



CRYSTAL GROWTH AND MAGNETIC PROPERTIES OF $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ ($0.90 \leq x \leq 1.00$)

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ABSTRACT

A large single crystal of $S = 1/2$ quasi-one-dimensional system $\gamma\text{-LiV}_2\text{O}_5$ was successfully grown by the flux method. Single crystals of nonstoichiometric $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ were also prepared. The electromagnetic properties of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ ($0.90 \leq x \leq 1.00$) were investigated. Li deficiency introduces nonmagnetic V^{5+} ($S = 0$) ions or holes in the magnetic V^{4+} ($S = 1/2$) linear chain. In $\gamma\text{-Li}_x\text{V}_2\text{O}_5$, the Curie-like increase of the magnetic susceptibility was observed at low temperature, but no evidence for a magnetic order was observed, in contrast to the 1-D cuprates. The electrical resistivity of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ decreases with Li deficiency at room temperature, but all compounds remain semiconductive. The temperature dependence of conductivity for the $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ does not obey any activation types except the stoichiometric $\gamma\text{-LiV}_2\text{O}_5$ ($E_a \sim 0.32$ eV). In $\gamma\text{-LiV}_2\text{O}_5$, the exchange integral through the corner of VO_5 square pyramid has been estimated to be about 3 times as large as that through the edge. Therefore the magnetic structure of $\gamma\text{-LiV}_2\text{O}_5$ can be considered to be an infinite double linear chain, rather than an infinite linear zigzag chain. © 2000 Elsevier Science Ltd

KEYWORDS: A. oxides, B. crystal growth, D. electrical properties, D. magnetic properties

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INTRODUCTION

Low-dimensional quantum spin systems have attracted considerable interest both experimentally and theoretically in recent decades. Quantum effects are most prominent in one-dimensional systems. Recently, the doping or substitution effect on low-dimensional spin systems with spin gap, such as the spin-Peierls compound CuGeO_3 [1] and the spin ladder compound SrCu_2O_3 [2,3], have received much attention. For instance, the substitution of a small amount of Zn for Cu in the spin ladder compound SrCu_2O_3 and the spin-Peierls compound CuGeO_3 leads to an antiferromagnetic long-range order [4] or the coexistence of a spin-Peierls state with a magnetically ordered state [5–7].

We have investigated vanadium oxides as low-dimensional magnetic systems with V^{4+} ion ($S = 1/2$). We have reported the magnetic properties of the vanadate family AV_2O_5 ($A = \text{Li, Na, Cs, Mg, Ca}$). It has been found that α' - NaV_2O_5 is a spin-Peierls system [8–11], CaV_2O_5 [12] and MgV_2O_5 [13,14] are two-leg spin-ladder systems with spin gaps, and CsV_2O_5 [15] is a dimer system with a spin gap. γ - LiV_2O_5 is a member of the lithium vanadium bronze oxides. Lithium intercalation in V_2O_5 produces six phases, viz, α , β , β' , ϵ , γ , and δ [16,17]. All these phases are formed from VO_6 octahedra and VO_5 pyramids, with distinct orderings. α - $\text{Li}_x\text{V}_2\text{O}_5$ is very similar to V_2O_5 and has a layered orthorhombic structure with identical vanadium sites. The monoclinic β bronze has three different vanadium sites forming a three-dimensional tunnel structure, within which the Li ion resides in octahedral sites. The β' phase is different from the β phase based on the mode of lithium insertion. Orthorhombic γ - LiV_2O_5 has a layer structure with lithium ions between the layers. In this structure, there are two crystallographic vanadium sites that form two kinds of zigzag chains, the shaded and the white zigzag chains, as shown in Figure 1 [18]. The valence states of the vanadium ions were inferred from the results of structural analysis to be V^{4+} for the shaded zigzag chains and V^{5+} for the white zigzag chains [18]. Within the layers, V^{4+}O_5 (shaded) zigzag chains are linked to V^{5+}O_5 (white) zigzag chains by corner sharing, as shown in Figure 1.

The magnetic susceptibilities of γ - LiV_2O_5 were first reported by Murphy et. al. [16], and more recently we reported that the magnetic susceptibilities of powder γ - LiV_2O_5 show good fits to the equations for a $S = 1/2$ one-dimensional Heisenberg antiferromagnetic linear chain model [15]. The fit gave $J = 308$ K (defined as $J\sum S_i S_j$), $g = 1.8$, and $\chi_0 = 1 \times 10^{-4}$ emu/mol [15]. γ - LiV_2O_5 does not show either a spin singlet state nor a magnetically ordered state as the ground state [19].

To investigate the magnetic properties, especially spin dynamics, in much more detail, it was crucial to grow single crystals of considerable size. In this study, we tried to grow single crystals, including large quasi-one-dimensional single crystals. We report the electromagnetic properties of single crystal of γ - LiV_2O_5 . It is very interesting how Li deficiency affects the $S = 1/2$ quasi-one-dimensional system γ - LiV_2O_5 . We also report the electromagnetic properties of Li-deficient samples of γ - LiV_2O_5 and discuss the magnetic structure of γ - LiV_2O_5 compared with other members of the vanadate family.

EXPERIMENTAL

Powder Sample Preparation. Powder samples of γ - $\text{Li}_x\text{V}_2\text{O}_5$ were prepared by a solid-state reaction of mixtures with appropriate molar ratios of LiVO_3 , V_2O_3 , and V_2O_5 . The weighed mixture was pressed into a pellet and heated at 600°C in an evacuated silica tube for

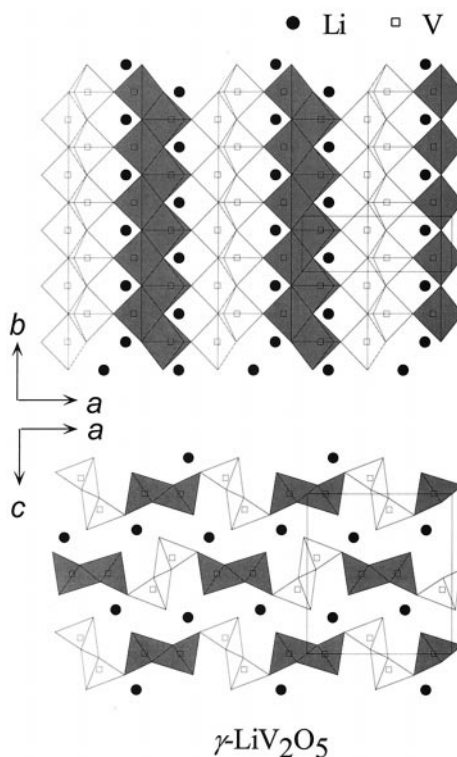


FIG. 1

Schematic crystal structure of $\gamma\text{-LiV}_2\text{O}_5$ projected onto the orthorhombic a - b plane and a - c plane. The filled circles represent Li^+ ions. The squares represent V atoms. The white and shaded square pyramids show two kinds of VO_5 pyramids (two crystallographic vanadium sites).

several days, with one intermediate grinding. No chemical analyses of the composition were carried out in the present study. The x in $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ was a nominal composition.

Single Crystal Growth. Single crystals of $\gamma\text{-LiV}_2\text{O}_5$ were grown from liquid phase, using LiVO_3 as a flux, by a method similar to that used for crystal growth of $\alpha'\text{-NaV}_2\text{O}_5$ [20]. The mixture of LiVO_3 and $\gamma\text{-LiV}_2\text{O}_5$ in the molar ratio of 9 (LiVO_3) to 1 ($\gamma\text{-LiV}_2\text{O}_5$) was sealed into an evacuated quart tube, heated at 700°C for 4 h, cooled to 550°C at the cooling rate of $2^\circ\text{C}/\text{h}$, and then cooled rapidly to room temperature. The flux (LiVO_3) was removed by washing with hot water. By this method, we obtained rather large ($\sim 10 \times 0.5 \times 0.5 \text{ mm}^3$) black single crystals. To obtain larger single crystals, the powder mixture of LiVO_3 and $\gamma\text{-LiV}_2\text{O}_5$ was put into a platinum crucible, with the obtained crystal as a seed crystal, sealed into an evacuated silica tube. The temperature profile employed for crystal growth is shown in Figure 2. A large single crystal with dimensions $18 \times 3 \times 2 \text{ mm}^3$ thus obtained is shown in Figure 3. All of the obtained single crystals were stoichiometric, because they were grown from the liquid of excess Li (LiVO_3 flux). Single crystals of nonstoichiometric $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ were prepared by heating a small crystal of stoichiometric $\gamma\text{-LiV}_2\text{O}_5$ embedded in a large

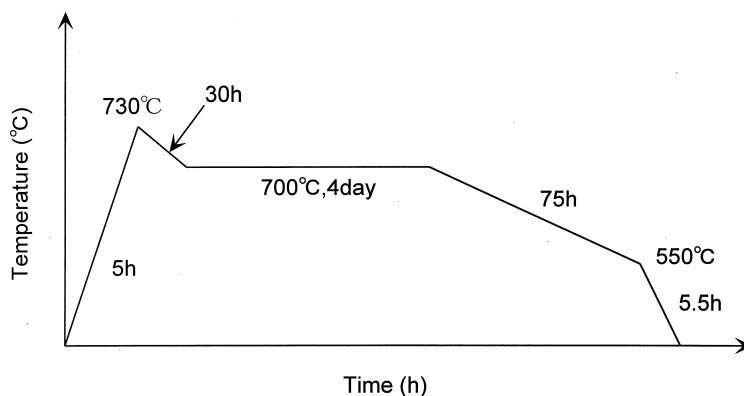


FIG. 2

Temperature profile employed for single crystal.

quantity of the powder sample of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ in an evacuated silica tube at 600°C for a week. It was determined by measurements of the magnetic susceptibility that the composition of the small crystals was identical to that of the large quantity of powder samples.

Power X-ray Diffraction, and Magnetic and Electronic Measurements. The sample characterization and the measurement of lattice parameters were made by powder X-ray diffraction, using a Mac Science MPX18 system with a rotating anode generator and a monochromator of single crystalline graphite for $\text{Cu K}\alpha$ radiation. The nonstoichiometric region of the γ -phase was examined by means of the powder X-ray diffraction. The magnetic susceptibility was measured with a Quantum Design SQUID magnetometer (MPMS5S). For measuring the magnetization of single crystal ($3 \times 2 \times 1 \text{ mm}^3$), we used sticky tape as a sample holder, because the contribution of the media holding the sample (e.g., grease) in the magnetic susceptibility can be ignored in this method. The electric resistivity measurements were made by an ordinary four-probe method using single crystals.

RESULTS AND DISCUSSION

The composition range of the single γ -phase was $0.90 \leq x \leq 1.00$ in $\text{Li}_x\text{V}_2\text{O}_5$ in the present work. This is in agreement with a previous report [17]. The compositional dependence of

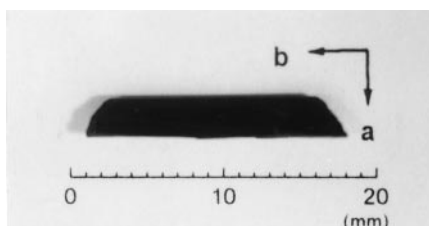


FIG. 3

$\gamma\text{-LiV}_2\text{O}_5$ single crystal.

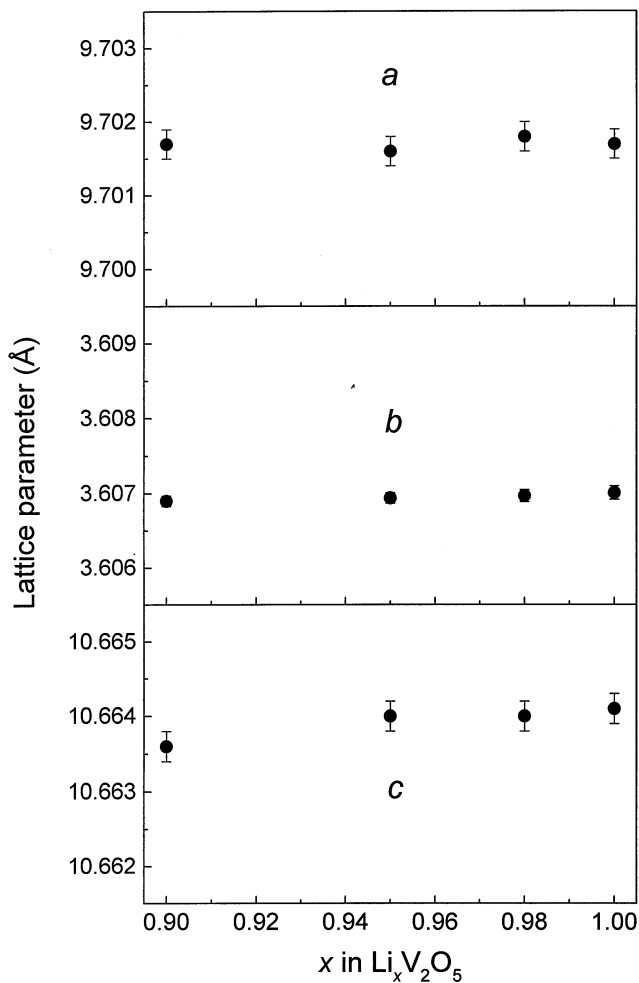


FIG. 4

Compositional dependence of lattice constants for $\gamma\text{-Li}_x\text{V}_2\text{O}_5$.

lattice constants in the $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ is shown in Figure 4. All lattice constants show a little change with an increase in Li deficiency. The Li ions between the layers may be so small as to affect the lattice constant in all axes, in contrast to the case of $\alpha'\text{-Na}_x\text{V}_2\text{O}_5$ [9].

Figure 5 shows the raw data of the magnetic susceptibility measured using single crystal of $\gamma\text{-LiV}_2\text{O}_5$. The magnetic susceptibility has a broad maximum at about 190 K in all directions, and its temperature dependence was in good agreement with that for powder sample reported previously [15]. The increase of the magnetic susceptibility at low temperature was not observed in all directions, in contrast to the results for the powder sample. This is attributed to the smaller defect concentration of the single crystal compared to that of the powder sample. The easy axis of magnetization is the a axis perpendicular to the zigzag chain. No evidence for a magnetic order was observed. This is in contrast to SrCuO_2 [21] and Sr_2CuO_3 [22], whose Neel temperatures are given in Table 1.

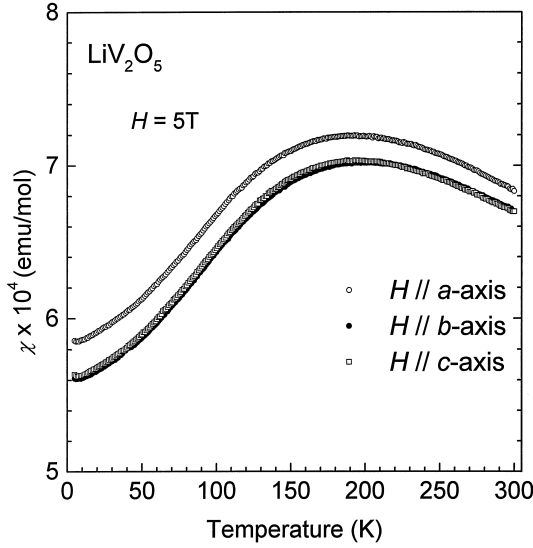


FIG. 5

Magnetic susceptibility of single crystal γ - LiV_2O_5 measured in a field of 1 T.

Figure 6 shows the magnetic susceptibility of the powdered γ - $\text{Li}_x\text{V}_2\text{O}_5$ below 80 K. Li deficiency introduces nonmagnetic V^{5+} ($S = 0$) ions into the magnetic V^{4+} ($S = 1/2$) linear zigzag chains and cuts the chains. A Curie-like increase of magnetic susceptibility, which was in proportion to the degree of Li deficiency, was observed at low temperature. But, as with α' - $\text{Na}_x\text{V}_2\text{O}_5$ [9], no evidence for a magnetic order was observed. This indicates that γ - LiV_2O_5 is an ideal 1-D magnetic system and the magnetic interchain interaction is very weak. The Curie constants obtained from fitting the magnetic susceptibility to Curie law between 5 and 15 K are given in Figure 7 as a function of y in $\text{Li}_{1-y}\text{V}_2\text{O}_5$. The dotted lines represent the $y/5$ and $y/6$ dependence, assuming free ion with $S = 1/2$ associated with Li deficiency. The Curie constant increases with a dependence between $y/5$ and $y/6$. Some theories [23,24] predict that the compositional dependence of the Curie constant lies between $y/4$ and $y/12$ in the spin-ladder system with spin gap. The observed small dependence of γ - $\text{Li}_x\text{V}_2\text{O}_5$ may be due to a quantum effect of low-dimensional magnets at low temperature.

The electric resistivity of γ - $\text{Li}_x\text{V}_2\text{O}_5$ was measured along the b axis (the linear chain direction) using single crystals. The inset of Figure 8 shows the resistivity of γ - $\text{Li}_x\text{V}_2\text{O}_5$ as

TABLE 1

Intrachain Coupling J (Defined as $J \sum S_i S_j$) and the Temperature of Magnetic Order for $S = 1/2$ Quasi-One-Dimensional Systems

	J/k_B (K)	T_N (K)
SrCuO_2 [21]	1800	2
Sr_2CuO_3 [22]	2200	5
γ - LiV_2O_5 [15,19]	308	

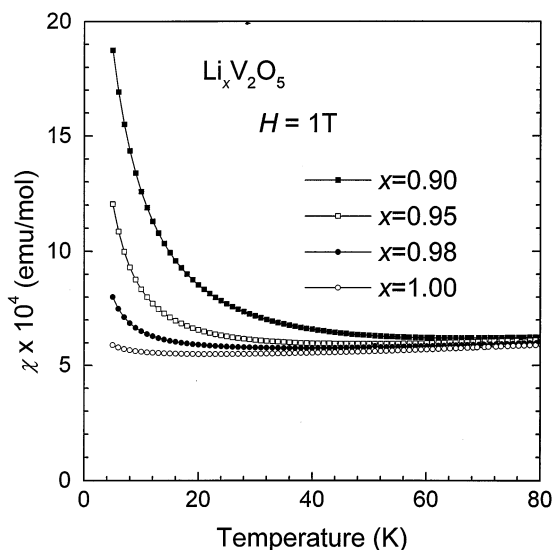


FIG. 6

Magnetic susceptibility of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ with $x = 0.90\text{--}1.00$ measured in a field of 1 T in the temperature range from 5 to 80 K.

a linear function of temperature. The resistivity of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ decreases with Li deficiency at 300 K, but all samples are semiconductive. Figure 8 shows the plot of the logarithm of the conductivity ($\ln \sigma$) vs. T^{-1} . The energy gap estimated by fitting the conductivity to the activation equation from 200 to 300 K is about 0.32 eV in the stoichiometric sample, while the conductivity of Li-deficient samples does not obey any activation types. This suggests that the carriers are possibly doped into 1-D chains in $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ by Li deficiency, but the conducting behaviors of doped samples are more complex.

In the $\gamma\text{-LiV}_2\text{O}_5$ system, Uemura et al. [25] have measured muon spin relaxation and observed the quantum fluctuation as observed in SrCuO_2 , although no magnetic order has been observed down to 2 K. Fujiwara et al. [19] have reported staggered- and uniform-spin fluctuation without magnetic order until 0.5 K, by ^7Li NMR measurements. These studies suggest that the one-dimensionality is quite good in $\gamma\text{-LiV}_2\text{O}_5$, compared with other linear chain systems. Still, the carrier-doping capacity of $\gamma\text{-LiV}_2\text{O}_5$ is a significantly different from those of SrCuO_2 [21] and Sr_2CuO_3 [22].

For the magnetic structure of $\gamma\text{-LiV}_2\text{O}_5$, it is considered that the structure consists of two nearest-neighbor magnetic exchange interactions with exchange integrals of J_{corner} ($\text{V}^{4+}\text{-O-V}^{4+}$) and J_{edge} ($\text{V}^{4+}\text{-V}^{4+}$), as shown in Figure 1. The spin-Peierls system $\alpha'\text{-NaV}_2\text{O}_5$ consists of $S = 1/2$ 1-D magnetic chain of corner-sharing V^{4+}O_5 pyramids with a single exchange integral J_{corner} [8]. The fit of χ to a Bonner-Fisher equation gives J_{corner} ($\alpha'\text{-NaV}_2\text{O}_5$) about 560 K [8]. On the other hand, CsV_2O_5 is a dimer system with only edge-sharing V^{4+}O_5 [11]. From fitting χ to the dimer model, J_{edge} (CsV_2O_5) is about 146 K [15]. We roughly estimated the exchange integrals of $\gamma\text{-LiV}_2\text{O}_5$ based on the two exchange integrals. It is a reasonable assumption that they depend only on local geometry of the bonds [26]. For corner-sharing pyramids (J_{corner}), the dominant process is superexchange (through

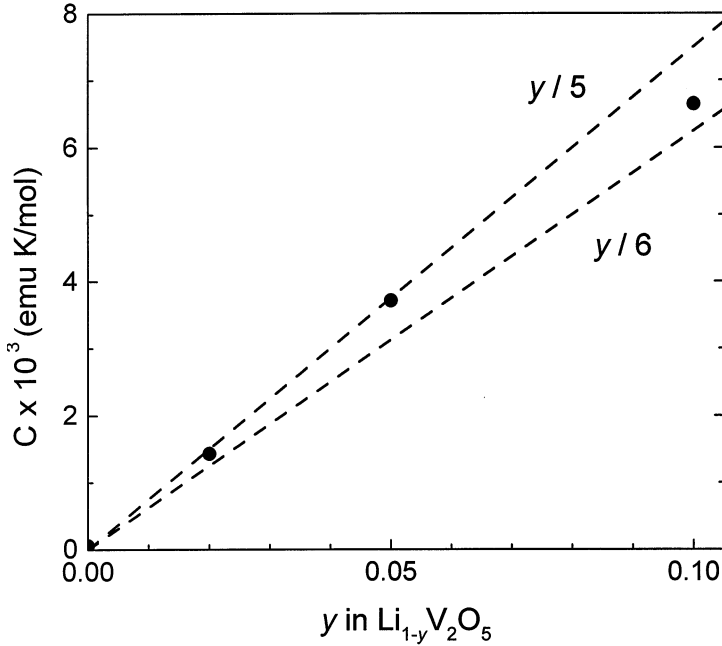


FIG. 7

Compositional dependence of Curie constant in γ -Li_{1-y}V₂O₅. The Curie constant was obtained from the fitting the magnetic susceptibility to Curie law between 5 and 15 K. The dotted lines represent the $y/5$ and $y/6$ dependence.

oxygen atom), and the exchange integrals are expected to depend on the local parameters defined according to [26]

$$J_{\text{corner}}(d_{\text{V-O}}, \theta_{\text{V-O}}) \propto \cos^4(\theta_{\text{V-O}}) d_{\text{V-O}}^{-14}$$

where the exponent is given by empirical laws concerning the dependence of the overlap integrals on distance [26]. For edge-sharing pyramids (J_{edge}), the origin of the interaction is not so clear. Assuming that it is due primarily to direct exchange between vanadium $3d$ orbitals, similar empirical laws predict that it should scale according to [26]

$$J_{\text{edge}}(d_{\text{V-V}}) \propto (d_{\text{V-V}})^{-10}$$

where $d_{\text{V-V}}$ is the vanadium–vanadium distance. The two exchange integrals of γ -LiV₂O₅ can be estimated to be J_{corner} about 568 K and J_{edge} about 183 K, from the above equations and crystal parameters [18]. The exchange integral J obtained from fitting χ to a Bonner–Fisher equation is about 308 K in γ -LiV₂O₅. The observed exchange integral J seems to be close to the difference between J_{corner} and J_{edge} , although the relation between the J and J_{corner} and J_{edge} is not so simple. In γ -LiV₂O₅, the J_{corner} is about 3 times as large as the J_{edge} . Therefore, the magnetic structure of γ -LiV₂O₅ can be considered to be an infinite double linear chain, rather than an infinite linear zigzag chain. The J_{corner} in γ -LiV₂O₅ is almost the same as that of spin-Peierls system α' -NaV₂O₅. But γ -LiV₂O₅ shows neither a spin singlet state nor a magnetically ordered state as the ground state. This may be due to the existence

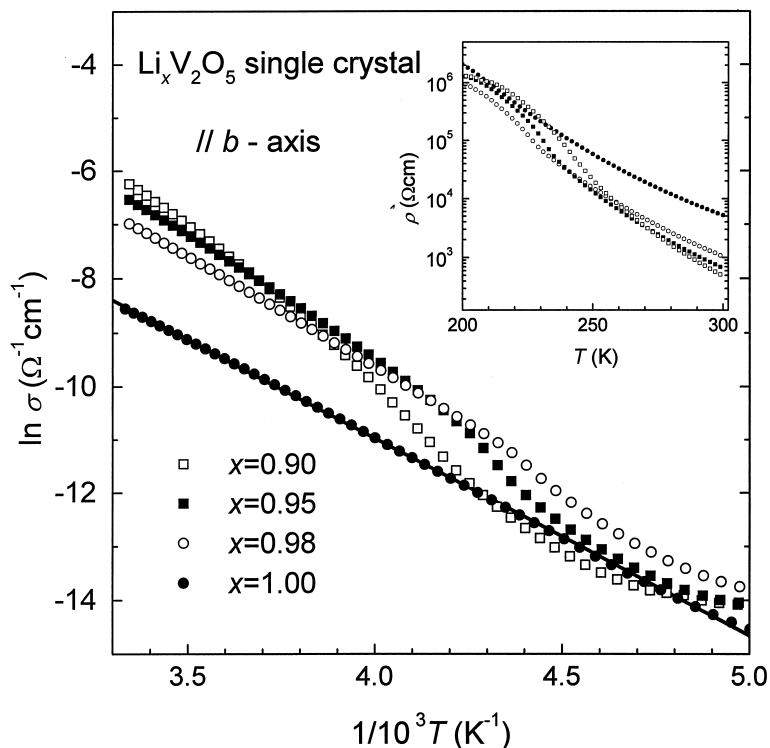


FIG. 8

Logarithm of the electric conductivity vs. $1/T$ of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$. The inset shows the resistivity of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ as a linear function of temperature.

of the double linear chain in $\gamma\text{-LiV}_2\text{O}_5$. The energy for the lattice distortion is too large to be compensated by the formation of spin-singlet because of the existence of the double linear chain in $\gamma\text{-LiV}_2\text{O}_5$.

In summary, single crystals of $\gamma\text{-LiV}_2\text{O}_5$ were successfully grown by a flux method. The largest crystal obtained by this method had the dimensions $18 \times 3 \times 2 \text{ mm}^3$. The easy axis of magnetization is the a axis perpendicular to 1-D chains. From Li deficiency, the Curie-like increase of magnetic susceptibility was observed in $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ ($0.90 \leq x \leq 1.00$) at low temperature, but, in contrast to the low-dimensional cuprates, no evidence for a magnetic order was observed. The electric resistivity decreases with Li deficiency at room temperature, although $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ remains semiconductive. The magnetic structure of $\gamma\text{-LiV}_2\text{O}_5$ can be considered to be an infinite double linear chain, rather than the zigzag linear chain, from a viewpoint of the exchange integral.

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REFERENCES

1. For a review, J.P. Boucher and L.P. Regnault, *J. Phys. I Fr.* **6**, 1939 (1996).
2. M. Azuma, Z. Hiroi, M. Takano, K. Ishida, and Y. Kitaoka, *Phys. Rev. Lett.* **73**, 3463 (1994).
3. K. Ishida, Y. Kitaoka, K. Asayama, M. Azuma, Z. Hiroi, and M. Takano, *J. Phys. Soc. Jpn.* **63**, 3222 (1994).
4. M. Azuma, Y. Fujishiro, M. Takano, M. Nohara, and H. Takagi, *Phys. Rev. B* **55**, R8658 (1997).
5. M. Hase, N. Koide, K. Manabe, Y. Sasago, K. Uchinokura, and A. Sawa, *Physica B* **215**, 164 (1995).
6. J-D. Lussier, S.M. Coad, D.F. McMorrow, and D.McK. Paul, *J. Phys.: Condens. Matter* **7**, L325 (1995).
7. J.P. Renard, K. Le Dang, P. Veillet, G. Dhalenne, A. Revcolevschi, and L.P. Regnault, *Europhys. Lett.* **30**, 475 (1995).
8. M. Isobe and Y. Ueda, *J. Phys. Soc. Jpn.* **65**, 1178 (1996).
9. M. Isobe and Y. Ueda, *J. Alloys Compd.* **262-263**, 180 (1997).
10. Y. Fujii, H. Nakao, T. Yoshihama, M. Nishi, K. Kakurai, M. Isobe, and Y. Ueda, *J. Phys. Soc. Jpn.* **66**, 326 (1997).
11. T. Yoshihama, M. Nishi, K. Nakasima, K. Kakurai, Y. Fujii, M. Isobe, C. Kagami, and Y. Ueda, *J. Phys. Soc. Jpn.* **67**, 744 (1998) and references therein.
12. H. Iwase, M. Isobe, Y. Ueda, and H. Yasuoka, *J. Phys. Soc. Jpn.* **65**, 2397 (1996).
13. M. Isobe, Y. Ueda, K. Takizawa, and T. Goto, *J. Phys. Soc. Jpn.* **67**, 755 (1998).
14. T. Mori, T. Yoshihama, M. Nishi, K. Nakasima, K. Kakurai, Y. Fujii, M. Isobe, and Y. Ueda, unpublished results.
15. M. Isobe and Y. Ueda, *J. Phys. Soc. Jpn.* **65**, 3142 (1996).
16. D.W. Murphy, P.A. Christian, F.J. DiSalvo, and J.V. Waszczak, *Inorg. Chem.* **18**, 2800 (1979).
17. E. Takayama-Muromachi and K. Kato, *J. Solid State Chem.* **71**, 274 (1987) and references in therein.
18. D.N. Anderson and R.D. Willett, *Acta Crystallogr. Sect. B* **27**, 1476 (1971).
19. H. Fujiwara, H. Yasuoka, M. Isobe, Y. Ueda, and S. Maegawa, *Phys. Rev. B* **55**, R11945 (1997).
20. M. Isobe, C. Kagami, and Y. Ueda, *J. Crystal Growth* **181**, 314 (1997).
21. M. Matsuda, K. Kastumata, K.M. Kojima, M. Larkin, G.M. Luke, J. Merrin, B. Nachumi, Y.J. Uemura, H. Eisaki, N. Motoyama, S. Uchida, and G. Shirane, *Phys. Rev. B* **55**, R11953 (1997).
22. K.M. Kojima, Y. Fudamoto, M. Larkin, G.M. Luke, J. Merrin, B. Nachumi, Y.J. Uemura, N. Motoyama, E. Eisaki, S. Uchida, K. Yamada, Y. Endoh, S. Hosoya, B.J. Sternlib, and G. Shirane, *Phys. Rev. Lett.* **78**, 1787 (1997).
23. M. Sigrist and A. Furusaki, *J. Phys. Soc. Jpn.* **65**, 2385 (1996).
24. Y. Iino and M. Imada, *J. Phys. Soc. Jpn.* **65**, 3728 (1996).
25. Y.J. Uemura, Y. Fudamoto, M. Isobe, and Y. Ueda, unpublished results.
26. P. Millet, C. Satto, J. Bonvoisin, B. Normand, K. Penc, M. Albrecht, and F. Mila, *Phys. Rev. B* **57**, 5005 (1998).