The Electronic Structure of Magnesium Hydroxide (Brucite) using *X*-Ray Emission, *X*-Ray Photoelectron, and Auger Spectroscopy

By **Derek E. Haycock, Masoud Kasrai, Christopher J. Nicholls,** and **David S. Urch,*** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

The *X*-ray emission spectra (Mg-$K_{\beta 1,3}$, Mg-$L_{2,3}$ M, and O-K_{α}), *X*-ray photoelectron spectra, and O-*KLL* Auger spectra from brucite, Mg[OH]$_2$, are reported. The electronic structure of brucite is discussed using these spectra and a simple Hückel molecular-orbital model. The spectra indicate that the strongest interaction exists between the oxygen and hydrogen of the hydroxide group, but that the Mg–O bond has some covalent character. An attempt to interpret the $2p^{-2}$ peak in the oxygen Auger spectrum using the O-K_{α} *X*-ray profile has met with only limited success.

THE combination of *X*-ray emission and *X*-ray photoelectron spectroscopies provides detailed information about the electronic structure of chemical bonds.[1,2] Results using these techniques together with Auger spectroscopy are reported in this paper for brucite, Mg[OH]$_2$. This study compliments previous work on periclase (MgO) [3,4] and spinel (MgAl$_2$O$_4$).[5] Brucite is especially interesting because of its layer structure. Within a layer each magnesium atom is surrounded by a nearly perfect octahedron of oxygen atoms,[6] whilst each oxygen is surrounded by a distorted tetrahedron of three magnesiums and a hydrogen atom. The magnesium atoms lie in planes with planes of oxygen atoms above and below them. The O–H bonds are more or less perpendicular to these planes. Brucite crystals are made up of such layers, weakly bound to each other by hydrogen bonding,[7] the hydrogen from the OH of one layer pointing towards the centre of the triangle formed by three OH bonds of the next layer.[8]

Because of this simple structure a simple interpretation of the electronic structure of brucite should be possible. Mg-$K_{\beta_{1,3}}$ *X*-ray emission lines from specifically orientated brucite crystals have been reported by Freund [9] who concluded that the two main peaks corresponded to Mg $3p$ character in the 3σ and 1π orbitals of OH. But this interpretation is at variance with that proposed a little earlier, by Freund and Scharpen,[10] based on *X*-ray photoelectron data. In this work, two or three peaks were observed depending on the orientation. The two main peaks in the photoelectron spectrum clearly corresponded to the two peaks in the Mg-$K_{\beta_{1,3}}$ *X*-ray emission spectrum. Freund here chose to base the interpretation of the spectra on the local O_h symmetry of the magnesium ion, proposing that the least tightly bound peak be due to the t_{1u}, σ molecular orbitals (m.o.s), the next peak to e_g, π orbitals, and the third peak to an a_{1g} orbital. Such a model implies Mg $3p$ character in only one set of m.o.s (t_{1u}) and, therefore, a single peak in the Mg-$K_{\beta_{1,3}}$ spectrum. However, the Mg $3d$ character, if any, present in the e_g orbitals could only give rise to a quadrupole transition to the 1*s* vacancy which would produce an emission peak of negligible intensity. The conclusions to be drawn from this model clearly do not agree with the observed Mg-$K_{\beta_{1,3}}$ spectrum. The model suffers from an additional drawback in that it requires π bonds to be more tightly bound than σ bonds.

In a study of the O-K_{α} *X*-ray emission spectra from single crystals of brucite in different orientations Freund [11] suggested that his results showed the 3σ and 1π orbitals in OH to be separated by 1 *ca.* -1.5 eV, again at variance with conclusions drawn from other experiments (*e.g.*, from the Mg-$K_{\beta_{1,3}}$ work it was proposed that the 3σ—1π separation was *ca.* 4 eV).*

The work described in this paper was undertaken in an attempt to provide a clearer picture of the bonding in brucite and to obtain an unambiguous interpretation of the *X*-ray spectra. To this end, *X*-ray emission, Mg-K_{β} and O-K_{α}, and valence-band *X*-ray photoelectron spectra have been assembled on a common energy scale provided by the photoelectron core-level data. Unfortunately, attempts to record Mg-$L_{2,3}$ M *X*-ray emission spectra failed due to sample decomposition. Oxygen Auger spectra were, however, obtained and are included in this paper.

EXPERIMENTAL

The brucite used in this work was cut from a massive specimen (location, Nevada, U.S.A.), provided by the Department of Geology, Queen Mary College. This sample was used directly in a Philips PW 1410 spectrometer to give Mg-$K_{\beta 1,3}$ and O-K_{α} *X*-ray emission spectra. Powdered brucite mounted on double-sided Sellotape was used in the

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa.

[1] D. S. Urch, in 'Electronic States of Inorganic Compounds: New Experimental Techniques,' ed. P. Day, Reidel, Dordrecht, The Netherlands, 1975, p. 449.

[2] V. I. Nefedov, 'Molecular Structure and Chemical Bonding,' Academy of Sciences, Moscow, 1975, vol. 3.

[3] C. J. Nicholls and D. S. Urch, *J.C.S. Dalton*, 1975, 2143.

[4] C. J. Nicholls and D. S. Urch, *J. Mol. Structure*, 1976, **31**, 327.

[5] D. E. Haycock, C. J. Nicholls, D. S. Urch, M. J. Webber, and G. Wiech, *J.C.S. Dalton*, preceding paper.

[6] G. Aminoff, *Geol. For. Forh. Stockholm*, 1919, **41**, 407.

[7] J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc.*, 1935, **A151**, 384.

[8] D. D. Elleman and D. Williams, *J. Chem. Phys.*, 1956, **25**, 742.

[9] F. Freund, *Phys. stat. sol.*, 1974, **B66**, 271.

[10] F. Freund and L. H. Scharpen, *J. Electron Spectroscopy*, 1974, **5**, 305.

[11] F. Freund, *Bull. Soc. chim. belges*, 1975, **84**, 101.

X-ray photoelectron and Auger spectra which were measured on a Vacuum Generators ESCA III photoelectron spectrometer. Full experimental details are given in the preceding paper.[5] In all these experiments the spectra were excited by *X*-irradiation. An attempt was made, however, with the help of Dr. R. Wiech, Physics Department, University of Munich, to obtain the Mg-$L_{2,3}$ M emission spectrum from brucite. This transition has an energy of *ca.* 45 eV, *i.e. ca.* 275 Å. At these wavelengths a grating spectrometer in which characteristic *X*-rays are excited by direct electron bombardment must be used.[12] Because the energy of irradiation is deposited in a very much thinner layer than when *X*-irradiation is used sample decomposition is much more likely. The spectrum that resulted from this work is shown in Figure 1(*a*) and is identical with the Mg-$L_{2,3}$ M spectrum from MgO [Figure 1(*b*)]. Since The Mg-$K_{\beta_{1,3}}$ and valence-band photoelectron spectra from Mg[OH]$_2$ and MgO differ greatly it is unreasonable to suppose that the same would not be true of the Mg-$L_{2,3}$ M spectra. The most prudent conclusions are that Figure 1(*a*) shows the Mg-$L_{2,3}$ M emission spectrum of magnesium oxide, not that of magnesium hydroxide, and that Mg[OH]$_2$ easily dehydrates under electron bombardment in a high vacuum (10^{-6} Torr).

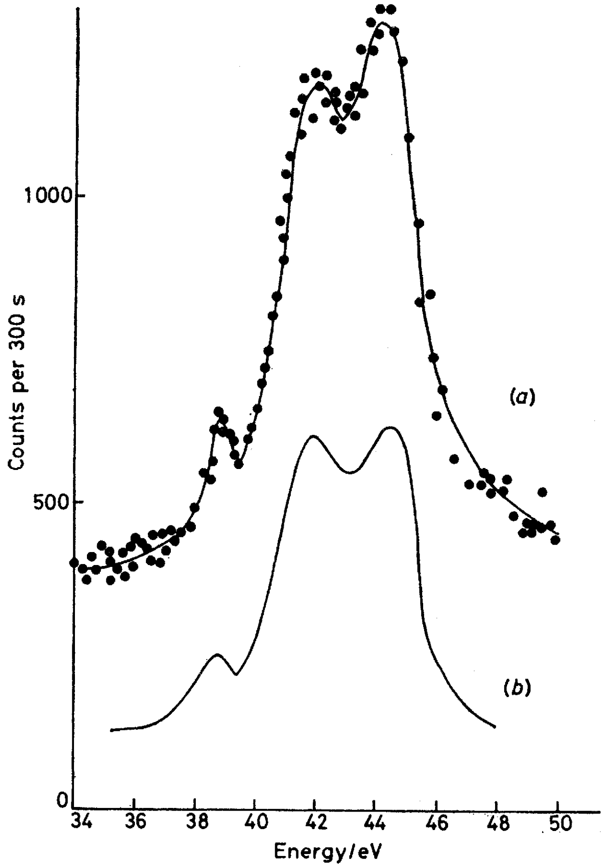

FIGURE 1 Mg-$L_{2,3}$ M *X*-ray emission spectra from (*a*) brucite and (*b*) periclase (MgO) using direct (*i.e.* electron-bombardment) excitation

RESULTS

The *X*-ray photoelectron ionisation energies are given in the Table. No corrections have been made for charging although the C 1*s* level is given as a reference. In Figure 2 the O-K_α and Mg-$K_{\beta_{1,3}}$ *X*-ray emission spectra have been placed on a common energy scale using the ionisation energies of O 1*s* and Mg 1*s*, together with the valence-band photoelectron spectrum. The main features of the latter are a peak at 31 eV principally due to O 2*s* and two much less-intense peaks at lower binding energies 17 and 13 eV. The relative lack of intensity of the list peaks indicates considerable O 2*p* character. This is confirmed by the coincidence of these two peaks with the two principal features of the oxygen *K* emission spectrum. The carbon 1*s* photoelectron signal had an intensity of *ca.* 2 500 counts s^{-1} so that a C 2*s* peak of the order of 100 counts s^{-1} could be anticipated in the valence-band (the photoelectron cross sections [13] for Mg-$K_{\alpha_{1,3}}$ radiation for C 1*s* : C 2*s* = 100 : 4.7). However, the contamination layer is unlikely to consist of isolated carbon atoms which would give rise to a single sharp C 2*s* peak; the layer is more probably graphitic

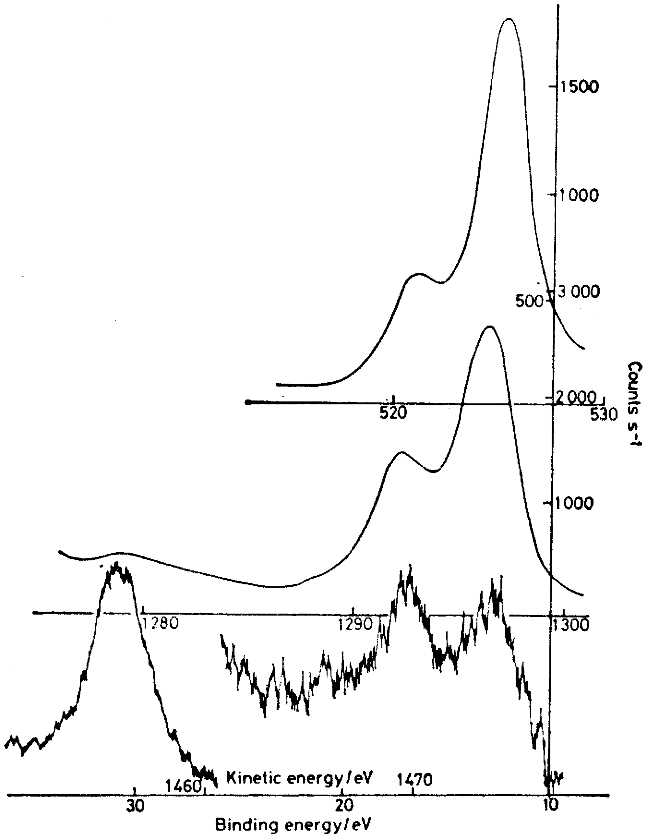

FIGURE 2 *X*-Ray emission spectra (O-$K\alpha$, upper; Mg-$K\beta_{1,3}$, middle) and the valence-band *X*-ray photoelectron spectrum (lower) from brucite (10—26 eV ratemeter full-scale deflection, 3×10^2 counts s^{-1}; 26—36 eV, 10^3 counts s^{-1})

Core-level ionisation energies (eV) for brucite (C 1*s* = 291.5 eV)

Mg	2*p*	56.2	O 1*s*	537.6
	2*s*	95.0		
	1*s*	1 309.4		

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[12] G. Wiech, *Z. Physik*, 1966, **193**, 490.

[13] J. H. Scofield, Lawrence Livermore Laboratory, Report UCRL-51326.

in character. The valence-band X-ray photoelectron spectrum of graphite [14] extends over nearly 20 eV with a broad maximum whose ionisation energy is 265—268 eV less than that for C 1s and another maximum 270 eV less tightly bound than the C 1s level. The breadth of the C 2s band in the graphite peak ensures a reduction in intensity relative to the C 1s peak [14b] so that count rates of the order of 10—20 counts s^{-1} are to be expected in the region of the maxima. These would be found at 24—27 and 22 eV, using the binding-energy scale of Figure 2. These energies are well clear of the two main brucite peaks at 13 and 17 eV and the anticipated count rates would be barely discernible above the experimental noise level. It is, however, possible that there is a weak peak at *ca.* 21.5 eV which could be associated with carbon contamination.

The dipole selection rule ($\Delta l = \pm 1$) which governs the probability of X-ray emission ensures that the oxygen K spectrum can be regarded as diagnostic for the presence of oxygen 2p character in atomic or molecular orbitals. The general appearance of the magnesium K_β emission spectrum is similar to that for oxygen, but it is interesting to note that the peaks are displaced to higher energies (on the ' valence-band energy scale ') by *ca.* 0.5 eV with respect to the oxygen and photoelectron peaks. It was possible using a Du Pont 310 curve resolver to deconvolute both the oxygen and magnesium emission peaks into just two main Gaussian components with relative intensities of 1 : 3.4 and 1 : 2 respectively (Figure 3).

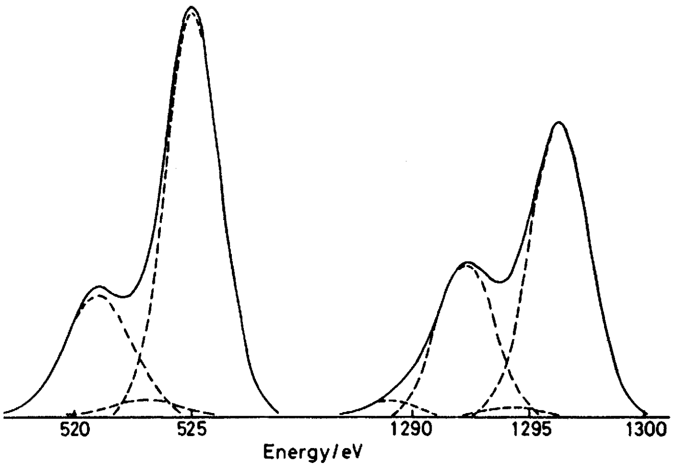

FIGURE 3 Deconvolution of O-K_α (left) and Mg-$K_{\beta_{1,3}}$ (right) X-ray emission peaks from brucite into Gaussian components

DISCUSSION

The dominant feature of the spectra presented in Figure 2 is the presence of two bands of molecular orbitals separated by *ca.* 4 eV. Since it is to be anticipated that the bonding between magnesium and oxygen should be quite ionic, the most covalent bond in brucite will be that of the hydroxyl group. Cade's SCF multi-ζ calculations on the bonding in [OH]$^-$ have shown [15] that the 2σ orbital is almost entirely O 2s, but that 3σ is an orbital with considerable H 1s as well as O 2p character. The 1π orbitals are O 2p lone-pair orbitals less tightly bound than 3σ by exactly 4.0 eV. The simplest and most obvious interpretation of the spectra is that the two peaks predominantly reflect the two least tightly bound orbitals of hydroxide, and that the magnesium ion (Mg^{2+}) acquires electronic charge by the formation of quite polar bonds with the oxygen atoms of hydroxide groups. The third prominent valence-band peak, especially in the photoelectron spectrum, is that of O 2s (*i.e.* 2σ) observed to be 14 eV more tightly bound that 3σ, somewhat less than the value of 17.7 eV calculated by Cade.

This simple picture provides a qualitative understanding of the general features of the electronic bonding in brucite but gives no clue as to the relative intensities of the peaks that should be found by X-ray spectroscopy. A simple repeating unit which can act as a model for the bonding in brucite is difficult to find since the local symmetry about each Mg is O_h, and that about each O is C_{3v}. If, however, two hydrogens are slightly displaced so that two OH bonds become collinear with an O–Mg–O axis, then the orthogonal properties of p orbitals enable the bonding in a brucite layer to be broken down into O–Mg–O units and HO–Mg–OH units provided that both oxygen 2s and magnesium 2s orbitals are ignored. Any one magnesium atom would participate in one HO–Mg–OH and two O–Mg–O units and the bonding in each and every unit would be orthogonal to that in all the other units. This is equivalent to orientating a hydroxide 3σ orbital exclusively towards one magnesium atom, rather than towards the centre of an equilateral triangle of three magnesiums, and to directing the two oxygen 2p orbitals perpendicular to the OH axis (1π) towards the other two magnesium atoms. The HO–Mg axis is extended to another hydroxide group which is moved to become coaxial with the first. The 1π orbitals of this hydroxide are arranged to point towards two other magnesium atoms, and so on throughout the layer.

If, for the purposes of a very simple Hückel-type m.o. calculation, all the resonance integrals are taken to be equal (β) and the Coulomb integrals of hydrogen and oxygen made equal (α) but that of magnesium is assumed to be less by 2β [*i.e.* α(Mg) = α − 2β], then the charge distribution in Figure 4 results. This calculation certainly overestimates the splitting between lone-pair 1π and OH (3σ bonding) energy levels in [OH]$^-$ caused by magnesium, but it does give some idea of the relative charge distributions in the two m.o. bands. If the total number of electrons associated with oxygen in the two O–Mg–O units is added and compared with the oxygen charge in the HO–Mg–OH unit, then a peak-intensity ratio of *ca.* 1 : 3.5 results for O-K_α. When the same summation is carried out for magnesium the ratio is 1 : 4. In this model *ca.* 0.8 e is found on the hydrogen. This is not an unreasonable result and the intensity ratio for the peaks in the O-K_α emission spectrum is in good agrement with experiment. The result for Mg-K_β is, however, poor. Indeed all attempts at other

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[14] (*a*) F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Cavell, R. A. Pollak, and D. A. Shirley, *Phys. Rev.*, 1974, **B9**, 5268; (*b*) K. Hamrin, G. Johansson, U. Gelius, C. Nordling, and K. Seigbahn, *Physica*, 1970, **1**, 277.

[15] J. Cade, *J. Chem. Phys.*, 1967, **47**, 2390.

parameterisation (*i.e.* variation of resonance integrals or Coulomb integrals for H, O, and Mg, inclusion of O 2*s*, *etc.*) failed to produce a result in which the ratio of peak intensities was less for magnesium than for oxygen. A facile solution would be to suggest that the approximations inherent in the simple Hückel model preclude a more accurate result. It seems likely that whilst more sophisticated calculations would give more accurate numbers they would be unlikely to reverse ratio trends.

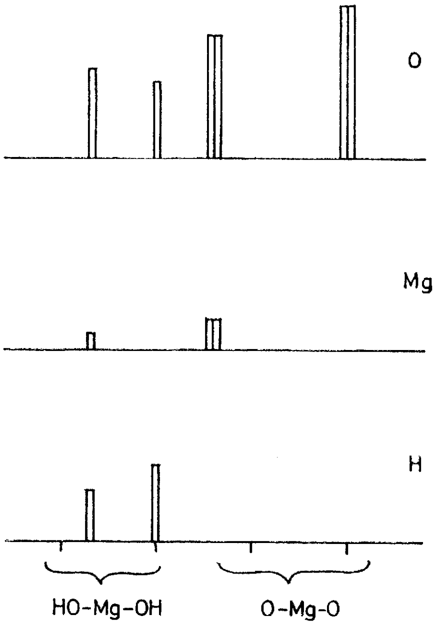

FIGURE 4 Molecular-orbital distribution of magnesium, 3*p*, oxygen 2*p*, and hydrogen 1*s* character in a Hückel model for brucite based on HO–Mg–OH and O–Mg–O units. Magnesium–oxygen covalency has been overestimated in these calculations so that the splittings in O–Mg–O units are exaggerated. The model used differs from the true structure for brucite in that the hydroxide axes are made collinear with certain O–Mg–O directions rather than being perpendicular to the brucite layer. The change from model to true structure will be associated with band broadening but with little change in relative band intensities. The relative amounts of O 2*p* character in the O–Mg–O and HO–Mg–OH bands should be compared with the peaks in the O-K_α *X*-ray emission spectrum; similarly the relative amounts of Mg 3*p* character can be compared with the Mg-$K_{\beta_{1,3}}$ spectrum

The factor that has so far been omitted from consideration is the presence, in the brucite crystal, of many contiguous layers each one hydrogen-bonded to the next. It is the effect which this hydrogen bonding may have on charge distributions which has been ignored. About any one OH group the hydrogen atoms from the hydroxide groups in the adjacent layer are arranged with three-fold symmetry. It seems reasonable, therefore, to expect these hydrogen atoms to interact with the 1π orbitals of OH rather than with the 3σ orbital. The 1π orbitals are the ones, in the model proposed above, that are involved in bonding in the O–Mg–O units. The symmetry of each unit ensures that of the two occupied m.o.s only the one with antisymmetric oxygen 2*p* orbitals can include any Mg 3*p* character, the other involving an in-phase (symmetric) combination of O 2*p* orbitals. The withdrawal of charge from the former type of orbital by hydrogen bonding can be considered in a five-centre system, thus: $\overset{\delta+}{\mathrm{H}}\cdots\mathrm{O{-}Mg{-}O}\cdots\overset{\delta+}{\mathrm{H}}$. It can easily be shown that, in the most tightly bound orbital with Mg 3*p* character, charge will move much more readily from the central atom than from the oxygens. Hydrogen bonding to the 'in-phase' orbital, $\overset{\delta+}{\mathrm{H}}\cdots\mathrm{O\ O}\cdots\overset{\delta+}{\mathrm{H}}$, must perforce remove charge from the oxygen. The effect of such hydrogen bonding will therefore be to remove a little charge from the least tightly bound orbitals which contain Mg 3*p* character and also from the least tightly bound oxygen orbitals. If this were to amount to 0.1 e per orbital in each O–Mg–O this would halve the amount of Mg 3*p* in the antisymmetric orbital, but reduce the amount of oxygen charge in the orbitals which contribute to the main O-K_α peak only by a small percentage. Thus the effect of interlayer hydrogen bonding would be to reduce the ratio of peak intensities in the Mg-$K_{\beta_{1,3}}$ spectra from a possible 1 : 4 to something nearer 1 : 2, whilst leaving the predicted intensity ratio for O-K_α peaks more or less unaltered at *ca.* 1 : 3.5.

Thus this simple model can at least qualitatively account for the observed ratios of peak intensities in the *X*-ray emission spectra. Also, as can be seen from Figure 4, orbitals which contain magnesium 3*p* character correspond to the more tightly bound orbitals both in the HO–Mg–OH and the O–Mg–O units. The median orbital energy for oxygen character will therefore be slightly less than for magnesium for both types of unit. It therefore follows from this model that the peaks in the Mg-$K_{\beta_{1,3}}$ spectrum should correspond to slightly higher valence-shell ionisation energies than those for the O-K_α spectrum when the spectra are compared on a common energy scale as in Figure 2. It is possible that the splitting observed by Freund [11] in one of his O-K_α spectra does in fact correspond to the separation between 'lone-pair' oxygen orbitals and magnesium bonding orbitals derived from O–Mg–O.

Magnesium 3*s* orbitals have so far been ignored in this model. They will interact with the 'in-phase' combination of lone-pair oxygen orbitals from O–Mg–O units or of hydroxide bonding orbitals (3σ) from HO–Mg–OH.

The local D_{4h} symmetry of one HO–Mg–OH and two O–Mg–O units about any one magnesium atom will make the irreducible representations of these orbitals, a_{1g} and $a_{1g} + b_{1g}$ respectively. The Mg 3*s* can thus interact with otherwise unperturbed oxygen lone-pair and hydroxide bonding orbitals altering their energies slightly and introducing Mg 3*s* character into both bands. Mg 3*s* orbitals can, therefore, easily be added to the bonding model. Since the 3*s* orbitals interact with only one orbital (a_{1g}) from two O–Mg–O units and with just one 'hydroxide bonding orbital,' it seems reasonable to suggest that amounts of Mg 3*s* character to be found in the two resulting m.o.s will be in the ratio 1 : 2 hydroxide bond : lone-pair bond since the oxygen-orbital coefficient in the hydroxide bond will be, in the approximation used above, $2^{-0.5}$. This in turn predicts an Mg-$L_{2,3}$ M spectrum for brucite very similar to that for Mg-K_β.

The omission of oxygen 2*s* orbitals from the initial model is more easy to justify than that of magnesium 3*s* because they are relatively tightly bound. Bonding orbitals of the right symmetry will be able to interact slightly and so introduce small amounts of character from other atoms, *e.g.* Mg-K_β' which can be seen as a very weak broad peak in Figure 2 at *ca.* 1 280 eV.[16]

If, as has been proposed above, the main atomic-orbital contribution to the valence bands of brucite at 13 and 17 eV is due to oxygen 2*p* character, the *X*-ray photoelectron spectrum should faithfully reflect the O-K_α emission spectrum both in peak position and in the relative intensities of the peaks (*cf.* spinel[5]). Whilst good correspondence is observed for peak positions, the relative intensities are quite different, the *X*-ray photoelectron peak at 17 eV being more intense than that at 13 eV rather than a quarter of its intensity. If the disposition of Mg 3*s* character [whose photoelectron cross section is a little greater than for O 2*p* (ref. 13)] is as anticipated above, then contributions from this atomic orbital to whatever extent could never explain the relative intensities of the *X*-ray photoelectron peaks. It has been suggested, however, that the peak at 17 eV is associated with strong covalent bonding between oxygen and hydrogen in hydroxide. The cylindrical symmetry of this group will enable O 2*s* as well as O $2p_z$ orbitals to participate in the bonding. This same symmetry will preclude O 2*s* from mixing with the 1π (O $2p_x$ and O $2p_y$) orbitals that give rise to the photoelectron peak at 13 eV. Thus an explanation for the unexpected intensity of the peak at 17 eV is the presence of oxygen 2*s* character in the 3σ molecular orbital. If it is assumed that the oxygen 2*p* contribution to the *X*-ray photoelectron spectrum should be related to the O-K_α emission spectrum then most of the intensity of the photoelectron peak at 17 eV must be due to O 2*s* character. Taking the main O 2*s* peak at 31 eV as an intensity reference, the amount of oxygen 2*s* participation in the 3σ m.o. is *ca.* 15%. This compares quite well with the theoretical estimate by Cade[15] of 20%.

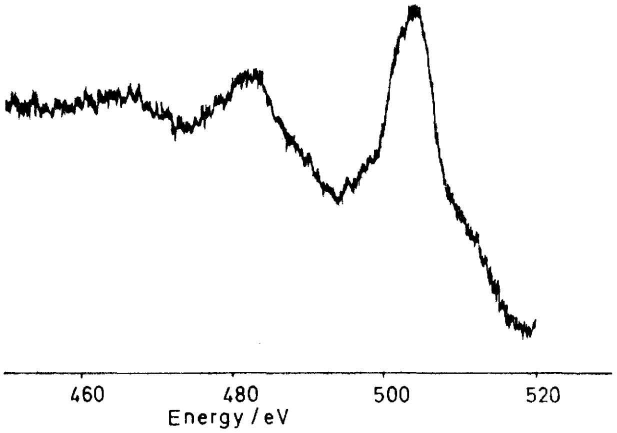

FIGURE 5 Oxygen *KLL* auger spectrum from brucite

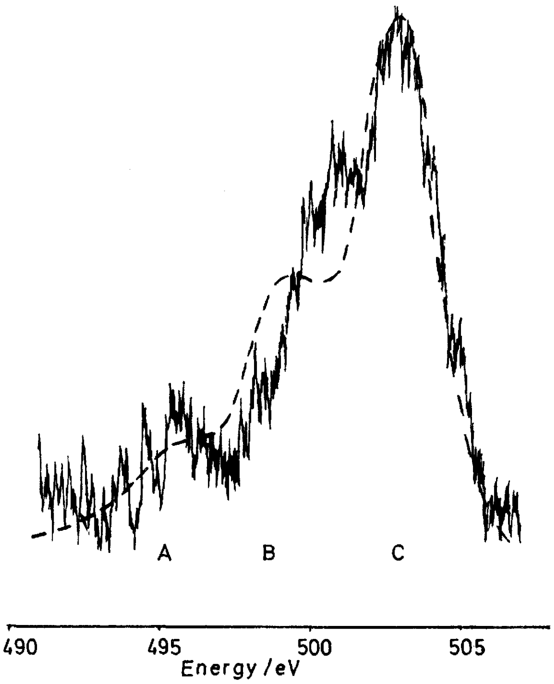

FIGURE 6 Peaks derived from the O $2p^{-2}$ configuration in the oxygen Auger spectrum of brucite

Finally, the effect of relaxing the local D_{4h} symmetry of this model to the observed D_{3d} symmetry about each magnesium needs to be considered. If six OH groups are orientated about a particular magnesium atom with their OH axes perpendicular to the plane of the magnesium atoms, then the interaction of the magnesium orbitals with the 3σ and 1π m.o.s can be considered very much as in the D_{4h} case to give rise to 'hydroxide-bands' and 'lone-pair bands.' Since however the orbitals utilised by every hydroxide group in this interaction are also shared with two other magnesium atoms, the interactions which could be considered as localised in D_{4h} will now be spread throughout each layer of the brucite crystal. This will somewhat broaden the sharp m.o. levels into bands. But this broadening is not excessive as has been demonstrated[3] for MgO. The orbital array and intensities considered for $Mg[OH]_2 \equiv HO{-}Mg{-}OH + 2O{-}Mg{-}O$ with D_{4h} symmetry can therefore be used for brucite as a whole with the proviso that sharp energy levels derived for the local unit be somewhat broadened in the bulk material. This is clearly borne out by comparison with the observed *X*-ray emission spectra where the main features can be rationalised as reflecting magnesium 3*p* or oxygen 2*p* character in the 'hydroxide' and 'lone-pair' bands. It would be extremely interesting to obtain spectra with much better resolution to see whether there is any further fine structure to be observed or whether band broadening has proceeded so far as to preclude this.

Auger Spectrum.—Figures 5 and 6 show the O-*KLL*

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

[17] R. G. Albridge, K. Hamrin, G. Johansson, and A. Fahlman, *Z. Physik*, 1968, **209**, 419.

Auger spectrum from brucite and the ^1S,^1D region in detail respectively. The resolution and intensities are not sufficient to warrant a discussion of the features that arise from $2s^{-2}$ and $2s^{-1}2p^{-2}$ configurations, but the ^1S, ^1D peaks from $2p^{-2}$ show both intensity and some structure. An isolated O^{2-} anion might be expected (by analogy with isoelectronic F^-)[17] to give rise to ^1S and ^1D states, derived from $2p^{-2}$, that were separated by *ca.* 3 eV and with an intensity ratio of *ca.* 1 : 4. This in no way corresponds to the observed spectrum in Figure 6. The O-*KLL* Auger spectrum from brucite is clearly complicated by the presence of oxygen $2p$ character in the molecular orbitals: the atomic model is no longer appropriate. Indeed, the spectrum shown in Figure 6 has superficial resemblances to the O-*KLL* Auger spectrum from water.[18] In that molecule oxygen $2p$ character is concentrated in three orbitals separated by 2 and then 3 eV.[19] In brucite the distribution of oxygen $2p$ character is known from the O-K_α emission spectrum. A simplified view may be obtained if it is assumed that the oxygen character is confined to two m.o.s ψ_a and ψ_b, then the oxygen $2p^{-2}$ configuration could arise from three possible orbital combinations ψ_a^{-2}, $\psi_a^{-1}\psi_b^{-1}$, and ψ_b^{-2}. If ψ_a and ψ_b are identified with the hydroxide band (3σ) and the lone-pair band (1π) then the energy separations between each of the three final Auger configurations will be *ca.* 4 eV. Since the relative intensity of oxygen $2p$ character in ψ_a and ψ_b is *ca.* 1 : 3.4 (from O-K_α) the relative intensities of the final Auger configurations (for O-*KLL* only) will be 1 : 3.4 : 10. Each of these configurations will give rise to ^1S and ^1D states separated by *ca.* 3 eV and with relative intensities of *ca.* 1 : 4. A combination of all these factors enables a prediction as to the overall O $2p^{-2}$ Auger peak shape to be made (broken line in Figure 6). The agreement for peak A and much of B is quite good, if C is taken as a reference point. However, the most prominent part of B is not explained and more detailed theoretical and experimental work is called for.

Conclusions.—A model using simple m.o. theory based on a strong covalent interaction between oxygen and hydrogen and a much more polar interaction to magnesium has been used to rationalise the *X*-ray emission and *X*-ray photoelectron spectra of brucite. Since satisfactory agreement between theory and experiment was obtained, it seems reasonable to conclude that the electronic structure of brucite does indeed correspond to these general ideas. Furthermore, in order to understand the relative structure of peaks in the oxygen and magnesium spectra it was necessary to postulate the existence of some hydrogen bonds between the layers of the brucite structure. The oxygen Auger spectra were also investigated. The use of *X*-ray emission spectra to aid in the interpretation of the Auger spectra of molecules was discussed and found to be of only limited value.

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[7/2155 *Received, 8th December*, 1977]

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[18] K. Siegbahn, Uppsala University, Institute of Physics, Report UUIP-880, 1974, p. 64.

[19] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, 1972, **94**, 1451.