Proc. Int. Symposium on Advances in Neutron Scattering Research, Tokai, 2000
J. Phys. Soc. Jpn. **70** (2001) Suppl. A pp. 64–66

Neutron Powder Diffraction on Novel Layered Cobalt Oxysulfide $Sr_2Cu_2CoO_2S_2$ in Strongly Correlated Electron Systems

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$Sr_2Cu_2CoO_2S_2$ is the strongly correlated antiferromagnet with T_N(=200 K). Above 200 K, this oxysulfide has the magnetic susceptibility with a broad maxium indicative of two-dimensional antiferromagnetic coupling in the square-planar CoO_2 planes. Below 80 K, the difference between zero-field cooled and field cooled magnetic susceptibilities are confirmed, suggesting that this oxysulfide exhibits a spin-glass-like (spin-frustrated) transition. From the neutron powder diffraction (NPD) experiment on $Sr_2Cu_2CoO_2S_2$, below 200 K we have observed the occurrences of new additional reflection peaks which can be indexed on the K_2NiF_4-type magnetic cell. These peaks can be therefore assigned to the square-planar CoO_2 planes with antiferromagnetic ordering. The magnetic reflection peaks are clearly seen in the NPD pattern at 75 K in the spin-glass-like region, indicating a possibility that $Sr_2Cu_2CoO_2S_2$ is the unusual spin-glass-like material.

KEYWORDS: layered transition-metal oxysulfide, strongly correlated electron system, neutron powder diffraction, two-dimensional antiferromagnet

§1. Introduction

Layered transition-metal oxysulfide $Sr_2Cu_2CoO_2S_2$ crystallizes in an unusual intergrowth structure[1–3] with alternating square-planar CoO_2 planes and anti-PbO type Cu_2S_2 layers separated by Sr^{2+} cations, as schematically depicted in Fig. 1. The $SrCoO_2$ unit is isostructural to the infinite layer high-T_C cuprate $Sr_{0.15}Ca_{0.85}CuO_2$, and the $SrCu_2S_2$ unit is of the $ThCr_2Si_2$ structure type. $Sr_2Cu_2CoO_2S_2$ is an antiferromagnetic semiconductor with magnetic anomalies[1,4] and belongs to the charge-transfer regime[5] of the well-known Zaanen-Sawatzky-Allen diagram[6] describing the strongly correlated electron picture. Electronic nature of the CoO_2 planes, which is isostructural with the CuO_2 planes of high-T_C cuprates, indeed shows the strongly correlated feature[5] and would be expected to be accounted for when the interaction of all the degrees of freedom (spin, charge, and orbital) are taken into consideration.

Layered compounds represent an active area of research due to their interesting physical properties including superconductivity, charge density waves, and two-dimensional (2D) magnetism.[7,8] In $Sr_2Cu_2CoO_2S_2$-type transition-metal oxysulfides, combinations of perovskite-like oxide and $ThCr_2Si_2$ type sulfide units are of great interest because of possible novel electronic and magnetic properties resulting from material interactions between the two types of layers. From the viewpoint of material design, by using these $Sr_2Cu_2CoO_2S_2$-type transition-metal oxysulfides, one can expect to design a new material that shows unusual properties. However, magnetic structure of the prototypical $Sr_2Cu_2CoO_2S_2$ are not understood yet. In this report, we will firstly report the neutron powder diffraction (NPD) study on $Sr_2Cu_2CoO_2S_2$ in strongly correlated electron systems in order to provide an important information on the magnetic nature in $Sr_2Cu_2CoO_2S_2$.

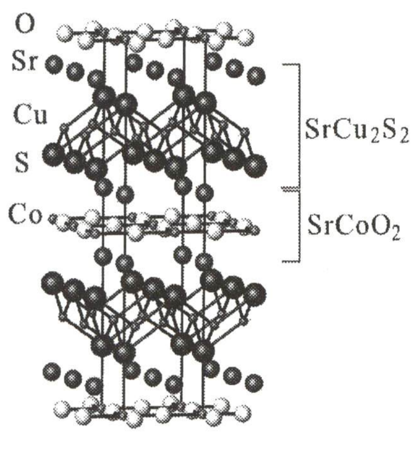

Fig. 1. Crystal structure of $Sr_2Cu_2CoO_2S_2$ (space group $I/4mmm$). Outline shows the crystallographic unit cell. The units are identified on the side of figure.

§2. Experimental

A polycrystalline sample of $Sr_2Cu_2CoO_2S_2$ was synthesized in an evacuated quartz tube containing pellets with appropriate mixture of SrS, Co, and CuO at 825 °C for 2 days. The products were ground into powder, pressed into pellets under 1 ton/cm^2, and sintered at 825 °C for 2 days. Obtained black polycrystalline samples were characterized by a powder x-ray diffraction (XRD) and an energy dispersive x-ray (EDX) spec-

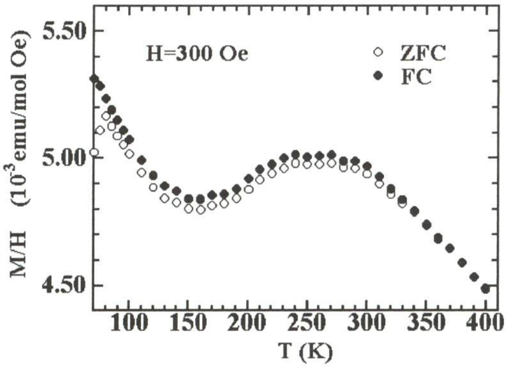

Fig. 2. Temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities of $Sr_2Cu_2CoO_2S_2$.

troscopy. In addition, the samples were characterized by a x-ray photoemmission spectroscopy (XPS) and a superconducting quatum interference device (SQUID) magnetometer.

The NPD patterns were obtained with Kinken powder diffractometer[9] 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). Neutrons with wave length 1.819 Å were obtained by the (331) reflection of Germanium monochromater and a combination of 12'-∞-open-22' collimator. The sample was put into a cylindrical aluminum with a thickness of 60μm and a diameter of 10 mm and was mounted in a closed cycle refrigerator. The diffraction data were analyzed using RIETAN[10] and FULLPROF[11] programs.

§3. Results and Discussion

The powder XRD patterns show that the prepared samples are single phases. The EDX analysis on the samples gives the atomic ratio Sr:Cu:Co:S close to 2:2:1:2 in $Sr_2Cu_2CoO_2S_2$, with an error of ± 0.1. The lattice parameters refined by the least squres method are $a = 3.981$ Å and $c = 17.625$ Å at room temperature, which are almost consistent with those in previous reports.[1,3] The line shape of Cu $2p$ XPS spectrum with no clear satellite is quite smilar to those of the formally mono-valent Cu compound. Co $2p$ XPS spectrum is quite smilar to those of strongly correlated di-valent Co compounds, suggesting that the square-planar CoO_2 plane belongs to the strongly correlated electron system such as high-T_C superconductors.[5]

The magnetic field dependences of the magnetization at 75 K, 130 K, and 300 K are linear, providing evidence for no ferromagnetic impurities in the samples. The temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities of $Sr_2Cu_2CoO_2S_2$ are shown in Fig. 2. The difference between ZFC and FC magnetic susceptibilities can be seen below 80K ($= T_1$), suggesting that this feature is smilar to that of $Ba_2Zn_2MnO_2As_2$[12] with isostructural square-planar MnO_2 planes and Zn_2As_2 layers. At 75 K ($< T_1$), the long time decay of the magnetization is observed and can be well described by the typical stretched exponential

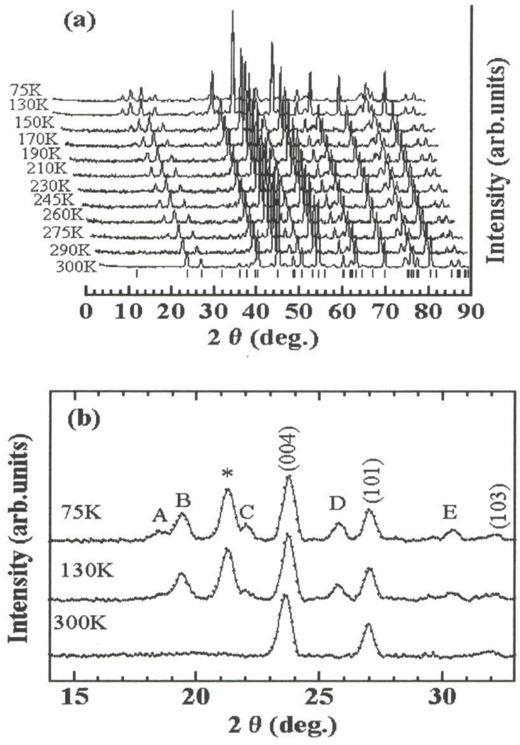

Fig. 3. (a) The neutron powder diffraction (NPD) patterns of $Sr_2Cu_2CoO_2S_2$ at various temperatures (75-300 K). Vertical marks show the positions of allowed reflections in the tetragonal crystallographic cell at 300 K. (b) The NPD patterns in the region of low scattering angle.

Table I. Positions and indices of magnetic reflections at 75 K.

Peaks	$2\theta_{obs}$ (deg.)	$2\theta_{calc}$ (deg.)	Indices
A	18.66	18.64	100
B	19.54	19.57	101
*	21.38		
C	22.10	22.15	102
D	25.91	25.90	103
E	30.50	30.43	104

form as seen in an usual spin-glass.[4] Above 200 K, the magnetic susceptibility indeed shows a broad maxium indicative of 2D antiferromagnetic coupling.[14] The antiferromagnetic transition temperature (T_N) can be obtained from measurements of the magnetic contribution $d\chi T/dT$, which is proportinal to the heat capacity.[13] Consequently, T_N can be determined to be 200K from the $d\chi T/dT$ vs. T plot. The T_N is almost consistent with the temperature (T_2) at which magnetic NPD peaks originated from antiferromagnetic CoO_2 planes disappear, as mentioned below.

Figure 3 shows the NPD patterns at various temperatures (75K-300K). The NPD pattern at 300K can be indexed with the tetragonal cell (space group I/4mmm) with $a = 3.981$ Å and $c = 17.625$ Å, which is in agreement with the previous study.[1] However, additional reflections peaks are clearly seen below 290 K. The new reflection (A-E) peaks, except of the (*) peak, can be indexed on a new cell with dimensions $a_{mag} = \sqrt{2}a$ and $c_{mag} = c$, following the selection rule: $h + k = odd$, as listed in Table I. This new cell and estimated indices are

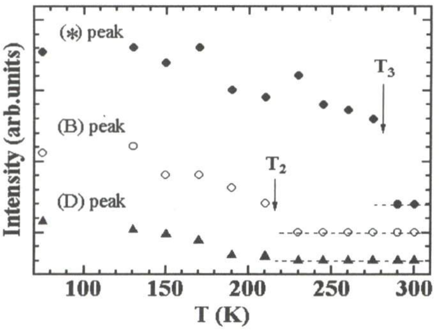

Fig. 4. Temperature dependence of three selected magnetic reflections (B, D, $*$) of $Sr_2Cu_2CoO_2S_2$.

the same as those normally seen for antiferromagnetic K_2NiF_4-type compounds with square-planar NiF_2-type planes. Consequently, the origin of the indexed (A-E) reflection peaks of $Sr_2Cu_2CoO_2S_2$, can be assigned to the square-planar CoO_2 planes with antiferromagnetic ordering.

The intensities of (B, D, $*$) peaks, which are tentatively measured as peak height above background, are plotted in Fig. 4 as a function of temperature in order to determine magnetic ordering temperatures. The intensities of (B,D) peaks disappears above 200 K ($= T_2$), indicating that the magnetic moments in the CoO_2 planes order antiferomagnetically below T_2. The T_2 is almost consistent with the T_N obtained from the $d\chi T/dT$ vs T plot, as noted above. On the other hand, the intensity of ($*$) peak disappears somewhat at 290 K ($= T_3$) above T_2. This feature suggests a possibility that the magnetic nature coming from the $ThCr_2Si_2$-type $SrCu_2S_2$ unit would be taken into account in order to understand the total magnetic structure of $Sr_2Cu_2CoO_2S_2$. A better understanding of the origin of ($*$) peak and the possibility of the magnetic moment formation in the the $ThCr_2Si_2$-type $SrCu_2S_2$ unit is of great importance and the next step to elucidate the anomalous magnetic properties in $Sr_2Cu_2CoO_2S_2$.

Finally, we would like to comment the unusual magnetic phases of $Sr_2Cu_2CoO_2S_2$. If $Sr_2Cu_2CoO_2S_2$ is a usual spin-glass, one can expect that it has no magnetic reflections peaks in the spin-frozen state. However, magnetic reflection peaks are clearly seen in the NPD pattern at 75 K. This feature indicates a possibility that $Sr_2Cu_2CoO_2S_2$ is an unusual spin-frustrated system in which some component of magnetic moments are only frozen. Futhermore, the magnetic susceptibility of $Sr_2Cu_2CoO_2S_2$ indeed shows a broad maxium indicative of 2D antiferromagnetic coupling.[14] It is of great importance whether short range 2D ordering[15] exists in the spin-frustrated phase or not. It is also of great interest whether 3D ordering can occur via interactions between two types of layers or not. Futher neutron diffraction HERMES experiments may help to resolve these crucial unanswered questions.

A detailed study of the magnetic structure of the novel layered oxysulfide $Sr_2Cu_2CoO_2S_2$ as a function of temperature is still in progress and will be published elsewhere.

§4. Conclusions

Magnetic nature has been investigated for the novel layered oxysulfide $Sr_2Cu_2CoO_2S_2$ which crystallizes in an unusual intergrowth structure with alternating square-planar CoO_2 planes and anti-PbO type Cu_2S_2 layers. $Sr_2Cu_2CoO_2S_2$ is the strongly correlated antiferromagnet with T_N(=200 K) obtained from measurements of the magnetic contribution $d\chi T/dT$. Below 80 K($= T_1$), the difference between ZFC and FC magnetic susceptibilities are observed, indicating that $Sr_2Cu_2CoO_2S_2$ exhibits a spin-glass-like (spin-frustrated) transition. Above 200 K($= T_2$), magnetic susceptibility shows a broad maxium indicative of 2D antiferromagnetic coupling in the square-planar CoO_2 planes. From the NPD HERMES experiment, below 200 K($= T_2$) we have confirmed the occurrences of new additional reflection peaks, which can be indexed on the K_2NiF_4-type magnetic cell and can be therefore assigned to the square-planar CoO_2 planes with antiferromagnetic ordering. The magnetic reflection peaks are clearly seen in the NPD pattern at 75 K in the spin-glass-like (spin-frustrated) region, indicating a possibility that $Sr_2Cu_2CoO_2S_2$ is the unusual spin-glass-like material.

Acknowledgements

Enlightening discussions with H.Kitô (ETL) and S.Anzai, S.Okada, T.Takeuchi (Keio Univ.) are gratefully acknowledged. The work was supported by a Grant-in-Aid for Scientific Reserach from the Ministry of Education, Science and Culture of Japan. The HERMES study was performed under the inter-university cooperative research program of the Institute for Materials Research, Tohoku University.

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