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LOCAL STRUCTURE CHANGES IN V_2O_3 BELOW AND ABOVE THE METAL–INSULATOR TRANSITION

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According to diffraction measurements of the *average* structure, V_2O_3 changes on heating from monoclinic to trigonal, accompanied by a 1.4% volume decrease, where some V - V distances decrease by about 0.11 Å, favoring the Mott - Hubbard mechanism of the phase transition from insulator to metal. Our x-ray absorption fine structure measurements of the *local* structure of the single crystal V_2O_3 show the same decrease in volume but no change in local symmetry in the transition, indicating that the phase transition contains a significant order–disorder component, contrary to the purely displacive model based on diffraction results. ©1997 Elsevier Science Ltd

1. INTRODUCTION

Vanadium sesquioxide (V_2O_3) undergoes a phase transition at 155 K [1]. In this sharp first - order phase transition the following changes occur: 1) insulating phase at low temperatures becomes metallic at elevated temperatures (resistivity drops by about 7 orders of magnitude); 2) antiferromagnetic phase transforms to a paramagnetic phase; and 3) crystal structure space group changes from monoclinic ($I2/a$) to trigonal ($R\bar{3}C$) with a 1.4% decrease in volume.

The phase transformations in V_2O_3 have been intensively studied as a function of temperature, pressure and dopant content in order to investigate the mechanism of the metal - insulator transition [1,2]. It is generally believed that the metal - insulator transition in V_2O_3 and other vanadium oxides is driven by the Mott - Hubbard (MH) mechanism, consistent with an abrupt expansion of the vanadium atoms distances (by 0.11 Åin V_2O_3) as the temperature is lowered below T_c. In this model, changes in V - V distances regulate the balance between the positive intra-atomic Coulomb repulsion energy of the electrons (U) and their bare band energy width W by changing the overlap between $3d$ V - V orbitals, thus determining the bandgap [3].

It should be emphasized that since the MH mechanism depends on the distance between the first few neighboring atoms and the corresponding overlap of their wave functions, the measurements of the *local* structure may help to determine whether this or some other mechanism holds. The *local* structure can differ from the *average* periodic structure as measured by diffraction if disorder is present. The information of the local structure can most be reliably quantified using the x-ray absorption fine structure (XAFS) method [4], explaining the motivation for the present investigation. Indeed we do find a difference between the *local* and *average* structures as described below.

An additional interest in metal - insulator transitions in general is explained by their being an example of a strongly correlated electron interacting system as is believed to be the case for high T_c superconductors. For example, $La_{2-x}Sr_xCuO_4$ and $La_{1-x}Sr_xVO_3$, when x increase, both undergo a transition to the metallic state together with disappearance of the magnetic order. Systems like these are a major challenge to theorists to understand the cause of such spectacular discontinuous (magnetic) insulator to metal transitions. The need for new experimental information is underscored in the statement by Mott in 1990: "For the [metal - insulator transition] phenomenon, there are

still as many theories as there are theorists" [5]. This statement has a familiar ring in the high T_c field.

It was found [6] that the low temperature insulating phase of V_2O_3 could be entirely suppressed by applying pressure greater than 26 kbar. Experiments with dopings with other 3*d* transition metals demonstrated that Ti - doped samples [1] behaved exactly as pure V_2O_3 specimens to which hydrostatic (isotropic) pressure was applied. On the other hand, Cr - doping acted as a negative pressure on the lattice, although the addition of Cr causes the lattice to expand anisotropically.

Room temperature experiments with doping [7] provide more information to be understood: lattice structure is reported trigonal at all concentrations, while the lattice parameters for Cr and Zr doped samples change abruptly during the metal - insulator phase transition as a function of doping. These changes in lattice parameters are similar to those in pure V_2O_3 during the metal - antiferromagnetic insulator transition, but without reduction of symmetry [1]. Lattice parameters of Ti doped samples change gradually, the structure is trigonal at all concentrations, and there is no phase transition.

In the present work, we investigated the local structure of pure V_2O_3 below and above the metal-insulator transition at ambient pressure. In our case the polarization of the synchrotron radiation in the plane of the electron orbit can be utilized to enhance the sensitivity of XAFS to the local structure. The measured XAFS signal

$$\chi(k) = \cos^2\Theta\chi_{\parallel}(k) + \sin^2\Theta\chi_{\perp}(k), \qquad (1)$$

where Θ is the angle between the polarization and the c-axis, and $\chi_{\parallel}(k)$ and $\chi_{\perp}(k)$ are the XAFS signals obtained with polarization parallel and perpendicular to the *c*- axis, respectively. This allows the separation of the V_0-V_1 pair (Fig. 1 a)) from the other V-V pairs since $\chi_{\parallel}(k)$ contains essentially only the nearest neighbor V_0-V_1 pair while $\chi_{\perp}(k)$ contains essentially only the other V-V pairs which lie nearly in the basal plane (Fig. 1 b)). This lowers the ratio between the number of adjustable variables and the number of independent points in XAFS data analysis.

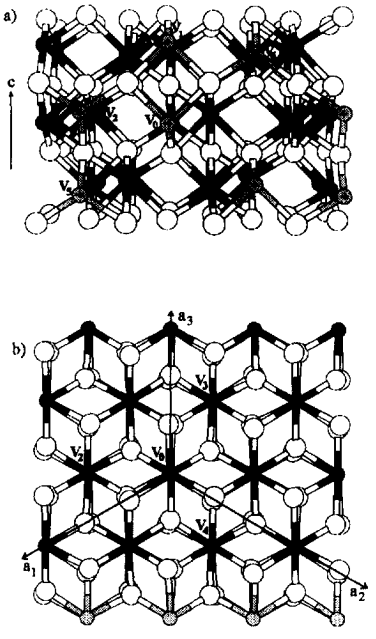

Fig. 1. Projections of the V_2O_3 trigonal structure on the planes: a) perpendicular to the 110 axis, b) perpendicular to 001 axis (in trigonal notation). The V atoms are dark circles, and O atoms are empty circles. Grey circles show V atoms within the top plane. Arrows show displacements of vanadium atoms under monoclinic distortions.

2. EXPERIMENT AND DATA ANALYSIS

The V_2O_3 crystals were grown in Ioffe Physical Technical Institute (St. Petersburg) by the Verneuil method. The powder for crystal growth was prepared by reducing high purity (99.999%) ammonium metavanadate (NH_4VO_3) in flowing hydrogen at 1000 °C for 12 h. The samples for measurements were cut from the crystals and after polishing and etching in hot 10% HNO_3 solution had the dimensions about 1.5 × 2 mm^2 and thickness 15 μm, (corresponding to the absorption edge step $\Delta\mu x \approx 2.5$ at V K-edge). To improve the stoichiometry, the samples were annealed at 1500 °C at the partial pressure of oxygen of about 0.1 mTorr. The *a*-*c* plane was parallel to the sample's surface. Resistivity measurements (following the procedure described previously [8]) demonstrated that the samples were single crystals of high quality: 1) resistivity dropped by 7 orders of magnitude above T_c with a jump width less than 0.2 K and a hysteresis loop width of 10 K, and 2) resistivity increased linearly with temperature in metallic phase.

XAFS measurements were performed at the National Synchrotron Light Source (NSLS) on beamline X11A at two temperatures below the phase transition for each orientation (80 K for polarization $\epsilon \parallel c$, 100 K for $\epsilon \perp c$, and 130 K for both orientations), and two temperatures above (200 K and 300 K). Cooling was performed using a Displex refrigeration system attached to a sealed copper cell containing the sample. Care was taken to prevent the crystal from fracturing on cooling due to the volume increase below the phase

transition. First, the sample was attached onto a thin aluminized mylar film through the surface tension of a droplet of alcohol. Then the mylar with the sample was oriented in the desired direction and attached to the sample cell using vacuum grease, so that only the tip of a corner of the sample was touching the copper holder. This assured both good thermal contact with the cell and lowered the probability for the sample to crack due to differential thermal contractions. Cycling through the phase transition and measuring data at 200 K both on the way down and up in temperature was used to check whether the sample cracked or not. The difference between the two so obtained XAFS signals at 200 K was within the statistical noise, thus confirming that no cracks appeared.

XAFS signals were analyzed by the UWXAFS software developed at the University of Washington [9]. To ensure compatibility, the same parameters were used to remove an atomic - like smooth background from all data sets, and the same k - range (between 2 and 14 $Å^{-1}$) was chosen for Fourier transforms. Theoretical scattering amplitudes and phases were generated using the FEFF6 code [10] for the monoclinic crystal structure model [11], chosen to describe the local structure of the samples below the transition temperature (155 K). Structural changes occurring during the phase transition in the local structure could be parameterized in the fit process as corrections to interatomic distances and, therefore, the chosen model would accommodate both phases.

The space group *I2/a* with four formulas per unit cell corresponding to the monoclinic structure of V_2O_3 is shown in Fig. 1 in the frame of trigonal axes. All of the V atoms have crystallographically equivalent environments but are labeled differently to distinguish their positions relative to the x-ray absorbing atoms. The monoclinic distortion of the trigonal structure could be visualized by "rotating" the V_0 - V_1 pair within the plane perpendicular to trigonal 110 axis, so as to move the V_0 - V_2 atoms towards the oxygen octahedra voids (see Fig. 1) [11]. This leads to the expansion of the V_0 - V_2 distances by 0.11 Åin the monoclinic phase compared to those in the trigonal structure. Such a difference in distances between the nearest neighbors can be easily detected in the fit of FEFF6 theory to the XAFS data. Fits to the data at the temperatures below (130 K) and above (200 K) the phase transition are shown in Figs. 2 a) and b) for both orientations. The results of the fits showed that the local structure of the samples remained monoclinic at all temperatures. The V - V nearest neighbor distances were directly determined from the fits and compared to the x-ray diffraction results (Fig. 3). Anharmonic corrections were found to be negligible. The V_0 - V_2 distance decreased above the transition by 0.070 ± 0.025 Å, but its absolute value remained 0.040 ± 0.025 Ålonger than given by the trigonal structure of the diffraction measurement. Another characteristic distance between V_0 - V_1 (Fig. 1 a)) remained about 0.025 ± 0.02 Ålonger than in the trigonal structure, consistent with the static displacement of V_0 and V_2 atoms in opposite directions in monoclinic structure. Mean-square deviations (σ^2) of V-V and V-O distances did not show significant change across the phase transitions, except for the V_0-V_1 bond where σ^2 changed from 0.0064 ± 0.0013 $Å^2$ at 130 K to 0.0113 ± 0.0024 $Å^2$ at 200 K. Further investigation is planned to understand the significance of this result.

To give further evidence of the lack of a purely displacive change in the local structure, we utilized the high sensitivity of XAFS signal to collinear arrangement of atoms. First described by Lee and Pendry [12], and emphasized by Teo [13], the enhancement of the forward scattering amplitude of the photoelectron, propagating from the absorbing atom "through" the first nearest neighbor to the next neighbor, and back to the absorber, was successfully employed previously in several cases to determine the bond angles between three nearly collinear atoms [14, 15].

The trigonal structure of V_2O_3 is characterized by a 6 - fold degeneracy of the coordination of V_5 - V_6 atoms (Fig. 1 a)). Another vanadium atom, V_0, is an intervening atom in a row: V_5 - V_0 - V_6 (Fig. 1 a)). This gives rise to the following set of photoelectron paths with the same half path length (7.38 Å): 6 - fold degenerate single scattering paths: $V_5 \rightarrow V_6 \rightarrow V_5$, 12 - fold degenerate focusing double scattering paths: $V_5 \rightarrow V_0 \rightarrow V_6 \rightarrow V_5$, and 6 - fold degenerate focusing triple scattering paths: $V_5 \rightarrow V_0 \rightarrow V_6 \rightarrow V_0 \rightarrow V_5$.

In the monoclinic structure, the displacements of vanadium atoms from their positions in the trigonal lattice destroy the 6 - fold degeneracy of the V_5 - V_0 - V_6 arrangement, splitting it into two groups of 4 - fold and 2 - fold degenerate collinearly arranged atoms, V_5 -V_0 - V_6' and V_5 -V_0 - V_6, with half path lengths of 7.47 Åand 7.255 Å, respectively.

The fit to the data within the range of 6.1 - 7.3 Åis shown in Fig. 2 where the trigonal model was also used to fit the data in this range for comparison with the monoclinic model. Figure 2 demonstrates that the monoclinic model gives a much better fit to the data than the trigonal. Figures 3 shows that the two distances remain split above the phase transition. This confirms the previous results and indicates that, locally, the structure remains monoclinic with a domain size of at least 7.3 Å.

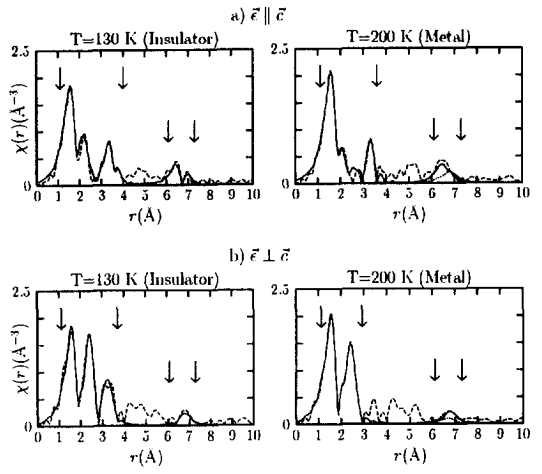

Fig. 2. Fourier transforms magnitudes of the k^2 - weighted XAFS spectra fitted with FEFF6 theory for monoclinic structure (solid) to the data (dash) at 130 K and 200 K for different orientations of the sample: a) $\epsilon \parallel c$ and b) $\epsilon \perp c$. Fits with trigonal structure model to the 200 K data within the higher r range are shown by dots. Fit ranges are indicated by arrows.

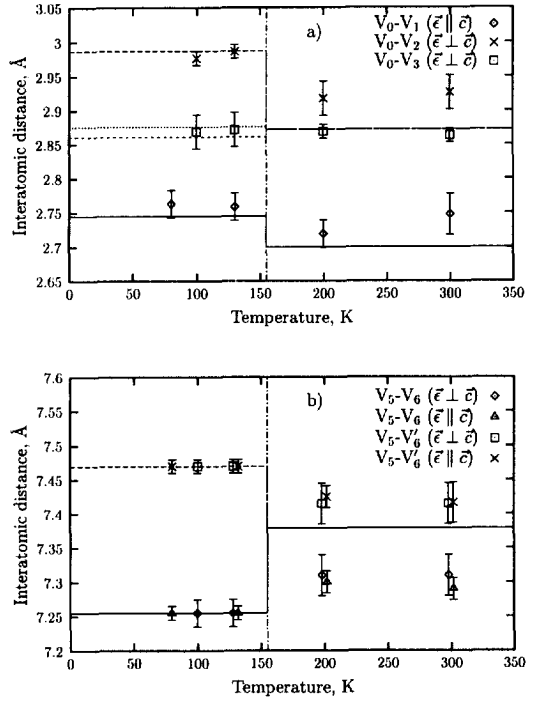

Fig. 3. V-V distances as determined by x-ray diffraction (lines) and XAFS (symbols) at 5 temperatures below and above the phase transition (vertical line): a) - nearest neighbors, b) more distant neighbors.

3. DISCUSSION

These results indicate that, locally, monoclinic distortions persist in the V_2O_3 above the phase transition temperature, though abruptly decreasing by 65 ± 20% at the phase transition as shown by the V_0 - V_2 distance of Fig. 3 a). The experimentally observed 1.4% decrease in the V_2O_3 volume, previously believed to be caused by the change in the unit cell dimensions between monoclinic and trigonal cells, can be explained mainly by the V_0-V_2 distances shortening in the monoclinic unit cell. Our estimates, using the change in V_0-V_2 distances obtained with XAFS, give 1.6 ± 0.3% decrease in the volume of the monoclinic unit cell.

The average trigonal structure, as ascertained by diffraction, therefore, is a result of averaging over unoriented monoclinic regions, which are small enough (and may dynamically change orientation), so that they do not individually produce sharp monoclinic diffraction peaks. Our XAFS results can only ascertain a lower limit to the region of 7.3 Åand give no information on the dynamics (the XAFS measurements are so fast ($\approx 10^{-15}$ sec) that no motion of atoms can occur). While the monoclinic region size is big enough to be detected by diffraction at low temperature (where three-fold twinned domains of the monoclinic cell [11] occur) it changes abruptly above the transition. This is another example, observed recently in perovskites [16] and high T_c superconductors [17], of a significant order - disorder component to what was previously thought to be a purely displacive transition. For example, XAFS measurements have indicated for the perovskite $PbTiO_3$ [16] that the local distortions from cubic symmetry below the ferroelectric T_c = 760 K remain large above T_c, yet diffraction indicates that the average structure becomes cubic in the weakly first order transition to the paraelectric phase.

4. SUMMARY AND CONCLUSIONS

In conclusion, our results show that the structural phase transition occurring in pure V_2O_3 is not the purely displacive transition with concomitant change of symmetry suggested by diffraction results. Rather, we obtained that the transition has both order - disorder and displacive character with locally monoclinic regions decreasing their correlation lengths from infinite to between 7 - 40 Å(where the monoclinic diffraction lines remain significantly broadened) above the metal - insulator transition, which leads to an average trigonal symmetry. The displacive character manifests itself above the transition by a decrease of monoclinic distortions within the domains by approximately 65%.

The wealth of information we obtained from these measurements should narrow the possible theoretical explanations. In particular, though the changes in some V - V distances are actually significantly less than given by the average structure, the change in volume is the same suggesting volume change is the more important parameter. The role of disorder and the lack of local symmetry change in the transition to the metallic and paramagnetic states needs to be accounted for in any theory. Obtaining a better understanding of these materials may also contribute to the understanding of other classes of materials containing correlated electrons such as strongly correlated metals and high-temperature superconductors.

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