PHYSICAL REVIEW B VOLUME 44, NUMBER 9 1 SEPTEMBER 1991-I

Spin-freezing behaviors in the layered perovskite $Sr_3V_2O_{7-d}$

Hiromi Niu,* Noburu Fukushima, and Ken Ando
Advanced Research Laboratory, Research and Development Center, Toshiba Corporation, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan
(Received 1 May 1991)

We have examined electrical and magnetic properties of the $Sr_3V_2O_{7-d}$ system. Electrical resistivity changes from metallic to semiconducting with decreasing oxygen content. Transport is governed by variable-range hopping of the electrons since the resistivity obeys the $\exp(AT^{-1/4})$ law at low temperature. Oxygen-deficient $Sr_3V_2O_{7-d}$ exhibits different temperature–magnetic susceptibility curves for zero-field-cooled and field-cooled measurements below about 15 K. We have measured also the field dependence of the magnetic susceptibility and the long-time relaxation of thermoremanent magnetization, which obeys the relationship $M_{\mathrm{TRM}}=At^{-a}$. The magnetic properties in the $Sr_3V_2O_{7-d}$ system, therefore, are interpreted to be spin-glass-like, caused by the localized V spins introduced by the disorder-induced localization.

Copper-based high-T_c oxides have certain common features, such as a two-dimensional crystal structure, a $\frac{1}{2}$ spin on the Cu^{2+} ion, and the existence of the "parent" antiferromagnetic insulators, which are considered to be clues both to elucidating the mechanism for high-T_c superconductivity and to searching for other high-T_c superconductors.

The layered perovskites $Sr_{n+1}V_nO_{3n+1}$ were recently described.[1,2] They possess all the above-mentioned features, including a metal-insulator transition in the $Sr_3V_{2-x}Cr_xO_7$ system.[3] Thus, they are attracting attention as possible high-temperature superconductors. The electronic states and the magnetic properties, however, have not been examined precisely. For example, the existence of magnetic order in the insulating Sr_2VO_4 has not been confirmed yet.

On the other hand, it has been reported that the magnetic susceptibility of the metallic $Sr_3V_2O_7$ system has both temperature-independent and Curie-Weiss terms,[2,4] but the fragmentary results of the susceptibility measurements are still far from representing a consensus about magnetic properties in this system.

In this work, we have made precise measurements of the magnetic susceptibility on the oxygen-deficient $Sr_3V_2O_{7-d}$ system, and observed irreversibility between zero-field cooling (ZFC) and field cooling (FC), the field dependence of the susceptibility and long-time relaxation of the magnetization below 15 K. These results indicate that this system exhibits a spin freezing behavior at low temperatures. At the same time, the conductivity of these oxygen-deficient samples can be described by the variable-range hopping scheme. Thus, the origin of the spin freezing character of this system may be the localized V spins introduced by the disorder-induced localization.

$Sr_3V_2O_{7-d}$ samples with various oxygen contents were prepared by the following method. A mixture of $SrCO_3$ and V_2O_3 was reacted at 1000 °C in air for 24 h. Then it was reground and pressed into pellets. Subsequently, the pellets were sintered at 1150 °C in dry H_2 (dew point −58 °C) for 10 h, and quenched from 1150 °C to room temperature in flowing H_2. Some of the quenched samples were annealed at 900 or 1000 °C in dry H_2 for 3 h. As the equilibrated partial oxygen pressures of the various vanadate oxides became higher with the rise in temperature, the oxygen content in the $Sr_3V_2O_{7-d}$ system was assumed to become smaller in the order samples quenched from 1150 °C, annealed at 1000 °C, and annealed at 900 °C. The oxygen contents, derived by the chemical analysis for the samples quenched from 1150 °C and annealed at 900 °C, were 6.69 and 6.73, respectively. The samples obtained were examined by x-ray diffraction and proved to be a single phase of $Sr_3Ti_2O_7$ structure. The temperature dependence of electrical resistivity and magnetization were measured for these samples.

Figure 1 displays the results of the electrical resistivity measurements in the $Sr_3V_2O_{7-d}$ system. The quenched sample shows a semiconducting property. The annealed samples, however, tend to show metallic conductivity as the annealing temperature is lowered. Thus, a decrease in the oxygen content in the $Sr_3V_2O_{7-d}$ system is considered to cause a transition from a metallic to a semiconducting state. The logarithmic electrical resistivity of the quenched sample at low temperatures is plotted versus $T^{-1/4}$ in Fig. 2. The conductivity is considered to be governed by variable-range hopping of the electrons, since the logarithmic resistivity obeys the $T^{-1/4}$ law. The low-

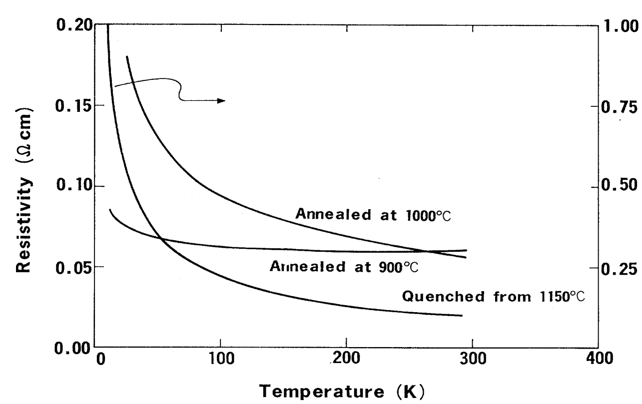

FIG. 1. Temperature dependence of electrical resistivity for $Sr_3V_2O_{7-d}$.

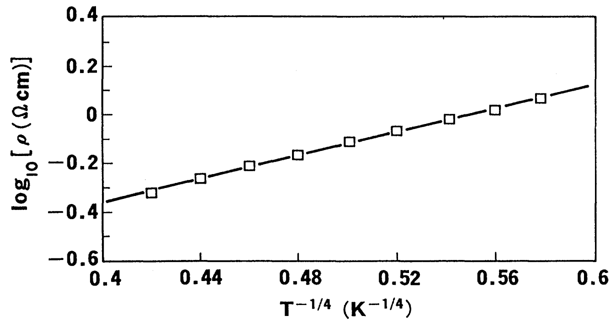

FIG. 2. Logarithmic resistivity ρ vs $T^{-1/4}$ plots for quenched $Sr_3V_2O_{7-d}$.

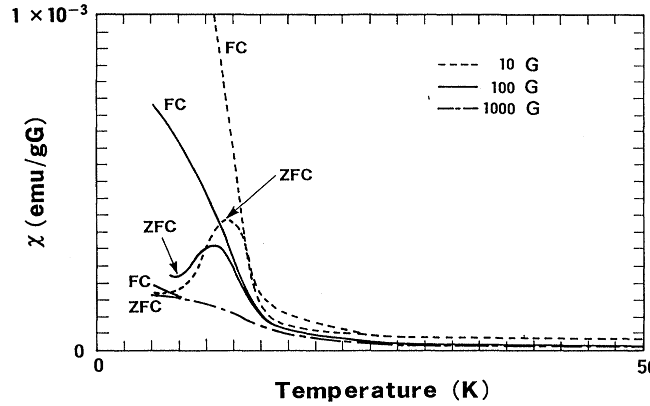

FIG. 3. Temperature dependence of magnetic susceptibility (χ) for quenched $Sr_3V_2O_{7-d}$. Measurements were carried out after zero-field cooling and field cooling. The measurement and cooling fields were 10, 100, and 1000 G, respectively.

temperature resistivity can also be fitted fairly well to the relation $\exp(AT^{-1/3})$. However, data are still insufficient to allow detailed discussion of the conduction.

We reported previously that the vanadium two-band overlap is considered to contribute to the metallic conduction in the $Sr_3V_2O_{7-d}$ system, and that replacement of V by Cr leads to the transition to the insulating state.[3] As x-ray photoemission experiments revealed a marked reduction in density of states at the Fermi level for the insulating sample,[5] this metal-insulator transition is now considered to be caused by band splitting between two V levels, assuming the electronic states of these layered-perovskite vanadates can be treated within a Mott-Hubbard insulator and "low-U" metal[6] formalism.

On the other hand, the transition to the semiconducting state observed in this study is now speculated to be a type of disorder-induced Anderson localization seen in the metal-deficient VO_x.[7] The $\exp(AT^{-1/4})$ dependence of the resistivity at low temperature and the magnetic properties described below are considered to support this model. This coincidence of the electrical properties and magnetic properties also rules out the possibility of an extrinsic cause, such as intergrain junctions, for the metal-insulator transition.

The temperature dependence of magnetic susceptibility in several applied fields for the quenched sample is illustrated in Fig. 3. The differences between ZFC and FC data are observed at low temperature. From this phenomenon, spin freezing is suggested to occur below the irreversibility temperature. The spin-freezing temperature (T_f) shifted to lower temperature with increasing field. At the same time, the peaks become smaller and broader.

Figure 4 shows the time dependence for thermoremanent magnetization M_{TRM} for the quenched sample at various temperatures. These were measured by removing the field, after the sample was cooled from room temperature to 10, 8, 7, and 5 K, respectively, in a 100 G field. Long-time M_{TRM} relaxation was observed. The gradient of relaxation tends to become large at higher temperatures. As the acquired data maintains linearity for log-log plots, the relaxation phenomenon is considered to be expressed by the following equation:

$$M_{TRM} = At^{-\alpha}, \qquad (1)$$

where M is magnetization. A denotes the M value for $t = 1$ s. The A and α values in Eq. (1) for various temperatures are plotted in Fig. 5. The α values rose at higher temperatures. This means an abrupt progress in relaxation at higher temperatures. The A values decrease linearly with the rise in temperature.

The magnetic properties in this system are considered to be very similar to those for spin glasses, since three features of a spin glass (magnetic-susceptibility irreversibility, the spin-freezing temperature and magnetic-susceptibility field dependence, and the thermoremanent magnetization long-time relaxation) are satisfied.

As mentioned above, oxygen-deficient $Sr_3V_2O_{7-d}$ exhibits variable-range hopping conduction and spin-freezing characteristics. The origin of the spin freezing for this system is considered to be the localized V spins, introduced by the disorder-induced localization, which interact via the conduction electrons. The exchange interaction is considered to be of the Rudermann-Kittel-Kasuya-Yoshida type, though some other mechanism by the localized electrons cannot be ruled out, as in the VO_x system.[8]

It should be pointed out that the temperature–magnetic-susceptibility curves for the field-cooled measure-

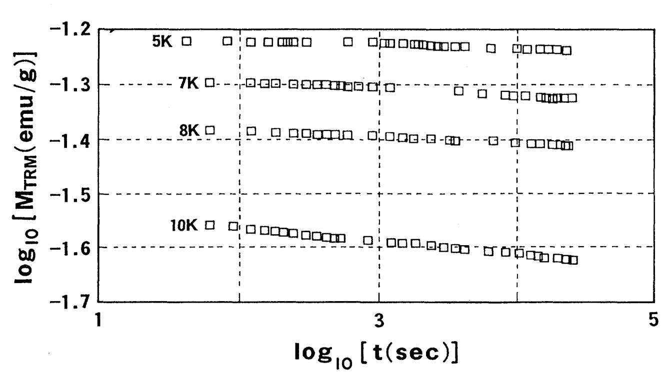

FIG. 4. Time dependence of thermoremanent magnetization (M_{TRM}) for quenched $Sr_3V_2O_{7-d}$. Measurements were carried out after cooling in a 100-G field for the measurement temperature and removing field.

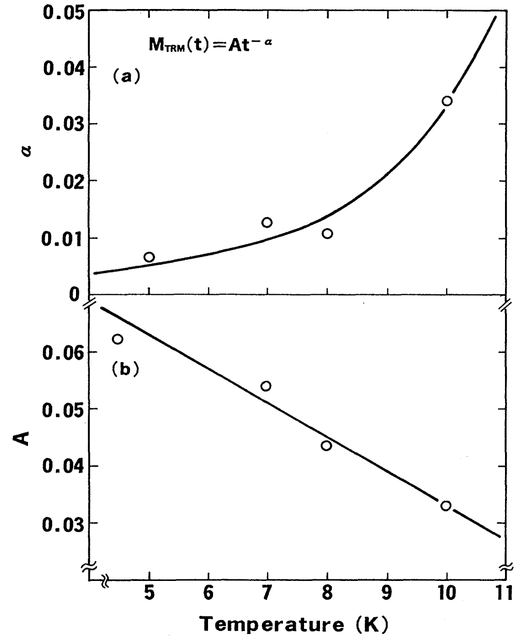

FIG. 5. A and α values derived from $M_{TRM} = At^{-\alpha}$.

ment in this system are different from those for the usual spin glass seen in dilute alloys, and the increase in the magnetic susceptibility below T_f does not obey the usual Curie-Weiss law. It is considered that the exchange interaction between the spins becomes small, due to the low mobility of the conduction carriers at lower temperatures, and is not sufficient to freeze the spins in random directions.

There are some early transition-metal oxides, which exhibit spin-freezing characteristics, such as VO_x,[8] and $Ti_{2-x}V_xO_3$,[9,10] in which the spin-spin interaction is expected to occur via partially localized d electrons. In the $Sr_3V_2O_{7-d}$ system, the conductivity was reduced as the oxygen deficiency increased, while the localized spin density increases. This situation resembles the case in VO_x. However, both conductivity and local spin density increase with increasing x in $Ti_{2-x}V_xO_3$. A comparison among these three compounds may yield information about the unusual behavior of the FC magnetization. However, we have not found any FC magnetization data in pertinent literature.

In summary, we have examined electrical and magnetic properties of the oxygen-deficient $Sr_3V_2O_{7-d}$ system. The electrical properties changed from a metallic state to a semiconducting state with decreasing oxygen content in this system. The magnetic properties for the oxygen deficient $Sr_3V_2O_{7-d}$ showed spin-freezing behavior. This change to a semiconductor in the electrical properties and appearance of spin-freezing behavior is attributed to Anderson localization, led by disorder introduced by the oxygen deficiency.

Measurements, such as the frequency dependence of the ac susceptibility cusp, are necessary to distinguish this spin-freezing property from other possibilities, such as superparamagnetism or dilute antiferromagnetism.

The authors would like to thank Dr. S. Tanaka and Dr. K. Inomata for useful discussions.

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*Present address: Metals and Ceramics Laboratory, Research and Development Center, Toshiba Corporation, Japan.

[1]M. Cryot, B. Lambert-Andron, J. L. Soubeyroux, M. J. Rey, Ph. Dehault, F. Cyrot-Lackmann, G. Fourcaudot, J. Beille, and J. L. Tholence, Solid State Commun. **85**, 321 (1990).

[2]Ayumi Nozaki, Hiroshi Yoshikawa, Takahiro Wada, H. Yamauchi, and Shoji Tanaka, Phys. Rev. B **43**, 181 (1991).

[3]N. Fukushima, S. Tanaka, H. Niu, and K. Ando, Jpn. J. Appl. Phys. **29**, 2190 (1990).

[4]N. Suzuki, T. Noritake, N. Yamamoto, and T. Hioki, Mater. Res. Bull. **26**, 75 (1991).

[5]N. Fukushima, S. Tanaka, H. Niu, and K. Ando (unpublished).

[6]J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[7]N. F. Mott, Philos. Mag. **24**, 935 (1971).

[8]T. Ohtani, K. Kosuge, and S. Kachi, Solid State Commun. **36**, 575 (1980).

[9]J. Dumas and C. Schlenker, J. Phys. (Paris) Colloq. **37**, C4-41 (1976).

[10]J. Dumas, C. Schlenker, J. L. Tholence, and R. Tournier, Phys. Rev. B **20**, 3913 (1979).