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The Band Gap Width of MgO under Compression in a Simple Tight-Binding Theory

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Abstract

The effects of the overlap integrals and the Watson potential on the variation of the band gap width of MgO under compression were investigated by a simple tight-binding model in the nearest- cation-anion and anion-anion interaction approximation. If all the integrals were adjusted so as to reproduce a known band structure and were scaled by the Harrison-Ciraci $1/d^2$-scaling law for the two-center integrals, the band gap width decreases as a crystal is compressed in this model. Then, the effect of the overlap integrals was examined by using a Slater-type 2p orbital and turned out to have an important role on the variation of the width. The overlap integrals reduce the effect of the $1/d^2$-scaling law to the half at most. Further, the effect of the Watson potential on the behavior of the width was investigated analytically by the first order perturbation theory, which resulted in a correction term of an approximate form, $1/d$. This correction improves further the former result and leads to, together with the overlap integrals, the behavior of the band gap width nearly constant at most. As expected, the higher excited states of Mg comes from Mg-3p states and the deeper states of O from O-2s give only negligible effects.

1. Introduction

In the last decade a considerable amount of researchs, by using the tight-binding method (Slater and Koster, 1954) with universal parameters within an approximation including the nearest-neighbor or the nearest- and next nearest-neighbor interactions, has been made on the physics of solids, such as electronic states, binding energies, elastic constats, and optical properties of crystals (reviewed by Harrison, 1980). In general, the two center integrals defined in the method are treated as adjustable parameters to satisfy experiments (Slater and Koster, 1954). In some applications, for example to very high pressure states relating to the lower mantle of the earth, experimental data are hardly expected and therefore some more information not based on experiments is needed in order the method to be useful.

For covalent solids or semiconductors an empirical tight-binging model with universal parameters for the two center integrals concerning only nearest-neighbor interactions has been found to be sufficient to reproduce electronic energy bands, especially for valence electrons (Panterides and Harrison, 1975). The universal parameters are useful, though qualitative, for predicting bonding properties for solids of which characters are not well known. In the model on-site integrals are taken to be equal to neutral atomic term values. This model can precict the band gap widths within a error of 20 percent (Harrison, 1980) but clearly fails to predict the band widths of ionic solids in which the highest electons originally belonging to cations are transferred to anion sites.

The most plausible approximation to ionic solids is to consider that valence electrons on cations are completely transferred to anion sites and bonding orbitals are composed only of anion valence electrons. This model inevitably takes into account of next nearest-neighbor (anion-anion) interactions in order to give the proper band width. This simplest model successfully reproduces valence bands in rocksalt-type crystals with another universal parameters which depend on valencies (Pantelides, 1975) but has nothing to say about the band gap width which is important for optical properties in ultraviolet.

It is obvious that in order to treat the band gap within a model, not as an empirical one, electrons originally in valence orbitals of cations should be included as ones in excited states. This model would contain more parameters than the above two models. In order to avoid a further complication, the overlap integrals between atomic orbitals on different sites are usually assumed to be zero. Though this is not a bad approximation as far as we treat bands in a normal state, it is not known whether this can be a good approximation in a study of the variation of bands in compressed states. It is considered that, therefore, in such a study, the overlap integrals should also be taken into account.

In general, the most simple tight-binding method is based on linear combination of atomic orbitals which are taken to be those of neutral atoms. For covalent crystals, it is successful but is doubtful for ionic ones. In ionic crystals, electrons originally on cation sites are transferred to anion sites to form a closed shell atom on each ion site (Gordon and Kim, 1972). This model based on free ion electronic charge distribution for each ion site gives rather accurate binding energies of these crystals in the nearest-neighbor approximation with the Madelung energy (Kim and Gordon, 1974). In actual crystals, these ions are stabilized by a potential formed from surrounding ions. The potential can be approximated by the Watson charged shell (Watson, 1958) and

the shell stabilized charge distribution further refines the results (Muhlhausen and Gordon, 1981a, 1981b). These results suggest that for the on-site integrals energy eigenvalues of shell stabilized ions will be adequate.

The purpose of this paper is to examine the behavior of the band gap width of MgO under compression by a simple tight-binding model. In the following, a summary of the basic technique for the tight-binding method will be presented, comparisons between bands obtained from various ways for MgO will be made, then the variation of the band gap width as a function of the nearest-neighbor distance will be disccussed. For atomic term values, Hermann-Skillman values (1963) of neutral atoms are used.

2. Theory

Bloch's function is given in a form;

$$\varphi_{s\lambda}^{k}=\frac{1}{\sqrt{N}}\sum_{n} e^{i\boldsymbol{k}\cdot(\boldsymbol{t}_n+\boldsymbol{\tau}_s)}\phi_{\lambda}(\boldsymbol{r}-\boldsymbol{t}_n-\boldsymbol{\tau}_s)$$

where $\boldsymbol{t}_n$ stands for the lattice translational vectors, $\boldsymbol{\tau}_s$ non-primitive vector of s-th atom in a primitive cell, ϕ_λ atomic orbibals with quantum number λ such as s, p, d and $\langle\phi_\lambda \mid \phi_\lambda\rangle=1$. N is the total number of cells in a solid. The eigenfunction of the Hamiltonian is a linear combination of the functions given above with assumed combination of s and λ;

$$\Psi_k=\sum_{s\lambda} C_{s\lambda}^{k}\varphi_{s\lambda}^{k}$$

Variational calculation leads to

$$\frac{\sum_{s\lambda} C_{s\lambda}^{k}\langle\varphi_{s'\lambda'}^{k} \mid H \mid \varphi_{s\lambda}^{k}\rangle-E^{(k)}\sum_{s\lambda} C_{s\lambda}^{k}\langle\varphi_{s'\lambda'}^{k} \mid \varphi_{s\lambda}^{k}\rangle}{\sum_{s\lambda s'\lambda'} C_{s\lambda}^{k*}C_{s'\lambda'}^{k}\langle\varphi_{s\lambda}^{k} \mid \varphi_{s'\lambda'}^{k}\rangle}=0$$

The Bloch's functions are not exactly orthogonal to each other, if they are formed from simply adding up atomic functions. Retaining, therefore, the overlap integrals, we obtain the secular equation,

$$\left|\langle\varphi_{s'\lambda'}^{k} \mid H \mid \varphi_{s\lambda}^{k}\rangle-E^{(k)}\langle\varphi_{s'\lambda'}^{k} \mid \varphi_{s\lambda}^{k}\rangle\right|=0$$

In latter disccusions, we will consider two cases; (1) the correction for the orthogonalization is thought to be absorbed in the parameters for the two-center integrals and (2) the overlap integrals are evaluated explicitly.

Matrix elements for MgO in the approximation including only nearest-cation-anion and nearest-anion-anion interactions are given in Table 1. In deriving this, on-site integrals concerning to two electrons with different quantum numbers are assumed to be zero. In the table Slater-Koster notations are

Table 1 Matrix elements in an approximation of the nearest-cation-anion and anion-anion interactions. The overlap integrals are also taken into account within the same approximation.

Mg	*O*			
s	p_x	p_y	p_z	
H_{11}	H_{12}	H_{13}	H_{14}	$H_{11}=E_s^{Mg}-E$
	H_{22}	H_{23}	H_{24}	$H_{12}=2i\{(sp\sigma)_1-S_1E\}\sin\frac{x}{2}$
		H_{33}	H_{34}	$H_{13}=2i\{(sp\sigma)_1-S_1E\}\sin\frac{y}{2}$
$\boldsymbol{k}\equiv\frac{1}{a}(x,y,z)$			H_{44}	$H_{14}=2i\{(sp\sigma)_1-S_1E\}\sin\frac{z}{2}$

$$H_{22}=E_p^0-E+2[(pp\sigma)_2+(pp\pi)_2-(S_2+S_3)E]\cos\frac{x}{2}\left[\cos\frac{y}{2}+\cos\frac{z}{2}\right]$$
$$+4\{(pp\pi)_2-S_2E\}\cos\frac{y}{2}\cos\frac{z}{2}$$

$$H_{23}=2[(pp\pi)_2-(pp\sigma)_2-(S_2-S_3)E]\sin\frac{x}{2}\sin\frac{y}{2}$$

$$H_{24}=2[(pp\pi)_2-(pp\sigma)_2-(S_2-S_3)E]\sin\frac{x}{2}\sin\frac{z}{2}$$

$$H_{33}=E_p^0-E+2[(pp\sigma)_2+(pp\pi)_2-(S_2+S_3)E]\cos\frac{y}{2}\left[\cos\frac{z}{2}+\cos\frac{x}{2}\right]$$
$$+4\{(pp\pi)_2-S_2E\}\cos\frac{x}{2}\cos\frac{z}{2}$$

$$H_{34}=2[(pp\pi)_2-(pp\sigma)_2-(S_2-S_3)E]\sin\frac{y}{2}\sin\frac{z}{2}$$

$$H_{44}=E_p^0-E+2[(pp\sigma)_2+(pp\pi)_2-(S_2+S_3)E]\cos\frac{z}{2}\left[\cos\frac{x}{2}+\cos\frac{y}{2}\right]$$
$$+4\{(pp\pi)_2-S_2E\}\cos\frac{x}{2}\cos\frac{y}{2}$$

used for the two-center integrals. For example $(sp\sigma)_2$ stands for the interaction between Mg-3s and the nearest O-2p electrons and $(pp\sigma)_2$ the one between the nearest O-2p electrons. The part of each matrix element concerning the overlap integrals can be derived by the same Slater-Koster procedure with Hamiltonian turned off to a unit operator. S_1 is the overlap integral between an oxygen s and the nearest neighbor oxygen s' but it is not used explicitly in the present study. S_2 and S_3 are the integrals between oxygen p's in a pi-configuration and in a sigma-configuration, respectively. S_2 is evaluated by using a hydrogen-like $2p_x$-function,

$$p_x=AZxe^{-\frac{z}{2}r}$$

where

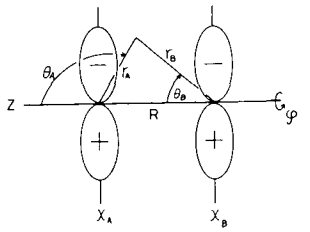

Fig. 1 A coordinate system for p-atomic orbitals in the pi-configuration.

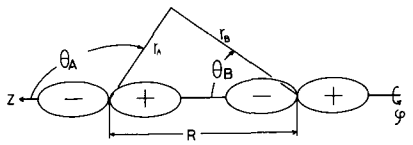

Fig. 2 A coordinate system for p-atomic orbitals in the sigma configuration.

$$A=\left(\frac{Z}{2}\right)^{\frac{3}{2}}\frac{1}{\sqrt{\pi}}$$

S_2 is, then,

$$S_2\equiv\langle p_x^A \mid p_x^B\rangle=A^2\iiint dv Z x_A e^{-\frac{Z}{2}r_A} Z x_B e^{-\frac{Z}{2}r_B}$$

where r_A etc. are defined in Fig. 1. Inroducing a spheroidal coordinate,

$$1<\xi=\frac{1}{R}(r_A+r_B)<\infty$$

$$-1<\eta=\frac{1}{R}(r_A-r_B)<1,\ \varphi=\varphi$$

we obtain the expression for the integral

$$S_2=\frac{1}{15}e^{-x}(x^3+6x^2+15x+15)$$

where $x=ZR/2$ and R is measured in atomic unit.
In evaluating S_3, we use hydrogen-like $2p_z$-function,

$$p_z=\left(\frac{Z}{2}\right)^{\frac{3}{2}}\frac{1}{\sqrt{4\pi}}Zre^{-\frac{Z}{2}r}\cos\theta$$

S_3 is obtained in a similar way as S_2,

$$S_3\equiv\langle p_z^A \mid p_z^B\rangle=\frac{Z^3}{2^5\pi}\iiint dv Z r_A e^{-\frac{Z}{2}r_A}\cos\theta_A Z r_B e^{-\frac{Z}{2}r_B}\cos\theta_B$$

$$=\frac{1}{15}e^{-x}(-x^4-2x^3+3x^2+15x+15)$$

(see Fig. 2)

3. Determination of parameters

Substituting proper values for k of symmetry points in the Brillouin Zone (B.Z.), we obtain following analytical expressions of band energies belonging to the irreducible representations at the given points;

(1) $E^{(\Gamma_1)}=E_s^{Mg}$

(2) $E^{(\Gamma_{15})}=\{E_p^o+4[(pp\sigma)_2+2(pp\pi)_2]\}/S$

(3) $E^{(X_{c'})}=\{E_p^o-4(pp\sigma)_2\}/(1-4S_3)$

(4) $E^{(X_{5'})}=\{E_p^o-4(pp\pi)_2\}/(1-4S_2)$

(5) $E^{(L_3)}=\{E_p^o-2[(pp\pi)_2-(pp\sigma)_2]\}/(1-2[S_2-S_3])$

(6) $E^{(L_1)}=\dfrac{1}{2\{1-4(S_1^2-S_2+S_3)\}}[E_p^o+E_s^{Mg}+24S_1(sp\sigma)_1$
$+4\{[(pp\pi)_2-(pp\sigma)_2]+S_2-S_3-\{[E_p^o+E_s^{Mg}$
$+24S_1(sp\sigma)_1+4\{[(pp\pi)_2-(pp\sigma)_2]+S_2-S_3\}]^2$
$-4\{1-4(S_1^2-S_2+S_3)\}\{4E_s^{Mg}[(pp\pi)_2-(pp\sigma)_2]$
$+E_s^{Mg}E_p^o-12(sp\sigma)_1^2\}\}^{\frac{1}{2}}]$

where $S=1+8\ S_2+4\ S_3$.

The band gap width which is at the center of B.Z. and the maximum band width of valence band which is at L in B.Z. (Pantelides, 1975) are given as

(7) $E_g=E^{(\Gamma_1)}-E^{(\Gamma_{15})}$

(8) $E_w=E^{(\Gamma_{15})}-E^{(L_1)}$

Values for the two-center integrals apeared in the matrix can be determined by setting the energies given in these equations equal to known values obtained either from experiments or more sophisticated calculations. In the process E_p^o is fixed to the atomic term value and, in order to compare the present result with published ones, S_2 and S_3 are temporarily set equal zero. $(pp\sigma)_2$ and $(pp\pi)_2$ are determined from the valence band widths in X direction, 4.93 and 1.97 eV, obtained from the pseudopotential calculation (Fong et. al., 1968), by using Eq. s (2), (3), and (4);

$$(pp\sigma)_2=0.678=3.02/d^2\ eV$$

and

$$(pp\pi)_2=-0.06=-0.27/d^2\ eV$$

The right most expressions are d^{-2}-scaling (Harrison and Ciraci, 1974) by the nearest-neighbor distance d measured in angstrom. Then E_s^{Mg} is determined from the band gap width being known to be 7.77 eV experimentally (Roessler and Walker, 1967) to be -4.14 eV relative to E_p^o by employing Eq.s (1) and (2). Finally $(sp\sigma)_1$ is determined from E_w experimentally obtained to be 7.0 eV (Fischer, 1970);

$$(sp\sigma)_1=1.50=6.67/d^2\ eV.$$

The situation that $(pp\sigma)_2$ is somewhat smaller than the value given by Pantelides, 0.93 eV, is compensated for by introducing $(sp\sigma)_1$ to give correct band energies. Harrison's universal parameters are too large. The ratio of $(pp\pi)_2$ to $(pp\sigma)_2$ is $-1:11$ which is again smaller than that of Pantelides, $-1:8$, but the difference is not thought to be severe, taking the roughness in his

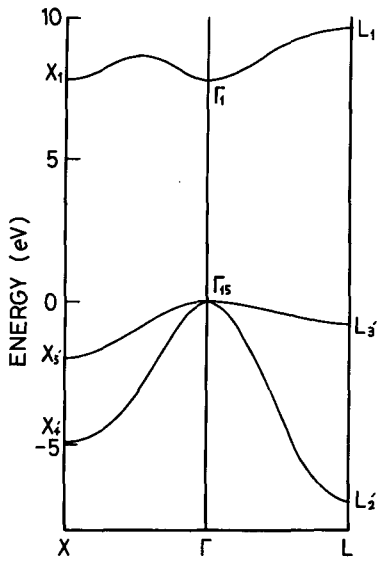

Fig. 3 The energy band in the directions of X and L from in the Brillouin zone.

estimation into account.

The band energies along the symmetry lines Δ and Λ are shown in Fig. 3. The valence band is identical with those calculated by Fong et. al (1968) and by Pantelides (1975) as a matter of course but the conduction band widths along Δ and Λ are about half and twice of those obtained by Fong et. al., respectively. Overall agreement is fairly good and comparable to that Harrison's theory (1980) attained for covalent solids.

4. Variation of band gap width

There are several methods to calculate the band gap width; (1) by subtracting the anion-p atomic term value from the cation-s one (Harrison, 1980), (2) by fitting empirical formulae to experimental values (Pantelides, 1975, (3) by using more sophisticated methods such as APW and pseudo-potential methods. Harrison's simplest method gives a rather good approximation, $E_g=$ 7.27 eV for MgO, but, as mentioned in the introduction, does not give correct dispersion consistently to valence bands in ionic solids. Harrison (1981) gave an approximate 'band gap width' which increased as d decreased, but it was not the true band gap width but merely a difference in energy between an average of

band levels arose from Mg-s's and that from O-p's. Pantelides's empirical formula gives poorer values than Harrison's but, as for the variation of E_g under compression, it seems to be consistent with APW results (Maeda, 1976; Bukowinski, 1980) in which E_g increases as a solid is compressed. Pantelides's formula does not necessarily mean that it can predict the behavior of E_g of a material under compression.

Apparently the first method gives constant E_g even under compression if free atomic term values are used. The present model, Eq. (7) with $S=1$, shows just the opposite tendency for the variation from APW results if Harrison-Ciraci $1/d^2$- scaling law for the two-center integrals is employed. It is apparent that use of the atomic term value for E_s^{Mg}, which results in $E_g=5.04$ eV, does not improve the situation.

To improve this, an effect of the overlap integrals, S_2 and S_3 contained in S, is examined. As a first step, the parameter Z is fixed in such a manner that a radius at which the hydrogen 2p-function has its maximum amplitude is set equal to the one at which the 2p-function of a neutral oxygen obtained by Herman and Skillman (1963) has its maximum; $Z=4.9646$. Since this hydrogen-like function with adjustable parameter Z can be regarded as a Slater-type orbital, the present approximation is one of the single-zeta-STO system used in chemistry (Huzinaga, 1980). It is probable that the actual 2p-orbitals of a doubly negative-charged oxygen are more difused than those of a neutral one even in a solid; Z may be lower than the above, and originally Slater gave $Z=4.55$ (see Huzinaga, 1980).

The variations of E_g with various Z in S as a function of d along with the one with $S=1$ are shown in Fig. 4. In the calculations, the two-center integral parameters, $(pp\sigma)_2$ and $(pp\pi)_2$, are re-evaluated by the same procedure as before and their variations are given in Fig. 5. The tendency of narrowing in E_g under compression is reduced as Z is decreased and at $Z=4.2$ the tendency is reduced to the half of the case of $S=1$, though the value of $Z=4.2$ is thought to be somewhat too small compared to Slater's value. It can be seen from Figs 4 and 5 that a smaller Z results in a smaller S, which means lower $E^{(\Gamma_{15})}$ and larger E_g, but it results in larger absolute values of the parameters, which hamper the former effect on E_g. The refinement in the variation of E_g by evaluating the overlap integrals explicitly means that, if we are interested in a compressed state, we must take account of S explicitly. It should be mentioned that, we used the $1/d^2$-scaling law in the calculation, taking the law as being empirical, though it is not known if it can still hold in the case that S is explicitly taken into account.

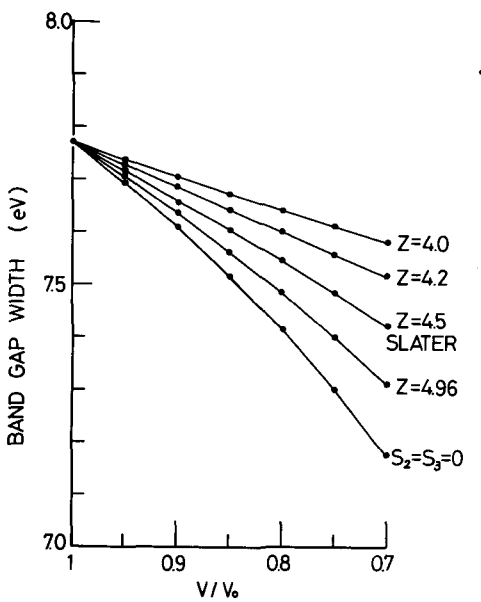

Fig. 4 The effect of the overlap integrals on the variation of the band gap width as a function of V/V_0, the specific volume, calculated with various Z, the parameter in the Slater-type orbital.

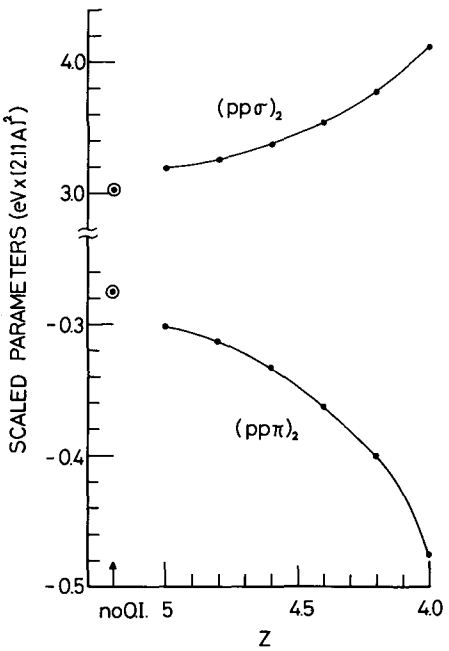

Fig. 5 The variations of the two-center integrals, $(pp\sigma)_2$ and $(pp\pi)_2$, being taken account of the overlap integrals with various Z, and the values obtained without taking the overlap integrals in to account, which are assigned 'no O.I.'.

Next we examine an effect of ionization because Gordon-Kim model (Gordon and Kim, 1972), in which each ion is thought to have a closed shell, successfully predicts physical quantities in compressed states of alkali halide (Cohen and Gordon, 1975) as well as those of ionic crystals in the normal states (Kim and Gordon, 1974). As a result of transferring electrons from Mg-site to O-site, doubly charged negative oxygen is formed though it is not stable as an free ion and must be stabilized by the surroundings. This stabilization might be achieved by the Madelung potential or Watson's potential caused by a ficticious charged shell around the ion but the first one was found to be not adequate (Watson, 1958). The Watson potential is expressed at each ion site as

$$V_w(r)=-\frac{q}{r_i}:\ r<r_i$$

$$=-\frac{q}{r}:\ r>r_i$$

where q is the inonic charge with the opposite sign from that of an ion concerned, eg., $q=2$ for doubly charged oxygen, r_i the ionic radius.

In order to obtain energy eigenvalues of shell stabilized (S.S.) ions, the Hatree-Fock equation must be solved numerically. Here we examine the effect of the Watson potential on the behavior of E_g analytically by using a rather crude model in which we assume that the potential can be treated as a perturbation. The basic idea is explained as follows. Suppose that MgO is in rocksalt structure with very large inter-atomic distance, d, and that a small amount of charge transfer (CT) occurs from Mg to O. Oxygen p-orbitals are modified by CT but stabilized by a potential which comes from the surrounding charges caused by CT and can be approximated by the Watson potential with small q. We assume that the orbitals modified then stabilized retain its original form approximately and the energy eigenvalue is not largely modified. In the next step, as d decreases by a small amount, additional CT occurs and the same process results not largely changed eigen- function and energy. Continuing this, we obtain an equilibrium state in which the eigen- function and energy might not be largely apart from the originals. This is supported by the fact that atomic term values of neutral atoms give rather good E_g (Harrison, 1980).

In the following, S is set unity in order for simplicity and for making clear the effect of Watson's potential. The oxygen p-function is assumed to be approximated by a hydrogen-like 2p-function as before, but in this case Z has a somewhat different meaning. The first order perturbation energy, W, becomes

$$\begin{aligned}W&=\langle p_z \mid V_w \mid p_z\rangle\\&=\frac{3}{4\pi}a_1^2\iiint d\varphi\sin\theta d\theta\cos^2\theta r^4 dr e^{-Zr}V_w(r)\\&=-a_1^2\frac{q}{r_i}\int_0^{r_i}drr^4e^{-Zr}-a_1^2q\int_{r_i}^{\infty}drr^3e^{-Zr}\\&=\frac{1}{12}Z^3q\left[e^{-Zr_i}\left(r_i^2+6\frac{r_i}{Z}+18\frac{1}{Z^2}+\frac{24}{Z^3}\frac{1}{r_i}\right)-24\frac{1}{Z^3r_i}\right]\end{aligned}$$

where

$$a_1=\left(\frac{Z}{2}\right)^{\frac{3}{2}}\frac{Z}{\sqrt{3}}$$

It must be mentioned that, although p-states are triply degenerate, the non-degenerate perturbation expression can be used because the perturbation here is

spherically symmetric so $\langle p_i \mid H \mid p_j \rangle$ with $i \neq j$ happens to be zero (Schiff, 1968).

The integral W as a function of the ionic radius, r_i, for fixed q and various Z is shown in Fig. 6. At the ionic radius of oxygen, 1.46A, W varies approximately as the inverse of r_i; this variation can be regarded as $1/d$-dependence of W if r_i varies proportionately as d does. This can hold whether V_w is sufficiently small, that is, small q, in which the perturbational calculation is legitimate, or not because W depends linearly on q. The actual value of W cannot be calculated from this model and, therefore, it should be adjusted so as to give correct E_g at normal state; $W = a/d$, where a is an adjustable parameter.

Then, E_g is given as

$$E_g = E_s^{Mg} - (E_p^o + W) - 4[(pp\sigma)_2 + 2(pp\pi)_2]$$

The variation of E_g depends on what value of E_s^{Mg} is used and is shown in Fig. 7 in which E_s^{Mg} varied from the Herman-Skillman value to the values obtained in the preceding section. It is considered that the Herman-Skillman value gives the Watson potential the maximum effect. It is clearly seen from the figure

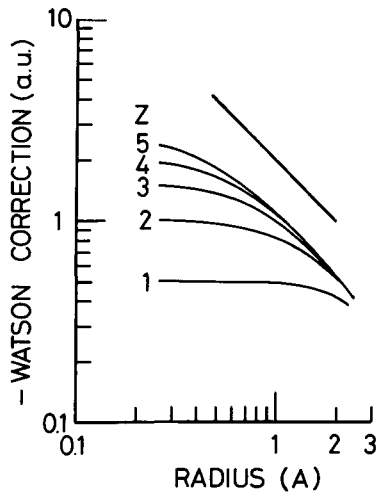

Fig. 6 The perturbation energy (in atomic unit) of the Watson potential as a function of the ionic radius (in angstrom). The inclination of the slanted line shows a 1/d-dependence of the energy at and around the ionic radius of oxygen 1.46A, where d is the interatomic distance.

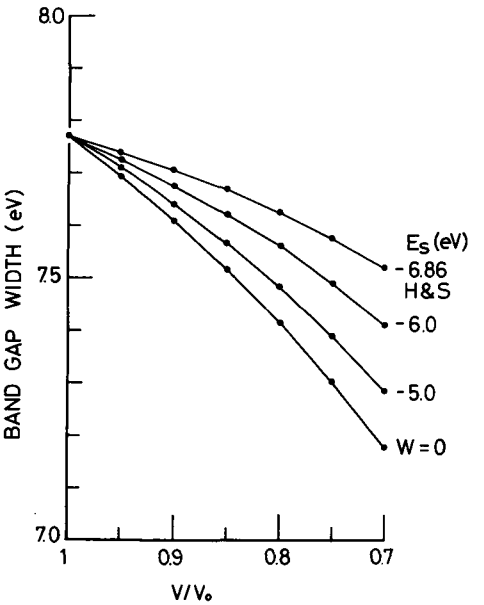

Fig. 7 The effect of the Watson potential on the band gap width as a function of the specific volume V/V_0 with various E_s^{Mg}. $E_s^{Mg} = -6.86$ means it was taken from Herman-Skillman value.

that this model reduces the tendency of narrowing E_g. Getting this result together with the effect of the overlap integrals discussed above, we can conclude that these two factors almost compensate the $1/d^2$-dependence of the two-center integrals and give E_g an almost constant feature under compression. As have already mentioned, Pantelides's empirical relation does not necessarily hold to predict the behavior of E_g of a material under compression and APW results are not quantitatively conlcusive though they would be qualitatively correct. To fix the behavior of E_g more precisely, numerical calculations of the Hartree-Fock equation for S.S. ions will be needed.

We will examine another possible factors to improve the calculation. Oxigen-2s electrons affect E_g by a small amount,

$$D_1=\frac{36[(ss\sigma)_1^2+(ss\sigma)_2^2]}{E_s^{Mg}-E_s^o+W}$$

(where W is the perturbation correction) which is obtained by a similar procedure deriving Table. 1 including the assigned orbitals under an assumption that the numerator is sufficiently smaller than the denominator and $S_1=S_2=S_3=0$. Evaluating newly appeared two-center integral parameters by again fitting calculated band energies to that by Fong et. al., we find D_1 has almost no effect on the variation of E_g. Addition of Mg-3p to the above approximation results a further additional term,

$$D_2=\frac{4[\{(pp\sigma)_2+2(pp\pi)_2\}^2+(ss\sigma)_1^2]}{E_g^{Mg}-E_p^o+W}$$

which is obtained by the same procedure as before. By a numerical evaluation this correction term turns out to be less effective as might be expected.

5. Summary

We investigated E_g and its behavior of MgO under compression by a simple tight-binding model in the nearest- cation-anion and anion-anion interaction approximation. For the two-center integrals, the Harrison-Ciraci $1/d^2$-scaling law was employed. First, all the integrals were taken to be adjustable parameters. E_g decreases as a crystal is compressed in this model. Then, the effect of the overlap integrals was examined by using a Slater-type 2p-orbital and turned out to have an important role on the variation of E_g. These integrals reduce the effect of the $1/d^2$-scaling law to the half at most. Further, the effects of the Watson potential on the behavior of Eg was investigated analytically by the first order perturbation theory, which resulted a correction term of an approximate form, $1/d$. This correction improves further the former result

and leads to, together with the overlap integrals, the behavior of E_g nearly constant at most. As expected, the higher excited states of Mg comes from Mg-3p states and the deeper states of O from O-2s give only negligible effects.

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