

Site Potentials and Valences in Copper and Silver Oxides

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Electrostatic potentials at atom sites have been calculated for a number of Cu and Ag oxides. It is shown that the potentials are approximately proportional to valence and may be used to determine valences in mixed-valence oxides. The data for Ag_3O_4 are consistent with metallic behavior, and the data for $\text{Ba}_2\text{YCu}_3\text{O}_7$ suggest that holes may be in part localized on O atoms. The role of Ba and other large atoms in facilitating oxidation of O^{2-} by Cu(III) is identified. Valency fluctuations $2\text{Cu(II)} \rightarrow \text{Cu(I)} + \text{Cu(III)}$ are found to be unlikely in oxides. The electron affinity of O^- is reevaluated and a value of -7.7 eV suggested. © 1990 Academic Press, Inc.

1. Introduction

The question of the valences of copper in mixed valence compounds is of considerable interest to, among other things, the interpretation of conduction mechanisms in copper oxide superconductors. The now classical crystal-chemical approach is in terms of bond valences, but as applied to compounds such as $\text{Ba}_2\text{YCu}_3\text{O}_7$ (1, 2) the method has not yielded entirely unambiguous results. There are, of course, a variety of spectroscopic methods (some are referenced below) that can be interpreted in terms of atom valences; however, this paper is concerned with an alternative method of using *structural* information to glean information about atomic valences.

The approach considered here is in terms of the classical ionic model of crystals. This will be shown to provide a useful diagnostic of atom valences in many instances. In particular, what is variously called the *Madelung potential*, *site potential* (as herein), or *electrostatic self-potential* (3) will be

shown to be a useful quantity. The site potential, ϕ_i at an atom site i , is just the electrostatic potential at that site due to the charge distribution of all the other ions in the crystal (considered as nonoverlapping spherical charges).

Although the ionic approximation is not generally a very useful starting point for predicting the detailed geometry or relative stabilities of crystal structures, it is of proven utility in providing a remarkably good estimate of the cohesive energy. This is because, in the ionic approximation, the energy is dominated by monopole terms in the charge distribution, whereas to predict structural details one has to consider ions as polarizable (introducing a number of very uncertain parameters) and consider higher moments of the charge distribution which will depend critically on the assumed polarizabilities. In the present context, the relevant observation is that site potentials, calculated assuming spherical, nonoverlapping charges at atom sites, are not very different from those used assuming nonspheri-

cal polarizable ions, whereas the gradients of the potential (field, field gradient) depend critically on the details of the assumed charge distribution (4).

An essential observation (5-7) is that the potential at an ion site scales approximately as the charge on the ion, i.e.,

$$\phi_i = -\alpha q_i, \quad (1)$$

with $\alpha \approx 12$ V when q is measured in multiples of the electronic charge e . The value of α also scales with the size of the atom concerned¹ but this effect is relatively small and we expect for a given cation (e.g., Cu⁺, Cu²⁺, Cu³⁺) that the site potential in an oxide will be a characteristic value approximately proportional to its formal valence. Indeed this will be shown to be the case.

It might be noted that Hoppe (8) and his collaborators have long used electrostatic calculations ("MAPLE" values) as powerful indicators of the validity of crystal structures and have been able to indicate misplaced atoms by what is in effect a consideration of site potentials. Relevant to this work are their calculations of site potentials in Cu(III) oxides and fluorides and Cs₂Cu(IV)F₆ which are discussed below. The present work is in the same spirit. In particular it is supposed that a value of α (as defined by Eq. (1)) for a given ion, that is different from the values normally found in well-characterized structures with unambiguous valences, is diagnostic of a wrong structure or (in the present context) a wrong assignment of valences. As such it has an heuristic value that one does not need to subscribe to the validity of the ionic model to appreciate.

2. Site Potentials in Cu and Ag Oxides

Site potentials are calculated by the Ewald method (3) at all the crystallographi-

cally distinct (i.e., not symmetry related) sites i (at r_i) as a sum of the contributions of all the other atoms j (at r_j) in the unit cell and those generated by the lattice translations:

$$\phi_i = \sum_j a_{ij} q_j. \quad (2)$$

The a_{ij} are in fact the potentials at a point $r_i - r_j$ in a primitive Bravais lattice (with unit cell the same as that of the structure in question) of point positive charges, neutralized by a uniform negative charge. Accordingly, if the charges in Eq. (2) do not add up to zero, the calculated potential is that for a crystal neutralized by an appropriate uniform charge distribution. The total electrostatic energy is the sum over all ions:

$$E_{el} = \sum \phi_i q_i e / 2. \quad (3)$$

In order to illustrate the variation of potential with valence, I have chosen the simplest possible compounds of Cu(I), Cu(II), and Cu(III) and the simplest known mixed valence Cu oxide (Cu₄O₃). Table I lists site potentials in Cu₂O, CuO (9), Cu₄O₃ (10),² NaCuO₂ (11, 12), and KCuO₂ (12, 13). The last two compounds are assumed to contain Cu(III); the only alternative is to assign charges other than -2 to oxygen.

Cu₄O₃ contains both Cu(I) and Cu(II) and their location in the structure is "obvious" from the structure: Cu(1) = Cu(I) is linear two-coordinated and Cu(2) = Cu(II) is square four-coordinated. However, to illustrate the possibility of determining valencies in mixed-valence crystals using site potentials, potentials are also calculated for the alternative distribution Cu(1) = Cu(II) and Cu(2) = Cu(I). Now one gets approximately equal potentials at Cu(1) and Cu(2) in contradiction to the proposed charge distribution. This illustrates the important

¹ Thus consider the isostructural crystals MgO and BaO for which $\phi = \pm 24$ and ± 18 V, respectively.

² Note that a misprint in Table 3 of Ref. (10) labels the positions of O(2) as 4a rather than the correct 4b of *I4₁/amd*. 4a is the site labeled L in Table I of this paper.

TABLE I
MADELUNG POTENTIALS (V) AT Cu AND O
IN SOME OXIDES

Oxide	Cu(I)	Cu(II)	Cu(III)	O(1)	O(2)	L
Cu ₂ O	-12.8			21.8		
CuO		-25.3		24.9		
Cu ₄ O ₃ ^a	-12.2	-24.7		22.4	23.5	2.9
NaCuO ₂			-32.7	24.8		
KCuO ₂			-33.1	24.2		
-(ϕ/z)	12.5	12.5	11.0	11.9		
Cu ₄ O ₃ ^b	-18.0	-18.9		23.0	15.5	10.9

Note. Entries in the penultimate row show the average potential (ϕ) divided by the formal valence (z) for the first four entries. L refers to an unoccupied site in Cu₄O₃.

^a Correct structure.

^b Structure with Cu(I) and Cu(II) interchanged.

point that in ternary etc. compounds in general one only gets reasonable potentials for a unique (correct) charge distribution (exceptions, such as the example of Ag₃O₄ below, are possibly indicative of delocalized electrons). Note also that in this incorrect structure there is a reduced potential at O(2) and a large positive potential at a vacant site labeled L , suggesting that O(2) would be better placed at L . In fact making that switch one recovers topologically (and very nearly metrically) the original correct structure.

Excluding the incorrect Cu₄O₃ structure the average values of α are all close to 12 V. Similar values for potentials at Cu(III) sites have been calculated by Bukovec *et al.* in Na₆Cu₂O₆ (14). It should also be mentioned that similar trends of potential with valence can be deduced in fluorides with Cu in different valence states such as Cu(II)F₂ (-21.8 V) (15), Cs₂KCu(III)F₆ (-32.6 V) (15), and Cs₂Cu(IV)F₆ (-40.0 V) (16).

Table II presents data for Ag₂O, AgO (17), and Ag₂O₃ (18); the assignment of AgO = Ag(I)Ag(III)O₂ is clearly preferred to Ag(II)O. The average value of α is 11.4

TABLE II
MADELUNG POTENTIALS (V) AT Ag AND O
IN SOME OXIDES

Oxide	Ag(I)	Ag(II)	Ag(III)	O(1)	O(2)
Ag ₂ O	-11.5				19.7
AgO ^a	-13.2		-30.8	22.9	
Ag ₂ O ₃			-32.6	23.7	22.2
-(ϕ/z)	12.4		10.6	11.1	
AgO ^b		-18.2	-25.8		21.0

Note. Entries in the penultimate row show the average potential (ϕ) divided by the formal valence (z) for the first three entries.

^a Ag(I)Ag(III)O₂.

^b Ag(II)Ag(II)O₂.

V, somewhat smaller than for the copper oxides, reflecting the longer bond lengths in the silver oxides.

Ag₃O₄ (19) presents a more difficult problem. The structure can be written Ag(1)Ag(2)₂O(1)₂O(2)₂, with the "natural" valence assignment (19) $q_{Ag(1)} = 2$, $q_{Ag(2)} = 3$. A second possibility is (by analogy with oxides like Fe₃O₄) $q_{Ag(1)} = 3$, $q_{Ag(2)} = \frac{5}{2}$. Finally one may take an average valence: $q_{Ag(1)} = q_{Ag(2)} = \frac{8}{3}$. Table III shows $\alpha = -\phi/q$ for these three possibilities. Note that in every case α is close to the average value (11.2 V), so in this instance we do not have a preferred valence distribution. I interpret this result to mean that more than one valence distribution is possible in accord with the "black metallic" appearance of this compound.

TABLE III
MADELUNG POTENTIALS (V)/VALENCE AT Ag
AND O IN Ag₃O₄

$q_{Ag(1)}$	$q_{Ag(2)}$	Ag(1)	Ag(2)	O(1)	O(2)
2	3	12.6	10.6	11.4	11.4
3	$\frac{5}{2}$	10.6	11.0	11.6	11.3
$\frac{8}{3}$	$\frac{8}{3}$	11.1	10.8	11.5	11.3

Note. The entries are $\alpha = -\phi/q$.

TABLE IV
SITE POTENTIALS IN $\text{Ba}_2\text{YCu}_3\text{O}_7$ (a-d) AND
 $\text{Ba}_2\text{YCu}_3\text{O}_6$ (e)

Ion	Coordinates	a	b	c	d	e
Ba	.5, .5, z_1	-17.3	-19.3	-18.1	-17.2	-17.6
Y	.5, .5, .5	-33.3	-27.9	-24.7	-32.2	-31.1
Cu(1)	0, 0, 0	-29.7	-30.8	-27.0	-22.3	-12.6
Cu(2)	0, 0, z_2	-29.0	-27.8	-24.5	-27.6	-27.0
O(1)	0, 0, z_3	23.4	19.6	20.1	18.8	19.8
O(2)	.5, 0, z_4	18.9	24.0	23.8	20.1	20.7
O(3)	0, .5, z_5	18.8	23.8	23.7	20.0	20.7
O(4)	0, .5, 0	26.9	18.9	19.4	20.0	3.2
L(1)	.5, 0, 0	10.9	2.0	2.4	5.8	3.2
L(2)	0, 0, .5	-0.4	6.4	5.5	0.8	2.5

Note. a: $q_{\text{Cu}(1)} = 3$, $q_{\text{Cu}(2)} = 2$. b: $q_{\text{Cu}(1)} = q_{\text{Cu}(2)} = \frac{7}{3}$. c: $q_{\text{Cu}(1)} = q_{\text{Cu}(2)} = 2$ plus one uniformly distributed + charge. d: $q_{\text{Cu}(1)} = q_{\text{Cu}(2)} = 2$, $q_{\text{O}(1)} = q_{\text{O}(4)} = \frac{1}{3}$. e: $q_{\text{Cu}(1)} = 1$, $q_{\text{Cu}(2)} = 2$, $q_{\text{O}(4)} = 0$.

Metallic behavior (superconductivity) is well documented in the mixed-valence compounds $\text{Ag}_7\text{O}_8\text{X}$ ($\text{X} = \text{F}, \text{NO}_3$, etc.) with an average charge $q_{\text{Ag}} = \frac{17}{7}$ (20).

3. Site Potentials in $\text{Ba}_2\text{YCu}_3\text{O}_6$ and $\text{Ba}_2\text{YCu}_3\text{O}_7$

Valences in $\text{Ba}_2\text{YCu}_3\text{O}_7$ remain a topic of considerable interest; bond valence analyses (1, 2) show that the "natural" assignment $\text{Ba}_2\text{YCu(III)Cu(II)}_2\text{O}_7$ is not likely. Accordingly the site potentials in this compound and in the related $\text{Ba}_2\text{YCu}_3\text{O}_6$ (in which valences can be unambiguously assigned) have been calculated for several charge assignments as indicated in Table IV.

The $\text{Ba}_2\text{YCu}_3\text{O}_7$ structure may be considered as derived from a triple-perovskite $\text{A}_3\text{B}_3\text{O}_9$ by removal of two oxygen atoms (from the sites labeled L(1) and L(2) in Table IV). A fragment of the structure is sketched in Fig. 1 to show the numbering of the atoms. The $\text{Ba}_2\text{YCu}_3\text{O}_6$ structure is derived from that of $\text{Ba}_2\text{YCu}_3\text{O}_7$ by removal of a third oxygen, labeled O(4). A large number of concordant determinations of the structure have now been made; I have chosen to use the coordinates of Capponi *et al.*

(21) and of Roth *et al.* (22). Different structural determinations yield potentials that differ by 0–0.3 V. To compare potentials at Ba and Y sites with what might be expected, we note that at Ba in BaO $\phi = -18.2$ V, and at Y sites in Y_2O_3 $\phi = -30.8$ V.

The "obvious" charge distribution with $q_{\text{Cu}(1)} = 3$ and $q_{\text{Cu}(2)} = 2$ (case a in Table IV) is not very satisfactory. The potential at Cu(1) is about 3 V less than expected and at Cu(2) about 4 V more than expected (compare Table I). There is also a large potential at L(1) instead of close to zero as expected.

The proposed (1) distribution with $q_{\text{Cu}(1)} = q_{\text{Cu}(2)} = \frac{7}{3}$ (case b in Table IV) is generally more satisfactory, but note now that the potentials at Ba and Y are several volts different from what might be expected.

Another possible charge distribution is provided by the suggestion (23–26) that the valences are all Cu(II) with the hole distributed over some or all of the O atoms. To test this hypothesis, I first calculate the potentials with $q_{\text{Cu}(1)} = q_{\text{Cu}(2)} = 2$ and neutralize the crystal with a uniformly distributed positive charge: this is symbolized $[\text{Ba}_2$

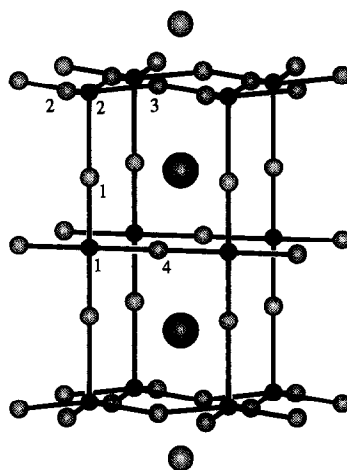


FIG. 1. The structure of $\text{Ba}_2\text{YCu}_3\text{O}_7$ showing the numbering of the O atoms (small light circles) and Cu (small dark circles). Y atoms are an intermediate size and Ba, large.

$YCu_3O_7]^- \cdot e^+$ (case *c* in Table IV). Note that now O(1) and O(4) have the lowest potentials, so finally (case *d* in Table IV) the hole is distributed over these sites so that $q_{O(1)} = q_{O(4)} = \frac{2}{3}$. This in fact appears to be a satisfactory distribution in so far as the potentials are now generally in accord with those expected (compare particularly with case *e*, that of $Ba_2YCu_3O_6$, in which the valence assignments are unambiguous (1, 2).

The question of valences is further considered in the next section. A key observation is that the lowest potential at oxygen in any proposed charge (valence) distribution is significantly lower than in the copper oxides of Table I. The reason is simple: part of the charge neutralizing O^{2-} is provided by Ba^{2+} which because of its large size is located relatively far away (compared to Cu^{2+}) and contributes relatively less to the potential at O^{2-} . We will see that this point is relevant to the question of whether Cu^{3+} will oxidize O^{2-} .

4. Energy Levels in Oxides

It has long been known (27–30) that the ionic model provides a useful first approximation to energy levels in the ground state of oxides and related materials. In this approximation the energy level of an ion is $-\phi e - I$, where I is the ionization energy of the free ion. Thus for CuO, the ionization energy of Cu^{2+} is 36.8 eV and the potential at Cu^{2+} is -25.3 V, so the Cu^{2+} level falls at -12.5 eV. Likewise, the ionization energy of O^{2-} is -7.7 eV (Appendix) and the potential at O^{2-} is 24.9 V, so the O^{2-} level falls at -17.2 eV, comfortably below Cu^{2+} . Imagine CuO to be oxidized (e.g., by adding a small Li dope) the holes introduced are then expected to fall on Cu rather than O. Similar arguments apply to other transition metal monoxides (27–29).

Consider now $Ba_2YCu_3O_7$: I start with the charge distribution $[Ba_2YCu_3O_7]^- \cdot e^+$

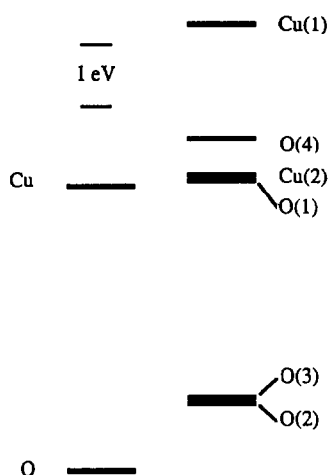


FIG. 2. Energy levels on the same scale for CuO (left) and $Ba_2YCu_3O_7$ (right).

discussed earlier and suppose that the extra positive charge will tend to be localized at the higher levels.³ The copper and oxygen levels calculated from the data in Table IV are as shown in Fig. 2. The O(2) and O(3) levels are well below Cu, but the other levels are much closer together. In particular, the diagram suggests that Cu(1) will be most oxidized, but that any positive charge on Cu(2) will be shared approximately equally with O(1) and O(2). It is interesting that Brown's (2) bond valence analysis (which, as he notes, does not preclude Cu–O charge transfer) suggests that the hole is 50% on Cu(1) and 25% on each of the Cu(2).

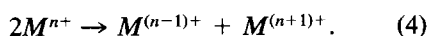
Detailed band structure calculations (31, 32) support the conclusions of the simple analysis given here. It may well be that the high T_c observed in some copper oxide superconductors is associated with the near degeneracy of the Cu and O levels (30); in that case one can see the importance of the

³ Of course the levels will move as the charge is added, but it may be expected that the qualitative picture will be correct. The same difficulty is inherent in any energy level diagram such as the MO diagrams favored by molecular chemists.

other ions in the structure in contributing to the potentials, in particular the effect of large cations lowering the potential at oxygen (or, in terms of Fig. 2, raising the O levels). Another role of the "big" atoms—that of allowing a high oxidation state to be attained—was identified earlier (1).

5. Valence Fluctuations: $2\text{Cu(II)} \rightarrow \text{Cu(I)} + \text{Cu(III)}$ etc.

The possibility of valence fluctuations such as $2\text{Cu(II)} \rightarrow \text{Cu(I)} + \text{Cu(III)}$ has also been suggested (33, 34) as important in Cu oxides. Consider the general case:



The energy increase for free ions is $\Delta I = I_{n+} - I_{(n-1)+}$. In the crystal this is offset by the gain in electrostatic energy which, if α is considered to remain constant, is given by (compare Eq. (3)) $E_{e1} = -(\alpha e/2)[(n-1)^2 + (n+1)^2 - 2n^2] = -\alpha e$. Thus in this approximation the energy increase for Eq. (4) in the crystal is $\Delta I - \alpha e$. For the first-row transition elements ΔI is largest for Ni(II) (17.0 eV) and Cu(II) (16.5 eV) (35) and thus substantially larger than the expected value of αe . On the other hand for Ag(II) (35) $\Delta I = 13.3$ eV and valence disproportionation (as observed in AgO) is more favorable.

It might be noted that in the superconductors based on BaBiO_3 there has been some discussion of the valence of Bi, with Bi(III) + Bi(V) being favored over 2Bi(IV) (36). For Bi(IV) $\Delta I = 10.7$ eV (35) so this result is to be expected.

The conclusion that Cu(II) is unlikely to disproportionate is disappointing in a sense because the process would be accompanied by a large shift of the anion positions and thus provide an attractive mechanism for strong electron-phonon coupling. Thus the structures of Cu(II)O and Ag(I)Ag(II)O differ mainly by displacement of O atoms by about 0.2 Å. The structure of $\text{CsAuCl}_3 = \text{Cs}_2\text{Au(I)Au(III)Cl}_6$ (37) is similarly related

to that of perovskite by small displacements of the Cl atoms.

6. Conclusions

The value of site potentials as diagnostics of valence in mixed valence crystals has been demonstrated. In $\text{Ba}_2\text{YCu}_3\text{O}_7$ they lead to a prediction that holes will be, at least in part, localized on O, in accord with a growing body of experimental and theoretical evidence. The role of large atoms such as Ba in affecting potentials in such oxides has been identified. Site potential calculations also show that disproportionation of Cu(II) in oxides is unlikely.

7. Appendix: The Electron Affinity of O^-

A major drawback to the application of the ionic model to oxides is that free O^{2-} (or for that matter any multiply charged anion) is unstable and unobservable. Thus the electron affinity of O^- can neither be measured nor calculated in any reliable *ab initio* way. Two ways around this impasse have been suggested: by extrapolation of ionization potential data of an appropriate isoelectronic sequence (37) or from a Born-Haber cycle applied to simple oxides (38). In this appendix I consider the merits of both these approaches in the light of the more accurate data now available and derive a revised value for the electron affinity of O^- .

Morris and Schmeising (37) extrapolated the ionization potentials of 10-electron ions by simple polynomial extrapolation and derived an often quoted value of -7.75 V for the ionization potential of O^{2-} . However they used an incorrect value for the electron affinity of F and the merits of polynomial extrapolation are dubious at best. Repeating their calculation with a value of 3.399 eV for the electron affinity of F (39) and ionization potentials of other ions from Moore (30) yields -6.3 V for the ionization potential of O^{2-} .

Edlén (40, 41) has considered at length the question of extrapolating ionization potential data to derive electron affinities. He determined that the best extrapolation formula is the simple three-parameter expression,

$$I = (R/n^2)[(\xi + a)^2 + b + c/(\xi + a)] \quad (5)$$

where R is the Rydberg constant, n is the principal quantum number, $\xi = Z - N + 1$ (where in turn Z is the atomic number and N is the number of electrons in the isoelectronic sequence), and a , b , and c are parameters to be determined from the data. This formula works well for the 10-electron sequence (predicting a value of 3.40 eV for the electron affinity of F from the data for Ne, Na⁺, Mg²⁺, and Al³⁺ for example). It predicts a value of -5.6 V for the ionization energy of O²⁻ ($\xi = -1$) from the data for F⁻, Ne, Na⁺, and Mg²⁺ ($\xi = 0-3$); however, I do not consider this value reliable as the extrapolating function has a minimum at $\xi = -1.15$ (thus predicting more positive ionization potentials for ξ less than this value) so it is not behaving in a physically reasonable manner. I have investigated several four-parameter functions based on Edlén's suggestions (41) and find that they all behave similarly.

The difficulty of extrapolating ionization potentials to multiply charged negative ions may be appreciated by examining the data for the difference in the first two ionization potentials for the 10-electron sequence. These data are shown in Fig. 3 together with a fifth-degree polynomial fit to the data for F⁻ to Si⁴⁺. This extrapolates to a value of $I_2 + I_1 = 7.8$ V for O²⁻. However it may be seen that the curve is concave downward and goes rapidly to zero, whereas one expects the difference in ionization potentials to be always positive (and to approach zero only as $\xi \rightarrow -\infty$). There must therefore be an inflection point on the curve about which the data for $\xi > 0$ give essentially no information. Thus I conclude that extrapolation of ionization potentials tells us only

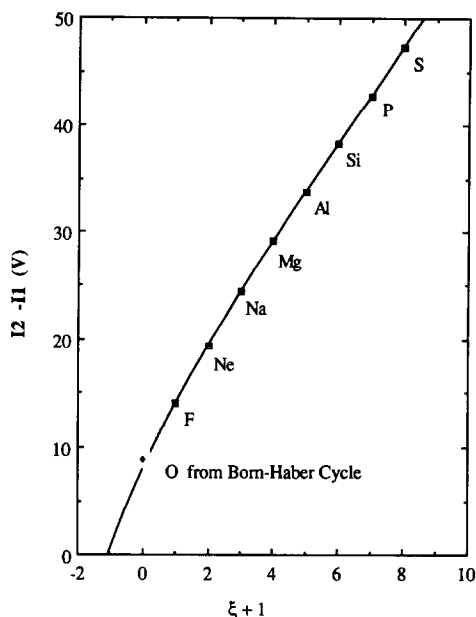


FIG. 3. Difference between the second and first ionization potentials for 10-electron ions. The point for O²⁻ is calculated from a Born-Haber cycle applied to MgO.

that $I_2 - I_1 > 7.8$ V. Thus with $I_2 = 1.46$ V (39), $I_1 < -6.3$ V.

The ionic model of cohesion is sufficiently familiar (3) that details need not be given here. The energy to separate the crystal with shortest internuclear distance r into ions is written $E = A/r - f(r)$, with the first term being the known electrostatic energy and $f(r)$ is a sum of short-range terms. The bulk modulus at $T = 0$ is then $K = -(2A/9V_0r_0)(1 + f''/f')$, where V_0 and r_0 are the equilibrium volume and internuclear distance. With $f(r) = e^{-r/\rho}$ (ρ a constant) one obtains⁴:

$$E = (A/r_0)(1 + 9KV_0r_0/A)/(2 + 9KV_0r_0/A). \quad (6)$$

⁴ It is well known (3) that omitting terms in r^{-6} (van der Waals energy) from $f(r)$ results in errors of less than 10% of that term, so that, in view of its small value for lighter ions and the uncertainty in estimating it, it is better omitted. A correction for zero-point energy has been included.

The right-hand side of Eq. (6) has been evaluated using bulk moduli for MgO ($K = 166$ GPa at 0 K) (37) and the other alkaline earth monoxides (43) together with thermochemical data (44) to derive the sum of the first and second electron affinities of O in the usual way (3). The results for $I_1 + I_2$ for O^{2-} are from the data for MgO, -6.2 ; CaO, -6.0 ; SrO, -5.8 ; and BaO, -5.6 eV. Neglect of van der Waals' energy will provide a correction (least important for MgO) that is increasingly more negative [and which may be larger than commonly supposed for heavier atoms (45)] so the value for MgO is preferred. Taken with value of $I_2 = 1.46$ V, one obtains $I_1 = -7.7$ V which I have used above. The value of $I_2 - I_1 = 9.1$ V is plotted in Fig. 3. It is clearly consistent with the data for the other ions.

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