STRUCTURAL MODELLING OF AMORPHOUS VANADIUM PENTOXIDE

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Abstract: Amorphous vanadium pentoxide (α -V_2O_5) is a component of many technically important semiconducting glasses. The transport properties are related directly to the material structure, and so in order to understand the transport mechanism the atom arrangement should be known. Much experimental work has been done to determine the short-range order in α -V_2O_5, but in view of contradicting conclusions the structure of the glass is still an open question. Thus, computer simulation techniques have been applied to get some insight into the structure of α -V_2O_5. In particular, the classical molecular dynamics (MD) simulations have been performed, using the original parametrisation of the interatomic interactions. Our effective interaction potential is derived from *ab initio* calculations of small hydrogen-saturated clusters VO_nH_n. The results of the MD simulations are discussed and compared to the available experimental data.

1. Introduction

Amorphous vanadium pentoxide (α -V_2O_5) is a component of many technically important semiconducting glasses, and forms a relatively new class of vitreous materials possessing electronic conductivity. Since electron transport depends on the structure, it is interesting to study the short-, and medium-range order in the glass. Various experimental methods, such as large-angle X-ray scattering (LAXS), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), IR-spectroscopy, Raman spectroscopy, have been applied in order to recognise the short-range order in amorphous V_2O_5, giving ambiguous information on the distances between atoms and on the shape of the basic structural units. Mosset *et al.* [1] showed that the oxygen co-ordination around the vanadium atoms in α -V_2O_5 is tetrahedral, similarly as in liquid V_2O_5. According to Nabavi *et al.* [2] both VO_4 and VO_5 units coexist in amorphous vanadium pentoxide. Dimitriev and Dimitrov [3], and Stizza *et al.* [4] conclude that structure of amorphous V_2O_5 is similar to the structure of its crystalline form, *i.e.* is composed only of VO_5 units. Moreover, Stizza *et al.* [4] note that the amorphous form of V_2O_5 reveals a higher regularity of the first co-ordination shell of vanadium atom then the corresponding crystal. Since the structure of V_2O_5 remains still controversial even as far as the short range order is concerned, an afford of computer structural modelling has been undertaken.

Computer simulation techniques have been applied to a wide range of structure modelling problems. Among other things they can be used as a powerful predictive tool, and give a more detailed (three dimensional) structural information then the experiment, which usually gives only two-dimensional representation of the structure [5-7]. In particular, the classical molecular dynamics (MD) simulations can yield full information on the structure and thermodynamic properties of solids and liquids, provided a correct parametrisation of the effective interaction potential is known. Because no potential parametrisation for amorphous vanadium pentoxide can be found in the literature, we had to perform suitable calculations ourselves. The calculations are based on the *ab initio* small cluster method [8-12]. Having obtained the paramerisation of a simple effective two-body interactions, the MD simulations were performed, and the resulting equilibrium structures were compared to the experimental data.

The paper is organised as follows. In Section 2 the experimental findings on the structure of crystalline and amorphous vanadium pentoxide are briefly reviewed. In Section 3 the results of the *ab initio* calculations within the small cluster method are presented and the parametrisation of a two-body interaction potential is given. Section 4 is dedicated to the description of our molecular dynamics (MD) simulations of the considered glass, and the simulation results are discussed and compared to the available experimental data. Finally, Section 5 contains concluding remarks.

2. The structure of crystalline and amorphous vanadium pentoxide

Enjalbert and Galy [13] reported a detailed structural study of crystalline V_2O_5, and concluded that the oxygen co-ordination around the vanadium atom should be described in terms of a square pyramid. The base of the pyramid is almost planar, and the vanadium atom is displaced from the basal plane by 0.47A towards the pyramid centre. The V-O distances equal to 1.779 A, 1.878 A, 2.017 A, and 1.577 A. Square pyramids share edges forming zigzag ribbons, and the ribbons share their corners forming layers (Figure 1).

Various experimental methods have been applied in order to obtain information on the short-range order in amorphous V_2O_5. Dimitriev and Dimitrov [3], in the base of their X-ray diffraction experiment conclude that the same VO_5 units occur in both vitreous and crystalline V_2O_5. Mosset *et al.* [1] develop a model of amorphous V_2O_5 in which the structure is built up from superstructural units comprising three tetrahedral VO_4 units (Figures 2, and 3). Stizza *et al.* [4] conclude that the amorphous form of vanadium pentoxide is build of layers of tetragonal pyramids, similarly as in crystalline V_2O_5, but the interatomic distance V-O in the vitreous structural unit is the same for all the vanadium-oxygen pairs, and equals to 1.85 A. This suggests a greater regularity of the vanadium atom neighbourhood in the α -phase then in the crystalline phase. Other authors claim that in amorphous V_2O_5 appear VO_5, V_2O_6, V_2O_7 and VO_4 structural units [14]. In view of contradicting conclusions of experimental works one can state, that the structure of the vanadium atom neighbourhood in α -V_2O_5 is still an open question. In what follows we describe the results of computer simulations aimed to elucidate the structure of the first co-ordination shell of the vanadium atom in amorphous vanadium pentoxide.

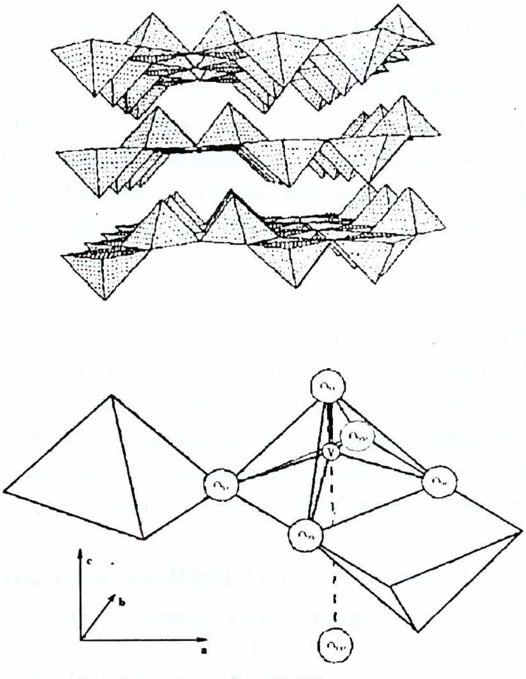


Figure 1. Network of VO_5 units after [13]

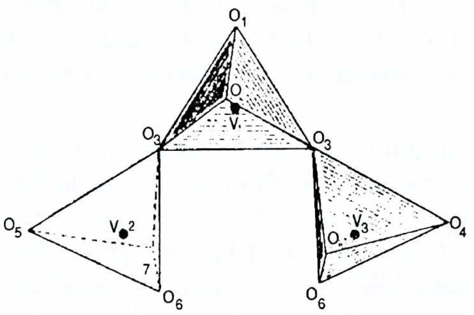


Figure 2. Superstructural unit comprising three tetrahedra [1]

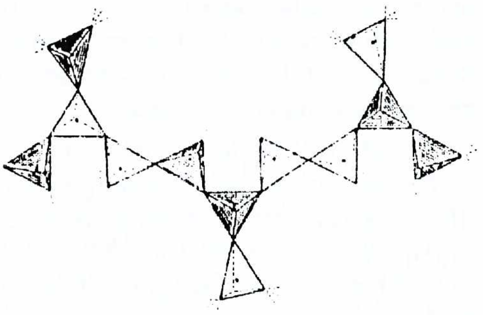
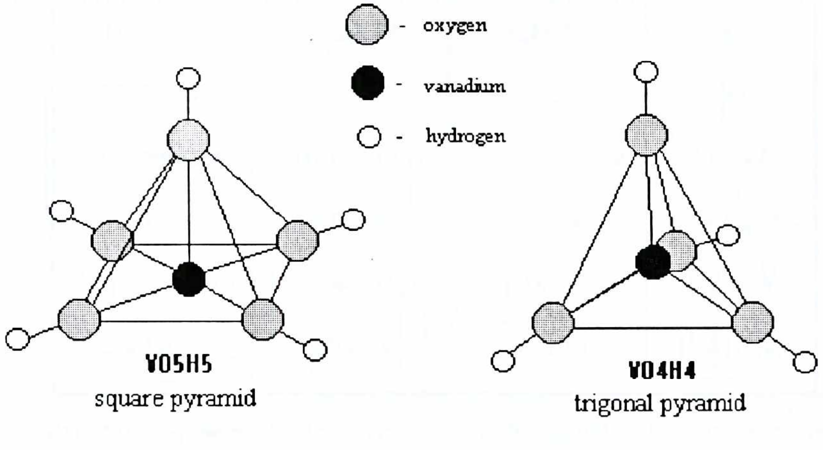


Figure 3.Superstructural units connected by corner sharing [1]

3. Effective two-body vanadium-oxygen and oxygen-oxygen interactions

Molecular dynamics (MD) simulations are at present widely used for structural modelling. The method consists in numerical solution of the classical many-body problem of interacting particles, so that the trajectories of all particles within a simulation box are found. At this point the laws of statistical physics are operative, that is, suitable averaging procedures over the atom trajectories yield the structural and thermodynamical information on the system [5-7]. Oxides have been commonly described by the ionic model with formal or partial ionic charges. The interactions between point charges arise from the long-range Coulomb forces between the ions, the short-range interactions come from the overlap of the electron charge clouds of the interacting ions. The total potential energy is the sum of n-body contributions to the potential, $n = 2,3,\ldots$. In the first approximation only two-body interactions can be taken into account. As far as the authors know, no potential parametrisation for amorphous vanadium pentoxide can be found in the literature. Thus, we have determined the parameters of the effective two-body interactions using the *ab initio* small cluster method [8-12].

In the MD simulations we calculate the components of forces between the i-th, and the j-th atom from the pair interaction potentials $V_{\alpha\beta}(r_{ij})$, which depend only on the distance r_{ij} the corresponding atoms. Here the indices α, and β denote the kind of atom (α,β = V, O). The chosen functional form of the short-range part of the pair interactions reads $V^{S}_{\alpha\beta}(r_{ij}) = A_{\alpha\beta} \exp(-r_{ij} \cdot \rho_{\alpha\beta})$ (the Buckingham potential). In calculating the long-range Coulomb interactions we allow for partial charges of vanadium and oxygen ions. The charges, as well as the $A_{\alpha\beta}$, $\rho_{\alpha\beta}$ parameters are to be determined in such a way, that the sum of the pair potential energies $V_{\alpha\beta}(r_{ij})$ within a small molecular cluster reproduces the *ab initio* energy of the same cluster.



VO5H5
square pyramid

VO4H4
trigonal pyramid

Figure. 1

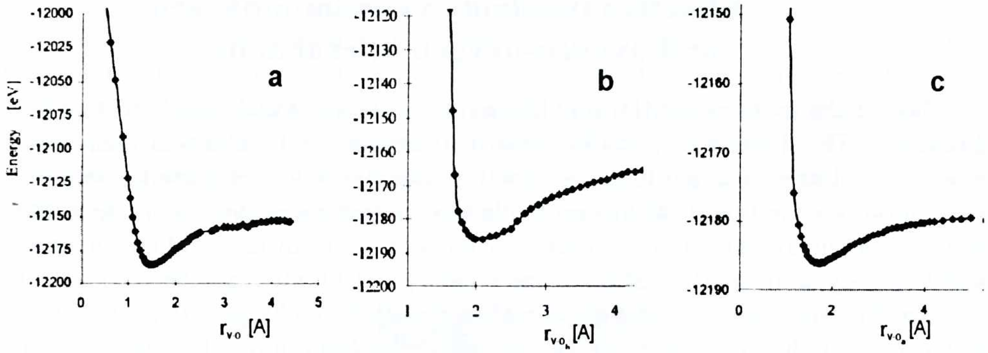


Figure 5. Results of the *ab initio* calculation on the VO_5H_5 cluster. Figure a: simple cluster size scaling, C_{4C} symmetry; Figure b: V-O_t = 1.75 A; Figure c: V-O_b = 1.75 A. O_t - apical oxygen, O_b - basal oxygen.

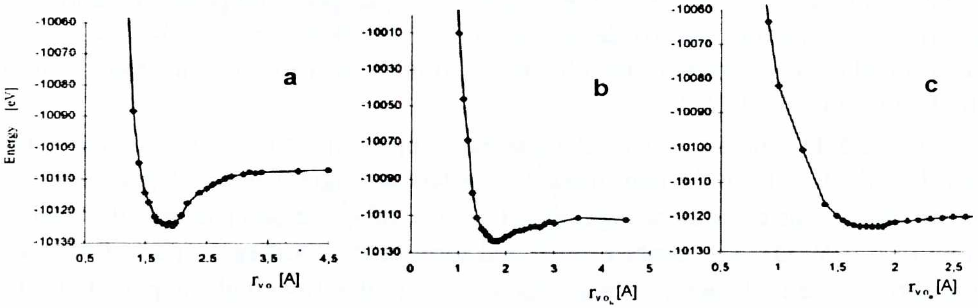


Figure 6. Result of the *ab initio* calculation on the VO_4H_4 cluster. Figure a: simple cluster size scaling, C_{3C} symmetry; Figure b: V-O_t = 1.75 A; Figure c: V-O_b = 1.75 A. O_t - apical oxygen, O_b - basal oxygen.

	Fit 1	**Fit 2**	**Fit 3**
Q_V	+2.5425	+2.56356	+2.49394
Q_O	-1.017	-1.02542	-0.997577
$A_{V\text{-}O}$ [J]	$8015.648\cdot10^{-19}$	$7930.949\cdot10^{-19}$	$7948.657\cdot10^{-19}$
$\rho_{V\text{-}O}$ [A^{-1}]	4.6359	4.6218	4.6352
$A_{O\text{-}O}$ [J]	$139061.41\cdot10^{-19}$	$132363.99\cdot10^{-19}$	$126975.56\cdot10^{-19}$
$\rho_{O\text{-}O}$ [A^{-1}]	10.1066	9.99778	9.9266

Table I. Parameters obtained by fitting of the parameters in the Buckingham potential to the results of the *ab initio* calculations.

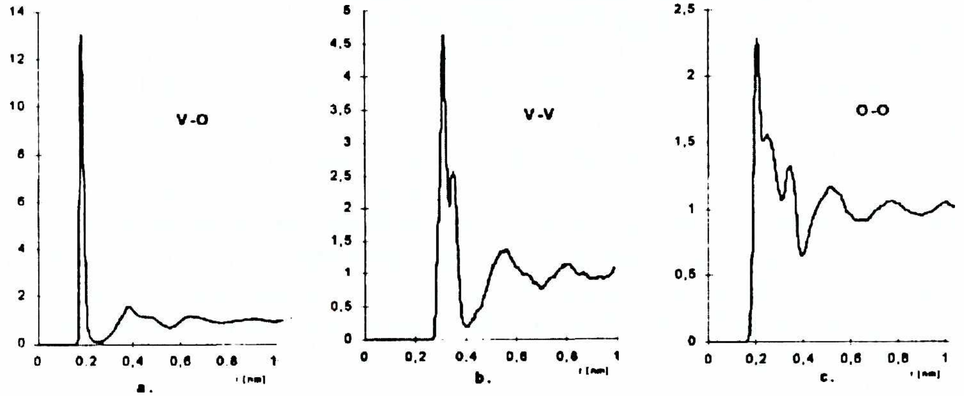
With the aid of Turbomole program [15] we have performed the Hartree-Fock (HF) calculations of potential energies for hydrogen-saturated molecular clusters VO_5H_5 (square pyramid, C_{4C} symmetry), and VO_4H_4 (trigonal pyramid, C_{3C} symmetry) (Figure 4). The 6-31g* basis set was used. The potential energy surface was obtained by repeating the HF calculations for the clusters of various V-O bond lengths in the range 0.5 - 5.0 A. Despite of the simple scaling of the cluster size, two other types of the cluster deformation were considered: changes of the base size at constant cluster height, and changes of the cluster height at fixed base geometry. The results for VO_5H_5, and VO_4H_4 clusters are presented in Figures 5, and 6, respectively.

Having obtained the *ab initio* energies of a sequence of small molecular clusters, the Powell method [16] has been used to find optimal parametrisation of the effective two-body V-O, and O-O interactions ($A_{\alpha\beta}$, $\rho_{\alpha\beta}$, $q_{\alpha\beta}$, α,β = V, O). Starting the optimisation program from different initial guess approximations, three different best-fitting sets of the parameters have been found (Table I).

4. Molecular dynamics simulation results and discussion

The classical molecular dynamics (MD) simulations have been performed in the microcanonical (NVE) ensemble. The atoms were assumed to interact by a two-body potential. The V-O interaction was parametrized as described in the previous section, and the V-V interaction parameters were taken from [17]. Coulomb forces were calculated with the aid of the standard Ewald method. The simulation box contained 2100 atoms. The systems were initially prepared in equilibrated molten state at 3000K, and then cooled down to 300K, passing equilibrium states at 2000K and 1000K. At each temperature the system was being equilibrated during 20000 femptosecond time steps, and sampled during other 10000 time steps. The MD calculations were realised for all three sets of the V-O interaction parameters.

Figures 7 and 8 show the radial pair distribution functions (RDFs), and angular distribution functions (ADFs), respectively, obtained from simulations with the first



a. b. c.

Figure 7. MD-simulated radial distribution functions, potential parametrisation 1.

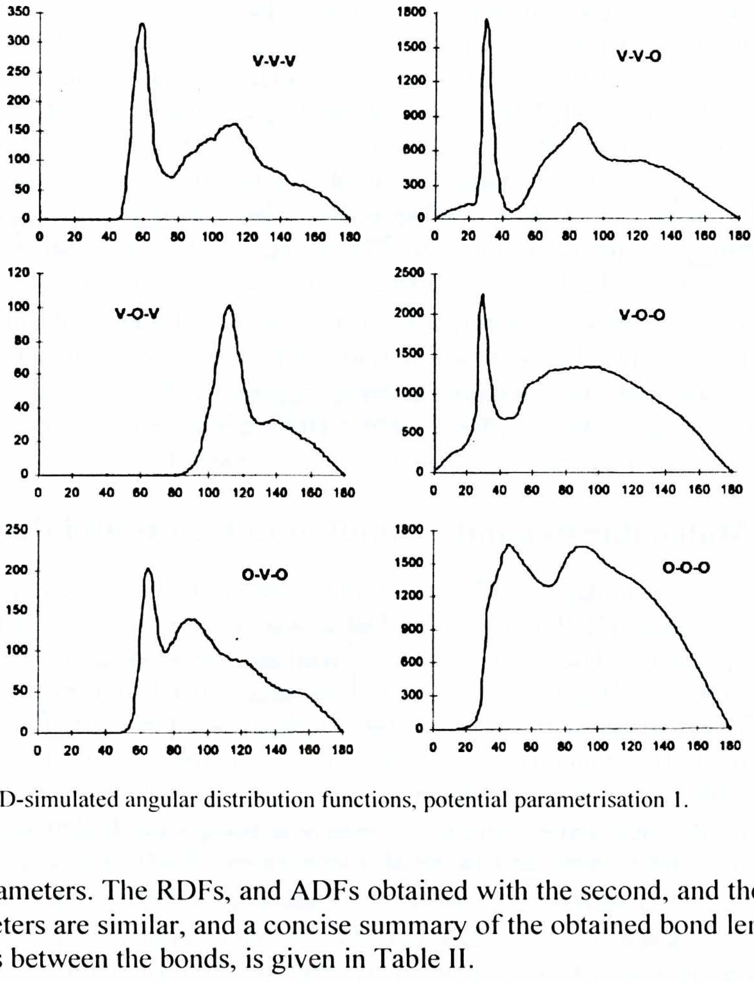


Figure 8. MD-simulated angular distribution functions, potential parametrisation 1.

set of parameters. The RDFs, and ADFs obtained with the second, and the third set of parameters are similar, and a concise summary of the obtained bond lengths, and the angles between the bonds, is given in Table II.

On the ground of the obtained radial and angular distribution functions, taking into account also the resultas of the Voronoi polyhedra analysis [19] we can conclude that a square pyramid is the basic structural unit in amorphous V_2O_5. This result agrees with the experimental evidence of [3] and [4], and remains in contradistinction with the results of [1] and [2]. Our results confirm the suggestion of Stizza *et al.* [4] that all the V-O distances in amorphous V_2O_5 have approximately the same length (~1.82 A). This means that the short range order in vitreous vanadium pentoxide shows the greater regularity than its crystalline form. The vanadium atom remains above the centre of the pyramid base and it is displaced from the basal plane by ~ 0.46 A towards the pyramid centre. The value is close to the corresponding distance in the crystalline phase (0.47 A, [13]). The neighbouring square pyramids share their edges and corners.

The comparison of our numerical results with the available experimental data is presented in Table III. The upper part of the table contains the experimental results

	Fit 1	**Fit 2**	**Fit 3**
V-O [A]	1.82	1.8199	1.82
V-V [A]	2.6 3.52	2.602 3.55	2.604 3.562
O-O [A]	2.574 2.878 3.52	2.545 2.839 3.55	2.602 2.909 3.562
O-V-O [°]	64.5 90 104.5 151	64.5 90 102.5 155	65 90 104.5 151
O-O-O [°]	45 53 63.4 90 135	45 53.9 63 90 135	45 53.13 63.4 90 135
V-O-O [°]	14.5 30 45	12.5 32.5 45	14.5 30.5 45
h [A]	0.4635	0.3928	0.4607

Table II. Geometric parameters of the vanadium atom first co-ordination shell obtained in the MD simulations. h is the displacement of vanadium atom from the base of the pyramid.

obtained by the various methods: large-angle X-ray scattering (LAXS) [3], extended X-ray absorption fine structure (EXAFS) [2], X-ray absorption near edge structure (XANES) [2], [4], IR-spectroscopy [2], [3], [14]. The lower part of the table summarises the results of our MD simulations based on potential parameters: 1. determined in the present work; 2. adopted in the standard way ($A_{\alpha\beta} = (A_{\alpha\alpha} A_{\beta\beta})^{1/2}$, $\rho_{\alpha\beta} = (\rho_{\alpha\alpha} + \rho_{\beta\beta})/2)$ from [17], and 3. determined for the V_2O_5 crystal [18], sets of parameters [A] and [B].

6. Concluding remarks

In the paper we have reported on the results of classical MD simulations of the structure of amorphous vanadium pentoxide. In the MD simulations a simple two-body interaction potential has been used. The potential has been parametrised within the molecular cluster *ab initio* method. Despite of the simplicity of the effective interaction potential, our MD results allowed to elucidate some doubts appearing in view of ambigous experimental results on the structure of the vanadium atom first co-ordination shell. However, the *ab initio* calculations that have been performed can

	V_2O_5	V - O [A]	V - V [A]	O - O [A]
EXPERIMENT	Dimitriev and Dimitrov [3]	1.85 (4.6) $[VO_5]$	------	------
	Mosset *et al.* [1]	1.75 (3.6) $[VO_4]$	------	------
	Stizza *et al.* [4]	1.85	------	------
	Nabavi *et al.* [2]	1.53 1.75 1.97	3.13 3.43	------
SIMULATION	Abrahamson [17]	1.8 (4.9)	3.52	2.52 3.6 4.9
	Dietrich *et al.* [18]	$1.84\ (6.7)^{a)}$ $1.78\ (5.3)^{b)}$	$3.12^{a)}$ $4.5^{a)}$ $3.17^{b)}$ $3.49^{b)}$	$2.08;\ 3.52^{a)}$ $4.36^{a)}$ $2.5;\ 3.54^{b)}$ $4.9^{b)}$
	Fit 1	1.82 (5.4)	3.18 3.52	2.08 2.56 3.52
	Fit 2	1.82 (5.5)	3.17 3.49	2.08 2.54 3.56
	Fit 3	1.84 (5.5)	3.19 3.52	2.12 2.56 3.56

Table III. The comparison of simulation results with the available experimental data. The V-O co-ordination numbers are given in brackets. a) data set A in [18]; b) data set B in [18].

serve as accurate input data for optimisation procedures applied for more realistic three-body effective interaction potentials. Such potentials will account for bond bending, and will lead to more exact description of the α -V_2O_5 structure. The work on the three-body potential parametrisation is in progress.

Acknowledgement

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