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The extent of zinc oxide solution in zinc chromate spinel

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ABSTRACT

Atomistic simulation methods have been applied to an ionic model and used to investigate the enthalpies of formation and reaction of defects in the spinel, ZnCr_2O_4 . For the stoichiometric material our results (i) suggest that small amounts of exchange disorder are expected and (ii) show that the formation enthalpies of Schottky and Frenkel defects are sufficiently high that negligible intrinsic disorder of these kinds is expected.

The possibility, suggested by experiment, that large amounts of ZnO may dissolve in the ZnCr_2O_4 lattice has also been investigated. However, the results of the calculations presented here rule out straightforward dissolution. On the other hand, they show that it is likely that the solubility of ZnO is substantially increased when the material is simultaneously oxidized. Unfortunately, the methods used to calculate the corresponding reaction energies in non-stoichiometric ZnCr_2O_4 are subject to some uncertainty arising from the variable nature of the second electron affinity of the oxygen atom. Nevertheless, the oxidation-driven mechanism is supported by the calculated variations of lattice parameter with composition, which are not subject to the same uncertainty.

§ 1. INTRODUCTION

There have been many studies of compounds with the spinel (MgAl_2O_4) structure. Many of these compounds, which we represent generally as AB_2O_4 , can be considered as strongly ionic oxides containing A^{2+} and B^{3+} ions. The *normal* structure (see fig. 1) is one in which all the A ions are on A-sites (tetrahedrally coordinated with neighbouring O ions) while all B ions are on B-sites (octahedrally coordinated with neighbouring O ions). Nevertheless, exchange disorder among the cations is common (see, for example, O'Neill and Navrotsky (1984)) and has been extensively studied. Some of these materials are interesting also because they may become non-stoichiometric, thus giving defective spinels; for example, at high temperatures excess Al_2O_3 may be dissolved in MgAl_2O_4 (Navrotsky, Wechsler, Geisinger and Seifert 1986). In general, however, while the dissolution of the B_2O_3 oxide in AB_2O_4 is known, the dissolution of the AO oxide occurs rather rarely. In addition, there is also the possibility of forming Schottky defects and three kinds of Frenkel defect. This wide range of structural defect reactions means that reliable calculations of the corresponding energies can be of particular value in understanding structural and thermodynamic data.

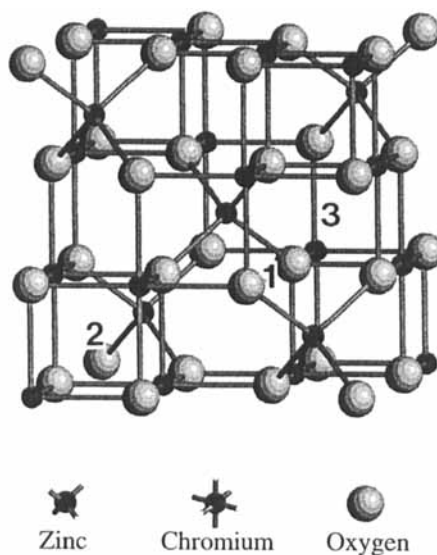
It is the object of this paper to apply these methods to one particular material in this

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Fig. 1



The spinel lattice; 1 designates the octahedral interstitial site, 2 and 3 the tetrahedral interstitial sites.

class, namely zinc chromate (ZnCr_2O_4). This material has potential applications as a sensor (Shimizu, Kusano, Kuwayama, Tanaka and Egashira 1990) and as a catalytic material (Bertoldi *et al.* 1988, Riva, Triferò, Vaccari, Mintchev and Busca 1988, Giamello, Fubino, Bertoldi, Busca and Vaccari 1989, Triferò and Vaccari 1991), but it is also interesting from a fundamental point of view because, rather unusually, it appears to take up large amounts of ZnO (Bertoldi *et al.* 1988). This conclusion followed from X-ray diffraction studies of specimens prepared by the calcination of carbonates co-precipitated from aqueous solution (Bertoldi *et al.* 1988). In addition, the catalytic activity of ZnCr_2O_4 appears to be particularly sensitive to composition. For example, it was recently reported that while stoichiometric ZnCr_2O_4 showed little activity towards the hydrogenation of carbon monoxide to methanol, a dramatic increase and a maximum in activity occurred once the zinc content of the material (believed single phase) reached $\sim 50\%$ (Triferò and Vaccari 1991). The present paper therefore focuses on the energetics of the formation of non-stoichiometric ZnCr_2O_4 .

As in the previous study by Jackson, Catlow and Thomas (1991), we shall regard the non-stoichiometric phase as a defective stoichiometric material that results from solution of ZnO in ZnCr_2O_4 . However, in this study we calculate the formation energies of an extended set of isolated defects and also of defect clusters. Oxidation of the non-stoichiometric material is also considered. These calculations are of energies of defects in a static lattice at constant volume. The usefulness of such quantities is to be found in two facts. Firstly, by invoking the quasi-harmonic approximation these energies can be equated to the corresponding defect internal energies at constant volume, u_v . Secondly, these internal energies in turn can be approximately equated to the corresponding enthalpies at constant pressure (or used with other information to give these enthalpies exactly if required). These two equalities therefore justify the direct use of energies calculated for a static lattice for the assessment of reactions of experimental or practical interest, although it should be added that in some

circumstances the associated entropies may also be significant. (For further details of these considerations see, for example, the review by Harding (1990)). These simplifications, of course, apply only to the energies of defects in the solid phase; for reactions involving a gaseous phase, e.g. oxidation, one requires the complete thermodynamic functions for that phase.

§ 2. METHODOLOGY

2.1. Model

We use an atomistic description of the solid which is essentially the classical Born model with full ionic charges. The energy function of the lattice is represented in terms of interionic potentials, although we include crystal field effects later. We first model the *perfect* crystal lattice. In the usual way this is described by defining a unit cell which is repeated throughout space using periodic boundary conditions as defined in terms of the crystallographic lattice vectors. We consider interactions due to long-range Coulombic forces, which are summed using Ewald's method, and also short-range forces that are described by using parameterized pair potentials (as discussed below). These short-range terms account for the electron cloud overlap and dispersion interactions which are significant only up to separations of a few lattice spacings. (In fact, in order to reduce the computational time, the short-range interactions are set to zero beyond 8.7 Å.) To obtain the parameters in the repulsive potential, the total energy of the crystal is minimized by allowing the ions in the unit cell and the lattice vectors to relax to zero strain. In the present calculations the Buckingham potential form was chosen to represent the short-range interaction energy of a pair of ions, $R(r)$, i.e.

$$E(r) = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}, \quad (1)$$

where A , ρ and C are parameters that depend upon the pair of ions being considered (see table 1). The oxygen–oxygen potential was assumed to be transferable between different oxides and was therefore determined by simultaneously fitting the lattice parameters of several related oxides. As a result, the range of oxygen–oxygen separations over which the potential is valid is correspondingly enlarged, which is an advantage when modelling lattice relaxation. The cation–anion potentials were first

Table 1. Short-range and shell model parameters.

Species	A (eV)	ρ (Å)	C (eV Å ⁻⁶)
Short-range parameters			
O ²⁻ :O ²⁻	9547.96	0.2192	32.0
Zn ²⁺ :O ²⁻	529.7	0.3581	0.0
Zn ³⁺ :O ²⁻	560.21	0.3470	0.0
Cr ³⁺ :O ²⁻	1204.18	0.3165	0.0
Cr ⁴⁺ :O ²⁻	1630.81	0.295	0.0
O ⁻ :O ²⁻	149734.35	0.1593	19.9
O ⁻ :Zn ²⁺	818.85	0.2977	0.0
O ⁻ :Cr ³⁺	6123.71	0.2292	0.0
Shell model parameters			
O ²⁻	$k = 6.3$ (eV Å ⁻²)	$Y = -2.04 e $; $X = +0.04 e $	
O ⁻	$k = 6.3$ (eV Å ⁻²)	$Y = -1.04 e $; $X = +0.04 e $	

e is the charge of the electron.

Table 2. Calculated dielectric constants (relative electric permittivities) of ZnCr_2O_4 .

$\epsilon_0 = 8.1924$
$\epsilon_\infty = 4.2558$

determined by using the approximate electron-gas method (Harding and Harker 1982). The parameters were then adjusted so that the calculated unit cell volumes of Cr_2O_3 , ZnCr_2O_4 and the three polymorphs of ZnO were accurately reproduced. The validity of the potentials was further verified by their success in reproducing the elastic and dielectric properties of the wurtzite form of ZnO . Further details of this and of the potential derivation process in general can be found in Binks (1994).

Once the perfect lattice has been successfully represented in this way, we can turn to the calculation of the defect energies. However, for this purpose we need to extend the model by including a representation of the electronic polarizability of the ions, since it has long been known that a good description of the dielectric properties is necessary for the accurate calculation of the energies of defects that bear a net electric charge. To this end, the oxygen ions are treated as polarizable and are described by the shell model (Dick and Overhauser 1958). In this, a massless shell of charge Ye is allowed to move with respect to a core of charge Xe . The charge state of each ion is therefore equal to $(X + Y)e$: in this study we used formal charges for all ions (e.g. O^{2-}). The ionic core and shell are connected by an isotropic harmonic spring of force constant k (see table 1). The shell charge and force constant were chosen in such a way that the high-frequency dielectric constants of a range of binary oxides, including ZnO , were correctly reproduced. In line with studies of many other oxides whose cations are significantly less polarizable than oxygen, we model all cations as rigid, unpolarizable ions (Catlow *et al.* 1977). The calculated dielectric constants of ZnCr_2O_4 are given in table 2. Unfortunately, there appear to be no experimental data with which to compare these predictions.

Later, when we consider changes in the stoichiometry of the crystal, it is necessary to consider the energy of the reaction by which oxide ions are formed from oxygen atoms. Since oxide ions are not stable in free space, this introduces some additional considerations (often referred to as the problem of the 'second electron affinity of oxygen'). The usual approach is to use a fixed value for this second affinity obtained by averaging values inferred by application of the Born–Harber cycle to a group of oxides, in the manner first indicated by Sherman (1932) and repeated by various authors since. Following subsequent studies of the matter by Mackrodt and Stewart (1979) and by Harding and Pyper (1995) we have abandoned the idea of a fixed value and instead use a specific value for each of the compounds in question. Our approach is described more fully in the appendix.

2.2. Defect simulation technique

The defect calculations follow the original method of Mott and Littleton (see, for example, the reviews by Catlow and Mackrodt (1982) and by Harding (1990)). In this method the lattice is partitioned into two regions: (i) an inner region I, roughly spherical, at the centre of which the defect is introduced and (ii) an outer region II containing the remaining crystal and which extends effectively to infinity. In region I, interactions are calculated explicitly so that the response of the lattice to the defect is modelled by relaxing the positions of all ions to zero force by means of a Newton–Raphson

minimization procedure. The response of region II is represented by using the Mott–Littleton approximation (Catlow and Mackrodt 1982, Harding 1990). In this study, the numerical calculations were performed by using the CASCADE code (Leslie 1982).

To ensure a smooth transition between regions I and II, we incorporate an interfacial region IIa in which ion displacements are represented in the Mott–Littleton approximation, but in which interactions with ions in region I are calculated by explicit summation. In the present calculations the radii of regions I and IIa were 8.9 Å and 34.1 Å, respectively. These sizes were chosen to be large enough to ensure that no appreciable change in the computed defect formation energies occurs when the regions are further increased in size.

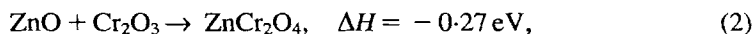
Discussions of models and their parameterization and of the methodology generally can be found in recent reviews (Catlow and Mackrodt 1982, Catlow and Stoneham 1989, Harding 1990, Harker and Grimes 1990).

§ 3. PERFECT LATTICE SIMULATION

As already mentioned, stoichiometric ZnCr_2O_4 crystallizes with a normal spinel structure. This has a slightly distorted face-centred cubic arrangement of oxygen ions with the metal ions occupying half of the octahedral and one-eighth of the tetrahedral sites enclosed within the anion sublattice (see fig. 1). Since the arrangement of cations is normal, the Zn^{2+} ions occupy all of the tetrahedral 8a sites and the Cr^{3+} ions fill all of the octahedral 16d sites. With this distribution, the calculated lattice parameter (fundamental cube edge) of the crystal is 8.340 Å. A range of room-temperature experimental values exists: 8.340 Å (Bertoldi *et al.* 1988), 8.359 Å (Leccabue *et al.* 1986), 8.330 Å (Battistoni, Dormann, Fiorani, Paparazzo and Viticoli 1981), 8.3275 Å (Dabkowska 1981, Pajaczowska and Piekarczyk 1981), 8.328 Å (Kino, Luthi and Mullen 1972) and 8.321 Å (Raccah, Bouchard and Wold 1966). The variation in the experimental values may indicate that it is hard to avoid the formation of non-stoichiometric material.

The extent to which the oxygen ions are displaced from perfect face-centred sites in the lattice is usually described by a single positional parameter u . (For perfect octahedral coordination $u = 0.375$; values greater than this imply that the anions have moved in a $\langle 111 \rangle$ direction away from the nearest Zn ion.†) For ZnCr_2O_4 our calculated value is 0.391 compared to the experimental value of 0.3899 (Raccah *et al.* 1966). This close agreement between the calculated and experimental u parameters is encouraging since, in a normal spinel, the u parameter reflects the balance between the Zn–O and Cr–O bond lengths and hence the Zn–O and Cr–O forces.

As already mentioned, the short-range potential used in this study was fitted empirically to the properties of a variety of perfect binary oxides. It is, of course, important to check that the model so obtained predicts that the mixed oxide is more stable than its component oxides. Indeed, as required, we find a negative reaction enthalpy for the reaction,



per molecule of product formed. This value is obtained from the lattice energies given

† In fact, this is an approximation to the true situation (see Grimes, Thompson and Kay 1983) but is quite sufficient for the present purposes.

Table 3. Comparison of calculated and experimental (Kino *et al.* 1972) elastic constants for $\text{ZnCr}_2\text{O}_4/10^{11} \text{ dyne cm}^{-2}$.

	Experimental	Calculated
c_{11}	25.58	34.74
c_{12}	14.24	16.29
c_{44}	8.46	15.25

in table 5, and is in acceptable agreement with the experimental thermodynamically determined enthalpy of -0.65 eV (Jacob 1976). However, it should be noted that in obtaining ΔH in this way, we have implicitly assumed that the second electron affinity of oxygen is the same in all three compounds. This discrepancy between the calculated and experimental values may be regarded as a measure of the accuracy of that assumption, although it may also be noted that the heats of formation of spinels from their component oxides (see, for example, Navrotsky and Kleppa (1968) and Knacke, Kubaschewski and Hesselmann (1991)) are rarely as large as the value -0.65 eV which Jacob obtained (1976). Nevertheless, this value is accepted by Knacke *et al.* and accordingly, as detailed in the Appendix, we use it to fix the second electron affinity of oxygen in ZnCr_2O_4 .

Finally, we wish to compare the elastic constants calculated for our model with those determined from measurements of the velocity of sound (Kino *et al.* 1972). These results, presented in table 3, show the calculated values to be somewhat higher than the experimental values. However, the cell parameter ascribed to the lattice by Kino *et al.* (1972), i.e. 8.328 \AA , implies, as we shall indicate later in § 6, that their material contained an excess of zinc. As such, their material would have incorporated a significant defect population, which limits the usefulness of a direct comparison with the calculated values. We feel satisfied with the accord between the experimental and theoretical elastic constants and therefore we did not make further use of the experimental constants in the potential fitting process.

§ 4. DEFECTS IN PURE ZnCr_2O_4

Following the perfect lattice study we investigated the formation of defects in the stoichiometric material. Among other things, this requires us to consider the occupation of the three types of interstitial site in the lattice (see fig. 1). In table 4, the interstitial defect energies for the Zn^{2+} , Cr^{3+} and O^{2-} ions are reported in sites 1 and 2. Since a negative energy implies stability, the octahedral interstitial site is clearly greatly favoured. Occupation of site 3 was found to be unstable with respect to displacement, during energy minimization, towards site 1. Consequently, we shall not consider these alternative tetrahedral interstitial sites further. Therefore, when we refer subsequently to interstitial sites we shall always mean octahedral interstitial sites of the type designated 1 in fig. 1.

The energies of the various basic defect reactions as obtained from the CASCADE calculations are given in table 5. From these we derive quantities of direct experimental interest. First of all, we consider the energies of formation of Schottky and Frenkel defects. The computed energies given in this way are as follows:

Schottky defects:

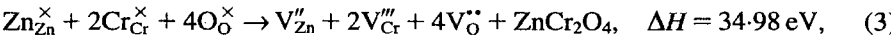


Table 4. Interstitial ion defect energies for the interstitial sites defined in fig. 1. Energies in (eV).

Interstitial site	Zn ²⁺	Cr ³⁺	O ²⁻
1; octahedral	- 14.66	- 40.56	- 10.79
2; tetrahedral	0.69	- 20.22	- 8.90

Table 5. Energies of basic defect reactions in eV.

Reaction ^{a, b}	ΔH
Lattice energies	
1 Zn _∞ ²⁺ + O _∞ ²⁻ → ZnO	- 39.34
2 2Cr _∞ ³⁻ + 3O _∞ ²⁻ → Cr ₂ O ₃	- 155.06
3 Zn _∞ ²⁺ + 2Cr _∞ ³⁻ + 4O _∞ ²⁻ → ZnCr ₂ O ₄	- 194.67
Vacancy formation	
4 Zn _{Zn} ^x → Zn _∞ ²⁺ + V _{Zn} ^{''}	25.98
5 Cr _{Cr} ^x → Cr _∞ ³⁺ + V _{Cr} ^{'''}	53.98
6 O _O ^x → O _∞ ²⁻ + V _O ^{••}	23.93
Interstitial formation	
7 Zn _∞ ²⁺ → Zn _i ^{••}	- 14.66
8 Cr _∞ ³⁺ → Cr _i ^{•••}	- 40.56
9 O _∞ ²⁻ → O _i ^{''}	- 10.79
Exchange disorder	
10 Zn _∞ ²⁺ + V _{Cr} ^{'''} → Zn _{Cr} [']	- 24.58
11 Cr _∞ ³⁺ + V _{Zn} ^{''} → Cr _{Zn} [']	- 53.83
Electronic reactions	
12 Zn _∞ ²⁺ → Zn _∞ ^{•+} + e _∞ ⁻	39.72 ^c
13 Cr _∞ ³⁺ → Cr _∞ ⁴⁺ + e _∞ ⁻	49.13 ^c
14 ½(O ₂) _∞ → O _∞	2.56 ^c
15 O _∞ + e _∞ ⁻ → O _∞ ⁻	- 1.46 ^c
16 O _∞ ⁻ + e _∞ ⁻ → O _∞ ²⁻	7.22 ^d
17 Zn _{Zn} ^x → Zn _{Zn} [•] + e _∞ ⁻	7.98
18 Zn _{Cr} ['] → Zn _{Cr} ^x + e _∞ ⁻	6.70
19 Cr _{Cr} ^x → Cr _{Cr} [•] + e _∞ ⁻	5.13 ^e
20 Cr _{Zn} ['] → Cr _{Zn} [•] + e _∞ ⁻	6.94 ^e
21 O _O ^x → O _O [•] + e _∞ ⁻	8.40
22 Zn _i ^{••} + 2Zn _{Cr} ['] → {Zn _i ^{••} :2Zn _{Cr} ['] }	- 2.05
23 V _O ^{••} + 2Zn _{Cr} ['] → {V _O ^{••} :2Zn _{Cr} ['] }	- 2.97
24 Cr _{Cr} [•] + Zn _{Cr} ['] → {Cr _{Cr} [•] :Zn _{Cr} ['] }	- 0.64

^a In all cases the subscript ∞ implies that the ion is in a state of rest at infinity, i.e. removed from interaction with any other matter.

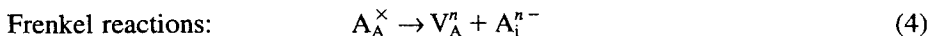
^b Apart from the first two entries, all reactions refer to ZnCr₂O₄. Energies of defect calculations have been obtained with the CASCADE code supplemented where necessary with empirical ionization energies of the free ions. Calculated energies are given to two decimal places, but, at best, only the first can be regarded as significant.

^c Emsley (1989).

^d See appendix.

^e Including crystal field correction (see text).

where ZnCr_2O_4 denotes the lattice molecule added to the crystal surface (or other sink or source for defects).



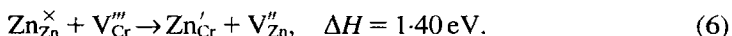
For intrinsic Schottky disorder (i.e. no significant concentration of other defects) the effective defect formation energy is $\Delta H/7$, i.e. 5.00 eV. For intrinsic Frenkel disorder the effective defect formation energy is $\Delta H/2$, i.e. 6.57 eV (oxygen Frenkel), 6.71 eV (chromium Frenkel) and 5.66 eV (zinc Frenkel). All these energies are so high that we should not expect, in practice, to observe intrinsic disorder of any of these types.

In addition, we also calculated the energy to exchange an octahedral Cr^{3+} ion with a tetrahedral Zn^{2+} ion,



The effective value for the formation energy of this 'anti-site' defect is thus 0.78 eV per defect. However, since the zinc site is tetrahedral, a chromium ion on such a site experiences an additional crystal-field destabilization of 1.64 eV per chromium ion (Dunitz and Orgel 1957), which increases ΔH to 3.20 eV, i.e. to 1.60 eV per defect. This is considerably less than the energies of formation of Frenkel and Schottky defects, so that we conclude that anti-site defects will be the dominant structural defects in the pure, stoichiometric material. This appears to be true rather widely in spinels, although we note that here the degree of exchange disorder will be quite small at all accessible temperatures. (Note, McClure (1957) suggests a slightly higher Cr^{3+} crystal field energy of 2.03 eV but the clear dominance of the anti-site defect is unaffected.)

Lastly, in order to complete the list of disorder reactions, we must consider the interplay of anti-site defects with Schottky and Frenkel defects. This occurs via the following reaction:



Since we find this reaction to be endothermic, it is clear that the occurrence of anti-site disorder will not significantly change the vacancy populations.

§ 5. DEVIATIONS FROM STOICHIOMETRY

5.1. *Solution of ZnO*

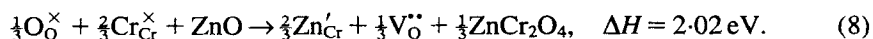
5.1.1. *Isolated defects*

The solution of ZnO in ZnCr_2O_4 leads to a material of composition $\text{Zn}_{(1+3x)}\text{Cr}_{(2-2x)}\text{O}_4$. There are a number of seemingly different ways by which the ZnO may be incorporated into the zinc chromate lattice, although, if we can assume thermodynamic equilibrium and therefore invoke one or more of the intrinsic defect reactions described in § 4, we can easily show that there is, in fact, only one independent way. Nevertheless, as the formation energies of these intrinsic defects are all high, the assumption of thermodynamic equilibrium may not be justified. We have therefore obtained the energies for several different reactions for the incorporation of ZnO in the lattice. Our consideration of all these shows that there are two solution mechanisms having energies of solution substantially lower than the others. In the first, some zinc

ions enter the chromium sub-lattice while others become interstitial according to the equation



whilst, in the second, oxygen vacancies are formed in place of zinc interstitials



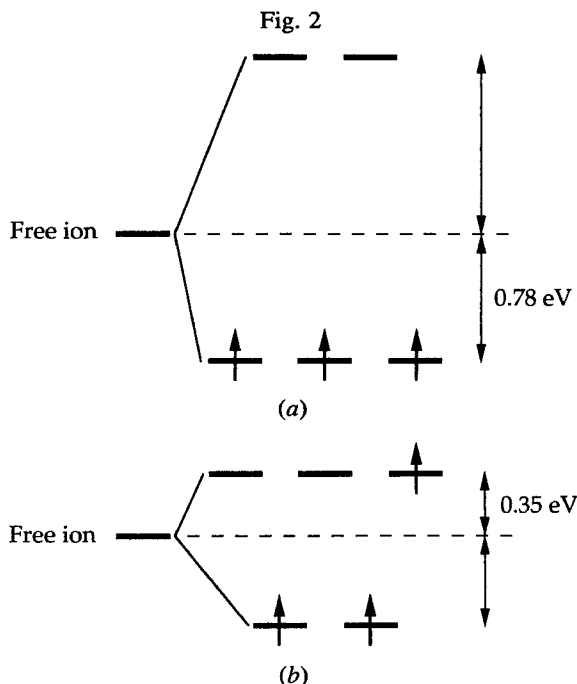
All other solution mechanisms that could be formulated by considering the equilibrium reactions (3)–(6) result in solution energies in excess of 5.77 eV per ZnO molecule. Thus, it seems from these results (i) that none of the reactions will lead to the dissolution of more than small fractions of ZnO in the lattice and (ii) that the most favourable manner in which excess ZnO can be accommodated as isolated defects into the lattice is by distributing the divalent zinc ions over both octahedral and tetrahedral sites with charge compensation provided by either oxygen vacancies or zinc interstitials. Nevertheless, although these inferences are valid, it should be noted that it is not necessarily correct to compare the enthalpies ΔH directly. Consideration of the ‘mass action’ equations for the equilibria corresponding to reactions (7) and (8), for example, shows that the correct comparison is between $4\Delta H_7/3$ and ΔH_8 , when, as here, only small amounts of ZnO will be dissolved. The small apparent preference for reaction (7) over reaction (8) is thus reversed. The conclusion thus far is therefore that the dissolution of ZnO will occur to a small extent via reaction (8), i.e. with the formation of oxygen vacancies.

5.1.2. Effect of defect clustering

So far it has been assumed that defects are isolated from one another, i.e. that no clustering occurs. If we now allow for the formation of bound nearest-neighbour triplets, $\{2\text{Zn}_{\text{Cr}}':\text{Zn}_i^{\bullet\bullet}\}$ in the case of reaction (7) and $\{2\text{Zn}_{\text{Cr}}':\text{V}_{\text{O}}^{\bullet\bullet}\}$ for reaction (8), the energies of the reactions are reduced to 1.21 eV and 1.03 eV, respectively, the corresponding total defect cluster binding energies being -2.05 eV for the zinc interstitial cluster and -2.97 eV for the oxygen vacancy cluster. The stronger binding of the oxygen vacancy cluster enhances the preference already noted in favour of the formation of oxygen vacancies. Even so, it is clear that none of the possible defect reactions as evaluated here will lead to the dissolution of sizeable fractions of ZnO and ZnCr_2O_4 . Since we have thereby considered all possible reactions in which none of the ions change their oxidation state, it remains to consider whether larger amounts of ZnO are likely to dissolve if we allow the material to be simultaneously oxidized or reduced. It is natural that we should concentrate attention on oxidation (a) because the experiments of Trifirò and Viccari (1991) were conducted in air at atmospheric pressure and (b) because we have seen that of the above reactions, that which leads to the formation of oxygen vacancies has the lowest energy of reaction.

5.2. Solution of ZnO under oxidizing conditions

To consider reactions in which the material becomes oxidized nevertheless presents us with a more difficult task. This is mainly because oxygen is incorporated into this (presumed) strongly ionic material as O^{2-} ions and this necessarily leads to the formation of electron holes. The accurate calculation of the energies of reactions involving such species is more difficult than that of reactions involving only structural defects. For example, Tomlinson's calculated enthalpies for the oxidation of the four transition metal oxides, MnO, FeO, CoO and NiO, were too large by some 1 to 2 eV



Splitting of the ground state energy of a Cr^{3+} ion by the crystal field at Cr and Zn sites in the spinel lattice; (a) Cr^{3+} ion on a Cr lattice site (O_h). Total energy splitting = 10Dq ; (b) Cr^{3+} ion on a Zn lattice site (T_d); total energy splitting = $\frac{4}{9} \times 10\text{Dq}$.

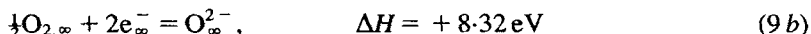
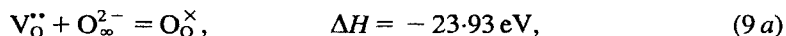
or more per incorporated O_2 molecule (see Tomlinson (1987) or Tomlinson, Catlow and Harding (1990)). Such inaccuracies may stem from two sources: (i) the holes are probably not localized on individual ions as assumed and (ii) since the O^{2-} ions are only stable against dissociation when confined by the Madelung potential well, their properties depend to some extent upon their surroundings. Another complication is that we may have to include changes in the crystal-field energies of the cations. Bearing in mind such limitations, we now describe the results of calculations made for non-stoichiometric material. The principal assumption of these calculations, additional to those presented in previous sections, is that the electron holes are localized on individual ions, but probably the main uncertainty in the numerical predictions arises from the indefinite nature of the second electron affinity of oxygen (here taken to be 7.22 eV; see appendix and table 5).

Assuming, therefore, that the holes are localized in this way, we first determined whether they reside mainly on zinc, chromium or oxygen ions, which we then regard as Zn^{3+} , Cr^{4+} and O^- ions, respectively. The energies of the basic electronic reactions are given in table 5. In finding these energies for the chromium ions, we have made a crystal field correction to the energy required to remove a d -electron by using the crystal field data of Dunitz and Orgel (1957). Following these authors, we assume that the Cr^{3+} ion is initially in a high spin, $S = \frac{3}{2}$ state. The correction term arises from the splitting of the d -orbital degeneracy by the crystal field and specifically from the fact that, in tetrahedral coordination, the t_{2g} orbitals, from which an electron is removed, are raised in energy, whereas in octahedral coordination they are lowered (see fig. 2). This correction increases the ionization energy of a Cr^{3+} ion on a normal chromium site

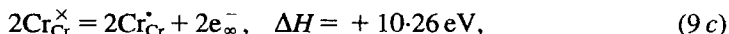
(octahedral coordination) by 0.78 eV, but reduces it by 0.35 eV for such an ion occupying a zinc site (tetrahedral coordination).

The calculated hole formation energies on each of these ions, when the electron is removed to a state of rest at infinity, are found to be: 7.98 eV to form a Zn^{3+} ion on a normal zinc site; 5.13 eV to form a Cr^{4+} ion on a normal chromium site; and 8.40 eV to form O^- on a normal oxygen site. In view of the possibility of exchange disorder, we also obtained the corresponding energies for a Zn^{3+} ion on a chromium site (6.70 eV) and for a Cr^{4+} ion on a zinc site (6.94 eV). Although the figure for O^- is probably the least reliable of all these, it nevertheless seems fair to conclude that these results show the holes to be principally localized on the chromium sub-lattice, as is thought often to be the case in transition metal oxides. However, because the states are probably less severely localized than we have assumed, the absolute values of these energies may be too high.

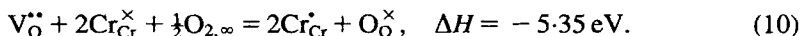
In § 5.1 we saw that the dissolution of ZnO in ZnCr_2O_4 (without the involvement of any other chemical component) is most likely to occur via reaction (8). In view of the creation of oxygen vacancies in this reaction, one might suppose that it would be facilitated by the presence of oxygen, which could release additional energy by filling the lattice vacancies. The reactions leading to this, in the conventional way, are



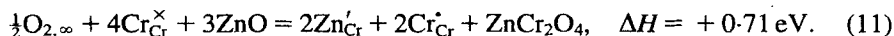
and



which, on addition, give



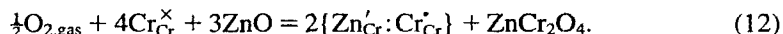
Here, as usual, the subscript ∞ means that the species is at rest at infinity. The energies (9c) and (10) include crystal field corrections. From (8) and (10) one obtains



We observe that the energy gained in reaction (10) is not enough to supply all that is required by (8), so that (11) remains endothermic.

This calculation assumes that the defects created, namely Zn'_Cr and the electron holes $\text{Cr}_\text{Cr}^{\bullet}$, are isolated from one another. In reality, of course, their Coulomb interactions will lead to the formation of some neutral pairs $\{\text{Zn}'_\text{Cr}:\text{Cr}_\text{Cr}^{\bullet}\}$ or even higher aggregates. If all the Zn'_Cr and the holes $\text{Cr}_\text{Cr}^{\bullet}$ are paired, but there are no interactions among the pairs, the cluster binding energy, 0.64 eV, reduces the enthalpy of reaction (11) to -0.57 eV. However, our estimates of the effect of the interactions between pairs indicate that the reaction enthalpy could even be as low as -1.1 eV, although this figure cannot be regarded as more than a rough estimate.

To see the significance of these results we must consider the thermodynamics of reaction (11), although, since this follows standard methods, we shall omit details. For this purpose we must modify eqn. (11) to correspond to the conditions of the experiment, i.e. we must replace $\frac{1}{2}\text{O}_{2,\infty}$ by $\frac{1}{2}\text{O}_{2,\text{gas}}$ to obtain



We plan to provide a detailed analysis of the thermodynamics of this reaction in

a later paper. Here we content ourselves by drawing attention to the salient features. First, in the corresponding equation of chemical equilibrium (see, for example, Schmalzried (1981)) we then have one-half the chemical potential of oxygen gas at the prevailing temperature and (partial) pressure on the left side. For air at 1000 K and 1 atm pressure this amounts to some -1.2 eV. We then see that the principal terms in ΔG will be (i) ΔH for reaction (12) and (ii) $-(\frac{1}{2})\mu_{O_2}$ (in which the entropy contribution is dominant). The first could be as low as the -1.1 eV obtained above, while, as just indicated, the second amounts to $+1.2$ eV for air at 1000 K and 1 atm pressure. Hence, ΔG could be as low as 0.1 eV under these conditions. It is therefore clear that significant dissolution of ZnO in $ZnCr_2O_4$ in the presence of oxygen is a distinct possibility, even at elevated temperatures. The dissolution would be driven by the configurational entropy gained when the population of defects is distributed throughout the host spinel lattice. Although this reasoning omits any consideration of the defect entropy terms arising from the changes which the defects cause in the lattice vibrations of the $ZnCr_2O_4$, we would not expect their inclusion to alter this broad conclusion. In a following paper we shall provide a more detailed analysis of the statistical thermodynamics of this system to support the conclusion. In the rest of this paper we shall turn to another use of these atomistic calculations which does not suffer quite so directly from the uncertainties introduced by the variable nature of the second electron affinity of oxygen but which lends further support to our conclusion. This concerns the prediction of changes in lattice parameter associated with the non-stoichiometry.

§ 6. LATTICE PARAMETER AS A FUNCTION OF ZINC CONTENT

The different defect reactions associated with ZnO solution give rise to different combinations and concentrations of defects. Since each defect has a characteristic defect volume, the different reactions give rise to different changes in volume, which can be related to changes in the average lattice parameter. The defect volume, \mathcal{V}_p , is given by (Catlow, Corish, Jacobs and Lidiard 1981),

$$\mathcal{V}_p = -K_T V(df_V/dV)_T \quad (13)$$

where K_T is the isothermal compressibility (calculated to be $0.7143 \text{ \AA}^3 \text{ eV}^{-1}$), V is the unit cell volume (580.09 \AA^3) and $(df_V/dV)_T$ is the variation at constant temperature of the defect formation Helmholtz free energy with cell volume (see Catlow *et al.* (1981) or Harding (1990)). It is implicit in the use of this relation that f_V is calculated with the system held at constant volume (as Mott–Littleton calculations invariably are). The defect volume, \mathcal{V}_p , is that appropriate to a system held at constant pressure, i.e. the usual experimental conditions. Here the creation of the defects is imagined to be carried out without attachment or removal of atoms or ions to surfaces. In other words, \mathcal{V}_p , calculated from eqn. (13) is merely the relaxation volume. In cases where such surface processes must be included for physical reasons, the appropriate contributions must be added to \mathcal{V}_p as given by eqn. (13); for example, in the thermal formation of Schottky defects one must add the molecular volume. Lastly, we note that for crystal models of sufficient sophistication one can use eqn. (13) to obtain the temperature dependence of \mathcal{V}_p . That would not be appropriate here; the calculations correspond to room temperature.

The calculated defect volumes of the elemental defects are reported in table 6. Consider the solution of ZnO via reaction (8) for isolated defects. If, for example, one molecule of ZnO is added to 10 formula units of $ZnCr_2O_4$ the increase in the volume of the system is given by the sum of the defect volumes (i.e. $\frac{2}{3} \times 4.01 + \frac{1}{3} \times 4.87$) plus

Table 6. Defect volumes in ZnCr_2O_4 calculated from eqn. (13).

Defect	$\gamma_p (\text{\AA}^3)$
$\text{V}_\text{O}^{\bullet\bullet}$	4.87
$\text{Zn}_\text{i}^{\bullet\bullet}$	7.78
Zn'_Cr	4.01
Cr'_Cr	-4.47
$\text{O}_\text{O}^{\bullet}$	1.61
$\{2\text{Zn}'_\text{Cr}; \text{Zn}_\text{i}^{\bullet\bullet}\}$	12.91
$\{2\text{Zn}'_\text{Cr}; \text{V}_\text{O}^{\bullet\bullet}\}$	6.84
$\{\text{Zn}'_\text{Cr}; \text{Cr}'_\text{Cr}\}$	-1.52
$\{\text{Zn}'_\text{Cr}; \text{O}_\text{O}^{\bullet}\}$	3.85

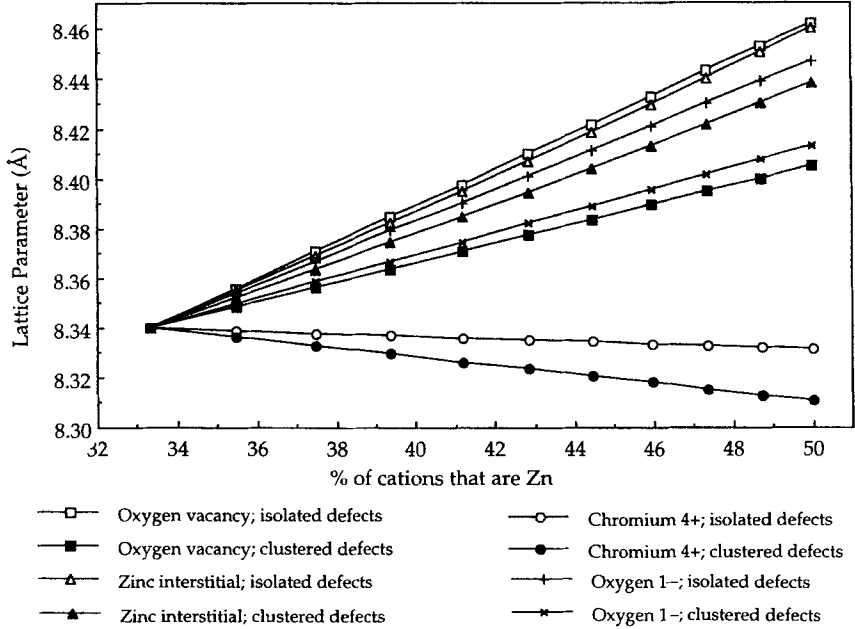
the increase due to the additional $\frac{1}{3}$ formula units of ZnCr_2O_4 . The lattice parameter of this material, $\text{Zn}_{1.06}\text{Cr}_{1.96}\text{O}_4$, can then be determined from the volume now of $10\frac{1}{3}$ formula units. In this manner it is possible to determine the change in lattice parameter as a function of zinc content for each reaction, assuming either isolated defects or defect clusters. The results of this are shown in fig. 3.

For each reaction, the lattice parameter varies linearly with zinc content, but the rates of variation are different. On the basis of the calculations given in §5.1 for reactions in the absence of excess oxygen, the *increase* in lattice parameter as a function of zinc excess is expected to follow that predicted by the lowest of the upper four lines, namely that for oxygen vacancy clusters. From §5.2, for the reactions expected at high oxygen activity, the lower of the two lines would predict the expected *decrease* in lattice parameter. For materials that are only partially oxidized, the lattice parameter will fall in between.

Figure 4 shows the experimentally observed lattice parameters of Bertoldi *et al.* (1988), other experimental values for materials whose zinc content had not been investigated explicitly and the predicted dependence of lattice parameter with zinc content under conditions of high oxygen activity (decreasing) and of low oxygen activity (increasing). It is apparent that all the experimental values either fall between or (in two cases) very close to the predicted lines. With respect to the data of Bertoldi *et al.* (1988), when only 5% excess zinc is present the lattice parameters are consistent with a fully oxidized material. At greater zinc excess, the theoretical values suggest that the lattice parameters show the presence of unoxidized material. Indeed, at both 11% and 17% zinc excess, the amount of unoxidized material depended upon the calcination temperature: in particular, these results suggest that a higher calcination temperature leads to a more fully oxidized material. This is possible since all samples were calcined for the same length of time (24 h, Bertoldi *et al.* (1988)), so that more unoxidized material is to be expected in material calcined at the lower temperature. In addition, Bertoldi (1988) found the presence of some ZnO in the 50% zinc samples.

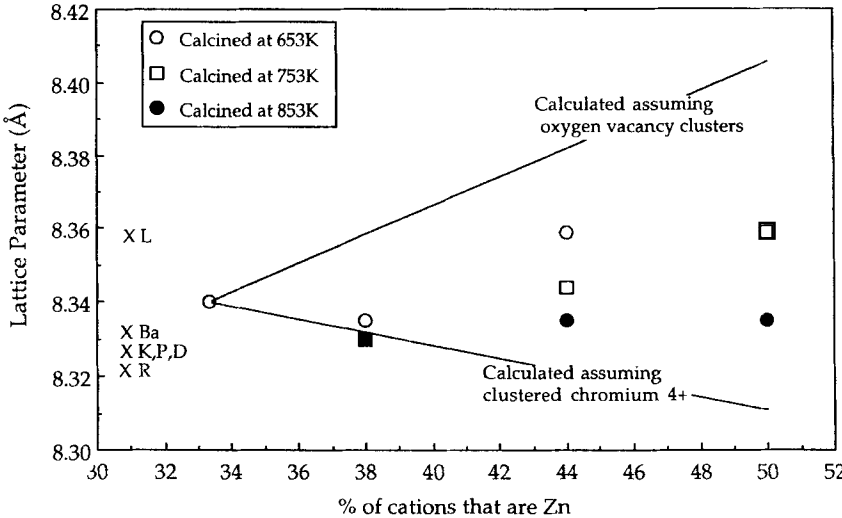
In §3 it was suggested that the variation in reported lattice parameter might result from the presence of non-stoichiometric material. From fig. 4 it is clear that the range in which those lattice parameters fall is indeed contained within the limits imposed by the calculations and by the experimental values of Bertoldi *et al.* (1988). Furthermore, the results suggest that the crystals synthesized by Raccach *et al.* (1966), Kino *et al.* (1972), Dabkowska (1981), and Pajaczkowska and Peikarczyk (1981), were far from being stoichiometric ZnCr_2O_4 but were rather fully oxidized, being essentially $\text{Zn}_{1.4}\text{Cr}_{1.6}\text{O}_4$.

Fig. 3



Variation of lattice parameter with zinc content.

Fig. 4



Comparison of predicted lattice parameters of zinc excess spinel with experimental values of Bertoldi *et al.* (1988). Additional experimental values, where the zinc content was not determined, are: L (Leccabue *et al.* 1986), Ba (Battistoni *et al.* 1981), P (Pajaczowska and Piekarczyk 1981), D (Dabkowska 1981), K (Kino *et al.* 1972) and R (Raccah *et al.* 1966).

In § 5.2 we ruled out the formation of O^- species as the charge-compensating ion for the oxidation reaction. This conclusion is supported by the lattice parameter calculations since the formation of O^- defects would be accompanied by a significant increase in the lattice parameter (see fig. 3).

Lastly, if the lattice parameter in fig. 4 predicted by eqn. (13) is extrapolated to the end member Zn_2CrO_4 , the value 8.284 \AA is obtained. This agrees reasonably well with the average bulk lattice value, 8.263 \AA , predicted by a perfect lattice calculation which we made on the basis of the same ionic model. The discrepancy may arise from the fact that the defect volumes used as input to eqn. (17) do not take account of defect-defect interactions.

§ 7. SUMMARY AND CONCLUSIONS

From the experiments of Bertoldi *et al.* it seems that zinc chromate spinel can act as a host for excess zinc up to a composition where nearly half the cations are zinc. This unusual behaviour has been investigated by considering the material as a solution of ZnO in stoichiometric ZnCr_2O_4 . The formation energies of isolated defects and defect clusters have been calculated and different mechanisms for the solution of ZnO have been compared. We can be confident that these calculations exclude the straightforward dissolution of ZnO in ZnCr_2O_4 to other than a very small extent. Nevertheless, we find that the defect reaction likely to lead to the highest solubility is one that leads to the creation of one oxygen vacancy for every three ZnO molecules dissolved (eqn. 8). Le Chatelier's Principle therefore suggests that the presence of oxygen gas, able to fill these vacant sites, will cause the reaction to proceed much further. Although our calculated free energies of reaction support this idea, we cannot yet be sure that the ionic model used in these calculations is able to predict the energies of oxidation to sufficient accuracy. However, we believe that the approach taken here to the question of the second affinity of oxygen is an advance on that used in some previous calculations (see appendix). More definitely, however, the changes in lattice parameter which we have calculated for the various reactions do appear to show that the observed behaviour is understandable in terms of the oxidation reaction (11), but not in terms of the straightforward dissolution reaction (8).

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APPENDIX

THE SECOND ELECTRON AFFINITY OF THE OXIDE ION IN CRYSTALS

The classical atomistic approach to ionic crystals, due originally to Born, has been extensively refined over the years and has been notably successful in recent times in predicting the properties of defects in these crystals (e.g. structures, energies and other characteristics; see, for example, Harding (1990)). This is true for many oxides as well

as for halides. Yet in one respect the halides and the oxides differ fundamentally; namely, the halogen ions F^- , Cl^- , etc., are stable with respect to dissociation into a free atom and an electron, whereas the oxide ion O^{2-} is only stable *within* the crystal. In free space O^- is stable, but O^{2-} is not. In the crystal O^{2-} is stabilized because it sits in a deep potential well created by the other ions of the structure (largely the Madelung potential well) (see, for example, Watson (1958), Mackrodt and Stewart (1979) and Grimes (1990)). Despite this difference, it has been usual for convenience of formal argument (e.g. the Born–Haber cycle) to treat the halides and the oxides in the same way by introducing a second electron affinity of oxygen as well as the first affinity (now known to be -1.461 eV). This second affinity is a positive quantity, i.e. work must be done to create O_{∞}^{2-} from O_{∞}^- and an electron. The instability of the free O^{2-} ion, which in fact has long been recognized (see, for example Sherman (1932)), nevertheless has an important implication for the practice of treating the oxides in the same way as the halides. For if the O^{2-} ion is only stable in the crystal, its properties, in particular the second affinity, would be expected to depend on the crystal environment. It follows, therefore, that the common practice of using an average value of the second affinity obtained by applying the Born–Haber cycle to one series of like compounds when making calculations for other compounds is basically inconsistent. The extent of the inconsistency has been emphasized by the quantum-mechanical analyses made by Mackrodt and Stewart (1979) and by Harding and Pyper (1995). The latter authors have emphasized that the second affinity is also closely tied to the particular representation of the overlap repulsion which is employed in the ionic model. For these reasons, variations of a few eV in the second affinity are found.

None of this is very significant unless one is concerned with changes in the composition (stoichiometry) of the oxide. But in those circumstances, the use of an inconsistent second affinity could lead to errors of this magnitude. Indeed, most attempts to calculate the enthalpies of oxidation and reduction of oxides have been unsuccessful, being in error by one or more eV. Although there may well be more than one reason for this failure in particular cases, the variability of the second oxygen affinity is almost certainly one significant contributor.

In this paper we have therefore used the Born–Haber cycle to fix the appropriate affinity for $ZnCr_2O_4$. The Born–Haber cycle in principle uses thermodynamic enthalpy data referred to standard conditions (298.15 K and a standard pressure formerly taken to be 1 atm or 101 325 Pa but now taken to be 0.1 MPa). However, adjustments of measured or calculated quantities (such as lattice energies) appropriate to other temperatures, being of the order of $R(T - 298.15)$ per mole, are generally negligible in comparison with the sought-for second affinity and are no greater than uncertainties in the calculated lattice energies. Also, the difference between the thermodynamic internal energies and the corresponding enthalpies are of the same order (in the case of gaseous phases) or much smaller (for solid phases). We have not therefore concerned ourselves with these corrections.

The Gibbs free energy of formation of $ZnCr_2O_4$ from ZnO and Cr_2O_3 at elevated temperatures (700–900°C) has been determined by Jacob (1976); the corresponding enthalpy is -62.76 kJ mol $^{-1}$ or -0.65 eV (independent of T over the range of measurement). The heats of formation of ZnO and Cr_2O_3 from their elements in their standard thermodynamic states are respectively, -350.5 kJ mol $^{-1}$ or -3.63 eV per molecule (Kaye and Laby (1986) quoted from CODATA) and -1135 kJ mol $^{-1}$ or -11.76 eV per molecule (Chase *et al.* 1985). The heats of sublimation of Zn and Cr metal at 298.15 K are, respectively, 130.4 kJ mol $^{-1}$ or 1.35 eV per atom and

397.5 kJ mol⁻¹ or 4.11 eV per atom (Chase *et al.* 1985). Spectroscopic data (ionization energies, the first electron affinity of oxygen and the energy of dissociation of the O₂ molecule) as given in table 5 have been taken from Emsley (1989). Conversion of units has been made according to Mills *et al.* (1993).

With the aid of this data and the calculated lattice energies of ZnO, Cr₂O₃ and ZnCr₂O₄ given in table 5 we have obtained the following values for the second electron affinity of oxygen:

$$\text{ZnO: } E_{\text{eall}} = 5.89 \text{ eV}$$

$$\text{Cr}_2\text{O}_3: E_{\text{eall}} = 7.78 \text{ eV}$$

$$\text{ZnCr}_2\text{O}_4: E_{\text{eall}} = 7.22 \text{ eV}$$

These values vary from compound to compound as expected from the work of Harding and Pyper (1995). We use the value 7.22 eV in all the calculations described here for ZnCr₂O₄. Calculated energies are given to two decimal places, but, at best, only the first can be regarded as significant.

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