Bands versus bonds in electronic-structure theory of metal oxides: Application to luminescence of copper in zinc oxide

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The fundamental issue of "bands versus bonds" in metal oxides is addressed through the direct comparison of results from scattered-wave cluster-molecular-orbital and augmented-spherical-wave band-structure calculations for zinc oxide and copper-impurity systems therein. It is shown that there is a close correspondence between the two types of calculations, both in regard to pure zinc oxide and the copper-impurity systems. The results lead to a coherent understanding of the luminescence of copper in zinc oxide.

I. INTRODUCTION

The electronic structures of metal oxides, particularly those based on metals with d and f electrons, have long presented a challenge to theorists addressing the electronic-structure-properties relationships in these materials.[1] This problem has been compounded by the recent discovery of high-transition-temperature (T_c) superconducting oxides such as $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$.[2] While conventional reciprocal- (or k-) space band-structure theory has been applied successfully to such oxides,[3] the localization of metal d and f electrons and their chemical bonding-antibonding relationships to the oxygen p electrons is more suitably analyzed from a "real-space" point of view such as cluster-molecular-orbital theory.[4] In the latter approach, the electronic structures of clusters representing appropriate local molecular environments in the oxides are calculated self-consistently but without the imposition of Bloch's theorem.[5] The cluster method has been used successfully for some time to address the local electronic structures of impurities and other point defects in semiconductors,[6] metals,[7] and phosphors,[8] while it also has been applied to amorphous semiconductors,[9] amorphous alloys,[10] magnetic material,[11] and most recently to high-T_c oxide superconductors[12] in order to determine their bulk electronic properties. Nevertheless, two questions remain: Can clusters adequately represent the electronic structures of solids, and how do cluster molecular orbitals connect to the Bloch states of conventional band theory? The present paper attempts to resolve this issue for the specific problem of copper impurities in zinc oxide by directly comparing the results of band-structure and cluster calculations. While the Cu/ZnO system is an interesting luminescent material[13] (see below), its theoretical study via both band-structure and cluster methods can also help to resolve the "bond-versus-bands" issue for metal oxides, in general. Additionally, there has been a long-term interest in the electronic structure and luminescent properties of zinc oxide phosphors.[14,15] Zinc oxide phosphors are often used for cathode-ray luminescence.[13] A large amount of experimental work has been performed to probe the electronic structure of the host material[16] and various dopants.[17] This system, therefore, provides an opportunity to compare the results from both theoretical techniques with experimental results.

Several models of luminescence[17-21] have been proposed to explain the electronic transitions in copper-activated phosphors. However, a clear theoretical description of the luminescent mechanism has not yet emerged. It is our aim to determine the luminescence mechanism of copper-activated zinc oxide using the energy levels obtained in the present calculation and to identify the correct model for luminescence of Cu-type activators in zinc oxide crystals. It is also hoped that the results of the present study will provide insight into processes involving multiphoton emission for excitation energies greater than twice the band gap of the host material.

In this paper the electronic structures for zinc oxide, as well as copper impurities in this host material, have been calculated by first-principles band-structure and molecular-orbital cluster methods. The electronic structure of copper in zinc oxide has previously been addressed using semiempirical cluster calculations.[22] In the present work the electronic structure of the host material

and the impurity ions will be obtained using the self-consistent-field scattered-wave $X\alpha$ (SW $X\alpha$) method.[5] Using the resulting molecular-orbital energies and wave functions, a coherent picture of the energy states and chemical bonding of divalent copper ions in ZnO will be developed. These results will be used to explain the available experimental data for the electronic states of divalent copper in zinc oxide. The electronic band structure of Cu/ZnO is also calculated using the augmented-spherical-wave method (ASW).[23,24] The band structure obtained by this method, which treats the phosphor as an extended and periodic system, will be compared with the electronic structure obtained by the cluster method. The relevance of the cluster and band-structure approaches in the study of impurity systems will also be discussed.

II. SUMMARY OF EXPERIMENTAL RESULTS

The electronic structure of zinc oxide has been extensively investigated. It crystallizes in the hexagonal wurtzite structure[25] and is transparent to visible radiation. In pure form the band gap is 3.4 eV.[15,16] However, because of intrinsic defects in the material, i.e., oxygen vacancies or zinc interstitials, this compound is usually found to have n-type conductivity, the Fermi level being 0.1 eV below the conduction-band minimum.

It is commonly believed that the divalent copper ions enter the crystal structure substitutionally for zinc.[14] The subsequent lowering of the atomic spherical symmetry by the crystal field removes the d-orbital degeneracy. Dietz et al. have measured the crystal-field splitting to be 0.71 eV. This is rather small compared to the crystal-field splitting of the d levels of copper in other tetrahedrally coordinated oxide crystals.[14,26]

The luminescence properties of divalent copper in zinc oxide were extensively investigated by Dietz et al.[14] and Dingle.[15] Dingle observed green luminescence at a temperature of 1.6 K with two zero-phonon lines separated by 0.1 eV. These were attributed to the isotope effect on the basis of the ratio of the intensity of these peaks, which was found to be 2.25±0.05. This is comparable to the ratio of ^{63}Cu to ^{65}Cu present (2.24). This ratio was also found to be constant over a wide range of temperatures and was found to be independent of the sample origin. The excitation peak was found to be 2.86 eV.[15]

On the basis of the measured components of the g tensor and the zero-phonon lines, Dingle ascribed the luminescence of Cu/ZnO to the excitation of the d hole at the copper site. Since the copper d-like level has to be above the Fermi level in order to hold a stable d hole, the binding energy of the d hole has to be greater than 3.3 eV. Furthermore, the excitation peak at 2.86 eV implies that the excited states should be at least 0.45 eV above the valence band. The measured values of g tensors in both the excited and the ground state indicate that while the hole in the ground state is localized at the copper center, the excited state is fairly delocalized. This indicates that the green luminescence results from a charge-transfer transition of an electron from the valence band (perturbed by the copper ion) into the d-like level of copper.

The luminescence mechanism of divalent copper proposed by Dingle is very similar to the mechanism proposed by Lambé and Klick.[19] However, the estimated position of the copper d-like level in the band gap is in conflict with the results obtained in earlier calculations,[22] which included covalency of copper in a semiempirical manner, and also with those obtained in the present work. The estimation of the binding energy of the Cu d hole in ZnO by Dingle[15] is based on the assumptions that (i) the crystal used in his experiment is essentially n type and (ii) the Fermi level is 0.1 eV below the conduction band. The latter assumption has led him to place the d-like levels due to copper very close to the conduction band. In order to get an n-type material, one has to prepare ZnO in a reducing environment, which will tend to reduce Cu^{2+} to Cu^{1+}. Since the luminescence is due to a paramagnetic center, it is obvious that the divalent copper ion is stable, and the Fermi level cannot be taken to be present where it appears in conventional n-type zinc oxide material. We believe, in view of the energy levels obtained in previous calculations[22] and in the present calculation that the Fermi level has to be low enough to obtain stable divalent copper impurities in ZnO.

III. THEORY

The calculations have been performed using the scattered-wave molecular-orbital (SW $X\alpha$) (Ref. 5) method and the augmented-spherical-wave (ASW) method.[2] Both techniques have been discussed extensively in the literature. In this paper we limit our discussions to a comparison of the methods.

Both the ASW and SW $X\alpha$ methods use muffin-tin potentials. The $X\alpha$ local-density approximation to the electron exchange correlation is employed.[27] The important difference between the two methods lies in the fact that the ASW method is a linear combination of atomic-orbitals type of approach with fixed energy atomic basis functions, whereas the SW $X\alpha$ method treats the energy as a free parameter that is determined by direct solution of the radial Schrödinger equation within each muffin-tin sphere. The one-electron energy eigenvalues are determined by the Rayleigh-Ritz variational procedure in the ASW method, whereas the scattered-wave method uses a multiple-scattering formalism to determine the molecular-orbital energy eigenvalues as in the Korringa-Kohn-Rostoker (KKR) method[28] of band-structure calculation.

Neither of the two procedures is specifically designed for studying the electronic structure of impurity ions in solids. The molecular-orbital method uses the cluster concept for this purpose. The use of this method for impurity ions in solids is based on two assumptions. First, the environment of the impurity ion in the solid can be simulated by a cluster of atoms representing the impurity and its neighbors in the host system with proper boundary conditions. Second, experiments suggest that impurity ions introduce localized states, and therefore a local approach will provide a proper description of the host-impurity interactions.

The band-structure approach utilizes the translational symmetry of the lattice by requiring that the one-electron

states obey the Bloch condition. The k dependence of the energy eigenvalues follows directly from this assumption. Incorporation of impurities into the host lattice breaks the translational symmetry. In order to circumvent this problem, one assumes that the impurity ions enter the host system in a periodic manner, i.e., one can describe the defect system in terms of a perfectly periodic lattice with a basis of atoms including the impurity ions. For a sufficiently dilute system, the corresponding lattice belongs to the same crystal system but is described with lattice vectors which are multiples of those of the host. The unit cells thus generated are called "supercells"[24] which contain integral multiples of the original basis of atoms, one of which is substituted for by an impurity atom.

A cluster-molecular-orbital procedure with an infinite number of atoms will lead to results similar to those obtained by the supercell band-structure calculations. Similarly, a band-structure calculation performed with unit-cell dimensions tending to infinity will reproduce the results of the infinite cluster calculation, since the corresponding Brillouin zone converges to a point in k space in this limit. The perfect translational symmetry assumed in the band-structure method can never be obtained in a cluster, irrespective of its size, due to the finiteness of the cluster size in space. The molecular-orbital procedures generally do not impose symmetry requirements on the cluster as the Bloch condition does in the band-structure calculations. The symmetry of the molecular orbitals and the degeneracy of the molecular-orbital eigenvalues required by symmetry follow directly from the Hamiltonian. Since a cluster containing any finite number of atoms cannot have translational symmetry, the Hamiltonian will not be translationally invariant. Therefore, in the limit where the cluster size approaches infinity, one will not be able to generate the k dependence of energy levels assumed in the band-structure calculation. In any case, the ideal translational symmetry and infiniteness of the crystal are mathematical abstractions exploited in band-structure methods to simplify the electronic-structure calculations involving crystals. Any real crystal is finite in space and has a well-defined surface limiting the extent of the crystal in space. Thus the infinite crystal as visualized by the Born–von Kármán principle is an approximation of a real crystal. The translational symmetry imposed by band-structure formalisms and the localized nature of orbitals in molecular-orbital theories are both approximations of the true state of solids. They should both be able to describe the observable properties of the crystals in a reliable manner. Finally, experimental (typically spectroscopic) probes of the electronic structure of a crystal may be better analyzed in terms of cluster-molecular-orbital excitations than Bloch states, especially if the crystal states of interest (e.g., impurity states) are inherently localized. These cluster-molecular-orbital excitations are real-space analogs of exciton states[29] derived from band structure, but lacking k-space dependence. In this paper our objective is to demonstrate this point of view. As will be shown, the two methods are complementary and, when used in a proper manner, they will lead to similar descriptions of the properties of solid-state systems.

IV. RESULTS

A. Cluster calculations

1. Zinc oxide

The electronic structure of zinc oxide is obtained by the scattered-wave approach using zinc-centered clusters with four nearest-neighbor oxygen atoms. The atomic separation between zinc and its nearest neighbors is taken to be 3.68 a.u. (1.95 Å). The cluster is enclosed inside a sphere carrying six units of positive charge for proper embedding of the cluster in the crystal. Ideal tetrahedral symmetry is chosen for the cluster. Inclusion of actual symmetry changes the relative separations among the energy levels by less than 0.2 eV.

The occupied valence molecular orbitals consist of two a_1, two e, one t_1, and four t_2 orbitals labeled in terms of the irreducible representations of the T_d point group. These orbitals appear in four distinct groups on the energy scale. The highest occupied molecular orbital (HOMO) belongs to the t_2 irreducible representation. Just below this level appears a molecular orbital of t_1 representation. The next group of molecular orbitals consists of one e, one t_2, and one a_1 type of molecular orbitals. They can be described as the oxygen bonding orbitals due to atomic $2p$-like electrons. The atomic zinc $3d$-like levels generate one t_2 and one e-like molecular orbitals. These are the metal oxygen bonding orbitals. The lowest-energy a_1- and t_2-like molecular orbitals are mostly due to the oxygen $2s$-like functions. These four groups of orbitals are responsible for the four photoelectron peaks observed at 3.1, 5.9, 8.9, and 21.1 eV.[30] Using these peaks, one can calculate the binding energy of the electrons corresponding to the last three peaks with respect to the top of the valence band. This gives us 2.8, 5.8, and 18.0 eV as the binding energies of the electrons in the inner three groups of molecular orbitals. Using the calculated energy levels, the binding energy of the inner groups of electrons turn out to be 2.06, 5.03, and 15.5 eV, which agree reasonably well with the observed values. One can improve the agreement by performing transition-state calculations for these energy levels. For a detailed discussion on the theoretical interpretation of the x-ray photoemission spectroscopy (XPS) and ultraviolet photoelectron spectroscopic measurements which provide similar results, one may refer to the work of Tossel.[31] Our results agree with his in all essential features.

The lowest unoccupied molecular orbital (LUMO) belongs to the a_1 irreducible representation. It is mainly composed of the $4s$-like atomic orbital of zinc and is very delocalized. The energy gap between the LUMO and HOMO energy levels is 3.9 eV, which is in reasonable agreement with the 3.4-eV optical band gap of the material. The lowering of the T_d symmetry of the cluster to C_{3v} will reduce the value of the gap by 0.2 eV, which would bring the theoretical value closer to the experimental value.

The scattered-wave results for the cluster representing zinc oxide provide a satisfactory explanation of those ex-

perimental results that depend on the relative ordering of the bulk energy levels. It will be shown that the results obtained by the cluster method agree very well with those obtained by the computationally more intensive band-structure method. This provides the basis for generating a global picture of the ordering of the energy levels of zinc oxide doped with copper by combining the energy levels of this cluster with those obtained for the copper-centered cluster.

2. Copper impurity in zinc oxide

The molecular-orbital wave functions and eigenvalues for divalent copper in zinc oxide are obtained using a $(CuO_4)^{6-}$ cluster. Since the divalent copper ions have the same Slater radius as zinc, we have assumed that there will be negligible relaxation of the lattice around the substitutional copper impurity. The important difference between copper and zinc is that a divalent copper ion has an unpaired hole in the atomic d shell. Therefore, one would expect a Jahn-Teller distortion of the lattice. However, we have not explicitly investigated this effect.

The value of the exchange-correlation parameter α has been taken to be 0.706 97.[32] The sphere radii of oxygen, copper, and the outer sphere have been determined using Norman's criterion.[33] The touching sphere criterion has been used. The radii for copper, oxygen, and the outer sphere are taken to be 2.0361, 2.1270, and 5.3321 a.u., respectively.

In isolated atoms, the binding energies of copper $3d$ electrons and oxygen $2p$ electrons are 9.53 and 8.935 eV, respectively. These values are obtained from atomic calculations using the Hartree-Slater procedure. Since the copper $3d$ electrons are more tightly bound than the $2p$ electrons of oxygen, the copper ion cannot completely donate two electrons to oxygen to give totally ionic bonding. The nature of bonding between copper and oxygen atoms will be substantially covalent. This is very different from the bonding of the other transition-metal ions (e.g., Mn, Fe, etc.) with oxygen for which the binding energy of the d electrons is less than that of the $2p$ electrons of oxygen. This is in keeping with the unique behavior of copper luminescent centers in oxides and sulfides. The significance of such $Cu(3d)$-$O(2p)$ covalent bonding to high-T_c superconducting cuprates[12] has also been elucidated in cluster models for these materials.

The molecular-orbital eigenfunctions and energy eigenvalues of the cluster are obtained using the spin-polarized version of the scattered-wave method. The occupied orbitals are composed of the same kind of orbitals as in zinc oxide. Since this is a paramagnetic system, the spin degeneracy is removed for all the energy levels.

The copper d-like orbitals give one t_2 and one e molecular orbital. The separation between the t_2 and e orbitals is 0.86 eV, which compares very well with the experimentally measured 0.71-eV splitting of the d orbitals measured for copper in zinc oxide.[14] The t_2 and e orbitals are further split by the exchange interaction. The magnitude of the exchange splitting is about 0.47 eV. These t_2 and e orbitals have 54% and 67% copper d character for the majority spin states and 48% and 58% copper d charac-

ter for the minority spin states. This indicates the expected strong covalency of copper oxygen bonding.

The next t_2 orbital for a minority spin state lies 2.88 eV below the t_2 orbital corresponding to the copper d hole. This compares very well with the excitation peak at 2.86 eV measured by Dingle.[15] This corresponds to a charge-transfer transition in which a hole in the upper t_2-like orbital is promoted to an oxygenlike t_2 orbital. This oxygenlike molecular orbital is significantly localized (58%) at the neighboring oxygen atoms.

In order to understand correctly the luminescence behavior of the divalent copper ion in zinc oxide, one needs to have a knowledge of the global picture of the energy levels of the impurity ions in the energy-level diagram for the host system. In the present paper we have used a very simple scheme to obtain a global picture of the energy-level diagram from the energy levels calculated for various clusters. We will show that this diagram not only explains satisfactorily the observed properties of the defect system, but is also consistent with the more rigorous band-structure approach.

The oxygen atoms near the copper center will experience the exchange-correlation effect due to a single spin localized at the copper ion in addition to the electrostatic field due to the formal charge at the copper center which is approximately the same as that due to a zinc ion. This will lead to a splitting of the otherwise spin-degenerate oxygenlike molecular orbitals. Thus it is reasonable to assume that the energy centroid of the split t_2-like orbital at the top of the valence band will be the same as the energy level associated with the t_2-like orbital at the top of the valence band of zinc oxide. Since the energy scale is rather arbitrary in the scattered-wave method, the matching of the energy levels thus described will lead to a unique picture of the energy-level diagram for this defect system. The energy-level diagram thus generated has been shown in Fig. 1. We have also used the observed band gap to define the position of the bottom of the conduction band.

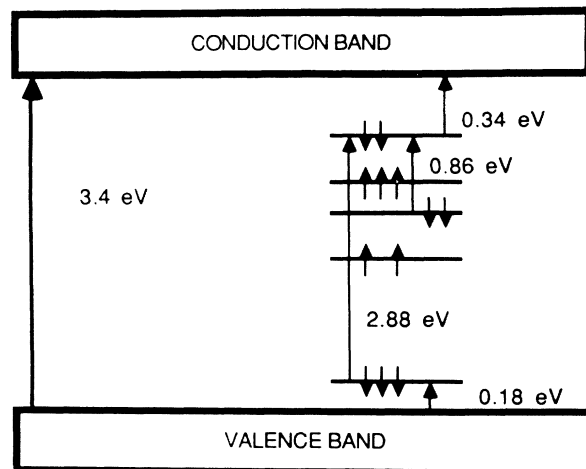From Fig. 1 the t_2 orbital localized at the oxygen

FIG. 1. Energy-level diagram for zinc oxide doped with copper.

atoms adjacent to copper is 0.18 eV above the top of the valence band. The luminescence process involves energy levels associated with the copper center and associated oxygen levels. The t_2 spin down state containing the copper d hole is 0.34 eV below the bottom of the conduction band. The d-like levels of copper start at 1.67 eV above the valence band.

The energy-level diagram presented in Fig. 1 is qualitatively similar to that proposed by Dingle.[15] He had assumed that the Fermi surface is only 0.1 eV below the conduction band. However, in our calculations we find it to be 0.34 eV below the conduction-band minimum. This is in keeping with the results obtained by the band-structure method described in Sec. IV B. If we assume the theoretical position of the Fermi surface, the theoretical and the experimental picture of the energy levels will be identical.

B. Results of band-structure calculations

Zinc oxide crystallizes in the Wurzite structure with two ZnO formula units in the hexagonal unit cell. The lattice parameters for pure ZnO are $a = 3.25$ Å and $c/a = 1.6021$. To study the electronic states of Cu/ZnO, it is necessary to simulate the local character of the copper impurity in the ZnO matrix. This has been performed in the following way: We have doubled the lengths of a and c to get a unit cell with 32 atoms and the copper substitutional point impurity on the zinc position is simulated by replacing one of the 16 zinc atoms by copper. The electronic states for this system ($Zn_{15}CuO_{16}$) have been investigated using a band-structure calculation. Such a calculation describes approximately the local character of the copper states because the nearest distance between two Cu atoms within the periodicity of the lattice is far, namely, 6.5 Å. This means that the energy bands $E(k,n)$ as a function of the wave vector k, and the band index n, are determined for $Zn_{15}CuO_{16}$ within a hexagonal unit cell of $a = 6.50$ Å and $c/a = 1.6021$.

The band-structure calculation has been carried out using the augmented-spherical-wave (ASW) method. One aspect of this procedure is that the crystal is separated into overlapping atomic spheres. The sizes of the atomic spheres are chosen in such a way that the total volume occupied by the atomic spheres is equal to the crystal volume. The size of the oxygen sphere is taken close to its ionic radius, $r_0 = 1.588$ Å. The radii of the zinc and copper atoms, which are taken to be equal, are $r_{Cu/Zn} = 1.89$ Å.

Within the band-structure calculation the oxygen $1s$ and the metal $1s$-to-$3p$ shells are treated as cores. Therefore, the lowest-lying electronic bands are the $2s$-like bands of oxygen.

The results of our calculation are shown in Figs. 2 and 3. In Fig. 2 the band structure of $Zn_{15}CuO_{16}$ is plotted for various symmetry lines of the Brillouin zone and Fig. 3 shows the density of states (DOS) for $Zn_{15}CuO_{16}$. The low-lying $2s$-like bands of oxygen at about -18 eV are only displayed in Fig. 3.

About 10 eV above the $2s$-like bands of oxygen one finds the $3d$-like bands of Zn. For pure ZnO, the $3d$-like bands of Zn are separated by a band gap from the $2p$-like
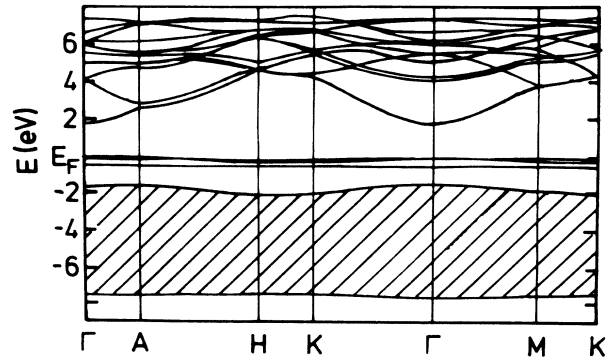

FIG. 2. Energy bands of the valence and conduction bands of Cu/ZnO based on a calculation of hexagonal $Zn_{15}O_{16}Cu$. E_F is the Fermi energy. For the 123 overlapping $3d$-like bands of zinc and $2p$-like bands of oxygen, the dispersion curves are only given for the 1st and 123rd bands. The five $3d$-like bands of Cu around E_F are partially resolved in this drawing.

bands of oxygen. For $Zn_{15}CuO_{16}$, however, this band gap is removed and the $3d$-like bands of Zn and the $2p$-like bands of oxygen overlap. The $3d$-like bands of zinc range from -7.5 to -5.5 eV and the $2p$-like bands of oxygen from -5 to -1.5 eV. This can be seen more clearly in Fig. 3. The $3d$-like bands of Cu are found 1.1 eV above the $2p$-like bands of oxygen. The Fermi energy E_F lies at the top of the $3d$-like bands of Cu with the conduction bands being separated by a band gap of about 2.0 eV from the $3d$-like bands of Cu. The two peaks of the $3d$-like bands of copper (see Fig. 3) correspond to the crystal-field splitting.

Next the charge Q_v inside the atomic spheres v (see above) is considered. For pure ZnO, one finds $Q_{Zn} = 1.956e = -Q_O$. For $Zn_{15}CuO_{16}$ there are five nonequivalent Zn atoms, eight nonequivalent oxygen atoms, and one Cu atom. The charge inside the copper sphere is equal to $Q_{Cu} = 1.723e$, which is distinctly less than that in
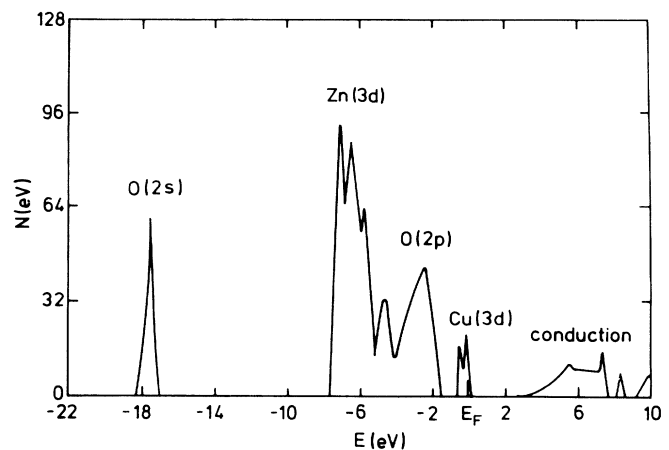

FIG. 3. Density of states for Cu/ZnO per electron volt and formula unit $Zn_{15}O_{16}Cu$. E_F is the Fermi energy. The energy scale ranges from the oxygen $2s$-like bands to the valence bands.

the Zn sphere of ZnO. For the oxygen atoms adjacent to the copper atom ($r_{Cu-O} = 1.991$ Å), $Q_{O,n} = -1.906e$, while for an oxygen atom far from the copper atom ($r_{Cu-O} = 6.924$ Å), $Q_{O,f} = -1.960e$. Similarly, one finds for Zn, $Q_{Zn,n} = 1.950e$ ($r_{Cu-Zn} = 3.209$ Å) and $Q_{Zn,f} = 1.992e$ ($r_{Cu-Zn} = 6.138$ Å). Therefore, the oxygen atoms close to the copper impurity are less negatively charged than average, and the zinc atoms closest to the copper impurity are less positively charged than the mean charge for zinc atoms.

Differences in the charge distribution among the various atoms can also be analyzed within the concept of partial densities of states $N_v(E)$. These are the DOS weighted by the norms of the wave functions inside the atomic sphere such that

$$Q_v = \int_0^{E_F} N_v(E) dE .$$

The sum over all partial DOS gives the total DOS shown in Fig. 3. In Figs. 4(a) and 4(b) the partial DOS are shown for those different atoms for which the partial charges Q_v are listed above, namely $N_{O,n}(E)$ is the par-
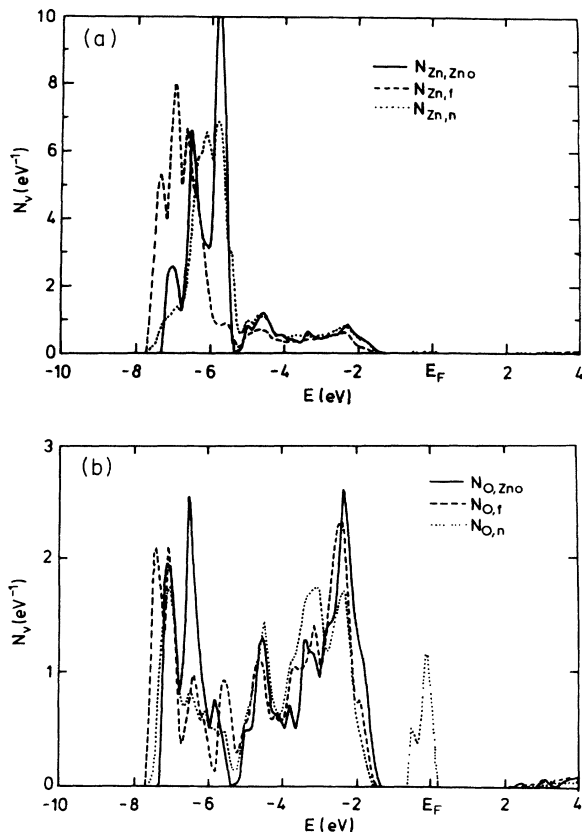
tial DOS for the oxygen atoms closest to the copper atom and $N_{O,f}(E)$ is the partial DOS for the oxygen atom far from the copper atom. The partial DOS $N_{Zn,n}(E)$ and $N_{Zn,f}(E)$ are defined similarly. For comparison, the partial DOS for pure ZnO $N_{Zn,ZnO}$ and $N_{O,ZnO}$ are also plotted.

We see from Figs. 4(a) and 4(b) that $N_{Zn,ZnO}(E)$ and $N_{O,ZnO}(E)$ are zero at about -5.2 eV which indicates that the $3d$-like bands of Zn and the $2p$-like bands of oxygen do not overlap. However, the partial DOS for Zn is nonzero in the energy range of the oxygen $2p$-like states above -5.2 eV. This is partly due to the distribution of the charge in the overlapping regions of the atomic spheres, and partly to a small covalent contribution to the chemical bonds.

Comparing the partial DOS of the zinc atoms for Cu/ZnO, one finds that the shapes of the curves for different Zn atoms look similar. However, the heights of the peaks are different and the peaks for $N_{Zn,n}(E)$ occur at higher energy values than for $N_{Zn,f}(E)$.

For the oxygen partial DOS one finds an additional effect: There is an extra peak in $N_{O,f}(E)$ which is missing in $N_{O,f}(E)$ (see Fig. 4). This shows that there is a partial covalent bond between the copper atom and adjacent oxygen atoms.

Finally, the optical transitions shall be considered. In a simple microscopic theory the imaginary component of the dielectric function $\epsilon(\omega)$ is related to the joint density of states $J(\omega)$ (Ref. 34), which is defined by

$$J(\omega) = \sum_{k,n',n} \sigma[E(k,n') - E(k,n) - \hbar\omega] .$$

Figure 5 shows the joint density of states (JDOS) for $Zn_{15}CuO_{16}$ calculated for transitions from levels below the Fermi energy into the d-like holes at copper.

The peak in the joint density curves of Fig. 5 at $\hbar\omega = 0.4$ eV correspond to transitions from the occupied $3d$-like levels of the copper impurities to the unoccupied $3d$-like levels of copper—that is, these are optical transi-

FIG. 4. (a) Partial density of states N_v for the Zn spheres in ZnO and Cu/ZnO. $N_{Zn,ZnO}$ is N_{Zn} for pure ZnO, $N_{Zn,f}$ is N_{Zn} for Cu/ZnO for a Zn sphere near the Cu sphere, and $N_{Zn,f}$ is N_{Zn} for Cu/ZnO for a Zn sphere far away from the Cu sphere. (b) Partial density of states N_v for the O spheres in ZnO and Cu/ZnO. $N_{O,ZnO}$ is N_O for pure ZnO, $N_{O,f}$ is N_O for Cu/ZnO for a O sphere near the Cu sphere, and $N_{O,f}$ is N_O for Cu/ZnO for a O sphere far away from the Cu sphere.
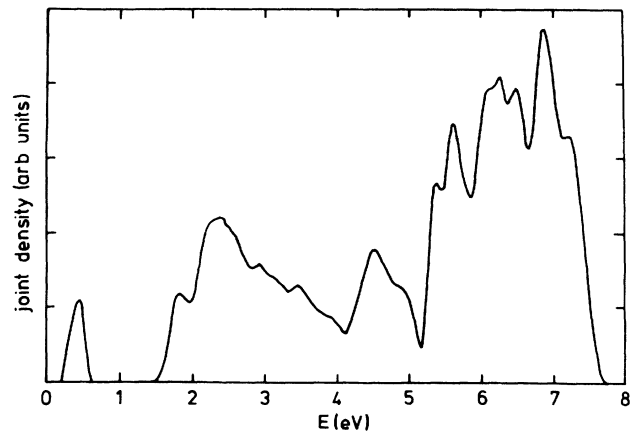

FIG. 5. Joint density for excitation into the Cu hole states in Cu/ZnO as determined from a spin-restricted band-structure calculation.

TABLE I. Comparison of results from cluster and band-structure calculations for ZnO/Cu.

	Experiment	Cluster theory	Band theory
Crystal-field splitting	0.71 eV	0.86 eV	0.45 eV
Excitation peak	2.86 eV	2.88 eV	2.5 eV
Band gap	3.4 eV	3.9 eV[a]	3.4 eV
		3.7 eV[b]	

[a]For T_d symmetry.

[b]For C_{3v} symmetry.

tions due to the crystal-field splitting of the d-like levels of copper. The second peak at $\hbar\omega = 2.5$ eV is due to charge-transfer transitions from the p-like bands of oxygen to the d-like holes of copper. The large maxima of $J(\omega)$ in the range 5 eV $< \hbar\omega < 8$ eV correspond to transitions from the d-like bands of Zn into the d-like holes of copper.

V. CONCLUSION

It is apparent that both the cluster molecular orbital and the band-theory calculations of electronic structure lead to the same qualitative description of the electronic states of Cu/ZnO. The band-gap energies found were nearly the same (Table I) and the copper d bands were found to lie inside the gap. The copper d band was found about to be 1.1 eV above the valence band in the ASW calculation compared to 1.5 eV found by the SW $X\alpha$ calculation. The crystal-field splitting and excitation peak from JDOS (Table I) are in reasonable agreement with those calculated from the cluster calculations. While the crystal-field splitting is not obvious in the band-structure plot (Fig. 2), the JDOS (Fig. 4) reveals a peak at 0.45 eV. Similarly, one finds the first excitation peak corresponding to excitation of an electron from the p band of oxygen to a d band of copper at 2.5 eV whereas the separation between the two bands from Fig. 2 is 1.1 eV. This apparent contradiction can be explained by the fact that the transition probability depends on the density of states. Therefore, the peak of a particular excitation is determined by the regions in the energy band where the density of states attains a maximum. This leads to a quantitative difference in the separation of band edges and the excitation peak measured by a photon probe. On the other hand, the cluster method yields discrete lines without any broadening. The discrete lines appear where the DOS is expected to be maximum. Therefore, the differences among the energy eigenvalues from a cluster calculation relate directly to the excitation peaks.

It appears (Table I) that the cluster method leads to better agreement with experimental measurements corresponding to impurity states. The new levels that appear in the band-structure calculations when the copper impurity is introduced show little k dependence—that is,

the states are localized. Cluster calculations are, therefore, expected to give better approximation to these impurity states. Furthermore, in the present case, the ASW calculations were performed within a spin-restricted formalism, whereas the cluster calculations include the exchange correlation. We feel that inclusion of the exchange-correlation effect, which is found to be of the order of 0.49 eV from the cluster calculation, would remove most of the discrepancies between the two methods.

Which of the two techniques is most suitable for studying spectroscopic properties of the impurity ions? It is clear from the present studies that the clusters can provide an accurate approximation to band-structure calculations in terms of ground-state properties. Similar conclusions have been reached before by other authors.[7,35] However, the present study indicates that the cluster method can provide reliable values for excitation peaks. This is of considerable interest in phosphor research, but questions such as the ordering of the impurity energy levels with respect to the bulk energy levels, the density of states in the conduction band, band widths, etc., cannot be reliably answered within the framework of cluster theories. Those parameters are important when studying problems related to host-impurity interactions, absorption above the band gap, interband Auger transitions, and many other properties related to the density of states and bandwidth of the material. We believe that both methods can, and should, be used in a complementary manner to obtain a more complete description of the solid-state properties of a material.

There has been a tendency among practitioners and critics of cluster calculations to assume that "bigger is better." However, it is clear from the present studies that a detailed analysis of the molecular orbitals of relatively small clusters compares very well to both experiment and the results of crystal band-structure calculations. While this may not be true in general for all types of materials (e.g., metals), we are confident in the generalization of these findings to other oxides. The general agreement between the present real-space cluster molecular orbital and k-space band-structure calculations for the Cu/ZnO system provides strong support for utilization of the cluster technique in other metal oxides where the band-structure calculation may be prohibitively time consuming.

[1]J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules* (McGraw-Hill, New York, 1974), Vol. 4, p. 216.

[2]*Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[3]J. Yu, A. J. Freeman, and J. H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[4]K. H. Johnson and R. P. Messmer, Synth. Metals **5**, 193 (1983).

[5]J. C. Slater and K. H. Johnson, Phys. Rev. B **5**, 844 (1972); K. H. Johnson and F. C. Smith Jr., *ibid.* **5**, 831 (1972).

[6]L. A. Hemstreet, Phys. Rev. B **15**, 834 (1977); N. Sahoo *et al.* Phys. Rev. Lett. **50**, 913 (1983); N. Sahoo, K. C. Mishra, and T. P. Das, *ibid.* **55**, 1506 (1985); M. Van Rossum *et al.*, Phys. Rev. B **26**, 4442 (1982).

[7]D. D. Vvedensky, M. E. Eberhardt, and M. E. McHenery, Phys. Rev. B **35**, 2061 (1987).

[8]K. C. Mishra, J. K. Berkowitz, B. G. De Boer, E. A. Dale, and K. H. Johnson, Phys. Rev. B **37**, 7230 (1988).

[9]K. H. Johnson, H. J. Kolari, J. P. deNeufville, and D. L. Morel, Phys. Rev. B **21**, 643 (1980).

[10]R. P. Messmer, Phys. Rev. B **23**, 1616 (1981).

[11]C. Y. Yang, K. H. Johnson, D. R. Salahub, J. Kasper, and R. P. Messmer, Phys. Rev. B **24**, 5673 (1981).

[12]K. H. Johnson, M. E. McHenery, C. Counterman, A. Collins, M. M. Donovan, R. C. O'Handley, and G. Kalonji, in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 563; K. H. Johnson, D. P. Clougherty, and M. E. McHenry, Mod. Phys. Lett. B **3**, 867 (1989).

[13]For ZnO/Zn phosphor see V. W. Leverenz, *An Introduction to Luminescence of Solids* (Dover, New York, 1968). This system has been listed as type-137 CRT phosphor in the Technical Information Bulletin by Sylvania Chemicals.

[14]R. E. Dietz, H. Kamimura, M. D. Sturge, and A. Yariv, Phys. Rev. **132**, 1559 (1963).

[15]R. Dingle, Phys. Rev. Lett. **23**, 579 (1969), and references cited therein.

[16]For experimental data on zinc oxide see F. A. Kroger, *The Chemistry of Imperfect Crystals* (North-Holland, New York, 1964).

[17]M. Schoen, Z. Phys. **119**, 463 (1942); Ann. Phys. **3**, 333 (1948).

[18]H. A. Klassens, J. Electrochem. Soc. **100**, 72 (1953).

[19]J. Lambé and C. C. Klick, Phys. Rev. **98**, 909 (1955).

[20]J. S. Prener and F. E. Williams, J. Electrochem. Soc. **103**, 342 (1956); J. Chem. Phys. **25**, 361 (1956); Phys. Rev. **101**, 1427 (1956).

[21]J. L. Birman, Phys. Rev. **121**, 141 (1961).

[22]W. Walter and J. L. Birman, in *Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 89.

[23]A. R. Williams, J. Kübler, and C. D. Gelatt Jr., Phys. Rev. B **19**, 1990 (1979).

[24]P. C. Schmidt, A. Weiss, S. Cabus, and J. Kübler, Z. Naturforsch., Teil A **42**, 1321 (1987).

[25]S. C. Abrahams and J. L. Bernstein, Acta Crystallogr. Sect. B **25**, 1233 (1969).

[26]R. Pappalardo, J. Mol. Spectrosc. **6**, 554 (1961); see also Dietz *et al.* in Ref. 14.

[27]J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972).

[28]J. Korringa, Physica (Utrecht) **13**, 392 (1947); W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[29]O. Madelung, *Introduction to Solid State Theory*, translated by B. C. Taylor (Springer-Verlag, New York, 1981).

[30]L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B **9**, 600 (1974).

[31]J. A. Tossel, Chem. Phys. **15**, 303 (1976).

[32]K. Schwartz, Phys. Rev. B **5**, 2466 (1972); Theor. Chim. Acta **34**, 225 (1974).

[33]J. L. Norman, J. Chem. Phys. **61**, 4630 (1974).

[34]F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972); M. Zwilling, P. C. Schmidt, and A. Weiss, J. Appl. Phys. **16**, 255 (1978).

[35]R. Podloucky, R. Zeller, and P. H. Dederichs, Phys. Rev. B **22**, 5777 (1980).