X-Ray Emission and Photoelectron Spectra from Magnesium Oxide: a Discussion of the Bonding Based on the Unit Mg_4O_4

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A simple molecular-orbital model for the bonding in magnesium oxide is developed using Mg_4O_4 (a cube with magnesium and oxygen atoms at alternate corners) as a basis. Extension to $Mg_{32}O_{32}$ indicates how the molecular-orbital description of Mg_4O_4 can be developed into the band structure for MgO. The qualitative predictions concerning the distribution of Mg 3*p*, Mg 3*s*, O 2*p*, and O 2*s* character amongst the various orbitals are checked by comparison with *X*-ray emission (Mg-$K_{\beta_{1,3}}$, Mg-$L_{2,3}$ M, and O-K_{α}) and also *X*-ray photoelectron spectra. The Mg_4O_4 model provides an adequate rationalisation of the principal features of the spectra, particularly of the split magnesium *X*-ray emission peaks.

MAGNESIUM OXIDE has a simple cubic structure: it is therefore to be hoped that the bonding between the magnesium and the oxygen will also be simple. The nature of the chemical bond between atoms can be studied in a particularly direct way by means of *X*-ray emission (*X*-e.m.) spectroscopy[1] since the transitions observed are those allowed by the Laporte selection rule for the emission of dipole radiation, $\Delta l = \pm 1$ (*i.e.* $p \rightarrow s$, s or $d \rightarrow p$, *etc*). *X*-Irradiation of a sample such as magnesium oxide therefore causes emission of a series of characteristic *X*-rays, magnesium $K_{\alpha_{1,2}}$ ($2p \rightarrow 1s$), $K_{\beta_{1,3}}$ ($3p \rightarrow 1s$), $L_{2,3}$M (3*s* and possibly $3d \rightarrow 2p$), and oxygen $K_{\alpha_{1,2}}$ ($2p \rightarrow 1s$). When the emission results from an electronic transition from a valence-shell orbital the structure of the observed *X*-ray peak can be directly related to the degree of participation of an atomic orbital in different molecular orbitals.[2] The various *X*-ray emission spectra can be referred to a common energy scale if the ionisation energies of the inner orbitals, to which the transition takes place, are determined directly using *X*-ray photoelectron (*X*-p.e.) spectroscopy.[3] *X*-P.e. spectroscopy also provides a convenient check on the *X*-ray emission data since the ionisation energies of the initial and final states for an *X*-ray transition can both be determined directly. Provided that Koopman's theorem[4] remains valid, it should be possible to relate the energy levels determined for the ionised species to those of the ground-state neutral molecule. The correctness of this theorem is assumed in the discussion below. The purpose of this paper is to present *X*-e.m. data and *X*-p.e. spectra for magnesium oxide and to show how these data may be interpreted using a simple molecular-orbital model, based on an Mg_4O_4 unit, for the bonding in this compound. These results are compared with other data and the interpretations that have been suggested using $[MgO_6]^{10-}$ as a basis.

EXPERIMENTAL

Magnesium $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, and oxygen $K_{\alpha_{1,2}}$ *X*-ray emission spectra were obtained from a sample of synthetic periclase which was very kindly supplied by the Mineralogical Department of the British Museum (Natural History), reference number BM 1952, 208. The powdered periclase was bound with terephthalic acid under pressure to form a pellet for determination of the magnesium spectra; for the oxygen spectrum the periclase was pressed into a copper mesh (this gave a less fragile disc than the one obtained by pressing the powdered sample alone). The emission spectra were excited by irradiation with a chromium-anode *X*-ray tube operated at 50 eV,† and 50 mA, in a Philips PW 1410 *X*-ray fluorescence spectrometer. In order to achieve the highest resolution the 'fine' soller collimator was used (150 μm × 100 mm). The magnesium *X*-rays were dispersed with an ammonium dihydrogenphosphate crystal (2*d* 1 064 pm, first order); a rubidium acid phthalate crystal (2*d* 2 612 pm, first order) was used for oxygen. Under these conditions the minimum peak width at half height would be *ca.* 0.5 eV for oxygen K_{α} and 1.0 eV for magnesium K_{α} and K_{β}, due to collimation alone. That the observed widths at half-height are *ca.* 2—3 times larger than these figures is

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† 1 eV ≈ 1.60×10^{-19} J.

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[2] D. S. Urch, *J. Phys.* (*C*), *Solid State*, 1970, **3**, 1275.

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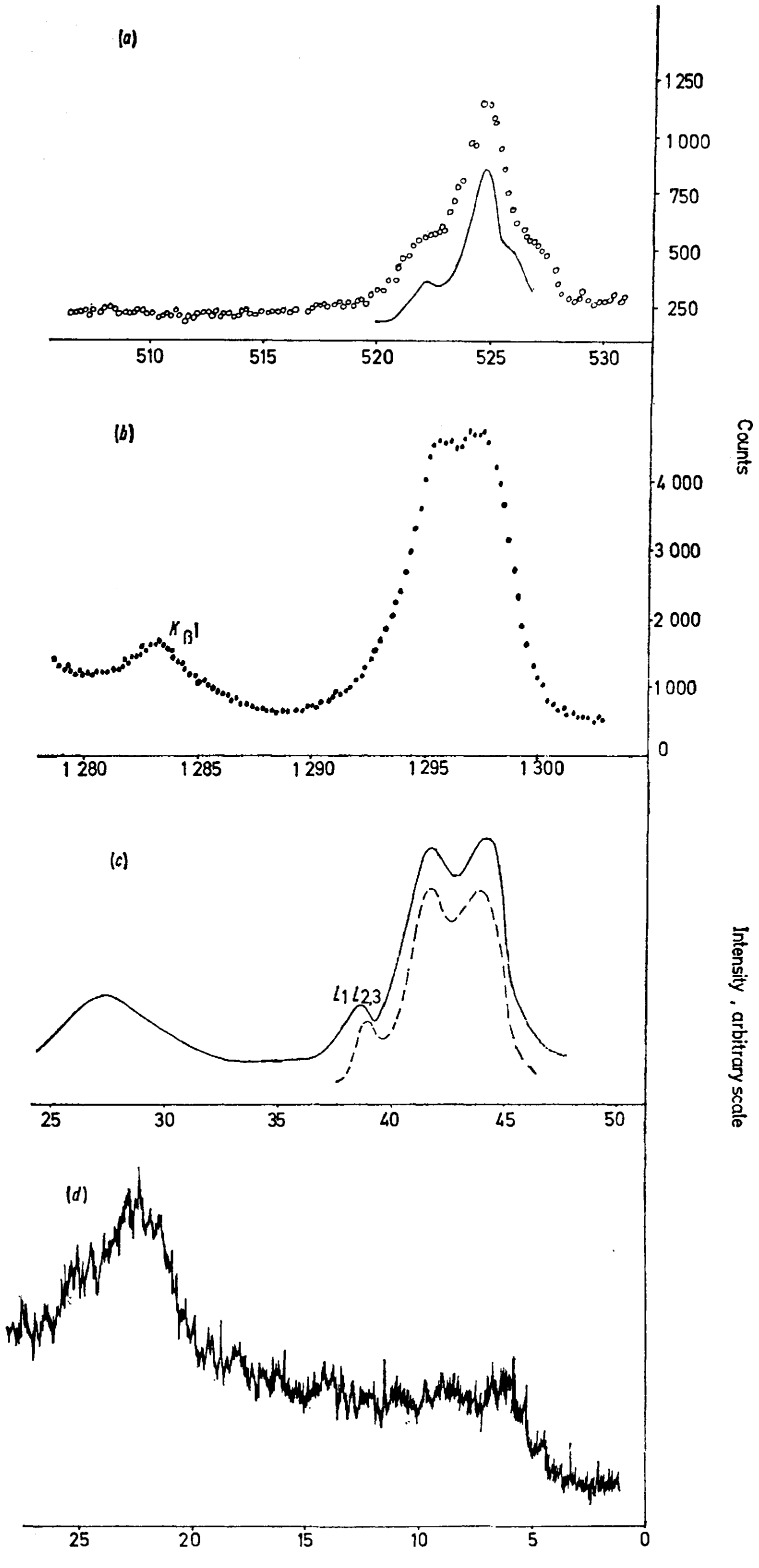

FIGURE 1 X-Ray emission and photoelectron spectra (*d*) from magnesium oxide: (*a*) O-$K\alpha$; (*b*) Mg-$K\beta_{1,3}$; and (*c*) Mg-$L_{2,3}$M. Inner-orbital ionisation energies determined by X-p.e. spectroscopy 532.2 (O 1*s*), 1 304.9 (Mg 1*s*), and 51.3 eV (Mg 2*p*). The full lines in (*a*) and (*c*) are from refs. 8 and 10, the broken line in (*c*) from ref. 9

due to a combination of many other factors, the most important of which are the natural linewidth and the mosaic nature of the diffracting crystal. In this work all the *X*-rays were detected using a proportional counter with a 1 μm window and argon–methane flow gas at atmospheric pressure. The output from the counter was amplified and analysed using Harwell 2 000 series electronics. Spectra were scanned automatically in steps of 0.1 eV; the duration of each count was 500 s.

Ionisation energies of the inner orbitals and also of the molecular orbitals of the valence band were determined by mounting powdered periclase on double-sided Sellotape in a Vacuum Generators ESCA III spectrometer. Radiation from an aluminium *X*-ray tube (12 kV, 40 mA) was used to stimulate photoemission. The analyser energy was set at 50 eV which restricted the peak width (at half-height) to a minimum of 1.8 eV. The spectra so obtained were referenced with respect to gold by repeating the irradiations with the sample pressed into a gold mesh. The data appear to be in good agreement with those of previous workers [5,6] but, bearing in mind the insulating nature of magnesium oxide and the difficulties associated with gold calibration,[7] this agreement may be fortuitous. This does not detract from the value of such spectra as a basis for lining up *X*-ray emission spectra since only the *relative* values of the inner-orbital ionisation energies are required.

RESULTS

The magnesium and oxygen *X*-ray emission spectra are shown in Figure 1. Zero on the common energy scale corresponds to the ionisation energy of the inner atomic orbital for each *X*-ray emission spectrum. The *X*-ray spectrum of oxygen as determined by Chun [8] has also been included because of its superior resolution. The Mg-$L_{2,3}$M spectra have been taken from Fomichev *et al.*[9] and also from Neddemeyer.[10]

DISCUSSION

One of the most striking features of Figure 1 is that the main peak of each spectrum is split, by approximately the same amount, and that the two components of each main peak line up underneath each other. This indicates contributions to two bands of molecular orbitals from valence atomic orbitals which give rise to Mg-$K_{\beta_{1,3}}$, Mg-$L_{2,3}$M, and O-K_α spectra. It is also interesting to note that the low-energy satellite peaks in the magnesium spectra line up with peaks at 21—25 eV in the p.e. spectrum, which presumably arises from orbitals with considerable oxygen 2*s* character.

The models which have been proposed [11-13] to explain the observed features of the emission spectra and which have been used as a basis for molecular-orbital calculations have all utilised the $[MgO_6]^{10-}$ unit. The magnesium is surrounded by an octahedron of oxygen ions. In such a model the 3*p* orbitals of magnesium belong to the irreducible representation t_{1u} as do symmetry orbitals which can be derived from 2*s* oxygen-ligand orbitals and also from oxygen 2*p* orbitals orientated along Mg–O axes. The interactions of these orbitals give rise to two occupied triply degenerate sets of orbitals, one mostly O 2*s* in character with only a small contribution from magnesium 3*p* orbitals and another in which the Mg 3*p* participation is somewhat larger but in combination with oxygen 2*p* orbitals. The model explains the gross features of the Mg-$K_{\beta_{1,3}}$ emission spectrum (a main peak and a less-intense low-energy satellite, K_{β}'),[2] but as Dodd and Glenn [11] and also Tossell [13] have shown it provides no reason as to why the Mg-$K_{\beta_{1,3}}$ (or the Mg-$L_{2,3}$M or the O-K_α) peaks should be split. Freund and Hamich [12] sought an explanation by postulating a 'forbidden' $3d \rightarrow 1s$ transition. Magnesium 3*d* orbitals of t_{2g} symmetry were considered to interact strongly with oxygen lone-pair orbitals of the same representation to form a strong π bond, more tightly bound than the t_{1u} σ bond. This provides two sets of orbitals, one σ and one π, both with Mg 3*p* character, and thus an explanation of the double peak. Tossell suggested that Mg–Mg interactions might well cause the Mg-$K_{\beta_{1,3}}$ peak to split. Dodd and Glenn proposed that the splitting was due to π interactions, but not involving forbidden transitions. The oxygen lone pairs in $[MgO_6]^{10-}$ transform as t_{1u}, t_{2u}, t_{1g}, and t_{2g}. It is therefore possible for the t_{1u} lone-pair orbitals to interact with the t_{1u} orbitals and so permit Mg 3*p* character to be present in both the σ and π bonds. A deficiency of these simple 'π-bonding in MgO_6' models is that it is very difficult to see why magnesium 3*p* character should be so equitably distributed between the σ and π bonds (as the almost equal intensity of the two components of the Mg-$K_{\beta_{1,3}}$ peak demands) and why the Mg-$L_{2,3}$M and O-K_α spectra should behave as they do.

It is clear that $[MgO_6]^{10-}$ can only give a poor description of the bonding in MgO; the Mg : O ratio is completely wrong and the charged carried by the model unit is absurd. Even so it is possible to extend calculations of this type and attempt to build up an approach to the true bond structure of MgO by considering units such as $Mg^{2+}([MgO_6]^{10-})_6$ in which a magnesium cation is thought of as surrounded not by six oxygen anions but by six $[MgO_6]^{10-}$ units.[14] When such a model is generalised to the indefinitely extended MgO lattice it is possible to appreciate why the Mg-$K_{\beta_{1,3}}$ peak is split into components of similar intensity. It seems, that this is due to π-type interaction between adjacent σ bonds in OMgO and MgOMg units, *i.e.* the delocalised analogue of the Dodd and Glenn proposal. Even so $[MgO_6]^{10-}$ remains a cumbersome unit on which to build a simple picture of the bonding in the MgO lattice. What is required is a small moiety which will better reflect the

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overall properties of the MgO macromolecule, a unit which will have the correct charge and the correct Mg : O ratio. In this paper a model for the bonding in MgO based on Mg_4O_4 with magnesium and oxygen atoms at alternate corners of a cube is described below and the predicted *X*-e.m. spectra are compared with experiment.

Mg_4O_4.—Consider a cube with magnesium and oxygen atoms at alternate corners so that the atoms are at the vertices of a pair of interlocking tetrahedra. The T_d symmetry of each unit can be used to simplify a consideration of the interactions between the magnesium and oxygen orbitals. From each atom a p orbital can be orientated to point to the centre of the cube (p_a orbitals); the other two orbitals (p_t) at each atom will be perpendicular to p_a. The valence-shell orbitals of Mg_4O_4 can then be classified: O 2*s* a_1, t_2; O 2p_a a_1, t_2; O 2p_t t_1, t_2, e; Mg 3*s* a_1, t_2; Mg 3p_a a_1, t_2; Mg 3p_t t_1, t_2, e. To simplify the discussion the following assumptions will be made: the O 2*s* orbitals can be considered separately because they are relatively tightly bound and the mutual interactions of the p_t orbitals can be considered, at least in the first instance, separately from the p_a and *s* interactions. Furthermore, since Mg 3*s* and Mg 3*p* orbitals have quite similar ionisation energies, it should be possible to use linear combinations of 3*s* and 3p_a [*i.e.* *sp* hybrids, $(2)^{-0.5}$ $(3s \pm 3p_a)$] without introducing serious errors into the subsequent arguments. When these assumptions and simplifications are made the interactions of *s* and p_a orbitals within the cube reduce to those of symmetry orbitals derived from O 2p_a and the hybrid orbitals Mg $2^{-0.5}$ $(3s + 3p_a)$. Within each monoatomic tetrahedron one bonding a_1 orbital (energy, $\alpha + 3\beta$) and three antibonding t_2 orbitals (energy, $\alpha - \beta$) are formed (bonding and antibonding relative to α, the coulomb integral from the original atomic orbital; β is the resonance integral between adjacent orbitals). The interaction between the symmetry orbitals of the two tetrahedra is particularly interesting. Let β' be the resonance integral for *adjacent* O 2*p* and Mg (3*s*, 3*p*) hybrid orbitals. Then the overall resonance-integral interaction between O 2*p* and Mg (3*s*, 3*p*) orbitals of a_1 symmetry is $3\beta'$, but for the corresponding orbitals belonging to the irreducible representation t_2 the integral is $2\beta' - \beta' = \beta'$. The a_1 interaction is thus approximately three times that for t_2 (only approximately because magnesium–oxygen interactions diagonally across the cube have been ignored; their inclusion would only enhance the a_1, t_2 interaction disparity). In the situation which exists in a very polar compound such as MgO, where the magnesium-orbital contribution to molecular orbitals is small, this results in the magnesium-orbital coefficient in the a_1 orbital being about three times that in each of the t_2 orbitals (see Appendix). But since the latter are triply degenerate, approximately equal amounts of magnesium character are associated with each energy level.

The interactions between p_t orbitals can be considered in a very similar way. The eight p_t orbitals associated with a homoatomic tetrahedron belong to irreducible representations e, t_2, and t_1; the mutual interactions of the p_t orbitals result in the e orbitals being the most tightly bound and t_1 the least tightly bound.[15] A consideration of the overlap integrals between the two tetrahedra for p_t orbitals suggests that the resonance integrals are less than for the p_a orbitals. The molecular orbitals that result from interactions between p orbitals tangential to the Mg_4O_4 cube therefore have less magnesium character than those derived fom p_a orbitals. This means that it should be possible to discuss magnesium emission spectra from a consideration of p_a-type interactions alone. The use of magnesium hybrid orbitals means that 3*s* and 3p_a orbitals behave in a very similar way and, since approximately equal magnesium character is associated with the p_a, a_1, and t_2 energy levels, the Mg_4O_4 model provides a simple explanation for the splitting of both the Mg-$K_{\beta_{1,3}}$ and Mg-$L_{2,3}$M spectra into two more or less equal components. A consequence of this approach to the bonding in magnesium oxide is the relegation of two of the three p orbitals on each oxygen atom to an almost non-bonding 'lone-pair' role. If this model is correct it should, of course, also provide an understanding of the peak shape of the O-K_α *X*-e.m. spectrum. When the p_a and p_t orbitals for oxygen in an Mg_4O_4 cube are considered together it is seen that eight (p_t — e, t_2, t_1) have a non-bonding role, that only one is clearly bonding (p_a, a_1), and that the p_a, t_2 orbitals which would be somewhat antibonding in the O_4 tetrahedron might well have on ionisation energy comparable with the p_t orbitals due to interactions with the magnesium p_a,t_2 orbitals. Thus the O-K_α spectrum is expected to show two features, a main peak (p_t and p_a, t_2) and a lower-energy peak (p_a, a_1) of relative intensity 11 : 1. An examination of Figure 1 shows that this is clearly not so. In order to resolve this problem it is necessary to consider the interactions between Mg_4O_4 cubes that give rise to the molecular-orbital bond structure in MgO itself. As a first step the interactions in $Mg_{32}O_{32}$ are discussed.

$Mg_{32}O_{32}$.—Consider an Mg_4O_4 cube (N) which shares each of its eight atoms with eight other cubes as partially shown in Figure 2. The four cubes which have oxygen atoms in common with (N) are (A), (B), (C), and (D) and the bridging oxygen atoms in the cubes (A)—(D) are designated 1. In this situation it is not possible to speak of p_a orbitals on the four oxygen atoms of cube (N), rather the interactions of p_a molecular orbitals in the four cubes (A)—(D) must be considered. The four a_1 orbitals from each of these cubes interact in (N) to give rise to more extensive molecular orbitals spread over (A)—(D) and (N) with symmetries a_1 and t_2. The new a_1 orbital is as in equation (1), where $\psi(X, p_a, a_1)$ indicates the molecular orbital, in cube (X) derived from O p_a and

$$\psi_{a_1,N} = \tfrac{1}{2}[\psi(A, p_a, a_1) + \psi(B, p_a, a_1) + \psi(C, p_a, a_1) + \psi(D, p_a, a_1)] \quad (1)$$

Mg (*s*, p_a) orbitals, which belongs to irreducible repre-

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[15] A. G. Massey and D. S. Urch, *J. Chem. Soc.*, **1965**, 6180.

sentation a_1. If magnesium character is ignored, $\psi(X, p_a, a_1)$ can be written approximately as (2) where 1—4 are the numbers of individual oxygen atoms in the

$$\psi(X, p_a, a_1) = \tfrac{1}{2}(O_1p_a + O_2p_a + O_3p_a + O_4p_a) \quad (2)$$

Mg_4O_4 unit, (X). These equations can now be used to relate interactions between the atomic orbitals in the individual Mg_4O_4 cubes with interactions between the molecular orbitals of the cubes themselves in (N). Thus the energy of $\psi_{a_1,N}$ is $\int\psi_{a_1,N}\ H\psi_{a_1,N} = \frac{1}{16}(16\alpha' + 12\beta)$ since only p_a orbitals on O_1 atoms interact; α' is the coulomb integral for the original molecular orbitals, *i.e.* $(\alpha + 3\beta)$. The resonance integral for interactions in (N) is thus 0.75β, *i.e.* just one quarter of the interactions between atomic orbitals with an Mg_4O_4 unit. Similar calculations and considerations show that all interactions with (N) are just one quarter of the corresponding interaction with Mg_4O_4. The symmetry relations that exist between local Mg_4O_4 orbitals and orbitals in (A)—(D) and (N) are indicated below:

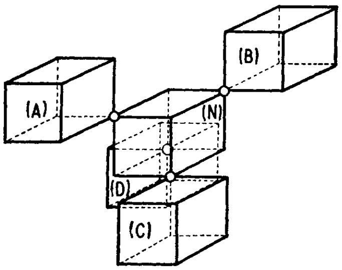

FIGURE 2 The model $Mg_{32}O_{32}$; only four of the eight constituent Mg_4O_4 cubes are shown clearly to indicate the juxtaposition of (A)—(D) and (N)

Orbitals in Mg_4O_4	Molecular orbitals in (A)—(D) and (N)
Mg (s, p_a), Op_a a_1	$a_1 + t_2$
Mg (s, p_a), Op_a t_2	$a_1 + e + t_1 + 2t_2$
p_a e	$e + t_1 + t_2$
p_t t_2	$a_1 + e + t_1 + 2t_2$
p_t t_1	$a_2 + e + 2t_1 + t_2$

The effect of allowing the four a_1 orbitals from the four Mg_4O_4 cubes (A)—(D) to interact *via* (N) is thus to generate four new molecular orbitals, but the energy difference between these new orbitals is just one quarter of the energy separation between p_a, a_1, and t_2 orbitals in Mg_4O_4.

Extension of the bonding from Mg_4O_4 to $Mg_{32}O_{32}$ thus acts as a perturbation of the basic orbital-energy scheme derived for Mg_4O_4. Furthermore when extensions beyond $Mg_{32}O_{32}$ are considered even smaller resonance integrals are found. In the limit the molecular orbitals whose energies are determined for Mg_4O_4 are the bases for bands of molecular orbitals in MgO. The shape of the bands can also be estimated: the new molecular orbitals in $Mg_{32}O_{32}$ derived from a_1 orbitals in Mg_4O_4 are found in only two energy levels, one singly the other triply degenerate. Orbitals interacting in this way generate an asymmetric band shape, with a tail on the more tightly bound side. The same asymmetry results from the interaction of e-type orbitals since of the new molecular orbitals e is the most tightly bound, then t_2 and t_1. The band shape which results has an asymmetric tail due to the more tightly bound 'e' orbitals. The t_2 orbitals from the p_a orbitals in an Mg_4O_4 cube give rise to $a_1 + t_2$ and $e + t_1 + t_2$ orbitals in $Mg_{32}O_{32}$ which of course give rise to the same type of band shape.

So far in $Mg_{32}O_{32}$ only interactions *via* the oxygen atoms have been considered. When comparable effects *via* magnesium atoms are contemplated they are found to be very much smaller because of the polar nature of the Mg–O bonds. This causes all magnesium atomic-orbital coefficients to be very small and thus the transmission of perturbations *via* magnesium atoms are equally small. The other four cubes of $Mg_{32}O_{32}$ therefore behave, at this level of approximation, as if they were isolated Mg_4O_4 units.

The implications of this 'extended' model for the oxygen K_a emission spectrum are quite interesting. The spectrum should show the basic bonding features of Mg_4O_4, but the peak shape should reflect the band structure of the solid and be asymmetric with a low-energy tail. If this is so, the observed spectrum should not be thought of as compound of two symmetric peaks but rather as a small low-energy feature superimposed on the low-energy tail of the main peak. When resolved in this way the relative intensity of the low-energy peak to the main peak is rather less than 10%, *i.e.* in accord with the requirements of the Mg_4O_4 model.

Oxygen 2s *Orbitals*.—The *X*-p.e. spectrum of the valence-band region of MgO showed a broad feature in the binding-energy range 21—27 eV, apparently with some structure corresponding to oxygen 2*s* orbitals. This peak lines up well with the Mg-$K_{\beta'}$ satellite which, it has been proposed,[2] arises from the small amount of magnesium 3*p* character present in molecular orbitals which are mostly oxygen 2*s* in character. In the Mg_4O_4 model the oxygen 2*s* orbitals have not been considered so far because they are relatively tightly bound and so can be treated separately. Their mutual interactions within an Mg_4O_4 unit give rise to one bonding orbital [a_1, energy $\alpha(O\ 2s) + 3\beta''$] and a trio of relatively antibonding orbitals [t_2, energy $\alpha(O\ 2s) - \beta''$] where β'' is the resonance integral between two oxygen 2*s* orbitals. This interaction is presumably the explanation for the general shape of the oxygen 2*s* p.e. spectrum: a main peak at 22.8 eV and a shoulder, less intense, at 25.2 eV. The magnesium 3*s*, 3*p* hybrid (p_a) orbitals of Mg_4O_4 will also belong to the same irreducible representations and interactions can therefore take place. Both magnesium 3*s* and 3*p* character should therefore be present in the 'oxygen 2*s*' orbitals giving rise to low-energy satellites in both the Mg-K_β and Mg-$L_{2,3}$ spectra: this is in fact what is observed experimentally.

Conclusions.—A model for the bonding in magnesium oxide based on Mg_4O_4 can be used to rationalise the magnesium X-ray emission spectra. When the model is extended to $Mg_{32}O_{32}$ the asymmetry of the oxygen K_α emission spectrum and the relative intensity of the low-energy satellite can both be understood. The unit Mg_4O_4 seems to be a suitable basis for more sophisticated molecular-orbital calculations of the electronic structure of magnesium oxide. The bonding model proposed here is not inherently different from models based on $[MgO_6]^{10-}$, but it provides a simpler and more direct explanation of X-ray spectra. It is of course possible to transform the molecular orbitals of Mg_4O_4 into those derived from extended $[MgO_6]^{10-}$ calculations by taking suitable linear combinations of molecular orbitals (equivalent orbitals).

APPENDIX

Effect of changing the Resonance Integral on the LCAO Coefficients in the Molecular Orbitals that result from the Interaction of Two Orbitals characterised by Different Coulomb Integrals.—Let the two orbitals be ψ_1 and ψ_2 with coulomb integrals α_1 and α_2 such that $\alpha_1 = \alpha_2 + \varepsilon\beta$, where β is the resonance integral. It is useful to retain β as the unit of energy; variation in the resonance integral is taken into account by use of the parameter c. The secular equations will therefore be (A1) and (A2), where $x = (\alpha_2 - E)/\beta$.

$$a_1(x + \varepsilon) + a_2c = 0 \qquad \text{(A1)}$$

$$a_1c + a_2x = 0 \qquad \text{(A2)}$$

By solving the corresponding determinant it can be shown that $x = 0.5\{-\varepsilon \pm \varepsilon[1 + (4c^2/\varepsilon^2)]^{0.5}\}$. Normalisation (with neglect of overlap) requires that $a_1^2 + a_2^2 = +1$. Therefore, $(a_2)^{-2} = (c^2 + x^2)/c^2$. In the special case of c being small relative to ε, and for the most tightly bound orbital, $c^2 \rightarrow 0$ and $x \rightarrow -\varepsilon$. Thus $(a_2)^{-2} = (c^2 + \varepsilon^2)/c^2 \simeq \varepsilon^2/c^2$ and, for a particular value of ε, $a_2 \propto c$.

In the particular case considered in this paper the interaction between the $Mg(p_a)a_1$ and the $O(p_a)a_1$ orbitals in Mg_4O_4 is characterised by a resonance integral of 3β and the interaction between $Mg(p_a)t_2$ and $O(p_a)t_2$ orbitals by β. Since quite polar bonds are formed it seems reasonable to assume that the value of ε is similar for the a_1 and t_2 interactions. It follows that the magnesium orbital coefficients in a_1 and t_2 are in the ratio of the resonance integrals, *i.e.* 3 : 1.

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