

# Local Structures in High Pressure Phases of V<sub>2</sub>O<sub>5</sub>

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The high-pressure behavior of layered V<sub>2</sub>O<sub>5</sub> is investigated using in situ Raman spectroscopy in a diamond anvil cell. Upon compression, the mode associated with the vanadyl V=O double bond at 997 cm<sup>-1</sup> softens and vanishes at about 10 GPa. Above 7 GPa, additional modes appear in the V–O stretching region, at lower wavenumbers than the V=O stretching oscillation. Such a behavior is interpreted as a pressure-induced five-to-six coordination change around the V<sup>5+</sup> cations, leading to a three-dimensional V<sub>2</sub>O<sub>5</sub> lattice. Upon decompression, intermediate phases are recovered.

## Introduction

The layered structure of vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>, is built up of VO<sub>5</sub> square pyramids sharing edges and corners.<sup>1</sup> The V atom, displaced toward the apex of the square pyramids due to the vanadyl V=O double bond, is distant from its basal plane by 0.470 Å. The sheets are held together by weak interlayer vanadium–oxygen interactions, V···O = 2.791 Å. The structure of V<sub>2</sub>O<sub>5</sub> is related to the structure of α-MoO<sub>3</sub>.<sup>2,3</sup> When one of the apical oxygen atoms is removed from each octahedron in α-MoO<sub>3</sub>, the structure of V<sub>2</sub>O<sub>5</sub> is obtained.

V<sub>2</sub>O<sub>5</sub>-based systems are thoroughly studied due to their semiconducting and catalytic properties. In all the systems, the V<sup>5+</sup> cations are partially reduced to a V<sup>4+</sup> valence state (a few atom percent).<sup>4</sup> The semiconducting properties arise from hopping of unpaired electrons between the V<sup>5+</sup> and V<sup>4+</sup> cations. A strong electron–phonon coupling is observed and the actual charge carriers are small polarons.<sup>5–8</sup> Supported vanadium oxide catalysts are widely used in industry for selective oxidations, ammoxidation of hydrocarbons, and selective reduction of NO<sub>x</sub>.<sup>9–12</sup> The open structure of V<sub>2</sub>O<sub>5</sub> favors molecular and ionic intercalations.<sup>1,13</sup>

There have been three reports on the high-pressure behavior of vanadium pentoxide to this date. Electrical resistance measurements by Minomura and Dricka-

mer<sup>14</sup> revealed that V<sub>2</sub>O<sub>5</sub> has a phase transition at about 10.5 GPa with a large increase in resistance. It is a semiconductor both below and above the transition. Suzuki et al.<sup>15</sup> examined crystallization of splat-cooled V<sub>2</sub>O<sub>5</sub> under high pressure. Amorphous V<sub>2</sub>O<sub>5</sub> crystallizes dramatically up to about 0.6 GPa. At higher pressures (2.0–6.0 GPa), crystallization occurs gradually and the crystallization temperature has a tendency to decrease with increasing pressure. Additionally, Suzuki et al.<sup>15</sup> synthesized a new modification of crystalline V<sub>2</sub>O<sub>5</sub> at high pressures. Volkov et al.<sup>16</sup> found that this phase, β-V<sub>2</sub>O<sub>5</sub>, is obtained in synthesis above 3.5 GPa and 873 K. The sample recovered to ambient conditions from 9 GPa and 873 K is tetragonal (ICDD-JCPDS 45-1074) and has the same X-ray pattern as the phase prepared earlier by Suzuki et al.<sup>15</sup> The β → α back-transformation occurs at 653 K at ambient pressure (the ambient pressure phase of V<sub>2</sub>O<sub>5</sub><sup>1</sup> is referred to as α-V<sub>2</sub>O<sub>5</sub>). Both α and β modifications are *n*-type semiconductors.<sup>5,16</sup>

In the reports by Suzuki et al.<sup>15</sup> and Volkov et al.,<sup>16</sup> there is no actual information on the structure of β-V<sub>2</sub>O<sub>5</sub>. On the other hand, comparison of the infrared spectra of the α and β phases<sup>16</sup> indicates that additional new bands are present in the β polymorph at 780 and 950 cm<sup>-1</sup>, at lower wavenumbers than the V=O bond stretching at 1020 cm<sup>-1</sup>. These two new bands may be interpreted as due to the 6-fold coordinated vanadium atoms in the high-pressure structure of V<sub>2</sub>O<sub>5</sub>, as could be inferred from previous reports on the pressure-induced coordination changes in vanadium compounds.<sup>17,18</sup> Also, the occurrence of these new bands along with the V=O oscillation in the infrared spectrum of β-V<sub>2</sub>O<sub>5</sub><sup>16</sup> further suggests that this phase is rather formed upon decompression and it does not necessarily represent the high-pressure polymorph(s) of V<sub>2</sub>O<sub>5</sub>.

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The motivation for this study is to begin to explore a variety of pure and intercalated crystalline modifications of  $V_2O_5$  that can be obtained using high-pressure, high-temperature methods. It could be hypothesized that the layered structure of pure  $\alpha$ - $V_2O_5$  might collapse at high pressure to form a more condensed phase. In particular, a close similarity of the  $\alpha$ - $V_2O_5$  and  $\alpha$ - $MoO_3$  structures under ambient conditions<sup>2,3</sup> prompts a search for the existence of other two- or three-dimensional  $V_2O_5$  polymorphs, related (or not) to the known  $MoO_3$  varieties.<sup>19–20</sup> These new phases, metastable upon decompression to atmospheric conditions, could allow for different intercalation chemistry and, in analogy to the  $MoO_3$  types, for different selectivity of catalytic reactions.<sup>10,21,22</sup> In this study the high-pressure behavior of  $V_2O_5$  at room temperature is studied using in situ Raman spectroscopy in a diamond anvil cell. This technique is a useful tool to investigate local symmetry and coordination changes around the  $V^{5+}$  cations at high pressures. It also provides invaluable information on the changes in bonding in response to changes in pressure.

### Experimental Section

Raman spectra, with spectral resolution of about  $2\text{ cm}^{-1}$ , were collected in the  $560\text{--}1130\text{ cm}^{-1}$  and  $10\text{--}620\text{ cm}^{-1}$  regions using a XY Dilor Raman spectrometer (1800 groove/mm gratings) in backscattering geometry with CCD signal detection. Raman scattering was excited using an  $Ar^+$  laser at a wavelength of 514.5 nm. The sample of  $\alpha$ - $V_2O_5$  (Aldrich) and CsI, as a pressure-transmitting medium, were loaded into a Mao-Bell-type diamond cell with type II-a diamonds, brilliant cut with  $600\text{ }\mu\text{m}$  culets, and a sample chamber diameter of  $250\text{ }\mu\text{m}$ . Pressures were determined from the  $R_1$  ruby fluorescence line.<sup>24</sup>

### Results and Discussion

The Raman spectrum of  $\alpha$ - $V_2O_5$  at ambient pressure (Figure 1) has already been analyzed by Wachs and Chan,<sup>9</sup> Hirata and Zhu,<sup>25</sup> and Fomichev et al.<sup>26</sup> The most important observation is that the Raman band at  $997\text{ cm}^{-1}$  is unique to  $\alpha$ - $V_2O_5$  and is not present in lower oxides of vanadium since they do not possess the vanadyl  $V=O$  double bonds.<sup>9</sup> Therefore, loss in the  $V=O$  stretching band at ambient conditions is due to the reduction of  $\alpha$ - $V_2O_5$  to lower oxides. The  $V^{5+} \rightarrow V^{4+}$  valence transition is also observed in the  $(1-x)V_2O_5 + xMoO_3$  solid solution series ( $x = 0.3$ ) as  $V^{5+}$  is replaced by  $Mo^{6+}$  cations.<sup>25</sup> As a result, the band at  $997\text{ cm}^{-1}$  shifts downward, broadens, and decreases in intensity with increasing  $x$ . It indicates the formation of polyhedra different from those in the parent structure of  $\alpha$ - $V_2O_5$ , reflecting the structural transformations as  $\alpha$ - $MoO_3$  is intercalated into  $\alpha$ - $V_2O_5$ . Thus, the softening

of the  $997\text{ cm}^{-1}$  band is associated with the increase of the short  $V=O$  bond and decrease of the interlayer  $V\cdots O$  distance. The decrease in intensity of this Raman band is due to the  $V^{5+} \rightarrow V^{4+}$  valence transition upon the  $Mo^{6+}$  substitution.

The pressure dependencies of the scattered Raman signal and observed Raman frequencies in  $V_2O_5$  upon compression are shown in Figures 1 and 2 and upon decompression in Figure 3. The spectra are neither scaled nor normalized and they have their absolute intensities as measured. The weak bands appearing at about 2 GPa can be accounted for by analysis of the normal modes in  $\alpha$ - $V_2O_5$ <sup>21</sup> (Figures 1 and 2). It is clearly seen that the intensities decrease monotonically with increasing pressure up to about 7 GPa. At this pressure, there occurs an abrupt change in Raman activity of the  $V_2O_5$  lattice, and all the spectra collected above 7 GPa are very weak. Below 7 GPa, the  $V=O$  stretching mode shifts downward and broadens. Also, other bands assigned to the deformational and lattice modes involving the predominant oscillations of the  $V^{5+}$  cation<sup>26</sup> have negative pressure shift. The abrupt change in intensity of the Raman scattering at 7 GPa is associated with the appearance of additional bands in the  $V-O$  bond stretching range ( $950\text{--}800\text{ cm}^{-1}$ ) and with the band splittings due to the lattice modes<sup>26</sup> below  $350\text{ cm}^{-1}$ . At higher pressures, the  $V=O$  stretching mode changes its pressure dependence, as do the deformational  $O-V-O$  modes at 478 and  $282\text{ cm}^{-1}$ . The divergence of the two lattice modes at about  $200\text{ cm}^{-1}$  is typical of the modes with the same symmetry that avoid crossing each other (Figure 2). It is remarkable that the  $V=O$  stretching mode vanishes at above 10 GPa, while the other  $V-O$  modes persist, except for the two shoulder features of the main band at about  $880\text{ cm}^{-1}$ . Upon decompression, the vanadyl oscillation is observed again at about 10 GPa; however, it is below 2 GPa that it becomes intense, relative to the other modes in the  $550\text{--}1100\text{ cm}^{-1}$  range. Comparison of the Raman spectrum of  $\alpha$ - $V_2O_5$  with the spectrum of the sample decompressed from 12 GPa to atmospheric pressure indicates that the latter is structurally different from  $\alpha$ - $V_2O_5$ , as it has additional bands in the  $1100\text{--}550\text{ cm}^{-1}$  wavenumber range. This is in agreement with the infrared spectrum of  $\beta$ - $V_2O_5$ , reported by Volkov et al.<sup>16</sup> It demonstrates hysteresis associated with the pressure-induced structural transformations in  $V_2O_5$ .

The results presented here were obtained during the room temperature experiments in which the only variable was pressure but not redox conditions. In consequence, the interpretation of the spectral changes, especially the ones concerning the  $V=O$  stretching mode, should rather be based on structural considerations, without taking into account the valence transitions of the  $V^{5+}$  cations. As discussed earlier, the structure of  $\alpha$ - $V_2O_5$  is related to  $\alpha$ - $MoO_3$ .<sup>2,3</sup> Hence, softening of the vanadyl bond stretching at  $997\text{ cm}^{-1}$  up to 7 GPa can be explained in a similar way as the structural changes in  $\alpha$ - $V_2O_5$  upon intercalation with  $\alpha$ - $MoO_3$  in the  $(1-x)V_2O_5 + xMoO_3$  solid solution series ( $x = 0.3$ ).<sup>25</sup> The pressure effect would be the formation of polyhedra different from those in the parent structure of  $\alpha$ - $V_2O_5$ , responding to the structural transformations into the  $\alpha$ - $MoO_3$  type due to the increase of the short  $V=O$  bond

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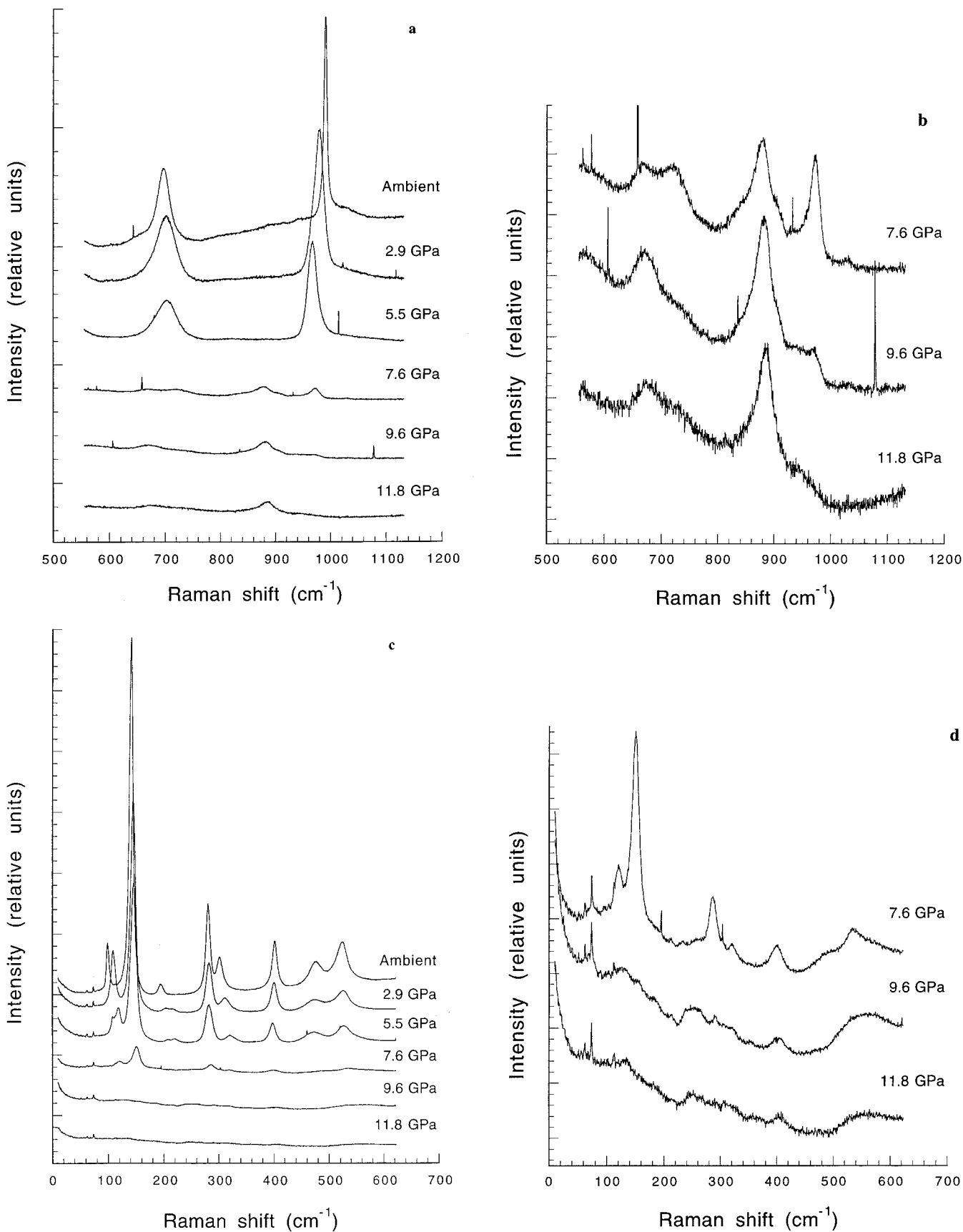
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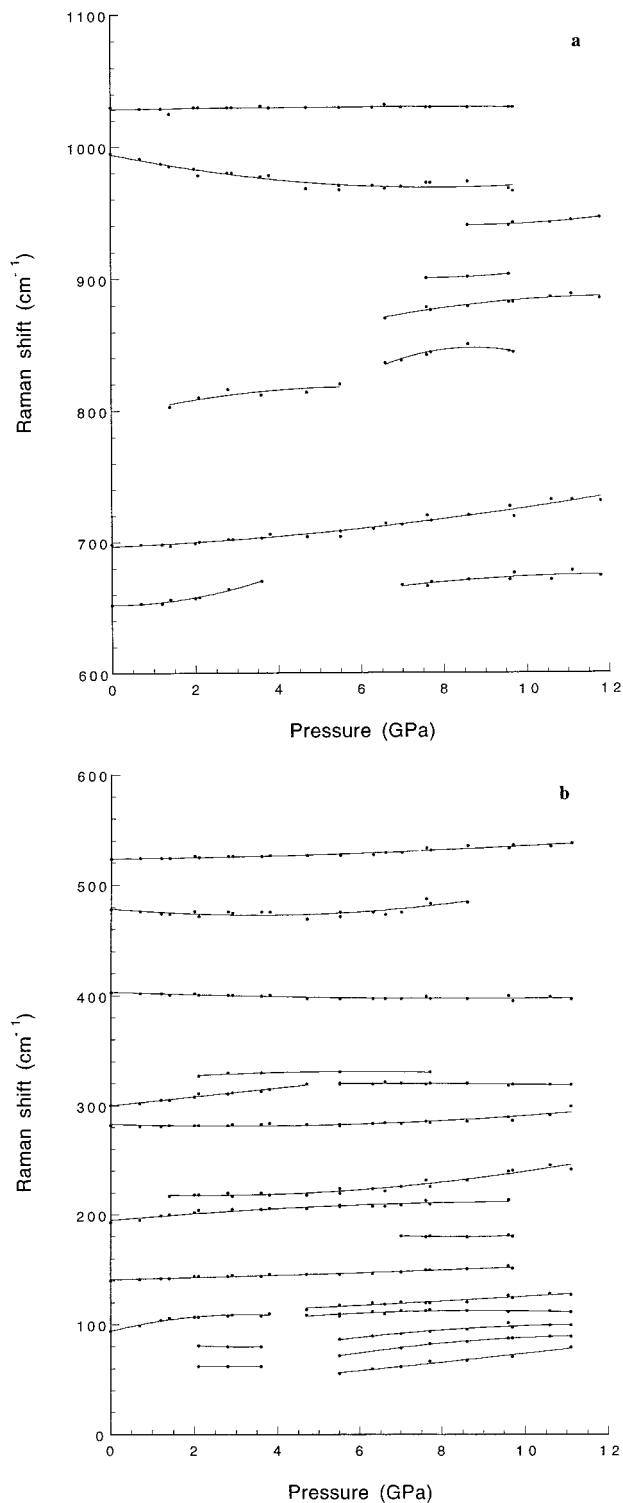
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**Figure 1.** Raman spectra of  $V_2O_5$  upon compression in the 560–1130  $cm^{-1}$  (a, b) and 10–620  $cm^{-1}$  (c, d) regions.

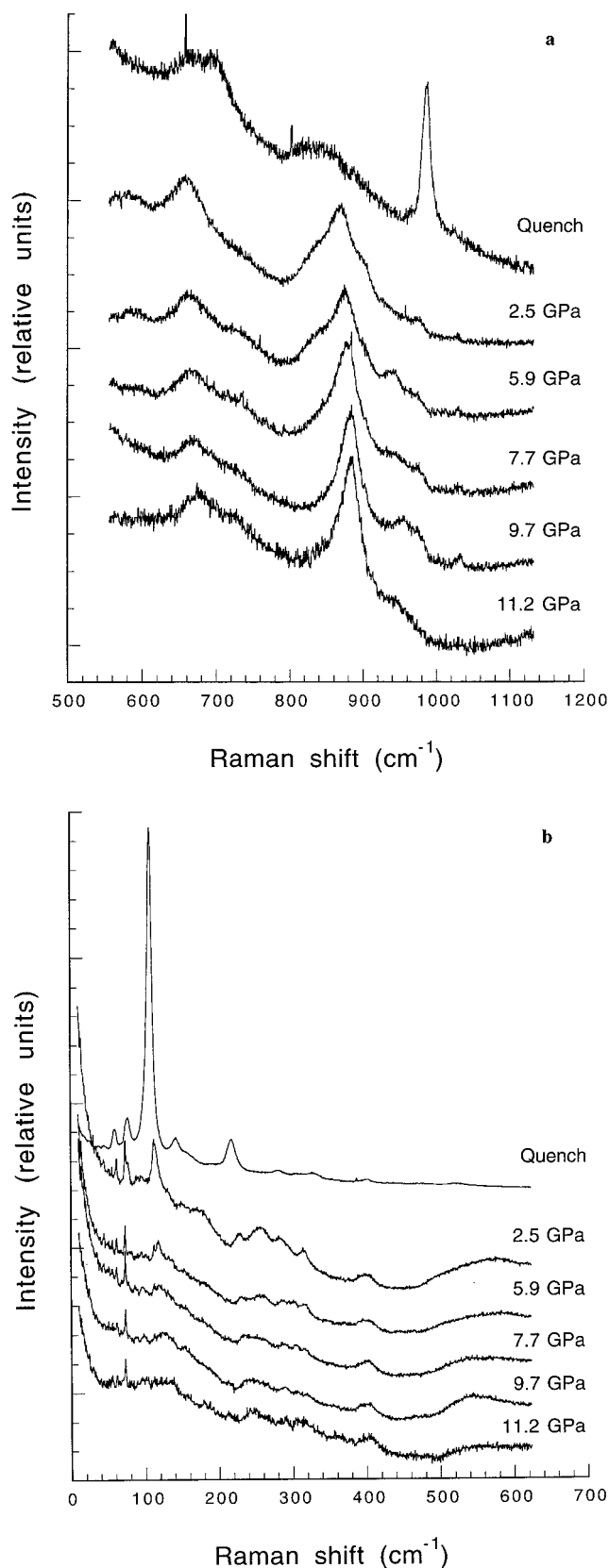
and decrease of the interlayer  $V\cdots O$  distance. Accordingly, at lower pressures the  $V^{5+}$  cations shift toward the center of their square pyramids. Such displacements also affect other vibrational modes with predomi-

nant contribution from the cations (the negative pressure dependence of Raman bands). When the cations are close to the basal plane of their square pyramids and do not shift away from the apex, the compressibility



**Figure 2.** Pressure dependence of Raman bands in  $V_2O_5$  upon compression. Lines are guides for the eye.

changes. It happens at about 7 GPa that the originally interlayer V and O atoms are close enough to form a bond. The appearance of the additional bands in the V–O stretching region can be considered as evidence for the pressure induced five-to-six coordination transformation in  $V_2O_5$ , attaining the structure of the  $\alpha$ - $MoO_3$  type.<sup>2,3</sup> Similar transitions have been observed in other vanadium compounds.<sup>17,18</sup> On the other hand, the decrease in intensity of the band at  $997\text{ cm}^{-1}$  cannot be explained by the  $V^{5+} \rightarrow V^{4+}$  valence transition upon compression. Instead, it should be noticed that the



**Figure 3.** Raman spectra of  $V_2O_5$  upon decompression in the  $560\text{--}1130\text{ cm}^{-1}$  (a) and  $10\text{--}620\text{ cm}^{-1}$  (b) regions.

intensity of the mode due to the vanadyl  $V=O$  double bond would depend on the extent of the  $\pi$ -type overlap between the V 3d and O 2p orbitals. Through the phase transitions at high pressures, this overlap would increase with additional redistribution of the  $\pi$ -type

electrons into six bonds at the distorted octahedral sites. Further analysis of the pressure-induced changes in  $V_2O_5$  could be based on the considerations of different polymorphs of  $MoO_3$ .  $\alpha$ - $MoO_3$  crystallizes in a layered structure,<sup>2</sup> the prototype of the  $\alpha$ - $V_2O_5$  lattice.<sup>3</sup>  $\beta$ - $MoO_3$ <sup>19</sup> and  $\beta'$ - $MoO_3$ ,<sup>20</sup> related to  $WO_3$ , are three-dimensional with corner-shared octahedra. The structure of  $MoO_3$ -II, obtained at high pressure and high temperature, is layered with a more efficient stacking sequence of the layers than the one in  $\alpha$ - $MoO_3$ .<sup>21</sup> The most important information on different polymorphs of  $MoO_3$  is that the Raman band in  $\alpha$ - $MoO_3$  at  $1000\text{ cm}^{-1}$  associated with the  $Mo=O$  bond is absent from the Raman spectrum of  $\beta$ - $MoO_3$ .<sup>19</sup> Both the  $\alpha$ - $V_2O_5$  and  $\alpha$ - $MoO_3$  layered structures are stabilized by the vanadyl  $V=O$ <sup>1,3</sup> and molybdenyl  $Mo=O$ <sup>2,3</sup> double bonds, respectively. The increased overlap of the  $Mo\ 4d$  and  $O\ 2p$  orbitals in  $\beta$ - $MoO_3$  is sufficient to stabilize its three-dimensional structure.<sup>19</sup> It also results in smaller cationic displacements and loss of the  $Mo=O$  bond. The main pressure effect on bonding in  $V_2O_5$  is an increase in the  $\pi$ -type overlap of the  $V\ 3d$  and  $O\ 2p$  orbitals, as demonstrated by the vanishing of the vanadyl  $V=O$  double bonds. Therefore, loss of the  $V=O$  stretching mode and shoulder features in the main band at about  $880\text{ cm}^{-1}$  in the Raman spectra above about 10 GPa (Figures 1 and 2) could be interpreted as a result of the pressure-induced tendency to change the dimensionality of  $V_2O_5$ , leading to the formation of a structure related to  $WO_3$ .<sup>19</sup> At pressures of 7–10 GPa, at which the  $V=O$  stretching mode and the additional new  $V-O$  stretching modes are observed, the structure would still have a layered character, expressed by edge-shared octahedra in sheets connected via corners. Such a structure would be similar to that of  $\alpha$ - $MoO_3$ .<sup>2,3</sup> Upon decompression, the three-dimensional topology of corner-shared octahedra is metastable due to the strong tendency of the  $V^{5+}$  cations to form the vanadyl  $V=O$  double bonds,<sup>1,3</sup> so the octahedra tend to transform into the square pyramids, which are stable under ambient conditions. It proceeds through a series of intermediates, in which successive octahedra cluster into the edge-shared units with different degrees of distortions. Such intermediate phases are metastably recovered to atmospheric pressure, as seen in Figure 3 and as demonstrated by Volkov et al.<sup>16</sup>

in their infrared spectrum of  $\beta$ - $V_2O_5$ , both data sets showing the addition of the octahedral  $V-O$  stretching modes to the  $V=O$  stretching oscillation. The relatively high temperature of the  $\beta \rightarrow \alpha$  (653 K) back-transformations at ambient pressure<sup>16</sup> indicates that the decompressed phases are to a large degree kinetically stable near room temperature.

This interpretation is helpful in understanding the observations by Minomura and Drickamer<sup>14</sup> that the resistivity of  $V_2O_5$  largely increases at about 10.5 GPa. It occurs at the pressure in which the vanadyl  $V=O$  double bonds are extinct and the vanadium atoms are at 6-fold sites (Figures 1 and 2). It shows that the semiconducting properties of  $V_2O_5$ , arising from the electron hopping between the  $V^{5+}$  and  $V^{4+}$  cations, change in response to the pressure-induced structural transformations. At ambient pressure, the charge carriers are small polarons and their mobility depends on the thermal activation of the lattice distortions and associated lattice vibrations.<sup>5–8</sup> Hence, an increase in the  $\pi$ -type overlap of the  $V\ 3d$  and  $O\ 2p$  orbitals at high pressure along with the corner-shared octahedral coordination around the  $V$  atoms would impede the thermally activated mobile species hopping among the trapping 6-fold sites. Such a semiconducting behavior of polaron systems through pressure-induced coordination changes could be general in other vanadium pentoxide-based compounds.

The existence of the high-pressure phases of  $V_2O_5$  with different local structures around the  $V^{5+}$  cations is noteworthy because their structural similarity to the  $MoO_3$  polymorphs suggests that they will have new intercalation chemistry. Various ionic and molecular intercalates, inserted in situ at high pressure, could selectively stabilize different decompressed phases and affect their properties. In addition, it has been shown that many catalytic reactions are sensitive to the structure of oxide catalysts.<sup>10,22,23</sup> It is still not known whether the catalytic activity of the high-pressure phases of  $V_2O_5$ , metastable upon decompression to ambient conditions, will be the same or different from the one in layered  $\alpha$ - $V_2O_5$ ,<sup>9–12</sup> the thermodynamically stable polymorph, at atmospheric pressure.

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