. MR of $Cu_{1-x}Ge_xCr_2S_4$ can be expressed as $\Delta\rho = aH^2 - bH^n$ below $T_m$ ($a$, $b$, and $n$ are temperature-dependent adjustable parameters, H: magnetic field). This unusual MR originates in coexistence of ferromagnetism and spin- glass like (meta magnetism) states for $Cu_{1-x}Ge_xCr_2S_4$. Electronic structures and magneto- transport properties for *p*- and *n*- type $Fe_{0.5}Cu_{0.5}Cr_2S_4$ were described in chap. 5. *n*- type $Fe_{0.5}Cu_{0.5}Cr_2S_4$ are ferrimagnet, and perform large negative MR about 0.1 ($MR = (\rho_H - \rho_0)/\rho_0$) at 340 K in a magnetic field of 6 T. We found that the MR for *p*-$Fe_{0.5}Cu_{0.5}Cr_2S_4$ is about twice as large as that for *n*- type $Fe_{0.5}Cu_{0.5}Cr_2S_4$ at $T_c$. XPS study revealed that the electronic structure of *p*- type $Fe_{0.5}Cu_{0.5}Cr_2S_4$ could be proposed as $Fe^{3+}_{0.5}Cu^{1+}_{0.5}Cr^{3+}_2S^{2-}_4$. On the other hand, the electronic structure of *n*- type $Fe_{0.5}Cu_{0.5}Cr_2S_4$ could be proposed as $Fe^{3+}_{0.5-\delta}Fe^{2+}_{\delta}Cu^{1+}_{0.5-\delta}Cu^{2+}_{\delta}Cr_2S_4$. These results suggest that the inhomogeneous valence of Cu and Fe gives the *n*- type conducting for $Fe_{0.5}Cu_{0.5}Cr_2S_4$. The strongly correlated electronic states, magnetism and transport properties for novel layered oxysulfides ($Sr_2CuMn_{1-x}Zn_xO_3S$, $Sr_{4-x}La_xCu_2Mn_3O_{7.5}S_2$) were surveyed in chap. 6, 7. Summary and prospects were described in chap. 8.

These results revealed that Cr- spinel and Mn- perovskite related sulfides have unusual magneto-transport effect, and these effects originate in these correlated electronic states.