

A Computer Simulation Study of Sodium in Hexagonal Tungsten Trioxide

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We report a computer simulation study of hexagonal tungsten trioxide and its sodium insertion compounds using static equilibrium techniques. Our model is based on previously derived interatomic potentials and uses a rigid ion approximation. The calculated lattice vectors are compared with experimental data. We show that simulation of sodium ions and electrons in this structure predicts incommensurate ordering and a compositionally dependent mobility. © 1989 Academic Press, Inc.

Introduction

The ion insertion compounds, or bronzes, of tungsten trioxide have been widely investigated because of their potential application in electrochromic display devices. A useful electrochromic material should be a good ionic and electronic conductor to provide rapid color change. However, in WO_3 , fast response times have only been obtained with hydrated films. WO_3 has a distorted ReO_3 structure of corner-sharing WO_6 octahedra and the compounds $M_x\text{WO}_3$ exhibit structures which depend on both the size of M and the value of x . Diffusion of the interstitial cations in these structures is generally slow (1), although high diffusivities have been measured for lithium in the mixed alkali bronzes cubic $\text{Li}_x\text{Na}_x\text{WO}_3$ and hexagonal $\text{Li}_x\text{K}_{0.3}\text{WO}_3$ (2, 3). The increased diffusivity in these materials has

been attributed to the increased bottleneck size found in bronzes which contain large cations and to the improved coulombic screening which results from the high electronic conductivity that occurs at high concentrations of interstitial ions.

Preparation of a metastable form of WO_3 with a hexagonal structure has been reported (4), and a (001) projection of this structure is shown in Fig. 1. The large hexagonal tunnels parallel to the c axis appear favorable for fast cation conduction. In this study we report the results of computer simulation of the hexagonal WO_3 lattice and the insertion of sodium into the structure. We have calculated the potential energy surface for a sodium ion in the hexagonal tunnel and describe how this is altered by the presence of both localized electrons and other sodium ions.

Techniques

Well-established static equilibrium techniques were used which have been de-

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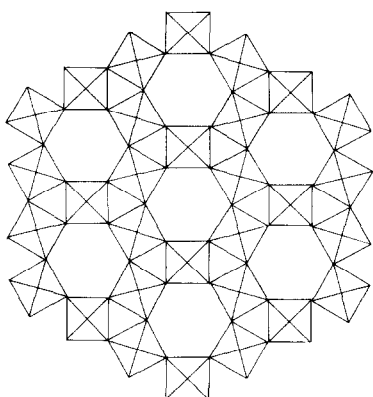


FIG. 1. (001) Projection of the hexagonal WO_3 structure.

scribed in detail elsewhere (5). Briefly, the program METAPOCS (6) uses specified ion pair potentials to relax the nondefective crystal structure to a minimum energy configuration by varying both the unit cell dimensions and the atomic coordinates. In these calculations all of the atomic positions are included, not just those in the asymmetric basis. No symmetry was explicitly included in the calculations. CASCADE (7) is essentially a vectorized version of the HADES III program (8) implemented on the Cray 1 at the University of London Computer Centre. CASCADE simulates point defects and defect clusters and calculates the energy required to introduce these into the perfect crystal. In this approach, the crystal is divided in two regions: an inner Region I, immediately surrounding the defects in which there is explicit lattice simulation using ion pair potentials, and a Region II, consisting of the remainder of the crystal which is treated as a dielectric continuum; Mott-Littleton theory is used to obtain the polarization in this region.

Interatomic Potential Model

The pair potential parameters used here were taken from a previous study of defects

in an idealized ReO_3 structure, used as a model for WO_3 (9). The earlier use of this model (9, 10) showed that it contained enough information to account for the structural behavior of nonstoichiometric WO_3 and we feel that the hexagonal polymorph could also be adequately modeled. The short-range interactions $V(r)$ take the form of a Buckingham function,

$$V(r) = A \cdot \exp(-r/p) - C \cdot r^{-6},$$

where A , p , and C are material parameters derived by fitting to measured crystal data. The parameters for the Na-O interaction were taken from a study by Walker and Catlow on beta aluminas (11). The parameters are given in Table I.

A simple rigid ion model has been used in which effects due to electronic polarization of the ions are not taken into account. This will result in a certain degree of inaccuracy. However, models which include polarizability require considerably increased computer time and it is felt that sufficiently interesting results have been obtained using this simplified model.

Results and Discussion

1. Lattice Relaxation and Energy Calculations

Trial coordinates and lattice vectors for the structure were calculated assuming a perfect lattice based on undistorted WO_6 octahedra. All of the atomic positions (not just those in the asymmetric basis) were in-

TABLE I
SHORT-RANGE PARAMETERS USED IN POTENTIAL MODEL

Interaction	A	p	C	Ref.
W. . . O	741.39	0.4383	0.00	(9)
O. . . O	22764.30	0.1490	17.89	(9)
Na. . . O	1226.80	0.30650	0.00	(10)

TABLE II
COMPARISON OF CALCULATED AND
MEASURED LATTICE PARAMETERS FOR
HEXAGONAL TUNGSTEN TRIOXIDE

	Calculated values	Measured values (4)
a (Å)	7.3698	7.298(2)
c (Å)	3.7299	3.899(2)
W-O ₁	1.8650	1.95
W-O ₂	1.8727	1.89

cluded in the calculation. The program METAPOCS was used to relax these parameters to a minimum energy configuration, the lattice energy of which was calculated to be -638 eV per unit cell or -2.05×10^4 kJ mole⁻¹. The relaxed lattice vectors and tungsten-oxygen distances are given in Table II where they are compared to X-ray diffraction data from Ref. (4).

Gerand *et al.* (4) report that superlattice reflections were observed in electron diffraction patterns which indicated that the c lattice parameter should be doubled. We attempted to observe this doubling in our simulation by using coordinates with a doubled c parameter and by repeating the calculations with slightly displaced ionic coordinates in order to lower the unit cell symmetry. However, in each case the relaxed coordinates showed the second layer of ions placed exactly above the first along the c axis, indicating no doubling of the c axis parameter in the calculation. Our potentials were derived for the cubic structure and may not include effects due to the lower initial symmetry which arises because of the displacement of the tungsten ions from the center of the octahedra. This displacement is stabilized by polarization of the oxygen ions. The absence of both of these effects may account for our inability to observe distortions to the lower symmetry phase.

Dickens and Kay (12) have reported that

the enthalpy of formation of hexagonal WO₃ is $-(840 \pm 1.0)$ kJ mole⁻¹ from solution calorimetry measurements. We have used this value to calculate the lattice energy E_1 from the Born-Haber cycle relations,

$$E_1 = S + \left(\frac{3}{2}\right)D_o + \Sigma I_w - 3\Sigma A_o - H_f,$$

where S , D_o , I_w , A_o , and H_f represent the energy of sublimation of tungsten trioxide, the energy of dissociation of oxygen, the ionization potentials of tungsten, the electron affinities of oxygen, and the enthalpy of formation of hexagonal tungsten trioxide, respectively. Using published data for these energies the lattice energy is calculated to be 1.88×10^4 kJ mole⁻¹. This is within 10% of the value found from our lattice simulation calculations.

Although the ion pair potentials used here were derived from the cubic crystal structure data, the reasonably close correspondence between our model and experimental data for the hexagonal form justifies confidence in our model. The following section describes how it has been extended to investigate the inclusion of sodium in the lattice using the parameters derived above.

Similar lattice relaxation calculations were performed on two bronzes:

- (i) Na_{0.165}WO₃: at this composition alternate tunnel sites are occupied.
- (ii) Na_{0.333}WO₃: every tunnel site is occupied.

The charge compensating electron was included in the calculation simply by replacing the W⁶⁺ lattice ion by a W⁵⁺ ion. This small polaron representation of the compensating electron (i.e., localized on a tungsten ion) is not thought to be unrealistic for at low insertion ion concentrations ($x < 0.3$) Na _{x} WO₃ behaves as a semiconductor with localized electrons (13).

Calculated lattice parameters for these compositions are given in Table III and it can be seen that both the a and c param-

TABLE III
CALCULATED LATTICE PARAMETERS FOR
HEXAGONAL TUNGSTEN BRONZES

	X value		
	0.0	0.165	0.333
a (Å)	7.3698	7.5016	7.6131
c (Å)	7.4598	7.5573	7.6502

ters increase with increasing sodium in concentration. An X-ray diffraction study of hexagonal tungsten trioxide and its sodium bronzes found that the a parameter increased but the c parameter decreased with increasing sodium ion concentration (14). The increase in the c parameter found in our calculations is likely to be a result of forcing the sodium ions to take up positions commensurate with the WO_3 lattice; in the next sections this is shown to be physically unrealistic. In addition at high sodium ion concentrations the electrons can no longer be treated as localized.

2. Ion Insertion Calculations

Initially we simply looked at the energetics of putting a sodium ion into the interstitial space in the hexagonal tunnel. It was specified either held fixed, that is, maintained in its position while the lattice re-

laxed around it, or allowed to relax with the surrounding lattice. In the former case the potential energy surface for the sodium ion in the hexagonal tunnel was determined and in the latter with the sodium ion allowed to relax, the minimum energy configuration was found.

The potential energy surface for an isolated sodium ion at the center of the hexagonal tunnel is shown in Fig. 2. The variation in potential energy is due to the interaction of the ion with the lattice. By plotting out the surface along the tunnel the enthalpy of migration is found to be 0.24 eV. The calculated distortions of the lattice around a Na^+ ion are very small, even when the ion is in the narrow part of the tunnel. This reflects the relative sizes of the tunnel and the sodium ion and is, of course, a requirement for fast sodium ion conduction.

The next series of calculations included the charge compensating electron in the defect configuration by replacing the W^{6+} lattice ion with a W^{5+} ion. In Fig. 3 the potential energy surface with an electron localized on the tungsten ion closest to position 0 is shown. The minimum energy for this configuration is -7.31 eV, whereas the sum of the energies for the isolated defects is -7.03 eV. The difference of -0.28 represents a trapping energy between the sodium ion and the electron.

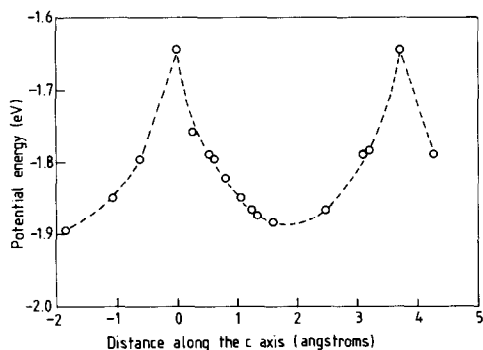


FIG. 2. Potential energy surface at the center of the hexagonal tunnel for a sodium ion in WO_3 .

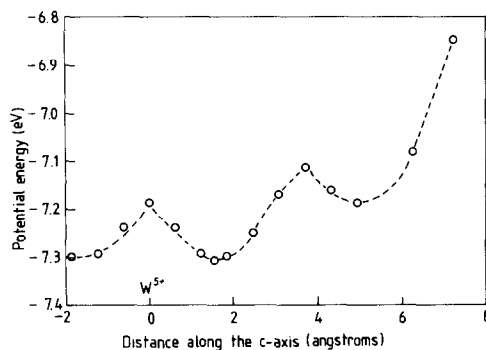


FIG. 3. Potential energy surface for a sodium ion close to a localized electron.

A series of energy calculations were carried out on clusters of sodium ions where the localized electrons were included; minimum energy configurations were determined. Calculations involving between two and eight ion-electron pairs were performed. The different configurations which were investigated included the following: simulation of all eight sodium ions in a single tunnel, simulation of one to four sodium ions in each of two adjacent tunnels, simulation of the sodium ions either in adjacent crystal layers perpendicular to the c axis or in the same layer, and a combination of these. The main points to emerge from these calculations are as follows:

The repulsive energy between sodium ions in the same tunnel is larger than the periodic potential associated with the host lattice. As a result of this the ions tend to move apart until they are separated by an empty tunnel site. This strong repulsive interaction causes the sodium ions to take up positions incommensurate with the WO_3 lattice; that is, the separation between sodium ions is not determined by the periodicity of the host lattice and is not a rational fraction of the c lattice parameter. Such incommensurate structures have been observed in hexagonal K_xWO_3 (15, 16). Our results provide an explanation of such behavior in terms of competing potential interactions; in this case the $\text{Na} \cdots \text{Na}$ interaction dominates the $\text{Na} \cdots$ lattice interaction.

The trapping energy between an electron localized at a tungsten ion and an adjacent sodium ion is of similar magnitude to the enthalpy of migration calculated for an isolated sodium ion. It is modified in larger clusters of ions. The most stable configuration found from these calculations was for two sodium ions in the same tunnel, separated by 6.9 \AA , with the localized electrons diagonally opposite each other in adjacent layers of WO_6 octahedra as shown in Fig. 4. All the other configurations which were in-

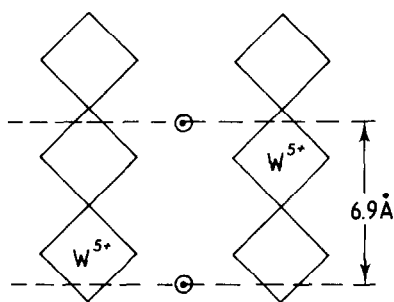


FIG. 4. Schematic cross section through the hexagonal tunnel in the (010) plane showing the lowest energy configuration for two sodium ions near two localized electrons. Dotted circles represent sodium ions.

vestigated were found to have higher energies per ion, and therefore lower trapping energies. The effect of these trapping energies will be to lower the mobility of the sodium ions. At low sodium concentrations, where isolated pairs of ions and electrons can exist, the trapping energy will be at a maximum. At sodium concentrations above approximately $x = 0.05$ the ions will interact and it will be reduced. For $x > 0.3$ the material is a metallic conductor and our model suggests it will also be a good ionic conductor. The model thus predicts a concentration-dependent mobility.

Approximate diffusion coefficients (D) may be calculated from the derived enthalpies (H_m) using a simple hopping model,

$$D = g(1 - c)Za^2\nu_0 \exp(S_m/R) \exp(-H_m/RT),$$

where g is a factor which includes effects due to lattice geometry and to correlations between successive jumps; $(1 - c)Z$ is the number of unoccupied nearest-neighbor sites; a is the jump distance; ν_0 is the attempt frequency, and S_m the entropy. R and T have their usual meanings. Using an approximate value of 10^{-12} for ν_0 , for no trapping H_m has been found to be 0.24 eV from which a diffusion coefficient at 363 K of $1.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ is calculated. If the trapping energy is included the enthalpy of mo-

tion becomes 0.55 eV and the diffusion coefficient is calculated to be $5.9 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$. In an experimental investigation of sodium diffusion in two hexagonal tungsten bronzes a chemical diffusion coefficient of $(4.1 \pm 1.3) \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ at 363 K was measured in $\text{Na}_{0.23}\text{WO}_3$ and $(5.4 \pm 2.9) \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ in $\text{Na}_{0.02}\text{WO}_3$ (17). Schlasche and Schollhorn (14) reported the electrochemical insertion of hydrogen and alkali ions into hexagonal WO_3 and find that the reaction is irreversible at low cation concentrations. Our results suggest that this is due to the increasing stability of the ion–electron pair.

By increasing the sophistication of our model to include electronic polarization effects we would expect to increase the trapping energy. Consequently our calculations underestimate these energies and therefore result in overestimates of mobilities in these structures.

To be suitable for use in an electrochromic display a material must exhibit good ionic and electronic conductivity across the composition at which the color change occurs. It appears that, while hexagonal Na_xWO_3 will be a good ionic conductor at high insertion ion concentrations where it is deep blue, bleaching the material results in much lower conductivities and thus long response times. Similar trapping effects are likely to occur in the cubic tungsten bronzes.

Conclusions

Static lattice simulation methods have been applied to hexagonal WO_3 and to sodium insertion in this material. We have calculated the lattice energy and unit cell vectors and these agree well with experimental data.

Calculations of sodium ions and electrons in the lattice have shown that, of the three competing potentials (ion–lattice, ion–ion, and ion–electron), the ion–ion in-

teractions dominate. This results in incommensurate structuring of the sodium ions with respect to the WO_3 structure.

Trapping of the ions near localized electrons is predicted, resulting in a decrease in the mobility of the ions. This effect will be most pronounced at low sodium ion concentrations where isolated pairs of ions can exist and accounts for the concentration-dependent mobility observed experimentally.

Acknowledgments

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