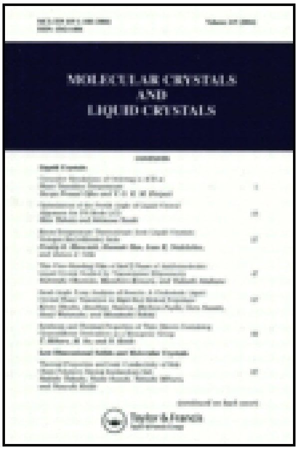

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Physical Properties of Vanadium Oxide Bronzes β-$A_{0.33}V_2O_5$ (A = Ca and Sr)

Masahiko Isobe [a] & Yutaka Ueda [a]

[a] Materials Design and Characterization Laboratory, Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo, 106-8666, Japan

Version of record first published: 27 Oct 2006

To cite this article: Masahiko Isobe & Yutaka Ueda (2000): Physical Properties of Vanadium Oxide Bronzes β-$A_{0.33}V_2O_5$ (A = Ca and Sr), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 271-276

To link to this article: http://dx.doi.org/10.1080/10587250008026152

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 271-276
Reprints available directly from the publisher
Photocopying permitted by license only

Physical Properties of Vanadium Oxide Bronzes β-$A_{0.33}V_2O_5$ (A = Ca and Sr)

MASAHIKO ISOBE and YUTAKA UEDA

Materials Design and Characterization Laboratory, Institute for Solid State Physics, The University of Tokyo, Roppongi 7–22–1, Minato-ku, Tokyo 106–8666, Japan

(In final form June 24, 1999)

The vanadium bronzes, β-$A_{0.33}V_2O_5$ (A= Ca and Sr) have been synthesized, and their electromagnetic properties investigated. They show phase transitions at 150K and 170K, respectively, accompanying with anomalies in the magnetic susceptibility and resistivity curves. These transitions are of charge order type. Below the transition temperature the magnetic susceptibility showed low dimensional behavior in both compounds, especially spin gap behavior in $Sr_{0.33}V_2O_5$. Such behavior is closely related to the crystal structure characteristic of the vanadium β-bronzes and a manner of ordering for magnetic V^{4+} ions at the transition.

Keywords: vanadium oxide bronzes; magnetic susceptibility; electric conductivity; phase transition

INTRODUCTION

The vanadate family of AV_2O_5 (A = Li, Na, Cs, Mg and Ca) has demonstrated a variety of low dimensional quantum spin phenomena of interests. We first found a spin-Peierls-like transition in NaV_2O_5[1]. The discovery of this anomalous transition triggered off extensive studies on NaV_2O_5[2-5]. At present there is a general consensus that NaV_2O_5 is converted from a quarter filled ladder to a state with charge order and spin gap in the transition. However, the mechanism of the transition has been an open question. In order to understand such a transition, it should be needed to search for other compounds which show a similar transition and investigate their structural and physical properties. Very recently, Yamada and Ueda have studied structural and electromagnetic properties of β-$A_xV_2O_5$ (A= Li, Na, Ag and Cu) in detail using single crystals, and they reported a transition accompanying with a charge order and a long range magnetic order as a ground state in β-$A_{0.33}V_2O_5$ (A= Na and Ag)[6].

The monoclinic β-phase has a characteristic V_2O_5 framework formed by edge/corner shearing VO_5 and VO_6, as shown in Fig. 1(a). There are three different sites for vanadium atoms: V1, V2 and V3. The V_2O_5 framework consists of three kinds of infinite double chains along the *b*-axis, as shown in Fig. 1(b). The V1 sites have six-fold, octahedral coordination and form a

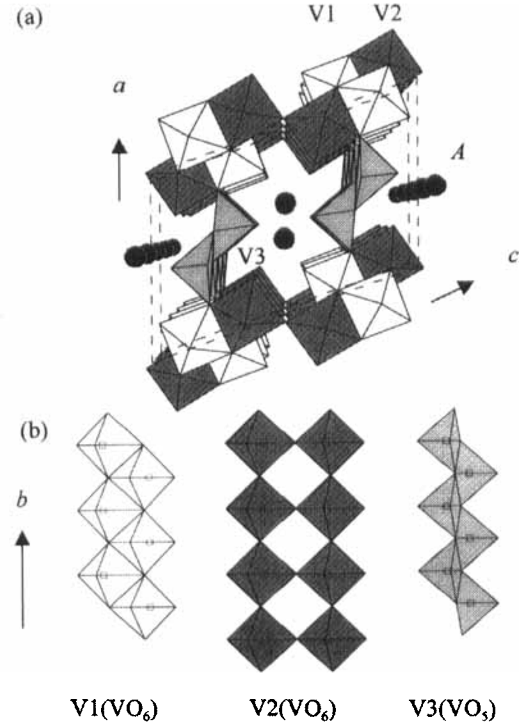

FIGURE 1 (a) Crystal structure of β-$A_{0.33}V_2O_5$ projected on the *a*-*c* plane. (b) The three types of V-chains running parallel to the *b*-axis.

zigzag chain by sharing the edges of VO_6 octahedra. The V2 sites with similar octahedral coordination form a ladder chain by sharing corners, and the V3 sites which have 5-fold square pyramidal coordination form a zigzag chain by sharing edges. A cations are located at the sites in the tunnel formed by the V_2O_5 framework. There are two equivalent sites for A, but two A sites at the same height along the b axis can not be occupied simultaneously. Therefore, the stoichiometric composition can be expressed as $A_{1/3}V_2O_5$, that is, AV_6O_{15}.

The β compounds with divalent A cations such as Ca^{2+} and Sr^{2+} were first prepared by Bouloux *et al*[7]. However, No report has been published on their electromagnetic properties up to now. We have synthesized powder samples of β-$A_{0.33}V_2O_5$ (A= Ca and Sr) and investigated their electric and magnetic properties. We observed similar transitions accompanying charge order and low dimensional behavior in the magnetic susceptibility below the transition, especially spin gap behavior in β-$Sr_{0.33}V_2O_5$. We will report the results in this paper and compare the physical properties of β-$A_{0.33}V_2O_5$ (A= Ca and Sr) with those of β-$A_{0.33}V_2O_5$ (A= Na and Ag).

EXPERIMENTAL

Powder samples of β-$Ca_{0.33}V_2O_5$ (β-$Sr_{0.33}V_2O_5$) were prepared by a solid state reaction of mixtures with an appropriate molar ratio of $Ca_2V_2O_7$ ($Sr_2V_2O_7$), V_2O_3 and V_2O_5. The weighed mixtures were pressed into pellets and heated at 650°C in an evacuated silica tube for several days with some intermediate grindings. Samples thus prepared were identified by X-ray powder diffraction (XRD) to be a single phase of the β structure. Magnetic susceptibilities were measured using a Quantum Design SQUID magnetometer. Electrical resistivities s were measured by an ordinary four-probe method.

RESULTS AND DISCUSSION

By XRD, we observed a superstructure with a lattice modulation vector $\boldsymbol{q}$ = (0, 1/2, 0) at room temperature in β-$A_{0.33}V_2O_5$ (A = Ca and Sr). This means doubling of the unit cell along the b axis. Such a superstructure was also observed in β-$A_{0.33}V_2O_5$ (A = Na and Ag) below room temperature and was caused from ordering of *A* cations along the *b* axis, that is, formation of *A*-chains where *A* cations and vacancies alternate with each other. The ordering of *A* cations has already been found in β-$A_{0.33}V_2O_5$ (*A* = Ca and Sr) at room temperature.

The magnetic susceptibility of $Sr_{0.33}V_2O_5$ showed a slight jump at around 170 K as seen in Fig. 2(a), which suggests some kind of a phase transition. Above the transition temperature (T_t) the magnetic susceptibility was almost independent of temperature, and below T_t it showed low dimensional behavior. The magnetic susceptibility of $Sr_{0.33}V_2O_5$ had a maximum around 50 K, decreased with lowering temperature and showed upturn caused by impurities or defects at low temperature. A small value of the magnetic susceptibility that is comparable to that for vanadium oxides with spin-singlet V^{4+}-V^{4+} pairs was obtained by subtracting this Curie term from the raw data of the magnetic susceptibility. No anomaly evidencing a magnetic order was observed. At the transition the lattice parameters showed a discontinus change, which suggests a first order transition. Moreover, the resistvity of $Sr_{0.33}V_2O_5$ measured by using sintered powder samples also changed from a semiconductive one above T_t to a much less conductive one below T_t. An NMR study has revealed that above T_t there exists only one kind of a V site in

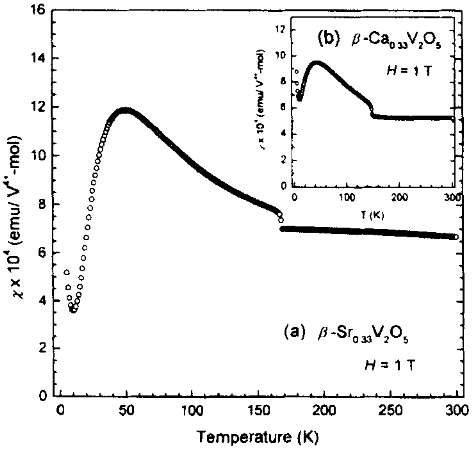

FIGURE 2 Temperature dependence of magnetic susceptibilities of β-$A_{0.33}V_2O_5$ (*A* = Ca and Sr).

the electronic state, while below T_t there exist two kinds of V sites which can be assigned to magnetic V^{4+} and nonmagnetic V^{5+} [8]. This strongly suggests a charge order transition or a charge disproportion at T_t.

$Ca_{0.33}V_2O_5$ also showed a similar phase transition at around 150 K and low dimensional behavior of the magnetic susceptibility below T_t, as shown in Fig. 2(b). The value of magnetic susceptibility at lower temperature is rather large in $Ca_{0.33}V_2O_5$ compared with that in $S_{0.33}V_2O_5$, and there is no anomaly evidencing any magnetic order. The resistivity and lattice parameters of $Ca_{0.33}V_2O_5$ showed the behavior similar to those of $S_{0.33}V_2O_5$.

We summarize the results in Table I. The β compounds with both monovalent and divalent A cations show similar charge order transitions but the behavior below T_t or the ground state is different between the A^+ and A^{2+} compounds. The A^{2+} compounds show low dimensional behavior without any magnetic order. On the other hand, the A^+ compounds show magnetic order at low temperature although they have a smaller amount of magnetic V^{4+} ions in comparison with the A^{2+} compounds.

The ratio of magnetic V^{4+} ions to nonmagnetic V^{5+} ions is 1 to 5 in the A^+ compounds and 1 to 2 (2 to 4) for the A^{2+} compounds. This difference is very suggestive when we consider the differences of the magnetic properties of both compounds in connection with their crystal structures. If the magnetic V^{4+} ions prefer only one of the three V sites, they can perfectly occupy one of the three chains in the case of A^{2+} compounds but they do only half of it in the A^+ compounds. Therefore the low dimensional character is expected to become more remarkable in the A^{2+} compounds rather than in the A^+ compounds.

TABLE I The comparison of the transition temperature (T_t) and ground state in β-$A_{0.33}V_2O_5$ (A= Na, Ag, Ca and Sr)

A	T_t	ground state
Na (1+)[6]	~ 135 K	antiferro. (T_N ~ 24 K)
Ag (1+)[6]	~ 90 K	antiferro. (T_N ~ 27 K)
Ca (2+)	~ 150 K	para. (gapless)
Sr (2+)	~ 170 K	para. (spin gap)

Actually, as described above, the Ca and Sr compounds show the low dimensional magnetic behavior below T_t; especially the Sr compound shows the spin gap behavior. Among one-dimensional magnetic systems, it is well known that a two-leg ladder system has a spin gap as a ground state. Then a possible scenario is as follows: A phase transition accompanying a charge order or charge disproportion occurs at T_t in the β-phase. At the transition, the magnetic V^{4+} ions preferably precipitate into the V2 sites in the Sr compound, and as a result the geometry of the two-leg ladder responsible for the spin gap behavior is realized. On the other hand, the magnetic V^{4+} ions occupy other sites, V1 or V3 in the Ca-compound, forming a 1-D magnetic chain, which shows neither magnetic order nor spin gap. In contrast, the magnetic chain forms insufficiently in the A^+ compounds, and a long-range magnetic order appears at low temperature.

Further investigations such as neutron scattering should be needed in order to confirm this idea. The transition in the β-phase should be compared with that in NaV_2O_5. In both compound the electronic state is uniform above T_t, and below T_t there exists clear charge differentiation. The transition is of second order in NaV_2O_5 while in the β-phase it is of first order.

CONCULUTION

The vanadium bronzes, β-$A_{0.33}V_2O_5$ (A= Ca and Sr) showed the phase transitions accompanying the charge order and low dimensional behavior in the magnetic susceptibility below the transition temperature, especially the spin gap behavior in $Sr_{0.33}V_2O_5$. Such behavior is closely related to the crystal structures characteristic of the vanadium β-bronzes and a manner of ordering for magnetic V^{4+} ions at the transition.

References

[1] M. Isobe and Y. Ueda, *J. Phys. Soc. Jpn.*, **65,** 1178 (1996).

[2] Y. Fujii *et al.*, *J. Phys. Soc. Jpn.*, **66,** 326 (1997).

[3] A. N. Vasil'ev *et al.*, *Phys. Rev. Lett.*, **81,** 1949 (1998).

[4] T. Ohama H. Yasuoka, M. Isobe, and Y. Ueda, *Phys. Rev. B*, **59,** 3299 (1999).

[5] H. Seo and H. Fukuyama, *J. Phys. Soc. Jpn.*, **67,** 2602 (1998).

[6] H. Yamada and Y. Ueda, *J. Phys. Soc. Jpn.*, to be published.

[7] J. C. Bouloux, J. Galy, and P. Hagenmuller, *Rev. Chim. Miner.*, **11,** 48 (1974).

[8] H. Yasuoka *et al.*, private communication.