# Pressure-Induced Superconductivity in $\beta$-$Na_{0.33}V_2O_5$ beyond Charge Ordering

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We report the discovery of a new superconducting phase in highly correlated $3d$ electron systems. The compound is $\beta$-vanadium bronze, $\beta$-$Na_{0.33}V_2O_5$, in which the charge-ordered phase collapses under hydrostatic high pressure and a pressure-induced superconducting phase appears around $T_{SC} = 8$ K, $P = 8$ GPa. This report presents the first observation not only of superconductivity in vanadium oxides but also of a phase transition from charge ordered to superconducting on a pressure-temperature ($P$-$T$) plane. The phase diagrams seem to have universal aspects across the classes of materials. This indicates a profound physics of superconductivity in highly correlated electron systems.

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Competition among ground states in a many-body electron system is a central problem in condensed matter physics. Such competition is described as a phase diagram in the space of thermodynamic parameters. A particularly dramatic example of a ground state is the large-scale quantum phenomenon of superconductivity. Several exotic phase diagrams, including a superconducting phase, have been observed in various systems, such as organic conductors, $4f/5f$ intermetallic alloys, and high-$T_C$ superconducting (HTSC) cuprates [1–4]. Exotic behaviors of them imply the possibility of a new mechanism of superconductivity beyond that explained by the BCS theory [5]. A new mechanism of superconductivity has been argued for several classes of materials above. A key term to describe the electronic nature of these compounds is high electron correlation, that is, the Coulomb interaction between carriers, which is ignored in the conventional physics of metals. As a good contrast to the HTSC cuprate, vanadium oxides have been investigated because they are highly correlated $3d^1$ electron (half-spin) systems in which the quantum fluctuation of the spin or charge is enhanced as well as it is by HTSC cuprates [6,7]. However, superconductivity has never been reported in metallic vanadium oxides. Many of these oxides show metal-insulator transitions (MIT) as decreasing temperature, accompanying charge ordering, namely, the oxides ground states are charge-ordered phases.

Recently, a quasi-one-dimensional (quasi-1D) metallic behavior and MIT accompanying charge ordering were reported in $\beta$-vanadium bronzes [8]. These compounds are represented as $\beta$-$A_XV_2O_5$ ($A =$ Li, Na, Ag, Ca, Sr, and Pb) and are mixed-valent oxides with $V^{4+}$ ($3d^1$) and $V^{5+}$ ($3d^0$). The stoichiometric composition in $\beta$-$A_xV_2O_5$ is $x = 1/3$ ($x = 0.33$). The monoclinic crystal structure is schematically illustrated in Fig. 1. $\beta$-$Na_{0.33}V_2O_5$ shows the MIT at $T_{CO} = 135$ K and, at the lower temperature $T_N = 25$ K, the antiferromagnetic (AF) ordered phase appears as the ground state of the insulating phase [8,9]. We note that this MIT is not a $2k_f$-CDW (charge density wave) or an SDW (spin density wave) transition, because a $2k_f$-CDW transition requires a spin singlet ground state [10] and because in SDW transitions a paramagnetic insulator phase does not exist below $T_{MI}$ [11].

The charge ordering at the MIT was first reported in a $^{51}V$ nuclear magnetic resonance (NMR) study [9] that revealed a rather uniform charge state above 135 K (the metallic phase), and both charge separation and charge ordering below 135 K (the insulating phase). In three vanadium sites (V1, V2, and V3; see the caption for Fig. 1), the Knight shifts indicate that the charge state of V3 becomes $V^{5+}$-like while those of V1 and V2 separate into $V^{5+}$-like and $V^{4+}$-like states. The evidence for the much clearer charge separation into $V^{4+}$ and $V^{5+}$ states was obtained from NMR in the AF phase below 25 K. Itoh *et al.* observed both the magnetic sites with internal fields of about 72 kOe, which is a typical value for $V^{4+}$, and nonmagnetic $V^{5+}$ sites with small internal fields that are hyperfine fields transferred from the magnetic $V^{4+}$ sites. On the other hand, an x-ray diffraction study has revealed an appearance of 6 times periodicity along the $b$ axis below 135 K [12]. The same 6-times periodicity was observed in the AF phase in both neutron magnetic diffraction and x-ray diffraction [13]. These results strongly support the occurrence of charge ordering in the insulating phase. We are now constructing a charge-ordered manner from the analysis of x-ray and neutron diffraction data. Our high-pressure experiments have been motivated by an interest in identifying the ground state that appears beyond the charge-ordered phase.

A high-quality crystal of $\beta$-$Na_{0.33}V_2O_5$ has been grown by the rf heating Czochralski method [14]. Using $NaVO_3$ as a solvent in a Pt crucible, we succeeded in growing centimeter-size single crystals. In high-pressure experiments, submillimeter crystals were prepared by cutting from a large crystal. We confirmed the excellent quality of the crystals used in the high-pressure experiments by

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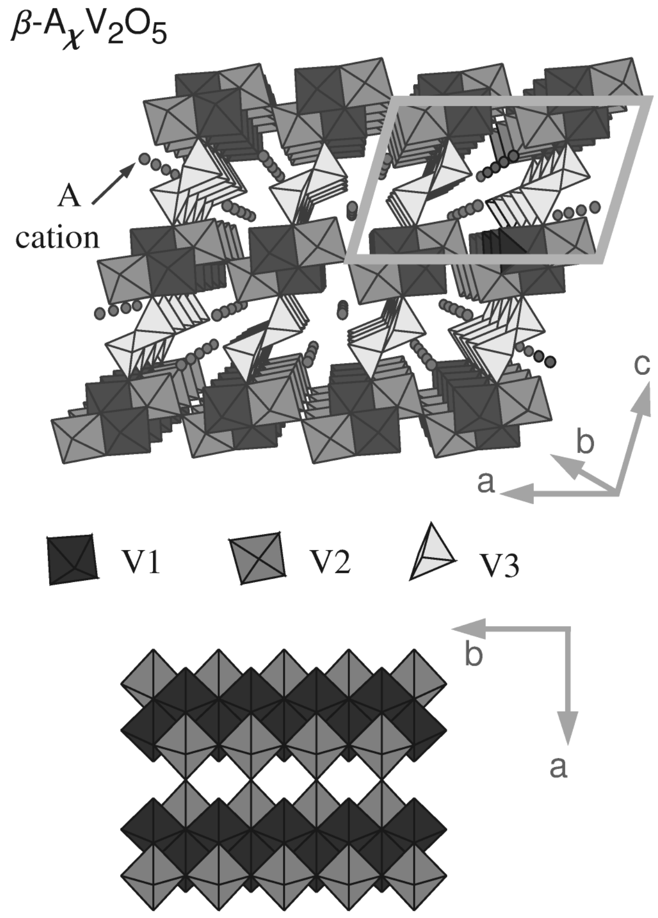

FIG. 1. The crystal structure of $\beta$-$A_XV_2O_5$. The $V_2O_5$ framework consists of three crystallographically independent vanadium atoms (V1, V2, and V3) and oxygen atoms, which are illustrated as chromatically different $VO_5$ pyramids and $VO_6$ octahedra. This framework has tunnels along the *b* axis, and *A* cations are aligned in this tunnel. At the stoichiometric composition $x = 1/3$, the ratio of $V^{4+}/V$ ions is 1/6 in the case of $A^+$ cations and is 1/3 in $A^{2+}$ cations. The stoichiometric composition $x = 0.33$ (1/3) is a singularity point where the system shows metallic behaviors. The slight nonstoichiometry (even if $x = 0.32$ or 0.34) of *A* cations spoils its quasi-1D metallic property. This means that the 1D electronic state on the $V_2O_5$ framework is very sensitive to imperfection in the Na ion array in the tunnels along the *b* axis, probably since the Anderson localization is not negligible in a 1D system.

various methods: electron-probe-microanalysis/scanning electron microscopy, NMR, powder and single-crystal x-ray diffraction (XRD). In the XRD measurements, the crystals included no detectable amounts of impurities. The stoichiometry of the crystals was checked by measuring magnetic susceptibility and resistivity, as a previous study found the electromagnetic properties highly sensitive to stoichiometry [8].

We used a cubic-anvil-type apparatus to apply hydrostatic pressure of up to 9 GPa. This apparatus is suitable for the observation of electrical properties of very frangible crystal under high pressure. We also used a pressure medium, composed of fluorinate and a methanol-ethanol mixture, to improve the hydrostatic pressure.

We measured resistivity along the *b* axis by a standard dc four-probe method under high pressure. Figure 2 exhibits the resistivity measured as a function of temperature under various high pressures. At ambient pressure, the resistivity increases slightly with cooling below room temperature, and suddenly jumps at $T_{CO} = 135$ K. As the pressure increases, the $T_{CO}$ shifts to low temperature, and finally the resistivity drops sharply at 8 GPa and 8 K. The

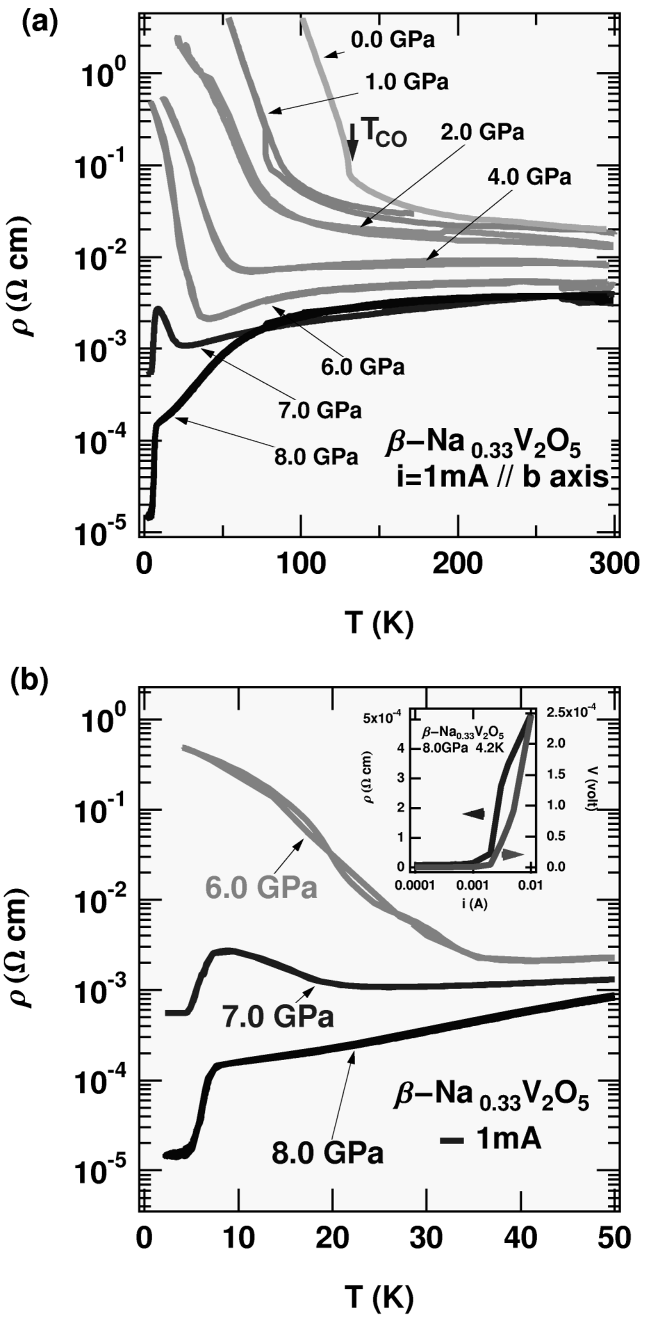

FIG. 2. Temperature dependence of resistivity under high pressures. (a) An overall range view. (b) A macrograph of the low-temperature region below 50 K. The inset in the lower panel exhibits a current-voltage curve at 4.2 K, 8.0 GPa.

resistivity at 8 GPa and 6 K is nearly zero within our experimental resolution of $\sim$10 nV for the voltage detection. This suggests strongly a superconducting state.

The resistivity measured at 7.0 GPa shows a peculiar temperature dependence: an upturn below 20 K and a drop at 9 K. Below 6.0 K, the resistivity reaches a constant value of about $6 \times 10^{-3}$ ($\Omega$ cm), as shown in Fig. 2(b). This suggests that the offset of the superconducting transition is 6.0 K at 7.0 GPa. This finite residual resistivity at low temperature might be due to a coexistence of superconducting and charge-ordered phases (granular superconductivity) at the boundary between those phases. Empirically, a granular superconductivity might show nonzero resistivity. Two explanations are possible for the coexistence of these two phases. One is the intrinsic phase coexistence in the equilibrium state (a first-order transition) and the other is the extrinsic one caused by inhomogeneity of pressure within the cell. At present, we cannot conclude which of these explanations is more likely.

In order to obtain further evidence of superconductivity, ac susceptibility was measured under high pressure using a pair of inductive coupled coils via a sample crystal. The experimental method is schematically illustrated in the inset of Fig. 3. In these experiments, using a lock-in amplifier, we observed a change in mutual inductance between a primary and a secondary coil. Here we note that capacitance should not change in changing temperature; that is, the observed change in mutual inductance should be attributed directly to the change in the sample's ac susceptibility. We also measured a change in mutual inductance around a superconducting transition of Pb metal using two coils, which were geometrically the same, as the inset of Fig. 3 also shows. The data were applied to calculate the superconducting volume fraction of the sample.

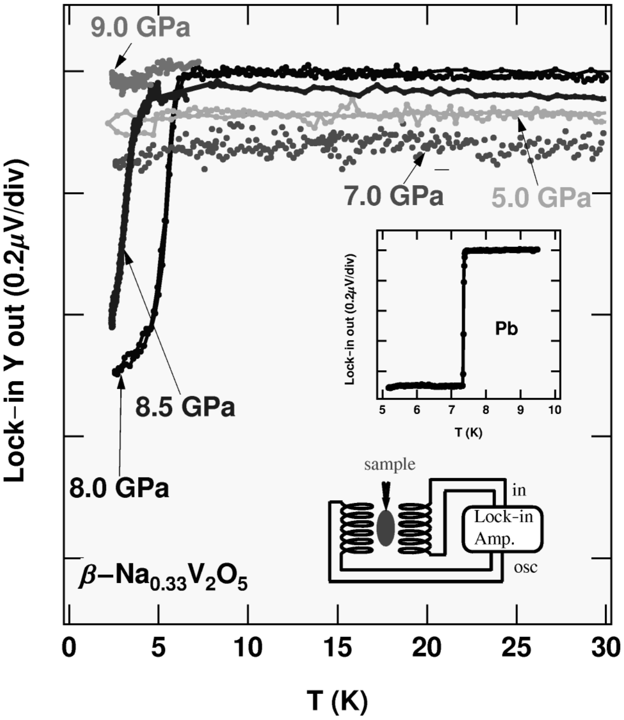

FIG. 3. Temperature dependence of ac susceptibility under high pressures. Drops in ac susceptibility under several pressures show the shielding effect of a superconducting transition. The insets show a shielding signal of Pb metal as a reference and a schematic view of the measurement method.

The ac susceptibility measurements ($\omega \sim 534$ Hz) under high pressures are shown in Fig. 3. The figure shows the temperature dependence of inductance (lock-in output) which corresponds to the real part of ac susceptibility. We observed a sharp drop in ac susceptibility at 6 K and 8.0 GPa. This shows the shielding that accompanies a transition to superconducting. From a simple proportional calculation (assuming that Pb metal has a 100% superconducting volume fraction), the superconducting volume fraction is estimated to be about 70%, high enough to confirm the superconductivity of this compound. Consequently, these ac susceptibility measurements, combined with the resistivity measurements, proved the pressure-induced superconductivity in $\beta$-Na$_{0.33}$V$_2$O$_5$. Further compression, beyond 8.0 GPa, decreases the superconducting transition temperature $T_{\mathrm{SC}}$, as shown in Fig. 3 (4 K at 8.5 GPa). At 9.0 GPa, $T_{\mathrm{SC}}$ falls below 2.0 K, the lowest temperature of this apparatus.

The disagreement between the onset temperature of resistivity (8 K) and that of ac susceptibility (6 K), as measured at 8 GPa, is a behavior seen often in oxide superconductors. It has been reported [15,16] that the onset of susceptibility coincides with the offset of resistivity. The absence of shielding at 7 GPa in ac susceptibility measurements may be due to a granular superconducting property.

The results are summarized in Fig. 4, a pressure-temperature ($P$-$T$) phase diagram. In this diagram, we also plotted the AF transition temperature $T_N$, which was determined from the dc magnetic susceptibility measurements by using a SQUID magnetometer equipped with a handmade pressure cell, available up to 1 GPa [17]. The $T_{\mathrm{CO}}$ decreases, while the $T_N$ increases with increasing pressure. A remarkable feature is the appearance of the superconducting phase at the critical point where the charge-ordered phase collapses under high pressure. This is the first observation of a phase transition from charge ordering to superconducting on a $P$-$T$ plane. This is also the first observation of superconductivity in vanadium oxides.

Recently it has been elucidated that various ground states compete with each other and considerably change in thermodynamic parameters such as magnetic field and pressure. For instance, the superconducting phases that compete with either the CDW/SDW or magnetic-ordered phase have been discovered in (TMTSF)$_2$PF$_6$ [1] ($\pi$-electron system) or CeCu$_2$Ge$_2$ [2] and UGe$_2$ [3] ($f$-electron system), respectively.

The obtained electronic phase diagram of $\beta$-Na$_{0.33}$V$_2$O$_5$ is similar to the diagrams of these other systems. There is,

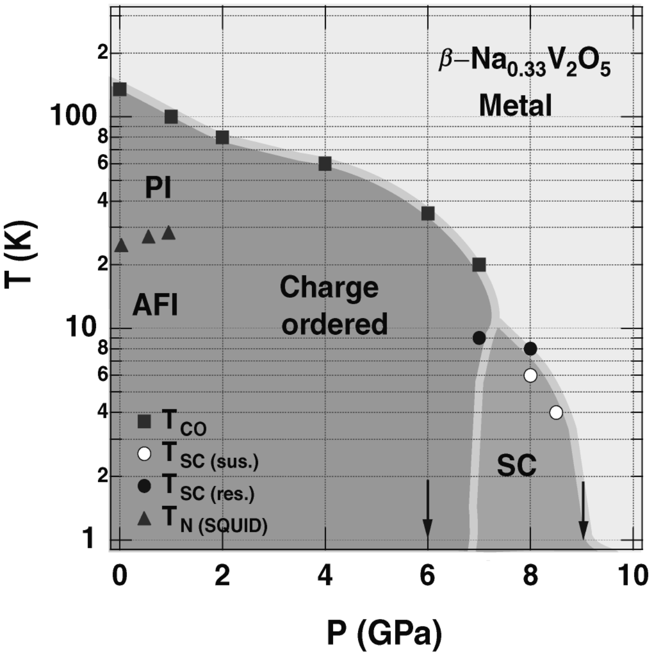

FIG. 4. The pressure-temperature (*P-T*) phase diagram of $\beta$-$Na_{0.33}V_2O_5$. $T_N$ (filled triangle) AF transition temperature, $T_{CO}$ (filled square) charge-ordering temperature, $T_{SC}$ (circle) superconducting transition temperature. The filled and blank symbols of $T_{SC}$ represent the onset temperature in resistivity and ac susceptibility measurements, respectively.

however, a significant difference between $\beta$-$Na_{0.33}V_2O_5$ and other systems. The $\beta$-$Na_{0.33}V_2O_5$ has a charge-ordered phase instead of an SDW phase in $(TMTSF)_2PF_6$, or instead of magnetic-ordered metallic phases in $CeCu_2Ge_2$ and $UGe_2$. This implies an important role for charge fluctuation in the superconductivity of $\beta$-$Na_{0.33}V_2O_5$, as opposed to spin fluctuation in $(TMTSF)_2PF_6$, $CeCu_2Ge_2$ and $UGe_2$. The insulating phase (charge-ordered phase) orders antiferromagnetically at 25 K in ambient pressure. Unfortunately, we could not determine whether the charge-ordered phase adjacent to the superconducting phase is antiferromagnetic or paramagnetic, because we have no apparatus precise enough to allow observation of the AF transition under high pressure, i.e., above 1 GPa. The phase diagram we obtained, however, does not exclude a role for spin correlation in superconductivity, because the pressure dependence of $T_N$ suggests the possibility of the Néel ordered state adjacent to the superconducting phase.

In spite of the differences between the present system and $\pi$-electron/$f$-electron systems, we emphasize the existence of a feature common to all classes of materials in the electronic phase diagrams. That feature is superconductivity near the transition of charge localization/delocalization. The 3*d* transition metal oxides that include high-$T_C$ cuprate superconductors constitute one of the main stages for highly correlated 3*d* electron systems. However, no *P-T* phase diagram with such a feature has ever been reported in them. $\beta$-$Na_{0.33}V_2O_5$ is the first 3*d* transition metal oxide found to have a characteristic *P-T* phase diagram in common with organic conductors and $4f/5f$ intermetallic compounds. There are many isostructural compounds in $\beta$-vanadium bronzes. The presence or absence of superconductivity under high pressure is a very interesting subject for the future.

In conclusion, we surveyed the electromagnetic properties of $\beta$-$Na_{0.33}V_2O_5$ under high pressures of up to 9 GPa, and we discovered a superconducting phase beyond the charge-ordered (paramagnetic or antiferromagnetic) phase. This is the first observation of a superconducting phase in vanadium oxides classified as highly correlated 3*d* electron systems. From this work, we obtained an electronic phase diagram for the *P-T* plane that looks similar to the diagrams for organic and/or heavy fermion pressure-induced superconducting compounds. We note that this work is the first observation of such a phase diagram in transition metal oxides.

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