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Charge order and quasi-one-dimensional behavior in $\beta(\beta')$-$A_xV_2O_5$

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Abstract

Quasi-one-dimensional conductor $\beta(\beta')$-$A_xV_2O_5$ (A=Li, Na, Ag, Ca, Sr, Cu) was investigated for its electric and magnetic properties. The β-$A_{0.33}V_2O_5$ (A=Li, Na, Ag, Ca, Sr) phases show a phase transition accompanied by a charge separation and a charge order. The low temperature phase of β-$A^{+}_{0.33}V_2O_5$ shows a long-range magnetic order at lower temperature whereas β-$A^{2+}_{0.33}V_2O_5$ shows a formation of spin gap without any magnetic order. The magnetic properties of the low temperature phases strongly suggest a linear chain for β-$A^{+}_{0.33}V_2O_5$ and a two-leg ladder chain for β-$A^{2+}_{0.33}V_2O_5$ as a charge ordered pattern of magnetic V^{4+} ions. A quasi-one-dimensional conductor β'-$Cu_{0.65}V_2O_5$ shows a superconducting transition under high pressure around 4 GPa at 5 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $\beta(\beta')$-$A_xV_2O_5$; Charge order transition; Quasi-one-dimensional behavior; Electromagnetic properties

1. Introduction

Recently low dimensional vanadium oxides AV_2O_5 (A= Li, Na, Cs, Mg, Ca) have drawn much interest because of their exotic behaviors resulting from an interplay among charge, spin, orbital and lattice degrees of freedom, particularly a phase transition accompanied with a charge-order and a formation of spin-gap in NaV_2O_5 [1]. The structures of AV_2O_5 take layer types consisting of V_2O_5 layers and interlayer A-atoms. The V_2O_5 layer adopts a special framework, so-called tréllis lattice, where a ladder or one-dimensional magnetic chain is realized according to a charge-ordered manner of V^{4+} (d^1, $S=1/2$) and V^{5+} (d^0). These compounds are situated as end members of vanadium bronze oxides $A_xV_2O_5$ which appear in the intercalation of A-cations between the layers of V_2O_5.

Some alkaline or alkaline earth atoms crystallize in a monoclinic structure called $\beta(\beta')$-structure with V_2O_5. The $\beta(\beta')$ bronze is the most famous compound among the vanadium bronze oxides. The $\beta(\beta')$ bronze has a one-dimensional structure rather than a layered structure [2,3]. Fig. 1a shows a projection on the *a–c* plane in the monoclinic $\beta(\beta')$-structure. The A-cations are located in the tunnel formed by a V_2O_5-framework and occupy the A-sites in the β-structure and A′-sites in the β'-structure, respectively. The A′-sites are different from the A-sites by 1/2 in the height along the *b*-axis. In the β-structure, the A-cations cannot occupy simultaneously two nearest-neighboring A-sites in the *a–c* plane but only either site, because the two A-sites are too close. Therefore the stoichiometric composition of the β-phase is $A_{1/3}V_2O_5$ or AV_6O_{15}. On the other hand, there is not such limitation of occupation of A-cations in the β'-phase. The two A′-sites can be fully occupied and therefore the stoichiometric composition is $A_{2/3}V_2O_5$ or $A_2V_6O_{15}$. Both β- and β'-structures have a characteristic V_2O_5-framework formed by the three crystallographically independent vanadium atoms (V1, V2 and V3) and oxygen atoms. The V_2O_5-framework consists of three kinds of infinite chain along the *b*-axis and each chain is a double chain, as shown in Fig. 1b. The V1-sites have a sixfold octahedral coordination and form a zigzag chain of edge-sharing VO_6-octahedra. The V2-sites with a similar octahedral coordination form a two-leg ladder chain of corner-sharing VO_6-octahedra and the V3-sites that have a fivefold square pyramidal coordination form a zigzag chain of edge-sharing VO_5-square-pyramids. From such structural characteristics the $\beta(\beta')$-$A_xV_2O_5$ has long been known as a quasi-one-dimensional conductor [4–6]. Actually two of the authors (HY and YU) reported a clear one-dimensional conducting behavior and a metal-insulator transition in β-$A_{0.33}V_2O_5$ (A=Na, Ag) [7]. In this paper we report a charge order transition and a

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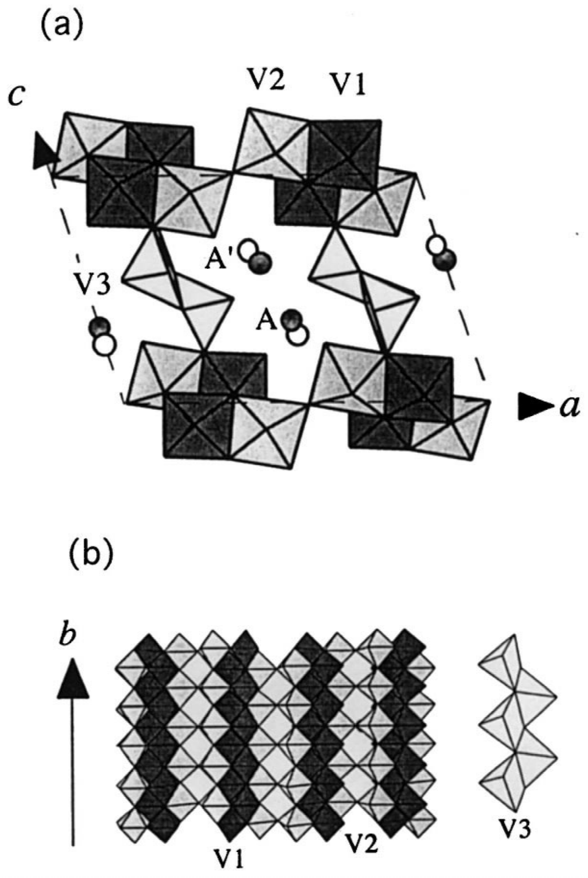

Fig. 1. (a) A schematic crystal structure of β(β′)-$A_xV_2O_5$ projected on a–c plane. V1, V2 and V3 represent crystallographically independent vanadium atoms. A and A′ are A-cation sites for β- and β′-phase, respectively. (b) Three kinds of chain formed by $(V1)O_6$, $(V2)O_6$ and $(V3)O_5$.

quasi-one-dimensional behavior as common properties in β(β′)-$A_{0.33}V_2O_5$.

2. Experimental

Powder samples were synthesized by a solid state reaction of V_2O_5, V_2O_3, and AVO_3 or $A(VO_3)_2$ for $A_xV_2O_5$ (A = Li, Na, Ag, Ca, Sr) and also CuO or Cu_2O for $Cu_xV_2O_5$ in an evacuated silica tube. AVO_3 or $A(VO_3)_2$ was prepared by a solid state reaction of V_2O_5 and A_2CO_3 or ACO_3 in air. Single crystals of $A_xV_2O_5$ (A = Li, Na, Ag and Cu) were grown by a self-flux method. The details of sample preparation were described in Refs. [7,8]. Single crystals of $A_xV_2O_5$ (A = Ca, Sr) have been unsuccessfully grown. Electrical resistivity was measured by an ordinary four-probe method with single crystals. Magnetic susceptibility and magnetization were measured using a SQUID magnetometer. NMR experiments were performed by a spin-echo method using a coherent pulsed spectrometer.

Table 1
β(β′)-$A_xV_2O_5$ investigated in this work

Compounds	V^{4+}/V^{5+}	T_t (K)	T_N (K)
β-$Li_xV_2O_5$ ($2.4 < x < 0.38$)			
β-LiV_6O_{15} ($x = 1/3$)	1/5	180	7
β-$Na_xV_2O_5$ ($0.23 < x < 0.35$)			
β-NaV_6O_{15} ($x = 1/3$)	1/5	136	24
β-$Ag_xV_2O_5$ ($0.23 < x < 0.41$)			
β-AgV_6O_{15} ($x = 1/3$)	1/5	90	24
β-$Ca_xV_2O_5$ ($0.30 \leq x < 0.34$)			
β-CaV_6O_{15} ($x = 1/3$)	2/4	150	–
β-$Sr_xV_2O_5$ ($0.30 \leq x < 0.34$)			
β-SrV_6O_{15} ($x = 1/3$)	2/4	170	–
β′-$Cu_xV_2O_5$ ($0.26 < x < 0.66$)			
β′-$Cu_{0.65}V_2O_5$	~2/4	–	$T_C = 5$ K

3. Results and discussion

The β(β′)-$A_xV_2O_5$ compounds investigated in this work are summarized in Table 1. All are mixed valent oxides of V^{4+} and V^{5+} whose ratio depends on the kind of A-cation and its composition. The stoichiometric β-compounds show some kind of phase transition at T_t as a common property, as shown in Table 1. At T_t the lattice parameters do not exhibit a significant change as shown in Fig. 2 but the phase transition is accompanied by a change of electric resistivity or specific heat [7]. The β-phase is a quasi-one-dimensional conductor with a metallic conductivity along the b-axis [7]. Fig. 3 shows the temperature dependence of electric resistivity of β-$A_{0.33}V_2O_5$ (A = Li, Na, Ag) measured along the b-axis. The resistivity changes from a metallic to semiconductive one at each T_t. Fig. 4 shows the temperature dependence of magnetic susceptibility for β-$A_{0.33}V_2O_5$ (A = Na, Ag, Ca and Sr). Na- or Ag-compound shows a slight change around T_t and a successive increase below T_t in the magnetic susceptibility, and then orders magnetically at lower temperature (T_N). On the other hand, the magnetic susceptibility for Ca- or Sr-compound has also a slight jump at T_t but below T_t it shows a low-dimensional behavior and does not show any evidence for a long-range magnetic order down to the lowest temperature. Especially the magnetic susceptibility of Sr-compound decreases to a very small value at low temperature, suggesting a spin-gap state as a ground state. The ^{51}V NMR studies confirmed a character of charge order transition at T_t. Fig. 5 shows the results of ^{51}V NMR for β-$Sr_{0.33}V_2O_5$ obtained by spin echo method with powder samples. Above T_t only one signal is observable, suggesting a uniform electronic state, while below T_t two signals can be observed. One is assigned to nonmagnetic V^{5+} sites with a very small and constant value of Knight shift and the other is due to the magnetic V^{4+} sites whose Knight shift shows a similar temperature dependence as the magnetic susceptibility. In ^{51}V NMR experiments using single crystals of β-$Na_{0.33}V_2O_5$ two signals with slightly different negative Knight shifts can be observed

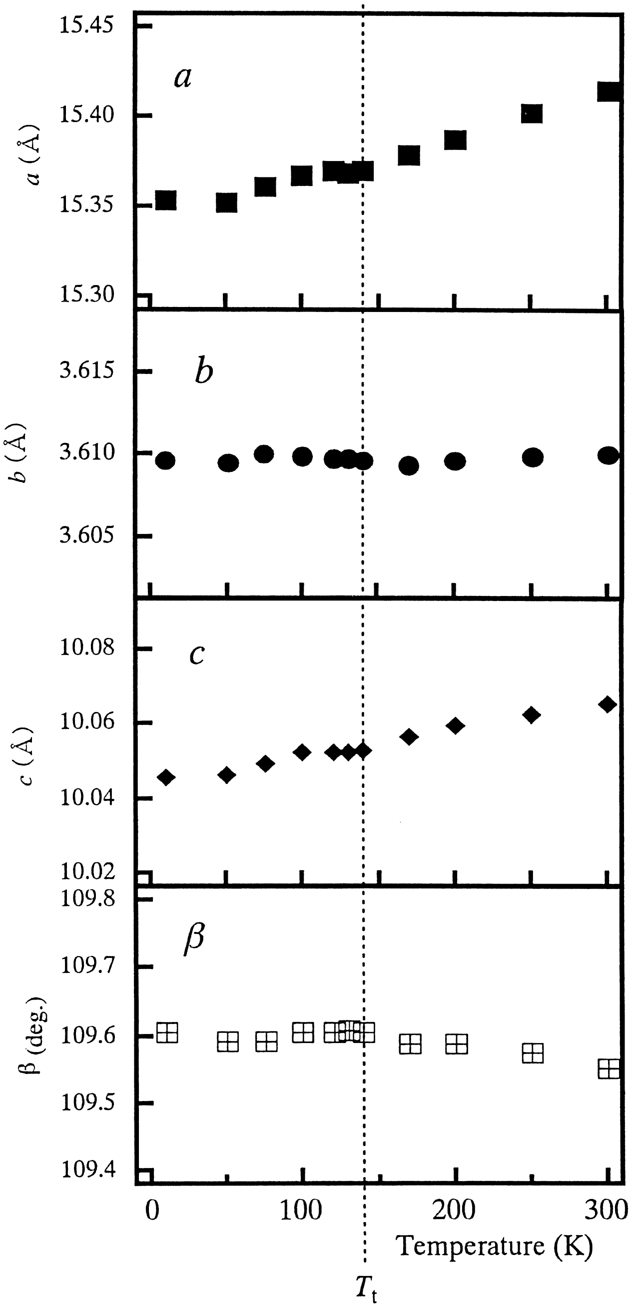

Fig. 2. Temperature dependences of lattice parameters of β-$Na_{0.33}V_2O_5$.

above T_t. From the analyses of the data, one with less Knight shift is assigned to the V3-sites and the other is to the V1- and V2-sites. Below T_t the V3-sites lose the Knight shift and the signal from the V1- and V2-sites splits into three, one of which has a large negative Knight shift and the other two have very small values of the Knight shift. Since the Knight shift corresponds to a local spin susceptibility at each site the sites with almost zero and large negative Knight shift can be regarded to be the nonmagnetic V^{5+}-sites and magnetic V^{4+}-sites, respectively. Below T_N we can observe four signals with the internal fields of 0, 16, 27 and 72 kOe in frequency-swept NMR under zero external fields [9]. The internal field of 72 kOe is a typical value for magnetic V^{4+} ions and the other three are the transferred hyperfine fields from the magnetic sites. These results indicate a rather uniform charge state above T_t and below T_t a clear charge separation and charge order. Particularly the NMR experiments with single crystals clearly show a charge transfer from the V3-sites to the V1- or V2-sites at T_t. The definite internal fields observed below T_N indicate that the magnetically ordered state is not a spin-glass like state but a long-range magnetic order.

Now we confirmed a charge separation and charge order transition at T_t in β-$A_{0.33}V_2O_5$. The magnetic properties below T_t give some information on charge-ordered manner. The compound with monovalent A^+-cation shows a maximum of magnetic susceptibility around 30 K and it orders magnetically slightly below the temperature at the maximum. On the other hand the magnetic susceptibility of the compound with divalent A^{2+}-cation has a maximum around 50 K and then decreases smoothly to a small value with decreasing temperature, suggesting a spin-singlet as a ground state. These results suggest a condensation of magnetic V^{4+} ions into one of the three V-sites, that is one of the three chains. The ratio of V^{4+} to total V ions is 1/6 in A^+-compound and 2/6 in A^{2+}-compound. In the β(β′)-structure there are three V-sites and each site forms a double chain (six chains in total), as shown in Fig. 1b. Therefore a low dimensional behavior of magnetic susceptibility cannot be expected in random distribution of magnetic V^{4+} ions into the three V-sites. When the magnetic V^{4+} ions preferably precipitate into one of the three V-sites at T_t they occupy half of the chain in A^+-compound and on the other hand fully occupy the chain in A^{2+}-compound, and as a result one-dimensional behaviors can appear in both cases. The magnetic susceptibility for A^+-compound shows a weak ferromagnetic behavior below T_N. Fig. 6 shows the magnetization curves of β-$Na_{0.33}V_2O_5$ measured along the *a*′-, *b*- and *c*-axis at 5 K. On the whole the magnetization increases almost linearly against applied field, as shown in Fig. 6a, suggesting an antiferromagnetic order. Looking at the curves in detail, however, the magnetization curve along the *b*-axis has a weak ferromagnetic component and furthermore a clear spin-flop is observed along the *a*′-axis (the direction perpendicular to the *b*–*c* plane) around 0.5 T, as clearly seen in Fig. 6b. A slight spin-flop behavior is also observed along the *c*-axis. These results indicate that the antiferromagnetic spin axis is perpendicular to the *b*-axis and parallel to the *a*-axis and it easily flops to the direction of applied field. The weak ferromagnetism originates in a spin-canting caused by Dzyaloshinsky–Moriya (DM)-interaction along the *b*-axis. A spin-canting angle can be estimated to be 0.2° from the *b*-axis. Since the DM-interaction is effective in a noncentrosymmetric relation between neighboring spins the magnetic V^{4+} ions are regarded to form a linear chain along the *b*-axis as shown

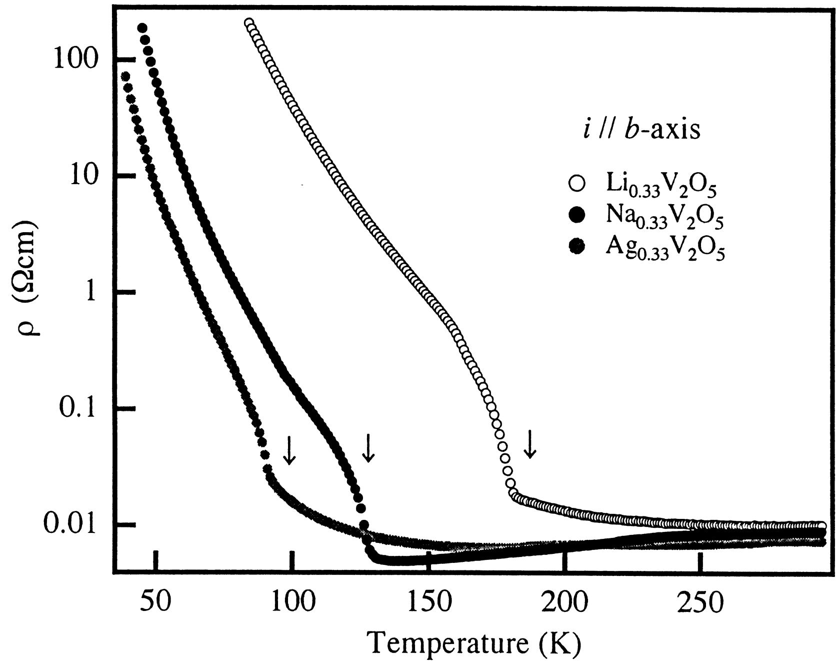

Fig. 3. Temperature dependences of electric resistivities of β-$A_{0.33}V_2O_5$ (A=Li, Na, Ag) measured along *b*-axis.

in Fig. 7a. The spin-gap behavior observed in A^{2+}-compound strongly suggests that the magnetic V^{4+} ions occupy the V2-sites to form a two-leg ladder chain as shown in Fig. 7b, because a two-leg ladder chain with $S=1/2$ is responsible for a spin-gap behavior without any help of lattice distortion.

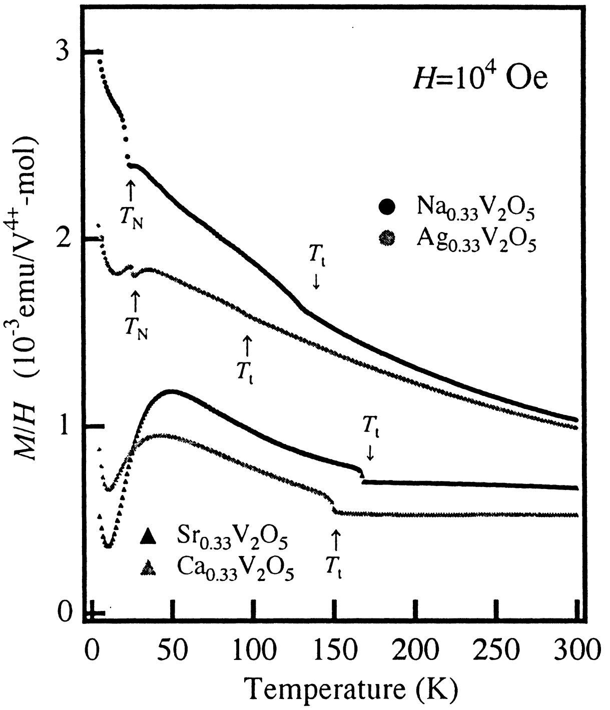

Fig. 4. Temperature dependences of magnetic susceptibilities of β-$A_{0.33}V_2O_5$ (A=Na, Ag, Ca, Sr).

Each β-compound has a wide nonstoichiometric region of A-cation, as shown in Table 1. The charge order transition is rapidly suppressed by the nonstoichiometry of A-cations and as a result the magnetic order disappears in the nonstoichiometric compounds [7]. The metallic behavior also disappears in the nonstoichiometric compounds, as reported in Ref. [7]. Therefore the β-phases show metal-insulator transitions as functions of both temperature and composition. The nonstoichiometry of A-cation results in a disorder of arrangement of A-cations, which could make metallic property unstable, particularly in a quasi-one-dimensional conductor. It also could weaken a charge-phonon coupling and suppress a charge

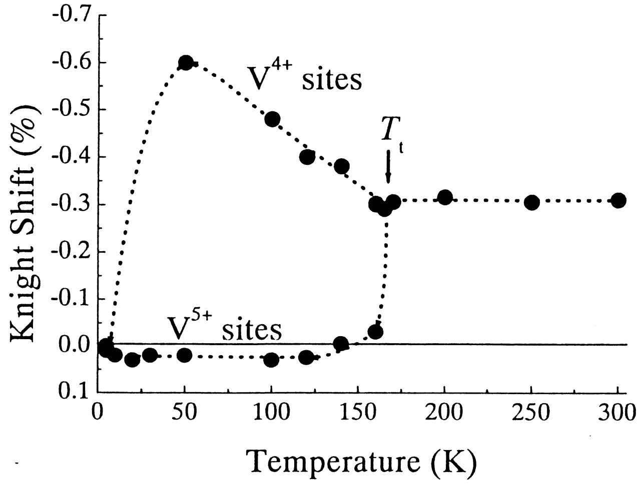

Fig. 5. Temperature dependences of ^{51}V Knight shift of β-$Sr_{0.33}V_2O_5$ measured using powder samples.

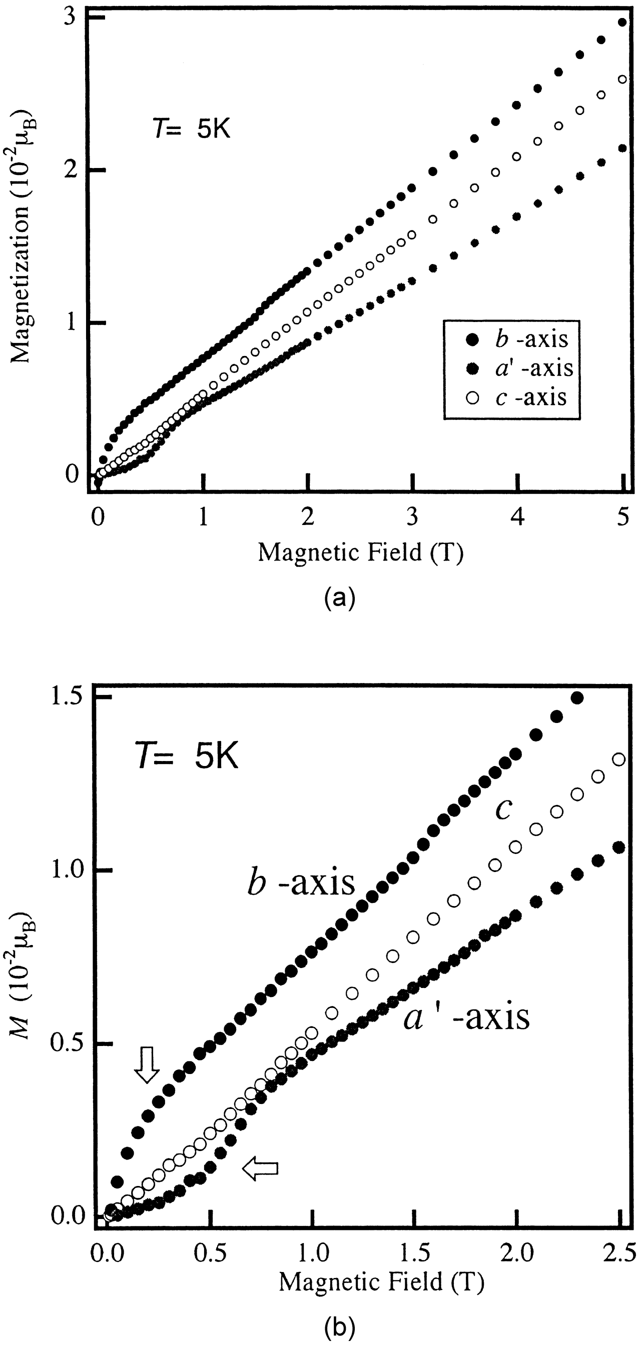

Fig. 6. Field dependences of magnetization of β-Na$_{0.33}$V$_2$O$_5$ measured along *b*-, *c*- and *a*′-axis at 5 K (a) up to 5 T and (b) up to 2.5 T.

transfer from the V3-sites to the V2- or V1-sites, and as a result the charge order transition could be suppressed.

The β'-Cu$_{0.65}$V$_2$O$_5$ is also a quasi-one-dimensional conductor but it does not show any electric or magnetic transition [8]. The stoichiometric β'-Cu$_{2/3}$V$_2$O$_5$ has been hardly synthesized in the present study. Very recently we observed a superconducting behavior in β'-Cu$_{0.65}$V$_2$O$_5$ under high-pressure around 4 GPa [10]. Beyond 5 GPa the superconducting behavior disappears. The β'-phase has a V$_2$O$_5$-framework similar to the β-phase in the structure and the mixed valent state of vanadium ions in β'-Cu$_{0.65}$V$_2$O$_5$ is close to that in β-A$^{2+}_{0.33}$V$_2$O$_5$ because the valence state of copper ions is considered to be Cu^{+}. The absence of a charge order transition in β'-Cu$_{0.65}$V$_2$O$_5$ may be due to absence of charge density in the V3-sites, that is the occupation of the V3-sites by V^{5+} ions. Actually a preliminary ^{51}V NMR experiment with single crystals of β'-Cu$_{0.65}$V$_2$O$_5$ have revealed that a signal assigned to the V3-sites has almost no shift [11]. If V^{4+} ions mainly occupy the V2-sites in β'-Cu$_{0.65}$V$_2$O$_5$ it may be regarded as a doped ladder system and therefore the observed pressure-induced superconductivity may be understood in a similar scenario in Sr(Ca)$_{14}$Cu$_{24}$O$_{41}$.

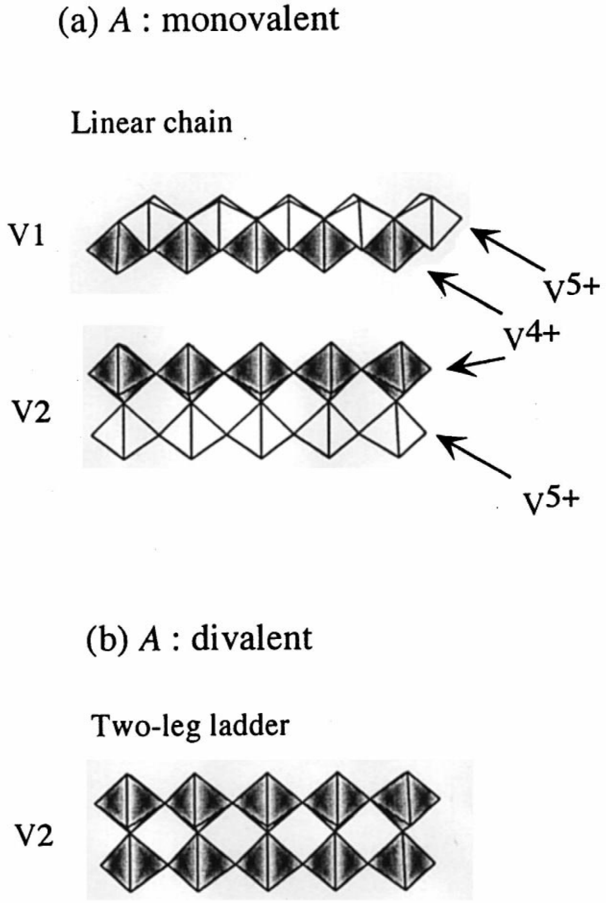

Fig. 7. Plausible charge ordered patterns for low temperature phases of (a) β-A$^{+}_{0.33}$V$_2$O$_5$ and (b) β-A$^{2+}_{0.33}$V$_2$O$_5$.

In summary, a quasi-one-dimensional conductor β-A$_{0.33}$V$_2$O$_5$ (A = Li, Na, Ag, Ca, Sr) shows a charge order transition at T_t. Above T_t the charge state is rather uniform. At T_t a charge transfer and a charge localization occur, and magnetic V^{4+} ions condense to one of the three V-sites. The low temperature phase of β-A$^{+}_{0.33}$V$_2$O$_5$ shows a long-range magnetic order at lower temperature and on the other hand that of β-A$^{2+}_{0.33}$V$_2$O$_5$ does a spin gap behavior without any magnetic order. The magnetic properties of the low temperature phases strongly suggest a linear chain for β-A$^{+}_{0.33}$V$_2$O$_5$ and a two-leg ladder chain for β-$A^{2+}_{0.33}V_2O_5$ as a charge ordered pattern of magnetic V^{4+} ions. A quasi-one-dimensional conductor β′-$Cu_{0.65}V_2O_5$ shows a superconducting transition under high-pressure around 4 GPa at 5 K.

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