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LOCAL STRUCTURES IN ALUMINUM OXIDE

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The relative stability of sixfold and fourfold coordination for Al ions by oxygens in the solid and liquid phases of Al_2O_3 is examined by treating several small clusters of this material within an ionic model.

Keywords: Molten salts; molecular structures

1. INTRODUCTION

The liquid structure of the high-temperature-melting oxides Al_2O_3 and Y_2O_3 has very recently been studied [1–3] by combining diffraction of X-rays from a synchrotron radiation source with levitation techniques for containerless confinement of the melt. The experimental results show a striking analogy in the behaviour of metal-ion coordination across melting between these oxides and the corresponding chlorides AlCl_3 [4–6] and YCl_3 [7]. Whereas the coordination of the Y^{3+} ions remains essentially sixfold after melting in both the chloride and the oxide, the coordination of the Al^{3+} ions changes on melting from sixfold to essentially fourfold in both compounds.

These similarities of coordination behaviour provide a further illustration of the fact that the stability of local structures in molten

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compounds is largely governed by the chemical activity of the metal ion [8, 9]. On a chemical scale of the elements such as that proposed by Pettifor [10], the chemical activity of Y is measured by a coordinate of 0.66 against a coordinate of 1.66 for Al.

However, the problem remains of how these local structures are connected into the crystalline and liquid structures. This question is especially intriguing for the two compounds of Al, since the often invoked explanation for the change from sixfold to fourfold coordination in AlCl_3 on melting is that a liquid of correlated Al_2Cl_6 dimers forms [4, 11], each dimer consisting of two AlCl_4 tetrahedra sharing an edge. A different explanation is needed for the connectivity of fourfold-coordinated local structures in liquid Al_2O_3 , as will be emphasized below by treating some relevant small clusters of Al and O ions within a simple ionic model.

2. LOCAL STRUCTURES IN CRYSTALLINE AND LIQUID Al_2O_3

The models that we examine are based on interionic potentials already used by Alvarez *et al.* [12] to carry out computer simulation work on the structure of small crystallites of $\gamma\text{-Al}_2\text{O}_3$. The effective pair potentials proposed by these authors have the simple form

$$V(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + \frac{e^2}{n(\sigma_i + \sigma_j)} \left(\frac{\sigma_i + \sigma_j}{r_{ij}} \right)^n \quad (1)$$

where q_i are the effective ionic charges, σ_i are the ionic radii and $n=9$. The values of these parameters that we have adopted in our calculations are reported in Table I. The ionic charges have alternatively

TABLE I Parameters for the interionic pair potentials in Eq. (1)

q_{Al}	q_O	$\sigma_{Al}(\text{\AA})$	$\sigma_O(\text{\AA})$
1.65	-1.10	0.52	1.02
3	-2	0.61	1.18

been taken from the work of Alvarez *et al.*, or set equal to the full valences. The values of the ionic radii have correspondingly been chosen so as to fit the observed Al—O bond length in the sixfold coordinated α -Al₂O₃ crystal, the ratio $\sigma_{\text{Al}}/\sigma_{\text{O}}$ being also taken from the work of Alvarez *et al.* (their values for the ionic radii are $\sigma_{\text{Al}} = 0.62\text{\AA}$ and $\sigma_{\text{O}} = 1.20\text{\AA}$).

An immediately relevant fact that emerges from our model for the sixfold-coordinated state is that, with both choices of the ionic charges in Table I, an isolated octahedral AlO₆ unit is found to be unstable against dissociation. However, on attributing a charge of $q_{\text{O}}/4$ to each of the oxygens we find that the AlO₆ unit is stabilized and that the value of the Al—O bond length in the α -Al₂O₃ crystal (1.91 \AA [1]) can be fitted with values of the ionic radii which are quite close to those of Alvarez *et al.* (see Tab. I).

The reduced charge on the oxygens in the AlO₆ unit can be interpreted, of course, as reflecting sharing of these ions between different Al ions in the crystal structure and the specific value of the reduction (a factor of 1/4) is dictated by the requirement of local charge neutrality. We recall in this regard that fractionalization of ionic charges as governed by local charge neutrality provides a very efficient method to evaluate the Madelung energy of ionic crystals by direct summation [13].

From the above calculation on the Al ^{q_{Al}} (O ^{$q_{\text{O}}/4$})₆ unit we move on without further adjustment of parameters to the fourfold-coordinated Al ^{q_{Al}} (O ^{$3q_{\text{O}}/8$})₄ unit. We find for it a stable tetrahedral structure with an Al—O bond length of 1.704–1.706 \AA , depending on the two alternative choices of q_{Al} and q_{O} in Table I. This result is to be compared with the value of 1.76 \AA reported by Ansell *et al.* [1] for the position of the first peak in the X-ray pair distribution function from their diffraction experiment on molten Al₂O₃. We stress that, as illustrated above, our results for the bond lengths are totally insensitive to the choice of the absolute values of the effective ionic charges. The total energy that we calculate for each unit and the values of its vibrational frequencies are instead sensitive to this choice. For this reason we shall in the following focus on relative values of the total energy (relative to the state of free ions) for different units, rather than on its absolute values.

3. CONNECTIVITY OF LOCAL STRUCTURES IN LIQUID Al_2O_3

In the light of the above results and with the aim of contrasting the structural behaviours of Al_2O_3 and AlCl_3 , we proceed to evaluate the stability of monomers and dimers of Al_2O_3 .

The stable structure that we find for the Al_2O_3 monomer is a symmetric trigonal bipyramid formed by a regular triangle of oxygens, with an O—O bond length of 2.19\AA , lying between the two Al ions, with an Al—O bond length of 1.59\AA and an Al—Al bond length of 1.93\AA . No data seem to be available for this molecule.

For the Al_4O_6 dimer we have instead found three different stable structures, which in order of increasing binding energy may be described as follows:

- (1) a symmetric structure formed by two fourfold-coordinated Al ions inside two distorted tetrahedra sharing an edge, with each terminal pair of oxygens being bound to a further Al ion (see Fig. 1.a);
- (2) a symmetric dimer formed by two bipyramidal monomers sharing two oxygens (see Fig. 1.b);
- (3) an asymmetric structure formed from the bitetrahedral one in Figure 1.a by breaking a tetrahedron in favour of attaching an oxygen tail to one of the terminal Al ions (see Fig. 1.c). For all these structures the values of the Al—O bond lengths and those of the O—O bond lengths in the pairs of bonding oxygens are similar to those that we have reported above for the Al_2O_3 monomer, whereas the O—O bond lengths for oxygen pairs involving terminal oxygens are considerably increased through distortions of the tetrahedra.

It is evident that, whereas fourfold coordination of the Al ions is met in both the structures of Figure 1.a and Figure 1.c, neither structure is relevant to the liquid structure of Al_2O_3 . In fact the symmetric structure in Figure 1.a is the most weakly bound, pointing again to ion sharing between neighbouring local structures as being crucial in determining the connectivity of the Al_2O_3 melt.

We have consequently examined the stability of an Al_2O_6 unit, for which we find the symmetric bitetrahedral structure shown in Figure 2 when we attribute the full q_{O} value of the charge to the two bonding

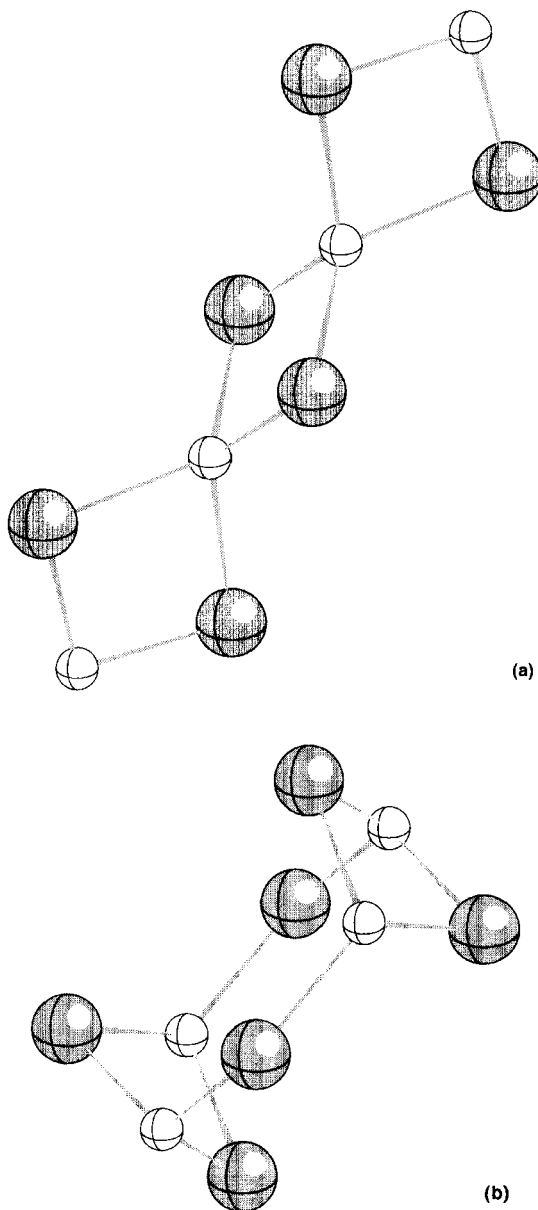


FIGURE 1 Stick-and-ball models of stable structures for the Al_4O_6 dimer, built with the equilibrium values of the structural parameters evaluated with interionic pair potentials. The small white spheres are Al ions and the large grey spheres are O ions.

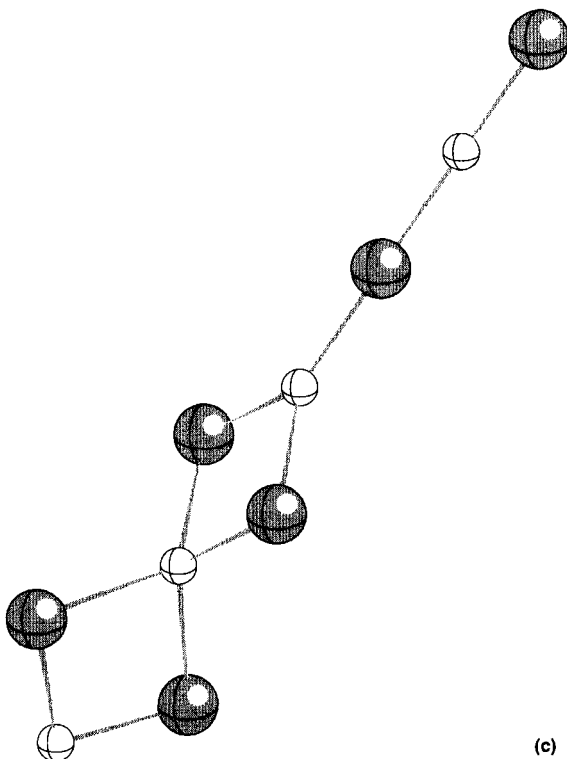


FIGURE 1 (Continued).

oxygens and a fractional charge of $q_O/4$ to each of the four terminal oxygens. The binding energy of this unit is much greater than that of any of the structures shown in Figure 1. The two tetrahedra are considerably distorted, the first-neighbour bond lengths being (with the notations O^B and O^T for bonding and terminal oxygens) $r_{Al-O^B} = 1.56 \text{ \AA}$, $r_{Al-O^T} = 1.85 \text{ \AA}$ and $r_{O^B-O^B} = 2.11 \text{ \AA}$, $r_{O^B-O^T} = 2.79 \text{ \AA}$, $r_{O^T-O^T} = 2.94 \text{ \AA}$.

4. CONCLUSIONS

In summary, we suggest that the liquid structure of Al_2O_3 can be viewed as formed from connecting basic units such as shown in Figure

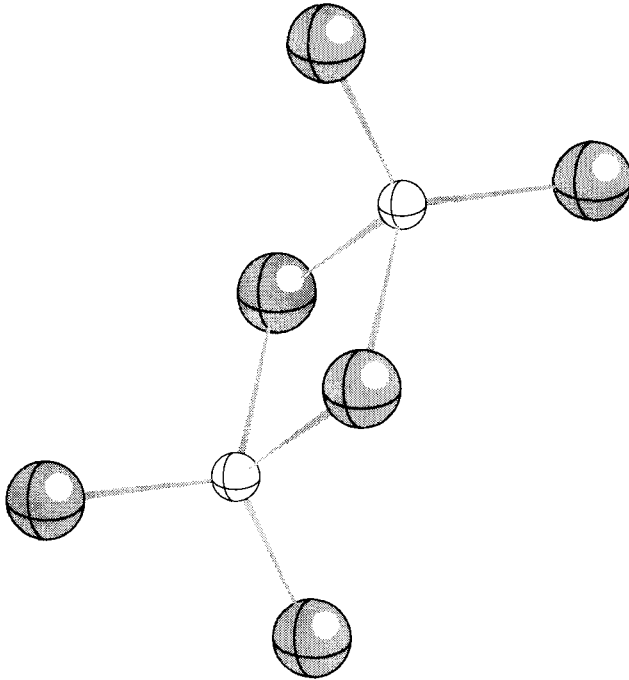


FIGURE 2 Stick-and-ball model of the stable structure for the Al_2O_6 unit, with fractional charges on the terminal oxygens as described in the text.

2 into a disordered network through oxygen sharing. A coordination number of Al ions by oxygens equal to 4 is consistent with the experimental value of 4.4 ± 1.0 [1]. We estimate an average Al—O bond length of 1.71\AA and an average O—O bond length of 2.78\AA , which are in crude accord with the positions of the first and second peak in the X-ray pair distribution function at 1.76\AA and 3.08\AA [1].

The predicted connectivity of the Al_2O_3 melt is therefore quite distinct from that of the AlCl_3 melt. It is nevertheless remarkable that, if one disregards the distortion of the tetrahedra in the Al_2O_6 unit and the fractional charges to be attributed to its terminal oxygens because of oxygen sharing between neighbouring units, the Al_2O_6 structure shown in Figure 2 resembles that of the Al_2Cl_6 dimer which is believed to be the basic constituent unit of molten AlCl_3 .

As a last remark we note that, from previous experience with calculations of the structure of small clusters within ionic models [14],

the values of the structural parameters that we have reported above may be expected to be quantitatively inaccurate owing to the extreme simplicity of the model in Eq. (1). In particular, inclusion of electronic dipoles on the oxygen ions can be expected to quantitatively modify the shape of the Al_2O_6 unit shown in Figure 2, in the direction of increasing the bond length for the pair of bonding oxygens and of reducing thereby the distortion of the bitetrahedron.

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