Magnetic and electronic nature of shandite-type type metallic ferromagnet $Sn_2Co_3S_2$ and its related compounds with Kagome lattices

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Pyrite- and shandite-type transition metal disulfides are both minerals that can be artificially synthesized. While Pyrite-types of MS_2 (M=Fe, Co, Ni,etc.) have been the subject of the intense research due to their variety of interesting physical properties [1, 2], few studies have been made of shandite-type $M_3A_2S_2$ (A=Sn, Pb, In, and Tl; M=Co, Ni, Rh and Pd) [3, 4] with two-dimensional Kagome lattices.

Earlier studies report that shandite-type $Co_3Sn_2S_2$ is a metallic ferromagnet with T_C (=177K), and that $Ni_3Sn_2S_2$ is a paramagnetic metal [3, 4]. In a solid solution of ferromagnetic metal CoS_2 (T_C =120K) and an antiferromagnetic Mott-Hubbard insulator NiS_2, ferromagnetism is gradually suppressed with Ni substitution [2]. However, the detailed Ni substitution effect in $(Co_{1-x}Ni_x)_3Sn_2S_2$ with 2-D Kagome latticesnot has been examined and the electronic nature is not clear. In this report, we discuss the hitherto unknown electrical and magnetic properties for $(Co_{1-x}Ni_x)_3Sn_2S_2$ [5] in comparison with $Co_{1-x}Ni_xS_2$.

Polycrystalline $(Co_{1-x}Ni_x)_3Sn_2S_2$ samples were carefully prepared by a solid state reaction method in a evacuated quartz tube and characterized by powder x-ray diffraction (XRD), Rietveld refinement using the Rietan 2000 [6], and x-ray photoemission spectroscopy (XPS). Electrical resistivity was measured at 10-300 K by the conventional dc four-probe technique. DC magnetization was measured by a superconducting quantum interface device (Quantum Design, MPMS) at 10-300K. Neutron powder diffraction (NPD) patterns were obtained with Kinken powder diffractometer [7] for high efficiency and high resolution measurements (HERMES) installed at the T1-3 beam hole of the guide hall at the Japan Research Reactor 3M (JRR-3M) in Japan Atomic Energy Research Institute (JAERI).

Figure 1(a) shows the temperature dependence of magnetic susceptibility (χ) for $(Co_{1-x}Ni_x)_3Sn_2S_2$ in field cooled (FC) conditions. $Co_3Sn_2S_2$ shows the ferromagnetic transition at 178K, which almost agrees with previous work [4]. With increasing Ni concentration (x), the magnitude of χ and T_C are gradually decreased as $Co_{1-x}Ni_xS_2$ [2], and ferromagnetism is suppressed above $x = 0.2$. However, unlike in the case of $Co_{1-x}Ni_xS_2$, there is no antiferromagnetic phase throughout the full range of composition. This Ni substitution effect indicates that the ferromagnetism on Kagome lattices originates from an exchange split of the Co 3*d* orbital, so substitution of Ni, which has one more electrons than Co, increases the number of electrons in the 3*d* orbital and suppresses the ferromagnetism on Kagome lattices.

As shown in the inset in Fig.1(a), the magnetization does not saturate up to 5.5T at 10K, unlike CoS_2. From the M-H curve we can roughly estimate a small saturation moment (p_s) of $0.2\mu_B$ per Co atom (which is slightly smaller than previous data ($0.29\mu_B$) [4]), while in CoS_2 p_s is $0.85\mu_B$.

$(Co_{1-x}Ni_x)_3Sn_2S_2$ are metallic with room temperature resistivities (ρ) of $10^{-3}\sim10^{-4}\Omega$cm and show a kink in resistivity at T_C, as shown in Fig.1(b). While, a hump at T_C appears in CoS_2, which has certain degree of localized moment.

The unsaturated magnetization, a small saturation moment, and the absence of a hump in resistivity indicate that $Co_3Sn_2S_2$ is an itinerant weak ferromagnet. These phenomena are different from those of $Co_{1-x}Ni_xS_2$, in which ferromagnetism is

also gradually suppressed with Ni substitution that develops antiferromagnetism, and the end member compound NiS_2 is a Mott-Hubbard antiferrmagnetic insulator.

While, the inverse susceptibility of $Co_3Sn_2S_2$ can be fitted to the Curie-Weiss law above T_C; from this fit, we obtain $p_{\rm eff}$ = 0.96 per Co. Figure 1(c) shows Rhodes-Wolfarth plots that plot T_C and p_c/p_s ($p_c = \sqrt{1+p_{eff}^2} - 1$) for metallic ferromagnets following Curie-Weiss law. The value of p_c/p_s is 1.9 for $Co_3Sn_2S_2$ and 1.8 for CoS_2 ($p_c/p_s \cong 1$ for localized moment system). According to the Rhodes-Wolfarth scheme, $Co_3Sn_2S_2$ has the same degree of localized moment as CoS_2. However, from our results, we cannot determine the magnetism of this compound, especially whether it has a localized moment or not.

Finally we would like to comment the NPD data at 10 K, 200 K ($T < T_C$) and 300 K ($T > T_C$) for $Co_3Sn_2S_2$ as shown in Fig.1(d). Indeed, magnetic peaks originated from magnetic long-range order shows the simple ferromagnetism on 2-D Kagome lattices, indicating the Mielke's prediction [10] that the ground states of Kagome lattices based on the Hubbard model is only one and exhibits the simple ferromagnetism in a finite range of the electron filling factor. The next step will be to reveal differences between the electronic structures of $(Co_{1-x}Ni_x)_3Sn_2S_2$ and $Co_{1-x}Ni_xS_2$ and to reveal the electron filling effect on ferromagnetism on the 2-D Kagome lattices.

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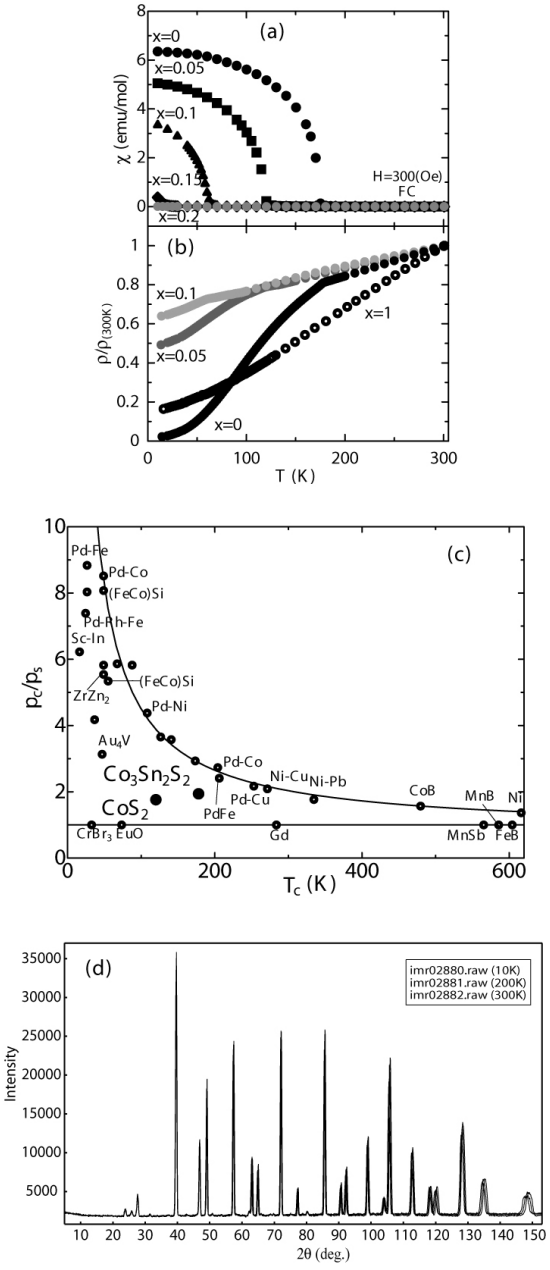

Fig. 1. (a) Magnetic susceptibility and (b) normalized electrical resistivity for $(Co_{1-x}Ni_x)_3Sn_2S_2$. (c) Rhodes-Wohlfarth plot [8, 9]. (d) Neutron powder diffraction data for $Co_3Sn_2S_2$.