Electrical Resistivity and Photoemission Spectra of Layered Oxysulfide $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$

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Abstract

We report temperature dependences of the electrical resistivity and photoemission spectra of $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ which is derived by the substitution of Ca and Ni for La and Cu in a wide-gap semiconductor (LaO)CuS with a layered structure. The temperature dependence of the electrical resistivity changes from semiconducting to metallic with the concentration x successively. The appearance of new density of states in the vicinity of Fermi energy is observed in the photoemission spectra. In the sample of $x = 0.03$, a semiconductor - metal transition occurs at 150 K with no specific heat anomaly. A resistivity increase proportional to $\ln T$ and a positive magneto-resistance are observed for $x = 0.03 \sim 0.06$ at low temperature.

Key words: oxysulfide, wide gap semiconductor, metal-semiconductor transition, resistivty minimum

An oxysulfide (LaO)CuS has a layered structure in which two types of slabs, La-O-La and S-Cu-S are stacked alternately along the *c*-axis. Its crystal structure is tetragonal and belongs to the space group $P4/nmm$. The S-Cu-S slab in which each Cu ion is surrounded by four S ions tetrahedrally, is expected to have a two dimensional electronic structure. Recently, this compound has attracted attention as a transparent *p*-type semiconductor with a strong photoluminescence at 400 nm due to an interband transition [**?**]. We have found previously a semiconductor to metal transition in the $(La_{1-x}Sr_xO)CuS$ [**?**] and $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ systems [**?**]. In order to understand the electronic states of these systems further, we have carried out electrical resistivity, magneto-resistance, photoemission, and powder X-ray diffraction measurements for $x = 0 \sim 0.07$.

All samples were polycrystals prepared by a solid state reaction of starting materials, La_2S_3 (99.9 %), La_2O_3 (99.9 %), Cu_2S (99.9 %), CaO(99.9 %), and NiS(99.9 %) powders. Powder material of La_2O_3 and CaO were preheated at 850 °C for 10 hours to remove hydroxides. Stoichiometric amounts of these starting materials were mixed under Ar atmosphere and pressed into a rectangular shape. The rectangular bars were sealed in evacuated quartz ampoules and sintered at 900 °C for 40 hours. The structure and lattice parameters of the samples were analyzed by powder X-ray diffraction (XRD).

Electrical resistivity and magneto-resistance(MR) measurements were made by means of a standard four-probe method. The temperature range of electrical resistivity measurements is 4.2 $\sim$ 300 K. The mag-

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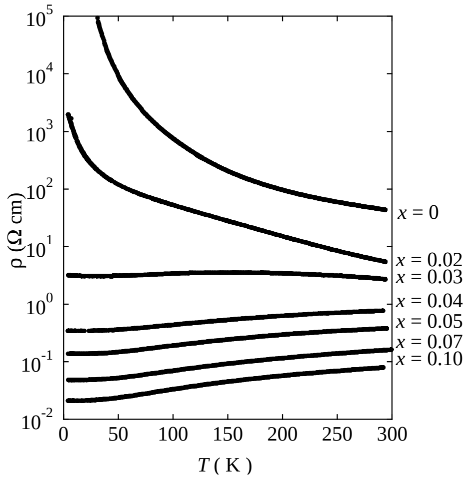

Fig. 1. The temperature dependences of the electrical resistivity of $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ for various values of x.

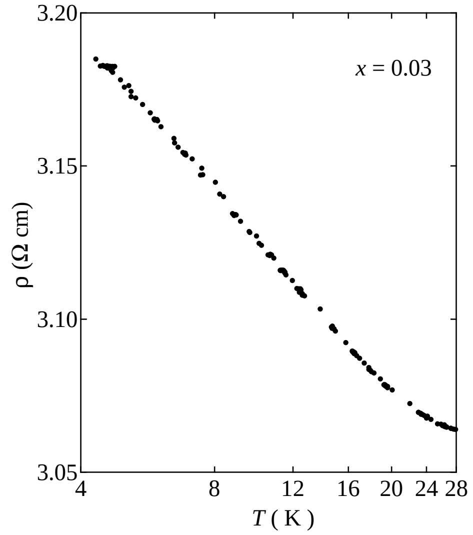

Fig. 2. The low temperature electrical resistivity for $x = 0.03$ against logarithmic temperature scale.

netic field dependence of MR was measured up to 9 T. Photoemission spectroscopies (PES) were carried out using synchrotron radiation(SR) as a excitation light source on BL-7 at HiSOR. A powder X-ray diffraction was measured using SR on BL02B2 at SPring 8 to obtain the structure and lattice parameters of these samples.

The lattice constants a and c of host crystal (LaO)CuS are 0.40030 and 0.85128 nm, respectively. The x dependences of a and c do not obeys the Vegard's law. The lattice constant a and c have a maximuma and a minimum at about $x = 0.03$, respectively. The charge distribution obtained by Rietveld / Maximum entropy method(MEM) shows that both La-O-La and S-Cu-S layers are electrically almost neutral and little exchange of charge occurs between them. This indicates that (LaO)CuS has a two-dimensional character. Fig. 1 shows the temperature dependences of the electrical resistivity of $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ for various x. Samples of $x \leq 0.02$ show semiconducting behaviors and the others ($x > 0.03$) are metallic. The absolute values of electrical resistivity decrease with increasing x.

The PES spectrum for $x = 0.10$ at $h\nu$= 40.8 eV indicates a finite density of state in the vicinity of Fermi energy, while the host crystal shows a p-type character. This indicates that new states are introduced by the substitution. The electrical resistivity for $x = 0.03$ shows a semiconductor - metal transition at 150 K without an anomalous specific heat. Such behavior is often observed in the layered materials which have a metallic and a semiconducting layer stacked alternately, such as Sr_2RuO_4 [?] and Na2CoO4 [?]. For the Ca single - doped system, such a transition is not observed and the electrical resistivity remains semiconducting up to $x = 0.10$. The origin of the resistivity maximum may be attributed to coherence - incoherence crossover along c direction of the metallic carriers introduced by the Ni substitution into the CuS layer. In the low temperature ranges, a resistivity minimum is observed for $x = 0.03 \sim 0.06$ metallic samples. The electrical resistivity increases almost linearly to $\log T$ with decreasing temperature as shown in Fig. 2 for $x = 0.03$. The resistivity increase is not observed at all for higher concentration than 0.06. In the high concentration range, the localization effct is surprpressed by the screening of the random potential. The sign of MR for $x = 0.03$ and 0.04 at 4.7 K is positive and increases with magnetic field up to 9 T, whereas the MR for $x = 0.07$ changes from negative in the low field range to positive in the high field range. No field dependence was observed within the measuring error for $x = 0$. The similar positive MR in the resistivity increase region is also found in $Cd_{1-x}Mn_xSe$:In [?].

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