

Structural Defects Effect on Ferromagnetism of Layered Oxysulfide (La_{1-x}Ca_xO)Cu_{1-x}Ni_xS

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Abstract

We have studied the effect of structural defects on magnetic properties of (La_{1-x}Ca_xO)Cu_{1-x}Ni_xS. The magnetization for samples containing less defects shows the magnetism consisting of a diamagnetism and a Pauli paramagnetism. Any ordered phase is not observed down to 2 K. A very weak ferromagnetic component is observed for non-stoichiometric system containing structural defects. These samples exhibit a well-defined hysteresis loop at room temperature. The Curie temperature obtained by the extrapolation of its temperature dependence increases with x . This ferromagnetism may be attributed to Ni and/or S related defects.

Key words: oxysulfide, wide gap semiconductor, structural defects, ferromagnetism

Diluted magnetic semiconductors(DMS) have attracted much notice in the last decade, because of their possibility for the application to spin electronics.

Layered oxysulfide (LaO)CuS which has two kinds of slabs, LaO and CuS, are stacked along c axis alternately is known as a p -type wide-gap semiconductor [1,2]. Since the top of valence band is consisted of Cu $3d$ and S $3p$ orbital, the appearance of ferromagnetism is expected by the hole doping into $3d$ band by means of the substitution of Ni for Cu. Furthermore, the structural defects of Cu, Ni, S may change its electronic state at the top of valence band. In our previous work, we found that the temperature dependences of their electrical resistivity change from semiconducting to metallic behaviors with the concentration x [3]. In this study, we focused our attention on the valence band modification caused by structural defects due to Ni and/or S deficiencies, and report on the magnetic properties of (La_{1-x}Ca_xO)Cu_{1-x}Ni_xS.

Two types of polycrystalline samples which belong to a stoichiometric system denoted by "system A" and a

non-stoichiometric system "system B" were prepared. In the crystal growth of system B, NiS and Cu₂S powders which were suspected to be non-stoichiometric were used in addition to La₂S₃, La₂O₃, and CaO, while elemental Ni, Cu, and S were used instead of NiS and Cu₂S for system A. Structural defects will be introduced into the CuS layer for the system B. The temperature and magnetic field dependences of magnetization are measured in the temperature range 4.2 ~ 300 K and magnetic field range -5 ~ 5 T. Powder X-ray diffraction(XRD) was measured using synchrotron radiation on BL02B2 at SPring 8. Its crystal structure analyzed by Reitveld method is tetragonal and belongs to the space group $P4/nmm$. The lattice constants (a , c) in the system B are (0.40030 nm, 0.85128 nm), (0.40006 nm, 0.85202 nm), and (0.40008 nm, 0.85168 nm) for $x=0$, 0.03, and 0.07, respectively. The x dependences of a and c have a maximum and a minimum, respectively at $x = 0.03$.

Fig. 1 shows the magnetization curves($M-H$) of $x = 0.03$ for system A and B at room temperature(RT). The magnetization of system B, M_B , increases rapidly

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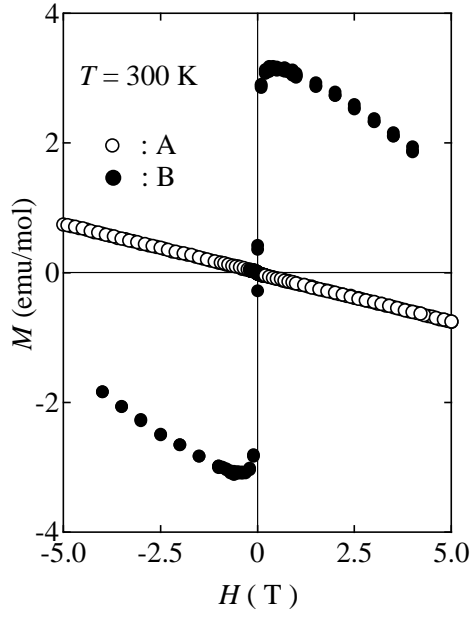


Fig. 1. Magnetization curves of $x = 0.03$ at room temperature in both systems

at low magnetic field and decreases linearly at high field. The rapid increase is due to a ferromagnetic component(FC) and the linear decrease is attributed to the sum of large diamagnetic component(DC) and a small Pauli paramagnetic component(PPC) of conduction carriers without temperature dependence. Thus, M_B is expressed as the sum of FC, DC, and PPC at RT. In the meanwhile, the magnetization of system A, M_A , decreases linearly with negative slope. Any ordered phase of system A is not observed down to 2 K. The observed ferromagnetism is attributed to Ni related defects.

Fig. 2 shows the temperature dependences of whole magnetization for $x = 0, 0.03$, and 0.07 in system B under the magnetic field $H = 1$ T. The samples of $x < 0.03$ are semiconductors and the other samples are metals. The diamagnetism is observed for the host crystal at RT and are almost unchanged against temperature. The Curie type paramagnetic component(PC), observed in all samples, is attributed to rare earth impurities contained in La. The samples in which Ca and Ni atoms are doped simultaneously have FC in addition to DC, PC and PPC. We carried out the separation of each component from whole magnetization by subtracting DC and PPC obtained from $M - H$ at RT. The temperature dependences of FCs with small saturation magnetization $0.052, 0.054 \mu_B/\text{Ni atom}$ for $x = 0.03$ and 0.07 , respectively, are shown in Fig. 3. The Curie temperature obtained by the extrapolation of the curve increases with x . The ferromagnetism is attributed to Ni and/or S related defects, because FC is not observed in any samples of system A. The abso-

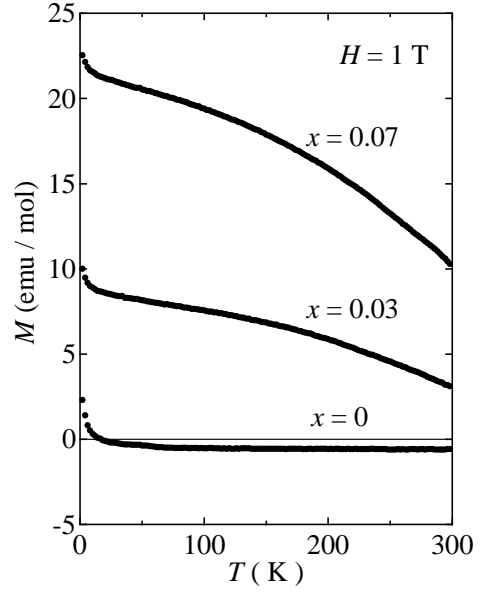


Fig. 2. The temperature dependence of magnetization of $x = 0, 0.03, 0.07$ under $H = 1$ T, for the system B.

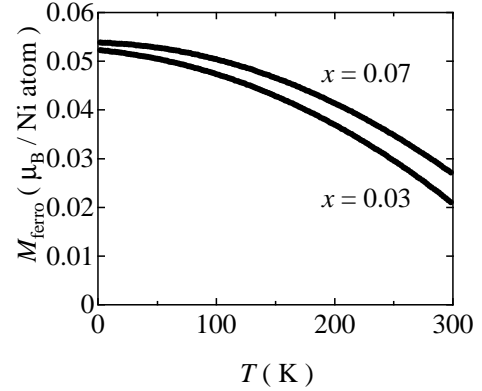


Fig. 3. The temperature dependence of FC in the system B.

lute value of apparent diamagnetism decreases with x , because PPC with positive sign increases with doped carriers. In the samples of system B, conductivity and ferromagnetism dependent on the concentration x are observed.

References

- [1] K. Ishikawa, S. Kinoshita, Y. Suzuki, S. Matsuura, T. Nakanishi, M. Aizawa, and Y. Suzuki, J Electrochem. Soc. 138, (1991) 1166.
- [2] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, and H. Hosono, Appl. Phys. Lett. 77, (2000) 2701.
- [3] K. Sekizawa, Y. Takano, K. Mori, K. Yahagi, Czech. J. of Phys., 46, Suppl.S4 (1996) 1943.