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Pressure-induced metallization and amorphization in VO₂(A) nanorods

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ABSTRACT:

A metallic state enabled by the metal-insulator transition (MIT) in single crystal VO₂(A) nanorods is demonstrated, which provides important physical foundation in experimental understanding of MIT in VO₂. The observed tetragonal metallic state at ~28 GPa should be interpreted as a distinct metastable state, while increasing pressure to ~32 GPa, it transforms into a metallic amorphous state completely. The metallization is due to V 3d orbital electrons delocalization, and the amorphization is attributed to the unique variation of V-O-V bond angle. A metallic amorphous VO₂ state is found under pressure, which is beneficial to explore the phase diagram of VO₂. Furthermore, this work proves the occurrence of both the metallization and amorphization in octahedrally coordinated materials.

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INTRODUCTION

Pressure-induced amorphization (PIA) has drawn great attention due to the fundamental importance in the fields of physics, chemistry, materials, and earth sciences [1–3]. Since the first observation in ice, PIA has been later discovered in several tetrahedrally coordinated materials including Si and SiO₂ [1,4–6]. Recently a breakthrough in this subject has been found, that PIA has also occurred in some octahedrally coordinated materials like TiO₂ and Y₂O₃, in which the PIA is strongly due to the nanometer size effect [7–11]. These results not only expand the range of PIA but also provide new members in size dependent amorphization.

Previous works are mainly focused on the microscopic structure and the driving forces of amorphization [1,4,5,12–14]. However, the physical property change in amorphization has also attracted increasing interest because of the importance of providing supportive evidence for amorphization and linking the macroscopic property to the microscopic structure [15]. Among various physical properties, pressure-induced metallization (PIM) is one of the most important concerns in the study of amorphization since the first discovery of a density driven metallization in semiconducting amorphous silicon, which stimulated a surge of study in various amorphous tetrahedrally coordinated materials, including Ge [2,16], GaSb [17], other alloys like Si-Ge alloy [18], and even glassy SiO₂, GeO₂ [19,20]. Up to now, most studies are limited on pressure-induced nonmetallic amorphous to metallic amorphous transition. Another interesting attempt is to induce metallic amorphous phase from a nonmetallic crystalline state under high pressure. However, to the best of our knowledge, only the tetrahedrally coordinated molecular crystal SnX₄/GeX₄ (X = halogen I, Br) [21–23] family has found the occurrence of both the metallization and amorphization, which is interpreted by the conducting chains due to the gradual growth of the tetrahedral halogen molecules [22,23]. Here we present an example with the occurrence of both PIM and PIA in an octahedrally coordinated VO₂ nanocrystal, which involves octahedron rearrangement and 3d orbital electrons delocalization during the phase transition, quite distinct from the reported molecular crystal, providing insights into the understanding of octahedrally coordinated materials.

As a strongly correlated electron model system, VO₂ has attracted long term interest since the first observation of MIT induced by changes in temperature, showing a huge change of conductivity at MIT which is accompanied by a structural transition from a monoclinic (*M1*)

insulating phase to a tetragonal (*R*) metallic phase [24]. Metallic phase transitions can also be effectively induced by external high pressures, an isostructural metallic *Mx* phase has been found in *M1* phase above 12 GPa [25,26] and a transient monoclinic *MT* metallic phase has also been observed around 11 GPa using ultrafast coherent phonon spectroscopy [27]. Recently, a metallic *X* phase has been observed in *M1* phase above 34 GPa [28]. A high pressure metallic phase even has been reported in other member V_2O_3 of the vanadium oxide family [29]. Besides *M1* phase, VO_2 also exhibits other polymorphs at ambient condition, $VO_2(A)$ is another metastable octahedrally coordinated phase, composed of edge and corner-sharing VO_6 octahedra [30] which is quite different from *M1* and *R* phase and the transformation from this structure to *R* is not reversible by changing temperature [31]. However, there is no study on the high pressure behavior of $VO_2(A)$ phase up to now which provides us another important and interesting system to explore MIT. Moreover, when the sample size reduces down to nanometer/submicrometer scale, it would be interesting to search for PIA in such an octahedrally coordinated nanomaterial. Here, using synchrotron radiation x-ray diffraction spectroscopy combined with Raman spectroscopy, IR spectroscopy, and first-principles calculations, we unveil the structure change and electrical property evolution of single crystal $VO_2(A)$ nanorods.

II. EXPERIMENTAL PROCEDURES

High quality $VO_2(A)$ nanorods were synthesized by a hydrothermal method [32]. High pressure measurements were generated by a diamond anvil cell (DAC) with argon (XRD and Raman) and KBr (IR) as the pressure-transmitting medium. Pressures were determined from ruby fluorescence techniques [33]. XRD measurements were carried out at X17C beamline of Brookhaven National Laboratory. Part of the XRD experiments were performed at 4W2 beamline of Beijing Synchrotron Radiation Facility. Raman measurements were conducted using a Renishaw inVia spectrometer with 514.5 nm laser excitation. IR measurements were carried out by a Bruker Vertex 80 V FTIR spectrometer belonging to our self-built system, part of the IR experiments were performed by U2A beamline of Brookhaven National Laboratory. The first-principles calculation on Raman spectra and phonon modes variation were performed on the basis of the density functional theory and pseudopotential methods [34], which are implemented in the CASTEP code.

III. RESULTS

A. Pressure-dependent XRD patterns

The pressure evolution of XRD patterns are shown in Fig. 1(a). All the Bragg peaks shift to larger angles upon compression. The diffraction peaks of argon appear at 4.8 GPa and last till the highest pressure 45.8 GPa, which is similar to Santillán's work in Mn_2O_3 [35]. $\text{VO}_2(\text{A})$ peaks disappear completely at 31.7 GPa, indicating the sample becomes amorphous. The Ar peaks disappear and no new peak emerges upon decompression, revealing the amorphization is irreversible. We further carried out HRTEM (high resolution transmission electron microscopy) and SAED (selected area electron diffraction) observations for the released sample, Figs. 1(b) and 1(c) show a totally disordered structure without any crystalline lattice.

B. Pressure-dependent Raman spectra

To further explore the structural change, we present a Raman spectroscopy study. According to first-principles calculation we assign the spatial modes, briefly, the peaks observed below 300 cm^{-1} , between 300 and 800 cm^{-1} , and above 800 cm^{-1} are assigned to lattice modes, VO_6 octahedra rotation, and antisymmetric and symmetric stretching of VO_6 octahedra, respectively. As shown in Fig. 2(a), all the vibrations exhibit a blueshift with increasing pressure, as expected for pressure-induced bond shortening. Above ~ 25 GPa, the blueshift can hardly be seen, while a slight redshift can be found in tendency, implying an enhanced interplay between octahedra as shown in Fig. 2(b). All Raman peaks disappear at 31.2 GPa, indicating the amorphization is completed. Upon decompression Raman spectra show no change, suggesting the amorphization is irreversible. The pressure-transmitting medium is argon, thus, the observed structural changes do not come from contaminated, chemically impure origins [36]. Raman results are in good agreement with XRD data.

C. Pressure-dependent infrared measurements

We further carried out infrared transmittance spectroscopy studies, as shown in Fig. 3(a). The low pressure spectrum shows vibrational bands characteristic of the insulator phase from 600 to 1000 cm^{-1} , which disappeared above ~ 28 GPa. Furthermore, we calculate the band gap approximately [37]. According to our first-principles calculations, there is an indirect

interband transition in VO₂(A), so we take $(\alpha d h \nu)^{1/2}$ as a function of the photon energy where α is the absorption coefficient and d is the sample thickness. By extrapolating the linear portion of the curve to the abscissa we obtained the band gap (E_g). At ambient condition E_g is 0.21 eV, which is the same as the theoretical value [38]. As shown in Fig. 3(b), E_g decreases gradually with the increased pressure and closes finally, revealing a PIM occurred. This is different from VO₂(M)'s metallization, in which PIM is accompanied with an isostructural transition [39]. Furthermore, we presented the reflectivity spectroscopy studies. As shown in Figs. 3(c) and 3(d), the reflectivity [32,40] increases abruptly at ~ 28 GPa, after which the reflectivity remains almost unchanged till the highest pressure 41.5 GPa. We use Drude model [32,41] to fit the experimental data and prove the metallic state under pressure, a similar method has also been used in the metallization of V₂O₃ [42]. These reflectivity results coincide with transmittance analysis, which further corroborates that the critical pressure of PIM (~ 28 GPa) is lower than that of PIA (~ 32 GPa).

IV. DISCUSSIONS

VO₂(A) can be regarded as a Mott insulator according to previous theoretical study [38]. At ambient conditions, the nearest-neighbor V-V1 (3.373 Å) in [110] layer, the nearest-neighbor V-V2 (2.771 Å), and the second nearest-neighbor V-V3 (3.102 Å) in the zigzag chain along c axis, are shown in Fig. S2 [32]. There are some similarities between the crystal structure of VO₂(A) and VO₂(M), as VO₂(M) also consists of VO₆ octahedra in three-dimensional framework and owns a zigzag chain along a axis with two different V-V distances 2.654 and 3.125 Å, and one V-V bond length 3.369 Å in [011] layer. Previous work on vanadium oxides indicate the electrical properties including electrical conductivity, carrier concentrations, and the MIT performance, are all strongly dependent on the microstructural characteristics at the atomic scale [43]. As Goodenough demonstrated [44], the critical separation value ($R_c \approx 2.93 \pm 0.04$ Å) of the 3d electron coupling interaction for both neighboring V³⁺-V³⁺ and V⁴⁺-V⁴⁺ ions can be deduced from semiempirical expressions, which have been well confirmed for an integral number of 3d electrons per cation in vanadium oxides. After that, Yao *et al.* pointed out a similar semiempirical expression for the separation of V 3d electrons, revealing that when the V-V distance is reduced to the critical distance (2.94 Å), the coupling interaction between 3d electrons leads to the itinerant electronic behavior in VO₂ [45]. Thus, for VO₂(A)

at ambient conditions, the larger V-V distances 3.373 and 3.102 Å are greater than the critical V-V interaction distance 2.94 Å, resulting in the localization of 3d orbital electrons both inside the pair in [110] plane and along *c* axis, which gives to the insulating behavior. The condition in VO₂(A) is similar to that in VO₂(M), as in VO₂(M) the V 3d electrons are localized in [011] plane and along *a* axis.

Table I shows the variation of V-V bond length in VO₂(A) upon compression. V-V1 represents the nearest-neighbor V-V bond in [110] plane, V-V2 represents the nearest-neighbor V-V bond along *c* axis, and V-V3 represents the second nearest-neighbor V-V bond along *c* axis. When the pressure reaches ~28 GPa, V-V1 distance is still greater than 2.94 Å, making 3d electrons localized in [110] plane, however, V-V3 bond length reduces to a value smaller than 2.94 Å, a condition that makes possible a delocalization of the 3d electrons among all V atoms along *c* axis, and the sample becomes metallic finally.

It is noticeable that in this research, the critical pressure of metallization is lower than that of amorphization, demonstrating the decoupling of the structural and electronic phase transitions. The tetragonal metallic phase observed in 28–32 GPa can be defined as an intermediate state. On compression the first transition is electronic: tetragonal-insulator to tetragonal-metal, and the second transition is structural: tetragonal-metal to amorphous-metal, thus, a Mott transition plays a major role in this MIT. Similarly, the separation of electronic and structural transition and the corresponding emergence of stable intermediate state among *M-R* transition have also been confirmed very recently in strained VO₂(M) film [46–48]. In the *M-R* transition, when the temperature reaches 340 K, the dual V-V bond lengths along *a* axis (monoclinic) change into one V-V bond length along *c* axis (rutile) with a distance of 2.853 Å shorter than critical value 2.94 Å, making electrons itinerant along *c* axis (rutile) and leading to the metallic behavior. In our research the situation is alike: when the pressure reaches ~28 GPa, V-V3 bond length along *c* axis reduces to a value of 2.933 Å smaller than critical value 2.94 Å, making electrons free to move along *c* axis and resulting in a metallic state finally.

From Rietveld refinements we can achieve the lattice parameters of VO₂(A) and the bond angle of V-O-V, these data are powerful to study the octahedra variation. Variation of relative lattice parameter *a/a*₀ and *c/c*₀ for VO₂(A) nanorods are shown in Fig. 4(a). Obviously VO₂(A) shows an anisotropic compressibility as *a* axis is more compressible than *c* axis.

Figure 4(b) shows the pressure dependence of the bond angle of V-O-V upon compression. V-O1-V represents the angle of two O atom shared octahedra along c axis, and V-O2-V represents the angle of two O atom shared octahedra in [110] plane. Upon compression there is a sharp decrease in V-O2-V at ~ 10 GPa, indicating a drastic distortion in [110] plane as the empty spaces are relatively easier to compress than the solid octahedra. After which the bond angle of V-O2-V increases gradually. To the bond angle of V-O1-V, the pressure dependence variation is negligible up to ~ 20 GPa, which is due to a denser arrangement of octahedra resulting in a lower compressibility along c axis. However, the bond angle of V-O1-V decreases sharply in the region of 20–25 GPa. Accompanied by the change of V-O2-V we suggest that this multiple rotation of the octahedra makes a huge variation in lattice. When the pressure is above ~ 25 GPa both bond angles change slightly.

This kind of discontinuous change in metal-oxygen-metal angles upon compression is related to the rodlike morphology. The nanorods have a preferred [110] orientation and a large L/D ratio (length/diameter ratio) [32], this could lead to an anisotropy of pressure effect in axial direction and radial direction. The anisotropic pressure effect, along with the large surface energy of the rods, may gradually result in soft mode and polyhedral tilt under pressure [49], generate potential nucleation centers for the phase transition and finally, transform a stable structure into an amorphous one. Thus, we suggest that the amorphization is consistent with the unique variation of bond angle. The PIA is similar to that which has been found in other systems like α -quartz [50], β -cristobalite [51], and zeolite [52].

V. CONCLUSIONS

In summary, observations of PIM and PIA in $\text{VO}_2(\text{A})$ nanorods have been performed by high pressure XRD, Raman spectra, IR spectra, HRTEM analysis, and first-principles calculations. A metallic state of $\text{VO}_2(\text{A})$ was found under high pressure, and then it transformed into an amorphous metallic form further at higher pressures. We propose that the mechanism for PIM and PIA are V $3d$ orbital electrons delocalization and the unique variation of V-O-V bond angle, respectively. The origin of metallization in this study is considered as a predominant Mott-like transition. From a broader perspective, the observed tetragonal metallic state and corresponding mechanism clarify a pathway in VO_2 's MIT.

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FIGURE CAPTIONS:

FIG. 1. (a) XRD patterns of VO₂(A) at various pressure. The peaks of Fe and Ar are marked by asterisk and triangle, respectively. (b) HRTEM and (c) SAED images are corresponding to the sample released from 45.8 GPa.

FIG. 2. (a) Raman spectra of VO₂(A) upon compression and decompression. (b) Pressure dependence of three modes above 800 cm⁻¹ upon compression.

FIG. 3. (a) IR transmittance spectra of VO₂(A) upon compression. (b) Pressure dependence of the band gap upon compression. (c) IR reflectivity spectra of VO₂(A) upon compression. Insets: Drude fits in the metallic phase. The black solid lines represent the experimental data, the red dashed lines represent model fits to the data. (d) Reflectivity change at selected photon energies upon compression.

FIG. 4. (a) Variation of relative lattice parameters a/a_0 and c/c_0 for VO₂(A) nanorods. (b) Pressure dependence of the bond angle of V-O-V in tetragonal phase upon compression.

TABLE I. Final refined V-V bond length of VO₂(A) around the metallization pressure by Rietveld refinements, V-V1 represents the nearest-neighbor V-V bond in [110] plane, V-V2 represents the nearest-neighbor V-V bond along c axis, and V-V3 represents the second nearest-neighbor V-V bond along c axis, respectively.

Pressure (GPa)	V-V1 (Å)	V-V2 (Å)	V-V3 (Å)
0	3.373(5)	2.771(4)	3.102(4)
19.5	3.204(7)	2.652(7)	2.968(8)
23.1	3.189(8)	2.642(8)	2.957(9)
27.3	3.143(7)	2.622(9)	2.933(6)
29.8	3.173(9)	2.614(7)	2.923(8)

FIGURES

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4