ubility or potentiometric methods. The resulting estimate for the stability constant of CuI is as expected for the class B metals and correlates very well with the value for AgI.

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Band Gap and Stability of Solids

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The presence of a good HOMO–LUMO gap in molecules has long been associated with structural and kinetic stability. Bartell's use of the second-order Jahn–Teller theorem highlighted this viewpoint when he showed how molecules with small gaps could distort to give more stable structures with larger gaps.[1] An example is the opening up of the gap on pyramidalization of ammonia. In studying the most stable substitution pattern of cyclobutadienes, Hoffmann identified the more stable (trans) $A_2B_2C_4$ isomer as the one with the larger HOMO–LUMO gap.[2] In organometallic chemistry as well, similar ideas apply. Whether the cis or trans form of $ML_4(CO)_2$ and ML_4O_2 species is more stable depends upon electron count. However, in each case for a given electron configuration the more stable structure is found to be the one with the larger gap. In fact, the concept that a small HOMO–LUMO gap signals a geometric distortion is well recognized in almost all areas of molecular chemistry. Notice that in all these examples the number and type of internuclear contact remain the same within each pair of examples. It is either the way the atoms are connected or the angles associated with pairs of bonds that change. In terms of the language of the method of moments, which we have used[3-6] extensively to study structural–electronic problems, the second moment of the electronic density of states remains invariant. There is, however, a less well established view that a correlation analogous to the one described above for molecules applies to solids. In this paper we show the formal connection between stability and band gap in solids by using a simple model that reproduces the results obtained via band structure computations. The model is easily transferable to molecules.

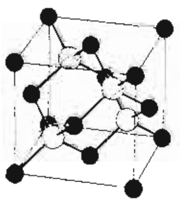
Gaps and Stability in Solids

In molecules the concept of isomerism is well established. The cis- and trans-substituted cyclobutadienes and transition-metal complexes mentioned above are a good example. In solids their equivalent is perhaps the possibility of "coloring" patterns of atoms over the sites of a given lattice.[3] The ZnS (sphalerite) structure may be described in several different ways. One route generates the structure by filling with Zn atoms all the upward-pointing tetrahedral holes of the cubic anion close-packing. A complementary pathway generates the structure by filling with S atoms all the upward-pointing tetrahedral holes of the cubic cation close-packing. In the derivative A_2XX' arrangement there can then be a variety of ways of ordering the X and X′ atoms over the S sites of either description. **1** and **2** show two possibilities.

Table I. Computed Band Gaps and Relative Stabilities for Different Ordering Patterns in Simple Solids

system	stoichiometry[b]	coordn environment	ΔE, eV[a]	E_g, eV
sphalerite	A_2XX'	2 + 2 (cation)	0	1.8
		3 + 1, 1 + 3 (cation)	0.3	1.5
rock salt	$AA'X_2$	3 + 3 (anion)	0	3.05
		4 + 2, 2 + 4 (anion)	0.5	2.40
defect ReO$_3$	$AX_{2.5}$	5[c] (cation)	0	2.84
		5[c] (cation)	0.2	2.80
spinel	$AA'_2X_2X'_2$	2 + 4 (cation A′), 2 + 2(A)	0	1.17
		3 + 3 (cation A′), 4 + 0(A)	0.17	1.15

[a] The most stable structure has $\Delta E = 0$. [b] In sphalerite the coloring is of P and S atoms in a fixed lattice of Zn, in rock salt it is of Mg and Zr atoms in a lattice of P atoms, in the ReO_3 structure it is of oxygen over an array of a prototypic transition metal (Mn parameters were used), and in the spinel it is of Mg and Sc over a close-packed array of P and S atoms. The details of the structures are shown in **1**–**6**. (Geometric details and orbital parameters are given in the Appendix.) [c] In these structures there are two different ordering patterns for the AX_5 square pyramids (see **7** and **8**).



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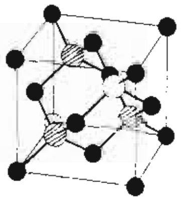
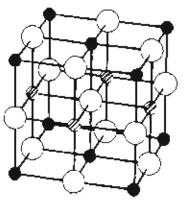


2

sphalerite : ● Zn, ▨ P, ○ S

Similarly, although the simple cubic structure is made up of three mutually perpendicular strings of atoms and can be viewed as a degenerate rock salt structure, there are other ways of ordering the Na and Cl atoms over the lattice. **3** and **4** show two possibilities for two different metal ions ordered over the octahedral hole of a close packing of halogen atoms. Table I shows the computed band gaps (E_g) and stabilities (ΔE) of four pairs of examples. The band structure calculations use the extended Hückel implementation of the tight-binding type method. The examples of Table I include the colorings of sphalerite and rock salt just described. The spinel structure (AB_2X_4) may be regarded as a rock salt/sphalerite hybrid in the sense that both octahedral and tetrahedral holes of the close packing are partially occupied. One of the examples of Table I compares the energies of two colorings (**5** and **6**) of the spinel structure. Coloring patterns do not always have to involve atoms; they can just as well involve vacancies. Thus, the final pair of examples (**7** and **8**) are two



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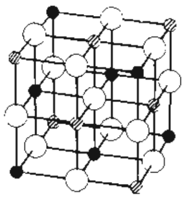

4

rock salt : ○ P, ● Mg, ▨ Zr

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(1) Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754.
(2) Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1979**, 240.
(3) Burdett, J. K.; Lee, S.; McLarnan, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3083.
(4) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1985**, *107*, 3050.
(5) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1985**, *107*, 3063.
(6) Burdett, J. K. *Struct. Bonding (Berlin)* **1987**, *65*, 30.

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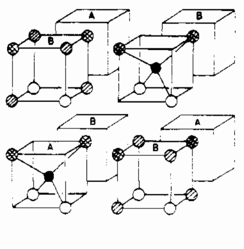

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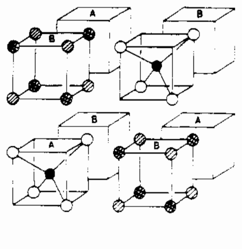
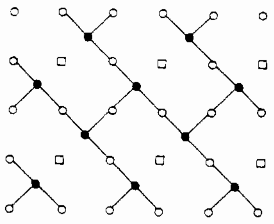


6

spinel : ● Mg, ⊘ Sc, ○ S, ⊛ P



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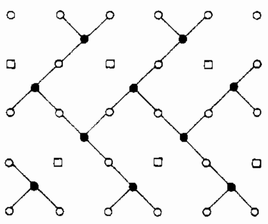
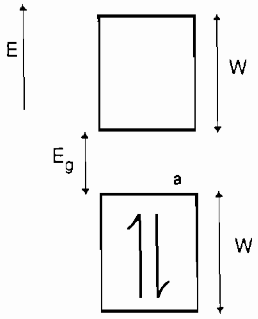


8

$ReO_{2.5}\square_{0.5}$: ● Mn, ○ O, □ O-vacancy

defect ordering patterns in the ReO_3-like structure of stoichiometry $AO_{2.5}$. The arrangement is similar to that in the perovskite structure. (Elsewhere we describe[7] the electronic factors responsible for the electron count dependence of the relative stability of these two structures.) We have chosen the metal electron configurations in all cases to correspond to d^0 (or in the first case d^{10}) metals, such that our examples correspond to closed-shell "octet" structures. An important point concerning the calculated stabilities and band gaps is the correlation between the two. Another point to notice about Table I is that the anion (or cation) coordination is different in each pair (see **1**–**8**). If we define the atomic coordination as $X + Y$, where there are X atoms of one type and Y atoms of another type, then in **1** the cation coordination is 2 + 2 (i.e. two anions of each type) but in **2** the coordination of the cation consists of an equal mixture of 1 + 3 and 3 + 1.

A Simple Model



9

9 shows a very simple model to describe the electronic state of affairs in an octet AX system, where A is a metal and X an electronegative element. Shown is a rectangular density of states for both valence and conduction bands. We set the energy zero arbitrarily halfway between the two and label the bottom of the valence band $E = b$, which means the top of the conduction band has an energy of $-b$. Likewise the top of the valence band is labeled $E = a$ and the bottom of the conduction band $E = -a$ (a, $b < 0$). The filled band of course is largely X in character, while the empty band is largely metal in character. The total electronic density of states is simply $N = \int_{-\infty}^{\infty}\rho(E)\,dE$ and the second moment $\mu_2 = 2\int_{-\infty}^{\infty}E^2[\rho(E)]\,dE$. In terms of the energy labels a and b the latter is just $\mu_2 = {}^2/_3N[a^2 + ab + b^2]$. The one-electron energy is given by $\epsilon = 2\int_{-\infty}^{E_f}E[\rho(E)]\,dE$, where E_f is the Fermi level. In terms of these other parameters $E = N(a + b)$ and $E_g = |2a|$. It is a straightforward matter to show by elimination of a and b that the energy and bandwidth are related by

$$\epsilon^2 = 2N\mu_2 - N^2W^2/3$$

and that the band gap is given by

$$E_g = [2\mu_2/N - W^2/3]^{1/2} - W$$

Table II. Parameters Used in EH Calculations

atom	orbital	H_{ii}, eV	$\zeta_1{}^a$	$\zeta_2{}^a$	$c_1{}^b$	$c_2{}^b$
Sc	3d	−8.51	4.35	0.4228	1.700	0.7276
	4s	−8.87	1.30			
	4p	−2.75	1.30			
Zr	4d	−8.65	3.84	0.6213	1.505	0.5798
	5s	−4.96	1.78			
	5p	−7.78	1.82			
Mn	3d	−11.67	5.15	0.5320	1.90	0.6930
	4s	−9.75	1.80			
	4p	−5.89	1.80			
Mg	3s	−8.00	1.04			
	3p	−5.00	1.04			
Zn	4s	−12.41	2.01			
	4p	−6.53	1.70			
P	3s	−18.60	1.88			
	3p	−12.50	1.63			
	3d	−7.00	1.40			
S	3s	−20.00	2.12			
	3p	−13.30	1.83			
	3d	−8.00	1.50			
O	2s	−32.80	2.275			
	2p	−14.80	2.275			

[a] Slater-type orbital exponents. [b] Coefficients used in double-ζ expansion.

Thus, if we assume that the second moment of the electronic density of states remains constant for the systems we wish to compare, just as for the molecular examples described above, both the stabilization energy and the band gap decrease as W increases. This correlation between stability and band gap is in the same sense as we computed for the real examples of Table I. Such a result should be true for a whole class of structural problems in the solid state. These are where the atoms in the structures being compared have the same coordination number and μ_2 is the same for both arrangements. Recall that μ_2 represents the "coordination strength" of the atoms concerned[6] via all the returning walks of length 2 that connect each atom with its neighbors. We have shown elsewhere[4,5] that at the half-filled band it is the structure with the smaller fourth moment which is more stable. The smaller fourth moment arises in practice from systems where the coordination environment is as symmetric as possible, and we have coined[6] the term "metriotic" to describe this state of affairs. Thus, notice that the symmetric 2 + 2 and rock salt 3 + 3 arrangements are more stable than their 3 + 1 and 4 + 2 isomers. In the spinel example notice that it is the coordination around the non transition metal (A = Mg) which appears to be important in determining the relative stability of the two patterns. Arguments using the same mathematical model can be derived for molecules where the continuous density of states is replaced by a small set of energy levels. Here the structure with the smaller fourth moment, and the one with metriotic use of the available orbitals, is the one more stable at the half-filled band and has the larger HOMO–LUMO gap. The argument may be reworked for a one-fourth- or three-fourths-full band (and indeed for other fillings). The result is a similar correlation between band gap and stability, even though at these two points it is the structure with the larger fourth moment that is more stable.

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(7) Burdett, J. K.; Kulkarni, G. *J. Am. Chem. Soc.*, in press.

If the second moments of the two structures are different, because of different internuclear distances or coordination numbers, then it is much difficult to make a correlation by using the one-electron model. It would predict, for example, that the system with the larger second moment is always the more stable, a result which is not at all reliable. Such one-electron ideas really only come into their own with structural problems that share the same second moment.

A Vital Difference

Solids and molecules, however, do differ in one very important respect. While zero- and small-gap molecules invariably distort (respectively via first- and second-order Jahn–Teller effects), metals (with zero gaps) are well-known in solids. In these cases it is not possible to lower the energy of usually two- and three-dimensional systems by distortion. While the energy at one point in the Brillouin zone may be lowered, the energy rises at another point. Thus whereas the correlation between the HOMO–LUMO gap and more stable structure applies to both coloring and distortional problems in molecules, in solids the distortion route is often frustrated.

Acknowledgment. This research was supported by the Office of Naval Research and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Appendix

The solid-state calculations employed the extended Hückel implementation of the tight-binding method. The atomic parameters used are given in Table II. In the band structure calculations, typically 20 k points were used in the irreducible wedge of the Brillouin zone. The geometries of the crystals were fixed at the values consistent with atomic sizes and the parent structure. The cubic unit cell edges used in the computations were as follows: sphalerite, $a_0 = 5.56$ Å; rock salt, $a_0 = 4.50$ Å; spinel, $a_0 = 10.627$ Å. In the case of the defect ReO_3 structure for the manganese oxide ($MnO_{2.5}\square_{0.5}$) a unit cell with an Mn–O distance of 1.87 Å was employed.

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Redox-Catalyzed Condensation of Hexaammineosmium(II) with Acetone

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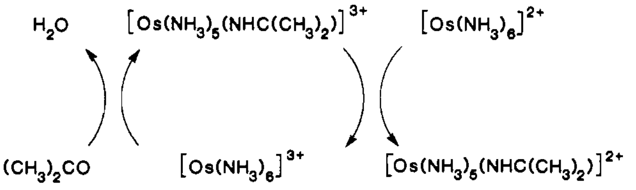

Figure 1. Redox-catalyzed condensation reaction of hexaammine-osmium(II) with acetone.

The nucleophilic activity of a transition-metal-coordinated ligand has both biological and synthetic significance. In the course of investigating the reactivity of $[Os(NH_3)_6](OTf)_2$ (OTf = $CF_3SO_3^-$) in nonaqueous media,[1] it was discovered that under anaerobic conditions this species condenses with acetone to yield a 2-propanimine complex of Os(II).[2] Spectroscopic and electrochemical data[3] of the resulting compound $[Os(NH_3)_5(NHC(CH_3)_2)](OTf)_2$ (**1**) indicate that the imine ligand is terminally bound, in contrast to the isoelectronic acetone analogue in which π coordination is observed.[4] A ^1H NMR spectrum of **1** displays inequivalent methyl resonances at 1.90 (3 H, s) and 2.09 ppm (3 H, s) and a broad peak at 12.65 ppm (1 H) corresponding to the imine proton. Trans- and cis-ammine resonances (4.05 and 3.73 ppm) appear in close proximity, contrary to what is observed for pentaammineosmium(II) complexes containing η^2-bound ligands.[5] A cyclic voltammogram of this material features a reversible couple at $E_{1/2} = -0.61$ V (NHE), which, in consideration of the electrochemical data reported for other pentaammineosmium(II) complexes,[5] would be inconsistent with η^2 coordination. The infrared spectrum of **1** includes absorptions at 1587 and 1432 cm^{-1}, the latter of which is assigned to the C–N stretch and is similar to that found for the complex $[Ru(NH_3)_5(NHCHPh)]^{2+}$ (1440 cm^{-1}).[6] When a sample of **1** is dissolved in MeOD for 1 h and reclaimed, its infrared spectrum no longer includes the higher energy absorption, indicating isotopic exchange. This 1587-cm^{-1} feature is tentatively ascribed to an N–H deformation.[7] When $[Os(NH_3)_5(NHC(CH_3)_2)]^{2+}$ is generated by dissolving $[Os(NH_3)_6](OTf)_2$ in acetone-d_6, a ^1H NMR spectrum of the reaction mixture shows ammine resonances similar to those described above, but the peaks at 1.90 and 2.09 ppm are absent. In addition, a broad singlet is present at 2.86 ppm, which we ascribe to the formation of H_2O, consistent with the stoichiometry

$$(CH_3)_2CO + [Os(NH_3)_6]^{2+} = [Os(NH_3)_5(NHC(CH_3)_2)]^{2+} + H_2O \quad (1)$$

A significant driving force for this reaction comes from the ability of the imine ligand to stabilize the Os(II) metal center through π-back-bonding.[8]

Reaction 1 is catalyzed by trace amounts of $[Os(NH_3)_6]^{3+}$ and is inhibited by acid. From these observations the formation of **1** is thought to occur through nucleophilic attack by an amidopentaamminosmium(III) intermediate (Figure 1), an observation that has previously been reported for Ru(III) and Pt(IV).[9] In the presence of trace amounts of Os(III),[10] **1** shows further reactivity in acetone over time. Cyclic voltammetry indicates that the reversible couple assigned to this species is slowly replaced by one at −0.42 V (NHE), suggesting further imine formation at the osmium center.

When a 0.5 N NaTFMS/DME solution of $[Os(NH_3)_6](OTf)_2$ is treated with excess acetaldehyde and trace amounts of Na^+MeO^-,[11] an intense orange color immediately develops. Cyclic

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[1] $Os(NH_3)_6(OTf)_2$ has been used in our laboratories as a potent one-electron-reducing agent ($E_{1/2} = -0.78$ V; H_2O; NHE). Synthesis: $Os(NH_3)_6(OTf)_3$ (250 mg) dissolved in acetone (10 mL) was stirred along with 5 g of activated magnesium under argon. After 2 h the resulting suspension was pipetted from the magnesium and filtered. The isolated yellow solid was washed with a 1:1 acetone/ether solution, dried under vacuum, and recrystallized from methanol and ether. $Os(NH_3)_6(OTf)_3$ was prepared from the direct reaction of $Os(NH_3)_5(OTf)_3$ in liquid ammonia. The synthesis of $Os(NH_3)_5(OTf)_3$ has been reported by: Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

[2] Under anaerobic conditions, $Os(NH_3)_6(OTf)_2$ (50 mg) was stirred in acetone (5 mL) for 6 h. Formation of the product was monitored by cyclic voltammetry ($E_{1/2} = -0.61$ V in acetone). Treatment with ether precipitated the final product. Anal. Calcd for $[Os(NH_3)_5(NHC(CH_3)_2)](OTf)_2$: C, 9.52; H, 3.52; N, 13.33. Found: C, 9.95; H, 3.33; N, 12.92.

[3] IR (KBr): 1587, 1432 cm^{-1}. ^1H NMR (acetone-d_6): 1.90 (3 H, s), 2.09 (3 H, s), 3.73 (12 H, b), 4.05 (3 H, b), 12.65 ppm (1 H, b). ^1H NMR (acetonitrile-d_3): 1.78 (3 H, s), 2.10 (3 H, s), 3.13 (12 H, b), 3.44 (3 H, b), 11.94 ppm (1 H, b). Cyclic voltammetry (scan rate 100 mV/s; acetone/0.5 N NaOTf; Pt^0 working electrode): $E_{1/2} = -0.61$ V (N H E).

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[5] Typically, pentaammineosmium(II) complexes containing a π-bound sixth ligand have 3+/2+ couples with $E_{1/2}$ greater than 0.0 V (NHE). See: Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.

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[8] Taube, H. *Pure and Applied Chemistry*; Pergamon: London, 1979; Vol. 51, pp 901–912.

[9] Evans, I. P.; Everett, G. W., Jr.; Sargeson, A. P. *J. Chem. Soc., Chem. Commun.* **1975**, 139.

[10] A trace of $[Os(NH_3)_6]^{3+}$ is added, which is thought to generate $[Os(NH_3)_5(NHC(CH_3)_2)]^{3+}$ in acetone. This latter species may be susceptible to further condensation.