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Superconductivity in anti-post-perovskite vanadium compounds

Bosen Wang & Kenya Ohgushi

Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.

Correspondence and requests for materials should be addressed to B.W. (bswang@issp.u-tokyo.ac.jp) or K.O. (ohgushi@issp.u-tokyo.ac.jp)

**Superconductivity, which is a quantum state induced by spontaneous gauge symmetry breaking, frequently emerges in low-dimensional materials. Hence, low dimensionality has long been considered as necessary to achieve high superconducting transition temperatures (T_C). The recently discovered post-perovskite (ppv) $MgSiO_3$, which constitutes the Earth's lowermost mantle (D'' layer), has attracted significant research interest due to its importance in geoscience. The ppv structure has a peculiar two-dimensional character and is expected to be a good platform for superconductivity. However, hereunto, no superconductivity has been observed in isostructural materials, despite extensive investigation. Here, we report the discovery of superconductivity with a maximum T_C of 5.6 K in V_3PnN_x (Pn = P, As) phases with the anti-ppv structure, where the anion and cation positions are reversed with respect to the ppv structure. This discovery stimulates further explorations of new superconducting materials with ppv and anti-ppv structures.**

S ince the discovery of high-T_C superconductivity in cuprates with the layered-perovskite (pv) structure[1], extensive effort has been devoted to finding other superconducting materials. After a quarter century of investigation, many layered superconducting families have been discovered, such as a ruthenate Sr_2RuO_4[2], boride MgB_2[3], hafnium nitride chloride[4], cobaltate $Na_xCoO_2 \cdot yH_2O$[5], an intercalated graphite C_6Ca[6], a chalcogenide Cu_xTiSe_2[7], and iron-based pnictides and chalcogenides[8,9]. The layered characteristics of the host crystal structures are widely believed to be essential in producing superconductivity due to the anisotropic electronic structures. This provides an important reference for the design of superconducting materials and the exploration of new mechanisms for superconductivity[1,2,4–6]. Recently, the ppv transition of $MgSiO_3$ was discovered using a laser-heated diamond anvil cell[10,11]. Consequently, this phase has received more attention because it is considered to be the main constitute of the Earth's lowermost mantle (D'' layer, *ca.* 2700–2900 km deep) (Fig. 1a). The ppv crystal structure is comprised of alternately-stacked SiO_6 octahedra and Mg atoms along the *b* axis and it has typical two-dimensional characteristics. This has motivated research into the physical phenomena of this phase, including superconductivity. However, ppv-$MgSiO_3$ is stable only under extreme conditions (120 GPa and 2200°C)[12] and is unquenchable to ambient pressure, which has restricted further research into chemical substitution and carrier doping of the structure. Therefore, there have been attempts to establish analogue materials that are stable under ambient conditions. Almost 20 ppv-type compounds have been identified to date, including the $MgGeO_3$, $NaIrO_3$, and $CaBO_3$ (B = Ru, Rh, Sn, Ir, and Pt) oxides, $Na(Mg,Zn)F_3$ fluorides and $(U,Th)MnSe_3$ chalcogenides[13–19]. As with perovskite-type materials, many interesting physical phenomena have been observed in ppv-type materials, such as metal-insulator phase transition[13] and low-dimensional magnetism[17]. However, no superconductivity has been reported so far for the ppv family, because most compounds with ppv structure are Mott insulators owing to the strong electron correlation effect.

In this letter, we report the observation of superconductivity in V_3PnN_x (Pn = P, As). These compounds crystallize in the filled Re_3B structure with the orthorhombic Cmcm (#63) space group, as depicted in Fig. 1b[20]. The positions occupied by the anions and cations are opposite to those of the ppv structure. Considering also the nomenclature of the anti-pv structure[21,22], we call this structure the anti-ppv structure (see crystal structure details in Section I of the Supplementary Information). The anti-ppv-type V_3PnN_x is composed of alternately-stacked NV_6 octahedral layers and PnV_8 bicapped trigonal prisms layers along the *b* axis, which gives rise to quasi-two-dimensional electronic states. Within the *ac*-plane, NV_6 octahedra are connected by edge sharing along the *a* axis and corner sharing along the *c* axis[20]. Here, we also notice that V-V metallic bonds play the key role in stabilizing this structure[20].

Results

Figure 2a presents the electrical resistivity (ρ) of V_3PnN_x (Pn = P, As) as a function of temperature (T). The room temperature resistivities ρ_{300K}, are approximately 340 and 240 $\mu\Omega$ cm for V_3PN and V_3AsN, respectively. ρ
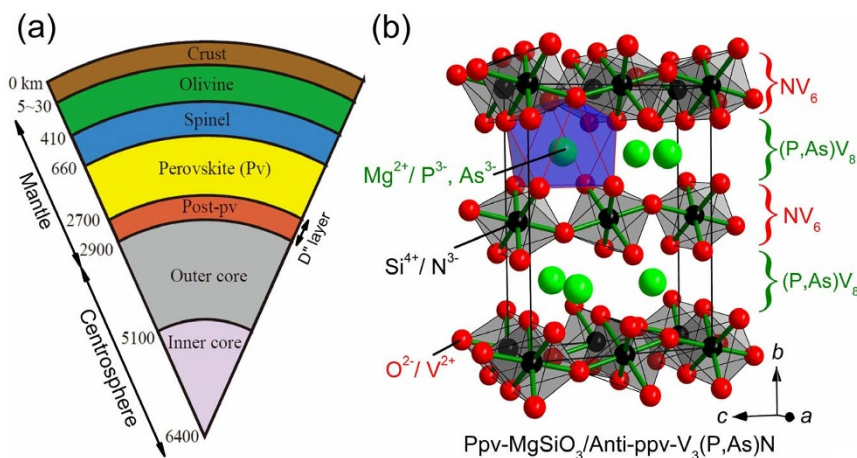
Figure 1 | Schematic illustration of Earth's interior and crystal structures of ppv-MgSiO$_3$/anti-ppv-V$_3$PnN. (a) The outermost solid shell is the crust composed of a variety of rocks. The mantle below the crust has layer structures corresponding to the structural transition induced by pressure in Mg-Si-O system. The lowermost layer is called the D'' layer, where the main constitute is the ppv-type silicate. The outer and inner cores below the mantle consist of liquid and solid iron alloys, respectively. (b) Crystal structure of ppv-MgSiO$_3$ and anti-ppv-V$_3$PnN (Pn = P, As) with the Cmcm (#63) space group. Solid lines represent a unit cell. The anti-ppv structure has layer structures composed of NV$_6$ octahedra and PnV$_8$ polyhedra.

decreases gradually with cooling (metallic behaviour) and drops sharply to zero at T_C = 4.2 and 2.6 K for V$_3$PN and V$_3$AsN (Fig. 2c), respectively, which indicates the appearance of superconductivity. The width of the transition temperature is narrow (ca. 0.3 K), which implies good sample quality. Figure 2d presents the magnetic susceptibility (M/H) under zero-field cooling (ZFC) and field cooling (FC) conditions at H = 10 Oe. The superconducting volume fraction estimated from ZFC data at 1.8 K are approximately 190 and 167% for V$_3$PN and V$_3$AsN, respectively. The volume fractions exceeding 100% is attributable to the polycrystalline nature of samples. The specific heat shown in Fig. 2e has a sudden increase around T_C. These results provide unambiguous evidence for the bulk superconductivity in V$_3$PnN (Pn = P, As).

Detailed measurements of the field-dependent resistivity and magnetization presented in Figs. 3a–f allow for better characterization of the superconducting state. The H-dependence of ρ (Figs. 3a–c) gives the upper critical field H_{C2}, as shown in Fig. 3g. There is another weak

transition above H_{C2} that originates from a small amount of the VN$_x$ impurity phase, as shown in Fig. S1(a). Close to T_C, H_{C2} is linearly dependent on T in accordance with the Werthamer-Helfand-Hohenberg theory[23]. Using the formula $H_{C2}(0) = -0.693T_C dH_{C2}/dT$ provided H_{C2} at the ground state; $H_{C2}(0)$ = 34.9 and 27.9 kOe was obtained for V$_3$PN and V$_3$AsN, respectively. According to the Bardeen-Copper-Schrieffer (BCS) theory[24], the H_{C2} value is related to the coherent length ξ, as $H_{C2} = \Phi_0/2\pi\xi^2$ (where Φ_0 is the magnetic flux quantum). Using this formula, ξ = 9.7 and 10.9 nm are obtained for V$_3$PN and V$_3$AsN, respectively. The magnetization isotherms at 1.8 K exhibit typical type-II superconductor behaviour (insets of Figs. 3d, 3f). The lower critical field H_{C1} was determined from the magnetic field, where the magnetization departs from the linear H-dependence (indicated by arrows in Figs. 3d, 3f). The temperature dependence of H_{C1} is well fitted with the empirical function $H_{C1}(T)$ = $H_{C1}(0)[1 - \alpha(T/T_C)^2]$ (where α is the fitting parameter), and the lower critical fields obtained at the ground state are $H_{C1}(0)$ = 207 and
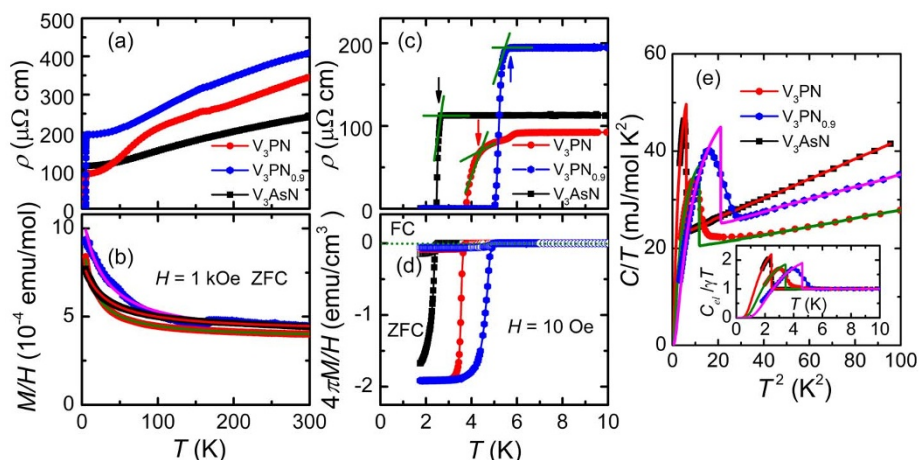

Figure 2 | Evidence for bulk superconductivity in V$_3$PnN (Pn = P, As). (a) Temperature (T) dependent resistivity (ρ) at zero magnetic field (H). (b) DC susceptibility (M/H) curve under the ZFC condition at H = 1 kOe. Solid lines indicate fitting results (see text). (c) Enlargement of low-temperature resistivity data. Arrows indicate the superconducting transition temperature (T_C). (d) Low-temperature M/H-T curve under ZFC and FC conditions at H = 10 Oe. (e) Temperature dependence of specific heat (C/T) at zero magnetic field. Solid lines indicate fitting with $C = \gamma T + \beta T^3$ in the normal state and the function based on the BCS model in the superconducting state. Inset shows the $C_{el}/\gamma T_C$ value, where C_{el} is the electron contribution of the specific heat. The solid curve is calculated from the BCS model with an isotropic gap.
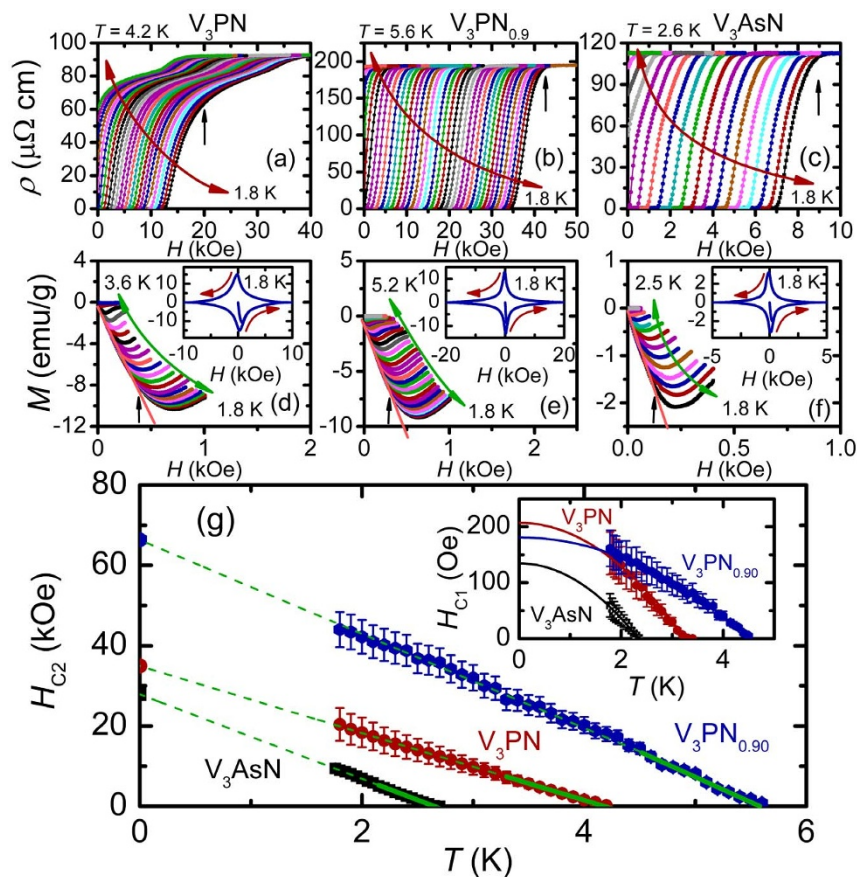
Figure 3 | Characterization of the superconductivity in V$_3$PnN (Pn = P, As). Magnetic field (H) dependence of (a–c) resistivity (ρ) and (d–f) magnetization (M) at fixed temperatures. Arrows in (a–c) indicate the upper critical field (H$_{C2}$) at 1.8 K. There is another weak transition above H$_{C2}$ that originates from a small amount of the VN$_x$ impurity phase, as shown in Fig. S1(a). Arrows in Figs. (d–f) indicate the lower critical field (H$_{C1}$), where M departs from the linear H-dependence. Insets in (d–f) are magnetization isotherms at 1.8 K over a wider H range. (g) Temperature (T) dependence of the upper and lower critical fields (H$_{C2}$ and H$_{C1}$). Solid lines indicate fitting results (see text).

134 Oe for V$_3$PN and V$_3$AsN, respectively (inset of Fig. 3g). The London penetration depths λ_L, and the Ginzburg-Landau parameters κ are estimated from the formula $H_{C2}/H_{C1} = 2\kappa^2/\ln\kappa$ with $\kappa = \lambda_L/\xi$ to be $\lambda_L = 157$ and 187 nm and $\kappa = 16.2$ and 17.2 for V$_3$PN and V$_3$AsN, respectively.

The appearance of superconductivity in both Pn = P and As compounds, as well as N-deficient systems (Fig. 4), indicate that the V-3d electrons are predominantly responsible for the emergence of superconductivity. The specific heat was closely examined to reveal bosons that act as the glue for Cooper pairs. The specific heat at the normal state can be well fitted using the function $C = \gamma T + \beta T^3$ (Fig. 2e), where the former and latter terms represent the electron and phonon contributions, respectively. We estimated $\gamma = 19.5$ and 22.0 mJ/mol K^2, and $\beta = 0.083$ and 0.20 mJ/mol K^4 for V$_3$PN and V$_3$AsN, respectively. The $\Delta C/\gamma T_C$ value (inset of Fig. 2e), where ΔC is the specific heat jump at T_C, is approximately 0.86 and 1.22 for V$_3$PN and V$_3$AsN, respectively. These values are slightly smaller than 1.43 expected for a typical BCS superconductor with a weak-coupling limit, which implies that the electron-phonon coupling is the glue for the Cooper pairs[24,25]. The Debye temperature was estimated to be $\theta_D = 489$ and 364 K for V$_3$PN and V$_3$AsN, respectively, using the relationship $\beta = 12\pi^4 NR/5\theta_D^3$ (where N is the number of atoms in a formula unit, 5, and R is the gas constant). It is worth noting that θ_D for V$_3$PN is larger than that for V$_3$AsN, because materials with smaller mass exhibit harder phonons. From the McMillan formula, $T_C = (\theta_D/1.45) \exp \{-1.04(1 + \lambda_{ph})/[\lambda_{ph} - \mu^*(1 + 0.62\lambda_{ph})]\}^{26}$, together with the assumption of the Coulomb pseudopotential $\mu^* = 0.15$, the electron-phonon coupling constants can be estimated as $\lambda_{ph} = 0.55$ and 0.54 for V$_3$PN and V$_3$AsN, respectively. These are typical values for phonon-mediated weakly coupling BCS superconductors[24,25,27].

On the other hand, the importance of a strong electron correlation effect manifests itself from an analysis of the Wilson ratio $R_w = \pi^2 k_B^2 \chi_s/3\mu_B^2\gamma$, where k_B is the Boltzmann constant, χ_s is the spin susceptibility, and μ_B is the Bohr magneton[28]. The magnetic susceptibility ($\chi = M/H$) in the normal state exhibits weakly T-dependent behaviour and can be well fitted to the formula $\chi = \chi_0 + C_{CW}/(T - \theta)$ (Fig. 2b), where χ_0 is a temperature-independent term, C_{CW} is the Curie-Weiss constant, and θ is the Weiss temperature. The fitting results give $\chi_0 = 4.13 \times 10^{-4}$ and 3.75×10^{-4} emu/mol, $C_{CW} = 1.09 \times 10^{-2}$ and 8.08×10^{-3} emu K/mol, and $\theta = -26.5$ and -13.0 K for V$_3$PN and V$_3$AsN, respectively. Using the obtained χ_0 values as χ_s, we acquire $R_w = 1.42$ and 1.45 for V$_3$PN and V$_3$AsN, respectively. The enhancement from the Fermi liquid value of 1 indicates a moderate electron correlation effect in the present compounds. Moreover, the ρ values in the normal state are in the order of 10^{-4} Ω cm (Figs. 2a, 2c), which is much larger than typical ρ values for conventional intermetallic compounds and indicates strong electron-electron interaction. Therefore, magnetic fluctuations originating from the strong electron correlation effect could not be excluded as the pairing glue for Cooper pairs.

Besides elucidation of the microscopic mechanism, identification of the chemical factors responsible for the appearance of superconductivity is important to further increase T_C in this new family of superconductors. Therefore, we have focused on the effects of N-defects on the superconductivity. The T_C values determined from
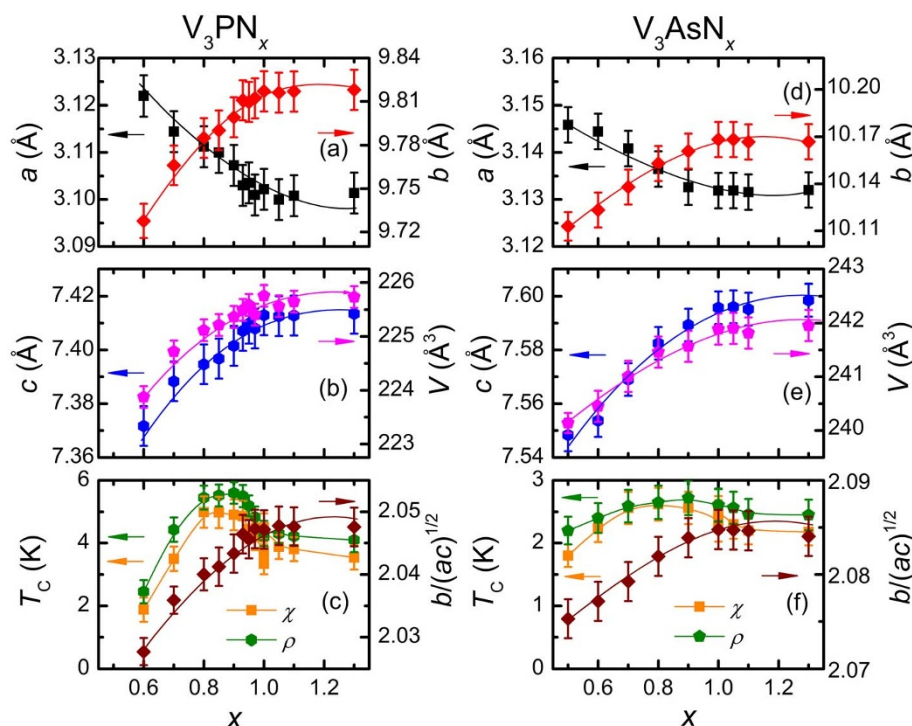
Figure 4 | Lattice parameters and superconducting transition temperature as a function of N-content (x). The values of a, b, c, V and T_C were determined from resistivity (ρ) and susceptibility (χ) data for (a–c) V_3PN_x and (d–f) V_3AsN_x. The $b/[ac]^{1/2}$ values, which quantify the two dimensionality of the systems, are also plotted in (c) and (f).

the low-temperature resistivity and magnetization of V_3PN_x ($x = 0.6$–1.3) and V_3AsN_x ($x = 0.5$–1.3) (x is the nominal composition, and the actual composition is expected to be less than 1) have been summarized in Figs. 4c and 4f (raw data are shown in Fig. S3 of supplementary information). For both cases, T_C is significantly enhanced with increasing x in the low x region, then decreases slightly after reaching a maximum at just below the stoichiometric composition ($x = 1$). The highest T_C achieved was 5.6 K for $V_3PN_{0.9}$, and the corresponding electronic properties are presented in Figs. 2a–e, 3b, 3e, and 3g. In addition, as x increases, the lattice expands along the b and c axes, and contracts along the a axis, which results in a slight increase of the unit cell volume. Here, we note that the $b/(ac)^{1/2}$ value, which quantifies the two-dimensionality of the system, is well correlated with the T_C values, as shown in Figs. 4c and 4f.

Discussion

On the basis of these experimental results, we now discuss the mechanism of superconductivity in V_3PnN. The strong correlation between T_C and $b/(ac)^{1/2}$ values suggests that the quasi two dimensionality of crystal structure plays an important role in the appearance of superconductivity. This suggestion is reinforced by the higher T_C for V_3PN than for V_3AsN. The former system has stronger intraplane coupling because the smaller atomic radius of P compared with that of As makes the in-plane V-V bond distances shorter, resulting in the enhanced hybridization of $3d$ orbitals in the plane; moreover, more ionic character of V-P bonds compared with V-As bonds due to the larger electronegativity of P than that of As also enhances the two-dimensionality of the system. Then, how this two dimensionality favor the superconductivity? If the electron-phonon interaction mediates Cooper pairs as suggested by electronic properties, the T_C value is considered to be enhanced by the larger density of states at the Fermi energy in low dimensional systems. Another possibility is that the electron correlation effect pronounced in the low dimensional crystal structure due to the smaller kinetic energy of electrons

stabilizes the superconducting states. Generally, T_C is known to be very sensitive to various factors in reported superconductors. Therefore, further detailed studies are required to identify the mechanism of superconductivity, especially on hybridization of the V-$3d$ and N-$2p$ bands, the direct-overlapping of V-$3d$ orbitals across two V atoms, and the change in carrier density introduced by N-defects.

To summarize, we have discovered superconductivity with maximum T_C at 5.6 and 2.6 K for V_3PN_x and V_3AsN_x with the anti ppv structure. Two-dimensionality is the key for the appearance of superconductivity; however, to elucidate the microscopic mechanism of superconductivity, further experimental and theoretical studies are required. These findings should stimulate future experimental and theoretical research on ppv-type materials to explore advanced functionalities.

Methods

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Acknowledgments

Author contributions

B.W. prepared the samples and carried out the experiments. The authors equally contributed to analysing the results. B.W. wrote the paper with assistance from K.O. K.O. directed the research.

Additional information

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