Superconductivity, charge order and magnetic transitions under high pressure in vanadium bronzes

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Abstract. The electric properties of $\beta$-vanadium bronze $\beta$-Na$_{0.33}$V$_2$O$_5$ have been investigated under high pressure up to 13 GPa. The metal-insulator transition accompanied by charge order is suppressed by pressure, and the superconductivity is observed around 7 GPa and 8 K ($T_c$). The superconducting phase adjacent to the charge ordered phase suggests an important role of charge fluctuation for the superconductivity. With further increase of pressure beyond 12 GPa, the superconductivity disappears in relevance to the appearance of a nonsuperconducting new phase.

1. Introduction

The discovery of pressure-induced superconductivity in $\beta$-Na$_{0.33}$V$_2$O$_5$ has accelerated the investigation of $\beta$-vanadium bronze family, $\beta$-$A_{0.33}$V$_2$O$_5$ (A = Li$^+$, Na$^+$, Ag$^+$, Ca$^{2+}$, Sr$^{2+}$ and Pb$^{2+}$) [1]. We have performed the investigation of $\beta$-$A_{0.33}$V$_2$O$_5$ under high pressure. As the results, all $A^+$-compounds show charge order transitions under ambient pressure and pressure-induced superconductivity [2]. A striking feature is superconducting phases competing with charge ordered phases, which suggests a significant role of charge fluctuation for the superconductivity. On the other hand, $A^{2+}$-compounds have not such superconducting phase and instead have nonsuperconducting charge disordered phases [3]. These results reveal the competition among various ground states in $\beta$-vanadium bronzes.

The common monoclinic crystal structure of $\beta$-$A_{0.33}$V$_2$O$_5$ consists of a characteristic V$_2$O$_5$-framework and $A$-cations. The V$_2$O$_5$-framework is formed by sharing the corners and edges of (V1)O$_6$, (V2)O$_6$ and (V3)O$_5$ polyhedra, where V1, V2 and V3 are the three crystallographically independent vanadium atoms. Each polyhedron forms three kinds of infinite chain along the $b$-axis. The V$_2$O$_5$ framework has tunnels surrounded by the three chains. The $A$-cations occupy the tunnel sites in a manner of zigzag type below the ordering temperatures and act as electron donors, namely $\beta$-vanadium bronzes are an electron doped system into a band insulator V$_2$O$_5$ in contrast to high $T_c$ cuprates as a hole doped system to a Mott insulator. The stoichiometric composition is $A_{1/3}$V$_2$O$_5$ or $A_{0.33}$V$_2$O$_5$. Reflecting these structural characteristics, $\beta$-$A_{0.33}$V$_2$O$_5$ are quasi-one-dimensional conductors with metallic conductivity along the $b$-axis. The $\beta$-$A_{0.33}$V$_2$O$_5$ show metal-insulator (M-I) transitions with a nature of charge order except Pauli paramagnetic Pb-compound. The ground states of the insulating phases of $\beta$-$A_{0.33}$V$_2$O$_5$ are antiferromagnetic ordered states, while those of $\beta$-$A^{2+}_{0.33}$V$_2$O$_5$ ($A$ = Ca and Sr) are spin gapped states.
The previous studies were done in the pressure region up to 10 GPa by using sintered WC anvils. Major aim of this paper is to report the detailed results of $\beta$-Na$_{0.33}$V$_2$O$_5$ studied under pressure up to 13 GPa.

2. Experimental
In the present study, electrical properties of $\beta$-Na$_{0.33}$V$_2$O$_5$ were investigated in much higher pressure region up to 13 GPa, by using cubic anvil type high pressure apparatus equipped with precisely scoured sintered diamond anvils. A drop of methanol-ethanol-water (16:3:1 in volume) mixture was used as pressure medium to ensure better hydrostatic pressure above 10 GPa and to avoid damage of sample crystal. The out of the drop-like pressure medium was filled with the second pressure medium, Fluorinert, to prevent the drop of methanol-ethanol-water from evaporating during long time experiments about several weeks. Sample crystals were grown in N$_2$ atmosphere by rf-heating Czochralski method using self-flux of NaVO$_3$ in a Pt crucible. The resistivity under high pressure was measured along the $b$-axis by ordinal 4-probe method.

3. Results and discussion
The temperature dependences of resistivity ($\rho$-$T$ curves) under several pressures are represented in Fig. 1. The charge ordering temperature (M-I transition temperature) decreases as pressure increases. Near the critical pressure (7.0 GPa) where the minimum absolute values of the resistivity reach about 100 $\mu$Ωcm, a sudden upturn caused by charge order and a clear drop by superconductivity are observed in $\rho$-$T$ curves. With a slight increase of pressure from the critical pressure, the $\rho$ reaches zero resistivity within experimental resolution. A sudden upturn and a successive clear drop but nonzero resistivity in $\rho$-$T$ curve near the critical pressure can be understood as the coexistence of charge ordered phase and superconducting phase. Such coexistence behavior is not due to inhomogeneous pressure but reflects a first order transition from charge ordered insulator phase to superconducting phase.

Fig. 1. Temperature dependences of resistivity ($\rho$-$T$ curves) for $\beta$-Na$_{0.33}$V$_2$O$_5$ under several pressures up to 10 GPa. Resistivity was measured by excitation current 100 $\mu$A along the $b$-axis, quasi-one dimensional conductive direction. The metal-insulator transition is suppressed by pressure and superconducting transition (inverted triangles) is observed around 7.0 GPa.
Figure 2 shows $\rho$-$T$ curves above 10 GPa in pressure-increasing and -decreasing (9.5 GPa) processes. The pressure of 9.5 GPa was determined from the superconducting transition temperature because the calibration of pressure was impossible in pressure-decreasing process. The $\rho$-$T$ curve at 11.2 GPa clearly shows superconducting transition. By a slight increase of pressure up to 11.8 GPa, the $\rho$-$T$ curve shows no longer any superconducting behavior, and then the $\rho$-$T$ curve at 9.5 GPa shows superconducting transition again. The clear superconducting transition at 9.5 GPa in pressure-decreasing process excludes a possibility of sample damage in the run beyond 11 GPa. These results imply the appearance of new nonsuperconducting phase beyond 11.8 GPa. Such a new phase at higher pressure is consistent with the results of an optical study on $\beta$-Na$_{0.33}$V$_2$O$_5$ under high pressure at room temperature [4]. Similar behaviors have observed in $\beta$-Li$_{0.33}$V$_2$O$_5$ in much serious manner, namely $\rho$-$T$ curve shows a drop but nonzero-resistivity, suggesting that a nonsuperconducting new phase appears almost simultaneously with a superconducting phase [5].

![Figure 2](image)

*Fig. 2. The $\rho$-$T$ curves of $\beta$-Na$_{0.33}$V$_2$O$_5$ above 10 GPa in pressure-increasing and at 9.5 GPa in pressure-decreasing processes. With a slight increase of pressure from 11.2 GPa to 11.8 GPa, the superconducting transition disappears. By going back to 9.5 GPa, the superconducting transition recovers.*

We summarize the obtained results in Fig. 3 as $P$-$T$ phase diagram. The charge order transition (M-I transition) is suppressed under high pressure and the superconducting state appears when the charge order melts. The superconducting phase is adjacent to the charge ordered phase. This suggests an important role of charge fluctuation for the superconductivity. On the other hand, the recent NMR study suggests that the antiferromagnetic state survives up to at least 6 GPa and therefore spin fluctuation also may play a role for the superconductivity. The present study reveals that a nonsuperconducting new phase exists in the higher pressure region above the critical pressure. The presence/absence of superconducting phase in $\beta$-A$_{0.33}$V$_2$O$_5$ could be closely related to such new phases. The superconductivity blooms in such competition among various ground states.
Fig. 3. Pressure-temperature ($P$-$T$) phase diagram of $\beta$-$\text{Na}_{0.33}\text{V}_2\text{O}_5$. CDO: charge disordered normal metallic phase, CO: charge ordered insulating phase, SC: superconducting phase, NSC: nonsuperconducting new phase.

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