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Bands versus bonds in sulfides: Theoretical investigation of the luminescence of copper in zinc sulfide

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The fundamental question of bands versus bonds has been probed through a direct comparison of results from scattered-wave cluster molecular-orbital and augmented-spherical-wave band-structure calculations for copper-activated zinc sulfide phosphor. These methods have been employed to develop a coherent understanding of the process of luminescence for various copper-luminescent centers. Our results for Cu^{2+}/ZnS support the Lambe-Klick model for excitation of infrared emission while calculations for $Cu^{+},Cl^{-}/ZnS$ and $Cu^{+},Al^{3+}/ZnS$ support the Schoen-Riehl-Klasens model for green emission. The present study indicates a close correspondence between the two types of calculations and illustrates the utility of using these techniques in a complementary manner to understand the electronic processes in solids.

I. INTRODUCTION

The electronic structures of solids, particularly those containing atoms having localized d and f electrons, have long presented problems to theorists interested in studying the electronic-structure-related properties of these systems.[1] While the conventional band-structure approach has been generally preferred for studying bulk properties because of the extended nature of the electronic states of periodic systems, the cluster method has been found to be suitable to analyze the electronic properties associated with impurities that introduce localized states in solids. However, application of these two alternative approaches has not necessarily been restricted by the above considerations. Although the electronic structures of dilute defect systems have been studied using "supercell" versions of band-structure methods,[2–4] the real-space description of bulk states by the cluster molecular-orbital approach has led to considerable success in describing the bulk properties of amorphous semiconductors,[5] alloys,[6] magnetic material,[7] and most recently high-T_c superconducting materials.[8] In a recent paper[4] describing the luminescence of divalent copper in zinc oxide, it was demonstrated that these techniques do not contradict each other in their description of the electronic structure of this system. It was shown that both the cluster and band methods can, and should, be used in a complementary manner to develop a complete model of the electronic structure, which is important for material design and development.

Our success in explaining the excited-state processes in zinc oxide using the cluster and band methods together gave us the confidence to apply both of these procedures to the very complex problem of luminescence of copper in zinc sulfide. In spite of the vast amount of experimental data published for this system over the past few decades, there does not exist any definitive picture regarding the excitation mechanism of copper-activated zinc sulfide. A number of alternative models have been proposed for the luminescence process of copper in ZnS.[9–13] In this paper, an attempt will be made to identify the correct mechanism using the energy eigenvalues calculated for small clusters and electronic energy bands for ZnS doped with copper. Both methods not only lead to similar pictures of luminescence, but also provide very useful results regarding the changes in electronic distributions due to changes in the oxidation state of copper and also the role played by coactivators in stabilizing a particular copper oxidation state. Additionally, there has recently been some interest in understanding the nature of the electronic states far away from the band extrema.[14] These states provide valuable information regarding the optical properties in general and interband Auger processes[15] in particular. The utility of the latter process in fabricating a multiphoton phosphor has been of interest to lighting research. It is hoped that the calculated density of states in the conduction band will provide information in this regard.

The cluster and band-structure calculations have been performed by first-principles scattered-wave $X\alpha$ (SW $X\alpha$)

(Ref. 16) and augmented-spherical-wave (ASW) methods,[17] respectively. Using the calculated molecular-orbital energy eigenvalues for different clusters describing the local environment of ions in ZnS, an energy-level diagram has been obtained. The correctness of the energy-level diagram is checked by the electronic bands obtained by the ASW method, and also by its ability to explain the existing luminescence data. These energy-level diagrams are in turn used to identify the correct luminescence model for copper in zinc sulfide.

II. LUMINESCENCE OF COPPER IN ZINC SULFIDE AND MODELS OF LUMINESCENCE

The luminescence of doped zinc sulfide is one of the most extensively studied subjects in the field of phosphors because of its use in a variety of optoelectronic devices. In the case of copper-activated zinc sulfide, there exists a vast amount of experimental data on the nature of the excitation of this phosphor,[18–21] and a number of models[9–12,22,23] have been proposed to explain the observed data. Most of these models propose classical energy-level diagrams and assume that the observed luminescence results from transitions among these energy levels. Although the correctness of such an approach is questionable because of relaxations in the excited state, these simple pictures provide much insight into the luminescence mechanisms and are useful in material design and quality control.[24]

Copper is assumed here to substitute for zinc atoms, although other sites have been proposed in the literature.[23,25] The copper ions can exist in either the monovalent or divalent oxidation state. In the latter case, there are nine electrons in the $3d$-like levels, which leaves a hole in the $3d$ shell of copper. The divalent copper ions are therefore paramagnetic. In the case of monovalent copper ions, the d shell is filled, resulting in a diamagnetic center.

A number of emission centers have been associated with copper.[22] We shall consider only three that have been definitively identified with copper impurities. They are the green center (Cu-*G*), the blue center (Cu-*B*), and the infrared center (Cu-ir). The Cu-*G* center is associated with the green emitting phosphor whose emission peaks at 2.38 eV, the corresponding excitation peak being at 2.95 eV.[18] Emission from the Cu-*B* center peaks at 2.67 eV, corresponding to the absorption peak at 3.35 eV.[18] The Cu-ir center at 0.95 eV correlates to the intense absorption peaks at 1.7 and 2.3 eV.[19] In addition to these peaks, one observes absorption at 3.7 eV due to optical transitions between the valence and the conduction bands.[18]

The nature of the Cu-ir center is believed to be well understood. The electronic transition at 0.95 eV has been identified as being due to a crystal-field transition[19,22,26] and therefore is associated with a divalent copper ion at a substitutional site. The early semiempirical ligand-field calculations tend to support this conclusion.[22,26] In Cu/ZnO, similar transitions have been studied by spin resonance and optical techniques[27,28] and have been identified as crystal-field transitions.[28,29,4] No electron-paramagnetic-resonance (EPR) signal has been seen for Cu-*B* or Cu-*G* centers, indicating that the green and blue transitions cannot be ascribed to a paramagnetic copper center.[23,29,30] Thus, these transitions are associated with monovalent copper impurities. In order to have a monovalent copper ion at a substitutional site, one has to codope zinc sulfide with trivalent cations or monovalent anions or create sulfur vacancies. These codopants or the anion vacancies compensate the charge imbalance due to monovalent copper ions substituting for divalent zinc ions.

If we identify the blue and green emissions with Cu^{1+}, the nature of the emission process becomes an enigmatic puzzle. Since the impurity states due to copper d-like levels are fully occupied, the electrons from the valence band can no longer be excited to these copper levels. For a typical excitation process by the 2537 Å photons from a mercury discharge, an electron-hole pair created by the incident photon has to migrate and recombine at a copper center to give a green or blue photon. This can occur in two different ways. (i) The hole is captured by the impurity center and then the itinerant electron in the conduction band makes a transition to fill the hole at the impurity center, which results in the emission of a photon. This is essentially the model of Riehl, Schoen, and Klasens (RSK). (ii) An electron from the impurity level makes a transition to fill the hole in the valence band, resulting in the photon emission. The hole at the copper site is eventually filled by the itinerant electrons in the conduction band. This is the Lamb and Klick (LK) model. The two models differ in their explanation of the ultimate emission process. In the LK model, the impurity level is placed very close to the bottom of the conduction band, whereas the other model (RSK) assumes that this level is probably a perturbed level of the valence band and thus close to the top of the valence band. There are also a number of other models[11,13] in which the role of the coactivator and other states has been brought into the picture. However, in our opinion all these models can be shown to be variations of the above two models.

In the present work, we extend the ligand-field band-theory model[12] to more rigorous band-structure and cluster methods. Attempts will be made to determine (i) the position of the energy levels of copper in both valence states with respect to the energy bands of the host lattice, and (ii) the effect of the codopants on the energy levels. Since these energy eigenvalues are determined for the ground-state geometry, we will make use of the calculated absorption peaks via the transition-state procedure for cluster methods or joint-density-of-states calculations for the band approach to distinguish between the various empirical energy schemes.

III. THEORY

This work uses the self-consistent-field scattered-wave molecular-orbital cluster (SW $X\alpha$) (Ref. 16) and the augmented-spherical-wave band-structure (ASW) (Ref. 17) methods. These two methods have been discussed extensively in the literature. In this paper, we limit our discussions to structural and computational parameters.

Structural information for zinc sulfide has been taken from crystallographic data.[31] It is known that zinc sulfide crystallizes in two extreme forms: cubic zinc blende and hexagonal wurtzite as well as a large number of intermediate polytypes. Most of the commercial phosphors use zinc sulfide with wurtzite structure as the host material. Primarily for this reason, the present calculations have been performed using the structural data for hexagonal zinc sulfide. The lattice parameter a and c/a ratio are 7.22 a.u. and 1.6329, respectively. The zinc atoms in zinc sulfide are tetrahedrally coordinated to four sulfur atoms. For a typical cluster calculation, a metal-centered cluster with its nearest neighbors is used. The effects of including next-nearest neighbors on the relative separation of the energy eigenvalues have been found to be insignificant.

The ASW band-structure calculations have been performed in the following manner. In order to extend the band-structure formalism to an aperiodic system like zinc sulfide doped with copper, we have made use of a quasiperiodicity assumption, i.e., we assume that the crystal still preserves its original crystal structure by reason of the occasional (assumed periodic) substitution of a dopant ion for a host ion, but the unit cells are larger than the original unit cells. This approximation is implemented via the supercell method.[2,3] In the present case, the unit-cell dimensions have been doubled to define the supercell, which forms the building block of the defect system. The supercell from zinc sulfide contains sixteen formula units of ZnS. The correctness of the supercell approach has been tested by comparing the energy bands and density of states calculated by using regular unit cells and supercells. The atomic radii are chosen so as to give total volume equal to the volume of the unit cell. Since the wurtzite structure contains many "octahedral" holes, empty spheres were used to fill up the empty space. Altogether, a typical supercell used in the present work contained 48 atomic spheres.

The radii of the zinc and copper atoms and the empty spheres are taken to be 2.22 a.u. These are similar in magnitude to the values used for Zn in our earlier paper.[4] The sphere radius for sulfur is taken to be 3.47 a.u. These choices for sphere radii lead to the observed band gap. The calculated energy bands are not significantly affected by minor variations of the sphere radii. The radii for the compensating chlorine and aluminum ions have been chosen to be the same as those for sulfur and zinc, respectively.

IV. RESULTS

A. Results from cluster calculations

1. Zinc sulfide

The local environment of zinc in zinc sulfide is simulated by metal-centered clusters with the nearest-neighbor sulfur atoms. Ideal tetrahedral symmetry is assumed for the cluster. The cluster is enclosed within a Watson sphere carrying six units of charge to simulate the Madelung potential produced by the rest of the crystal. The exchange-correlation parameters α for Zn and S atoms are taken to be 0.706 73 and 0.724 75, respectively.[32] The atomic radii for the ions have been chosen using the Norman criterion.[33] Calculations were performed using both touching and overlapping spheres. Although the absolute values of the energy eigenvalues are affected by the choice of touching or overlapping spheres, the relative separation among them is affected very little. In this work we will report the results obtained by using the touching-sphere condition with an inner Watson sphere.

Using the standard molecular-orbital representations of the T_d symmetry group, it can be shown that the occupied valence orbitals consist of two t_2, one a_1, one e, and one t_1 type of molecular orbital due mostly to the $3p$-like states of sulfur, one t_2 and one e molecular orbital arising from the $3d$-like states of zinc, and one t_2- and one a_1-like state due the sulfur $3s$-like atomic orbitals. The highest occupied state belongs to the t_2 irreducible representation and has 69% sulfur $3p$ character. This orbital has a 6% contribution from the $4p$- and $3d$-like states of zinc atoms. The importance of the admixture of zinc $3d$-like states has been discussed earlier in relation to the catalytic properties of zinc oxide.[34] The other valence orbitals, except for the t_1 orbital, that are identifiable with the sulfur $4p$- and $3d$-like states, have comparable admixtures with the zinc states. The t_1 state is an artifact of the cluster simulation and is mostly localized at the surface sulfur atoms. With infinite clusters, these orbitals would disappear as one expects from group theory.

The zinc $3d$-like levels are found to be separated by a gap of 4.0 eV from the bottom of the sulfur $3p$-like band. The splitting of the $3d$ band is found to be 0.6 eV, which is rather small compared to typical crystal-field splittings of the transition-metal ions. These orbitals also have 4% admixture of the sulfur states.

The lowest unoccupied energy level is due to the Zn $4s$-like state and belongs to the a_1 representation. The separation between this level and the highest occupied level is found to be 4.15 eV. Electronic transitions between these levels correspond to charge-transfer excitation across the fundamental energy gap, which has been measured to be 3.8 eV for ZnS, in good agreement with the calculated value of 4.15 eV.

2. Divalent copper in ZnS

It is commonly believed that copper ions substitute for zinc in zinc sulfide. Both ions have nearly identical ionic and Slater radii. It is therefore assumed that a substitutional copper ion would not induce any lattice distortion in its neighborhood, although a divalent copper ion may lead to a Jahn-Teller distortion of the lattice. In this paper, all the calculations involving copper ions have been performed assuming copper as a substitutional impurity ion without any lattice relaxation.

The energy eigenvalues and eigenfunctions associated with the copper center have been calculated using the spin-polarized version of the scattered-wave program. The α parameter for copper is taken to be 0.709 67. The sphere radius has been chosen to be the same as that for zinc.

Divalent copper has nine $3d$-like electrons. It is expected that the molecular-orbital energy levels associated with the $3d$-like levels of copper will play a very important role in the luminescence process due to this center. This is the crucial assumption in the ligand-field band-theory model for the copper centers.[12,22] The d-like energy levels split into one t_2 and one e molecular orbital. Since the t_2 level is not filled, there can be excitation from the e level to the t_2 level. The energy required for this excitation will be the same as the crystal-field splitting of these levels. This splitting has been calculated to be 0.93 eV, which compares very well with the experimentally observed splitting of 0.85 eV.[19]

The e and t_2 molecular orbitals are further split by exchange polarization. The magnitude of the exchange splitting is calculated to be 0.23 eV, which is rather small compared to the crystal-field splitting.

The $3p$- and $3s$-like atomic levels due to sulfur lead to valence-band states similar to those found for the zinc sulfide cluster. The highest occupied t_2 level lies about 1.98 eV below the t_2 state associated with the nonbonding level due to copper $3d$-like states. An e molecular orbital lies about 2.3 eV below that level. These separations agree very well with the observed intense absorption bands at 1.7 and 2.3 eV associated with the Cu-ir center.[19] These excitations can therefore be assigned to transitions of electrons from the valence band to the copper d-like level. These charge-transfer transitions are very similar to the absorption peaks observed for divalent copper in zinc oxide,[27,28] which have been conclusively identified as charge-transfer transitions both by theory[4,22,26] and experiment.[28] These transitions probably derive their strength from the strong admixture of sulfur $3p$-like states in the molecular orbitals involved in the transition process.

3. Monovalent copper ion

The energy eigenvalues and eigenfunctions for a monovalent copper ion are calculated using a cluster similar to that used for a divalent copper ion. It is assumed that the copper ion carries one unit of charge and the $3d$-like states are filled. The question of charge compensation has not been addressed using the cluster technique. This problem is studied in the band calculations.

The effect of the change of oxidation state is noticeable in the electronic charge distribution and eigenvalues. The nonbonding states due to copper $3d$-like levels are more localized at the copper site. The charge-density contributions to the t_2 and e levels due to copper ions are found to be 58% and 78%, respectively. This is less than, but comparable to, the values obtained by Tossel.[35] The differences are probably due to the overlapping-sphere approximation used in his work.[35] Similar to his observations, the contributions of the copper $3d$-like states to the nonbonding metallic states are found to be lower than those calculated for the divalent copper. The crystal-field splitting also decreases from 0.93 to 0.60 eV. The t_2 level moves up in the band gap with respect to the top of the valence band. The separation between the t_2-like nonbonding metallic state and the top of the valence band, which belongs to the same irreducible representation, changes from 1.9 to 2.37 eV for monovalent copper. No transition between these levels is possible since both these levels are fully occupied.

B. Band-structure results

1. Zinc sulfide doped with divalent copper

Electronic band-structure calculations for zinc sulfide with divalent copper impurities are performed using the ASW supercell method. Copper ions are assumed to substitute for zinc in zinc sulfide in a periodic manner. The supercell used in this calculation corresponds to a fundamental unit cell of a hexagonal crystal, whose formula unit and unit-cell content can be described as $Zn_{15}CuS_{16}$.

For pure ZnS, the band gap at the Γ point is calculated to be 3.8 eV, in good agreement with experiment. The relative ordering of the energy bands is very similar to those obtained by earlier workers.[36] In the case of Cu^{2+}, no dramatic changes in the energy bands are noticed, since the energy bands due to copper $3d$-like states and the top of the valence band overlap. However, in the density-of-states (DOS) plot (Fig. 1), a minor peak near the top of the valence band can be seen. Analyses of the partial density of states indicate that this peak is due to the $3d$-like states of copper.

The energy bands between -6.0 and -7.0 eV are predominantly due to the atomic $3s$-like states of sulfur. One finds that the energy bands resulting from the $3d$-like states due to zinc lie between the sulfur $3p$ and $3s$ bands. The conduction-band states between 10.0 and 30.0 eV have been calculated in order to study optical excitations and interband Auger processes. The DOS plot (Fig. 1) indicates a nearly constant density in the conduction band.

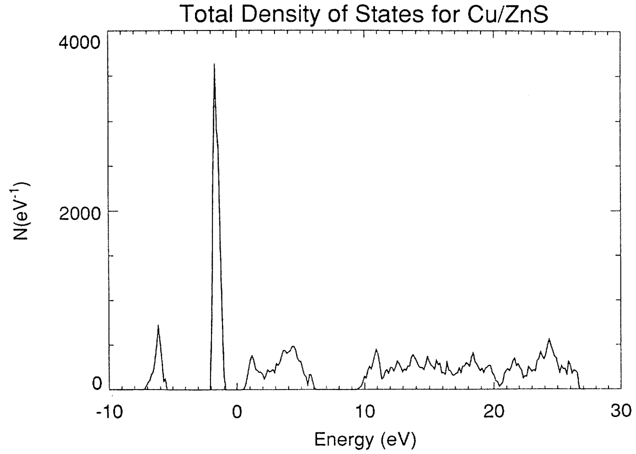

FIG. 1. Density of states due to Cu/ZnS per electron volt. The peak near 6.0 eV is due to the $3d$ bands of copper. Although the excitation of the divalent copper ions is similar to the LK model, the energy levels associated with the impurity ions are not located near the bottom of the conduction band.

The partial density calculations indicate that the sulfur 3*d*-like bands overlap strongly with the 4*s*- and 4*p*-like conduction bands. Since the excitation of an electron from the valence band to the conduction band depends on the availability of states in the conduction band, the nature of the DOS in the conduction band suggests that beyond the band edge the optical absorption would not show any dramatic drop in intensity due to lack of electronic states. The admixture of sulfur 3*d*-like states would contribute strongly to the transition probability for these charge-transfer transitions.

Next, we consider the charge Q_v inside each atomic sphere. For pure ZnS, Q_{Zn}, Q_{S}, and Q_{emp} are 1.84, -1.6, and -0.23, respectively. (The subscript "emp" denotes empty spheres.) In the case of Cu/ZnS, Q_{Cu} is found to be 1.55, suggesting charge transfer to divalent copper.

Finally, the optical properties of Cu/ZnS are considered. Two possible modes of excitation have been considered: (i) excitation of electrons from the valence band to the empty 3*d*-like state, and (ii) excitation from the *d*-like states to the conduction band. The former simulates the model proposed by Lambe and Klick[10] and the latter that by Schoen, Riehl, and Klasens.[9] The absorption peaks have been obtained by calculating the joint density of states (JDOS) $J(\omega)$ using the equation[37]

$$J(\omega)=\sum_{\mathbf{k},n,n'}\delta(E(\mathbf{k},n')-E(\mathbf{k},n)-\hbar\omega)\ , \tag{1}$$

where n' and n represent the energy bands involved in the excitation.

In Fig. 2, excitations from the valence band to the empty *d* state of copper are presented. It is obvious that there are at least three peaks: 0.75, 1.53, and 2.07 eV. The first peak can easily be identified with the crystal-field transition. The cluster calculations yielded a value of 0.93 eV, which agrees very well with the experiment.[19] The other two peaks can be identified with the charge-transfer transitions[18] discussed earlier.

The JDOS for excitations from the *d* band to the conduction band present no features in addition to the onset of absorption near 3.8 eV corresponding to excitations across the band gap. Thus, these JDOS calculations along with the cluster results indicate the correctness of the Lambe and Klick model[10] for the Cu-ir center.

2. Cu^{1+} *coactivated with Cl and Al*

It has been established that the Cu-*G* or Cu-*B* centers are not due to paramagnetic copper ions.[23] The luminescence of these centers has to be understood assuming a monovalent oxidation state for copper. In the case of monovalent copper, excitation of electrons from the valence band to a copper *d*-like band cannot occur. Therefore, the excitations would involve either the valence- or the conduction-band electronic states of the host. It is known that the green center can be excited by 2.95 eV radiation,[18] which is less than the band gap of the host material.

In a stoichiometric zinc sulfide crystal, a monovalent copper ion at a substitutional zinc site can be stabilized by codoping either with a monovalent anion at the sulfur site or a trivalent cation at the zinc site. Usually, chlorine or aluminum ions are chosen for this purpose. The dopants and their codopants have to be incorporated in equal concentrations to obtain monovalent copper ions.

3. *Chlorine as codopant*

The supercell used for this calculation consists of fifteen zinc, one copper, fifteen sulfur, and one chlorine atom. The copper and chlorine atoms occupy sites adjacent along the crystallographic *c* axis. Therefore, the space-group symmetry of the supercell crystal remains the same as that for Cu/ZnS.

The energy bands and DOS are shown in Figs. 3 and 4. Unlike the divalent copper case, one finds that the bands

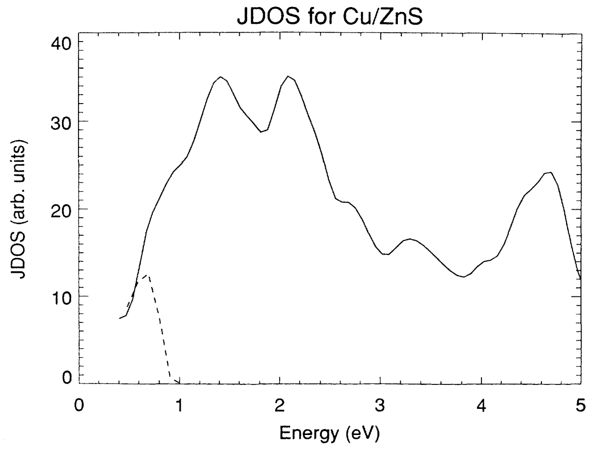

FIG. 2. Joint density of states for excitation into the Cu hole states in Cu/ZnS. The dashed curve gives the peak for the crystal-field transition due to the copper ion.

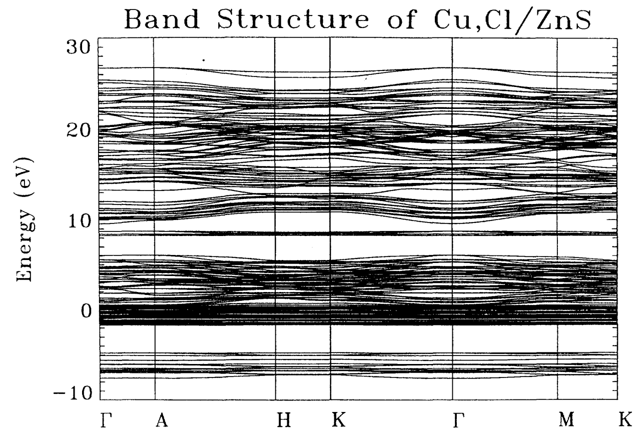

FIG. 3. Energy bands for Cu,Cl/ZnS based on a calculation of hexagonal $Zn_{15}CuClS_{15}$. The Cu 3*d* bands appear between 8.0 and 9.0 eV. The 3*s*-like bands of chlorine are not shown.

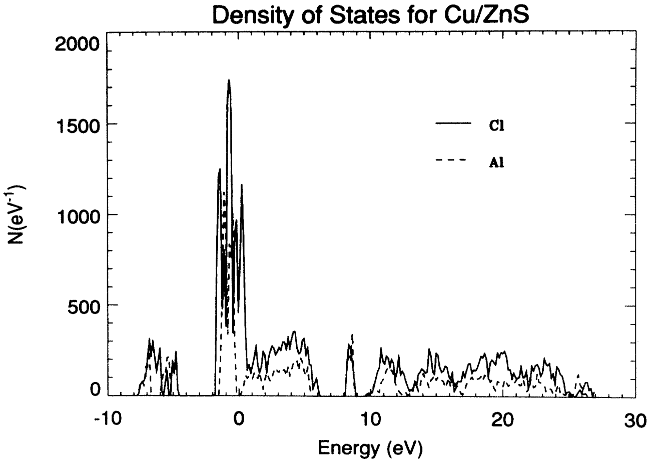

FIG. 4. Density of states per eV for Cu,Cl/ZnS and Cu,Al/ZnS shown by solid and dashed lines, respectively. Note the peak due to the $3d$-like levels of Cu in the band gap. Although the excitation of monovalent copper can be explained in light of the RSK model, the $3d$-like bands lie closer to the conduction-band minimum.

due to the d-like states of copper appear in the energy gap. The bands due to copper $3d$-like states are flat, indicating the localized nature of these copper states justifying the local cluster approach. An increase in the separation between the copper $3d$-like band and the top of the valence band with the change in the oxidation state of copper, as seen in the band calculations, is also observed in the cluster results. The d bands appear approximately 1.5 eV above the valence band, which compares reasonably well with the separation of 1.7 eV calculated by the cluster method (the separation between the e molecular orbital due to copper $3d$ electrons and the t_2 level at the top of the valence band).

The partial density of states indicates significant bonding between chlorine and the adjacent copper impurity. The partial-density-of-states calculation also indicates strong admixture of copper $3d$-like states and chlorine $3p$-like states. The charges within the atomic spheres are found to be 1.20 and -0.98. The charges within the other atomic spheres are not very strongly affected.

Finally, we considered the JDOS for excitations (Fig. 5) from the occupied levels, which include the valence-band states and the impurity states in the band gap, to the conduction band. There are two peaks at 2.6 and 3.1 eV before the onset of band absorption. These transitions agree very well with the absorption peaks at 2.95 and 3.35 eV.[18] The lower excitation peak leads to green emission at 2.38 eV.[18]

The transition at 2.6 eV involves excitation from the copper d band to the conduction band. This transition creates a hole in the d band and the green emission results from the transition of an electron in the conduction band into the empty state in the copper $3d$ band. The two models (LK and RSK) differ in their placement of the hole in the final state before the green emission. In the RSK model, the hole is in the copper $3d$-like band, whereas the LK model assigns it to the valence band. Thus the present calculation provides support for the RSK model for the Cu-G center.

4. *Aluminum as codopant*

Aluminum ions are also used as codopants for monovalent copper activators in zinc sulfide. It is believed that the aluminum ions substitute for zinc. A trivalent ion substituting for a divalent ion charge compensates for a monovalent ion at a divalent site. However, there are two problems associated with aluminum-ion substitution. First, the Slater radius for aluminum is about 0.15 a.u. smaller than for zinc. Therefore, one anticipates an unknown amount of lattice relaxation in the case of aluminum substituting for zinc. Second, it is not possible to accommodate an aluminum ion at a nearest-metal site without drastically lowering the symmetry of the supercell and correspondingly increasing the computational complexities of the problem. We tried supercells containing two aluminum and copper ions per unit cell, in which case, because of the equivalence of the two copper and two aluminum ions, we could use a smaller supercell containing only one copper-aluminum pair, still on the second-nearest metal sites, and 24 atomic spheres.

The electronic energy bands indicate the impurity states due to monovalent copper in the forbidden gap. The DOS plot (Fig. 4) shows that the states due to copper $3d$ electrons in the band gap are similar to those for CuCl/ZnS. However, the effect of the aluminum ions on the band structure is not obvious from this plot. The partial densities due to Cu, Al, and Zn indicate that the aluminum ions add impurity states near the bottom of the conduction band and that these states are due to the atomic $3s$-like levels of aluminum.

The electronic structure of the monovalent copper ion charge compensated by aluminum is similar to that compensated by chlorine. The JDOS for excitations from the copper $3d$-like bands to the conduction-band states is

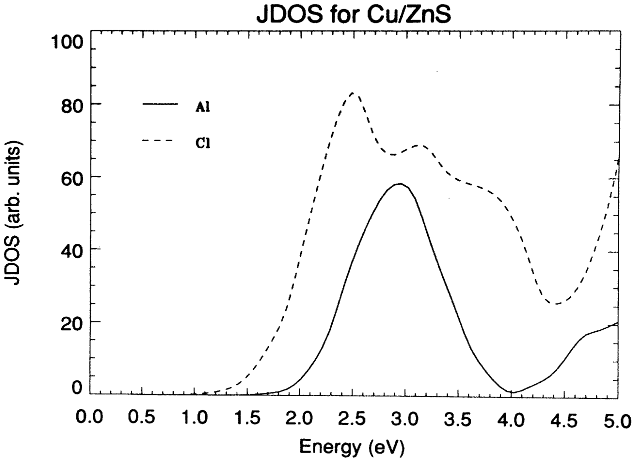

FIG. 5. Joint density of states for excitation of electrons from the valence band and the Cu $3d$-like bands to the conduction-band states for Al- and Cl-codoped zinc sulfide.

shown in Fig. 5. The first peak at 2.9 eV compares very well with the excitation peak at 2.95 eV observed for the Cu-*G* centers. The peak position differs from those for the chlorine-coactivated copper. This could be because of the higher assumed concentration of copper or the fact that the interaction between the copper and aluminum ions is mediated through the intermediate sulfur ions while the copper ions interact directly with chlorine in Cu,Cl/ZnS. The excitation process of monovalent copper compensated by aluminum is similar to that for chlorine compensation.

V. CONCLUSION

The results from the present calculations suggest that the cluster molecular-orbital method, combined with band-structure calculations, can provide a more realistic picture of the electronic structure of a solid-state system. The results from the two methods are found to be complementary. It is found that the excitation peaks are better explained by the cluster method if the states are very localized, but questions such as the ordering of the impurity levels with respect to the host states, the density of states in the conduction band, bandwidths, etc., cannot be reliably answered within the framework of the cluster theory. Such parameters are needed to study problems involving host-impurity interactions, absorption beyond the band edge, interband Auger transitions, and many other properties that require a detailed description of the density of states.

One of our main objectives was to determine the excitation processes of copper in ZnS using the calculated energy eigenvalues. We have succeeded in identifying the nature of transitions involving the Cu-ir and Cu-*G* centers. Although the excitation processes for the Cu-ir and Cu-*G* centers are very similar to those proposed by the LK and RSK models, respectively, the nature and origin of the various energy levels involved in the excitation process are found by theory to be very different from what is assumed in these models. It is also observed that the convergence of self-consistent-field cycles is better when the charge-compensating pairs are close to each other. Although the convergence strictly proves nothing. we tend to believe, based on our present study, that the charge-compensating ions prefer to be as close as possible. This is consistent with simple electrostatic attraction between ions of opposite charges, such as Cu and Cl, or that between Al and Cu, which is mediated by the intervening S atoms.

We are encouraged by the results of these calculations, as well as the earlier calculations[4] for ZnO, which indicate that such studies are useful in the design and improvement of luminescent materials. We look forward to the day when new phosphors can be designed by suitably combining theoretical results with minimal experimental work.

ACKNOWLEDGMENT

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[1] J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules* (McGraw-Hill, New York, 1944), Vol. 4, p. 216.

[2] R. A. Evarestov, Phys. Status Solidi B **72**, 569 (1975).

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

[4] K. C. Mishra, P. C. Schmidt, K. H. Johnson, B. G. DeBoer, J. K. Berkowitz, and E. A. Dale, Phys. Rev. B **42**, 1423 (1990).

[5] K. H. Johnson, H. J. Kolari, J. P. de Neufville, and D. L. Morell, Phys. Rev. B **21**, 643 (1980).

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

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

[8] K. H. Johnson, M. E. McHenry, 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. Krisin (Plenum, New York, 1987), p. 563; K. H. Johnson, D. P. Clougherty, and M. E. McHenry, Mod. Phys. Lett. B **3**, 867 (1989).

[9] M. Schoen, Z. Phys. **119**, 463 (1942); Ann. Phys. (Leipzig) [Folge 6] **3**, 333 (1948); H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953); N. Riehl and H. Ortmann, J. Phys. Radiat. **17**, 620 (1956).

[10] J. Lambe and C. C. Klick, Phys. Rev. **98**, 909 (1955), J. Lambe, *ibid.* **100**, 1586 (1955); J. Lambe and C. C. Klick, J. Phys. Radiat. **17**, 663 (1956).

[11] J. S. Prener and F. E. Williams, J. Phys. Radiat. **17**, 667 (1956); J. Electrochem. Soc. **103**, 342 (1956); J. Chem. Phys. **25**, 361 (1956); Phys. Rev. **101**, 1427 (1956).

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

[13] G. E. Arkhangel'skiy, N. N. Grigor'ev, A. V. Lavrov, and M. V. Fok, Proc. Lebedev Phys. Inst. **175**, 55 (1988).

[14] A. N. Botoev,, E. Yu. L'vova, and M. V. Fok, Proc. Lebedev Phys. Inst. **175**, 1 (1988).

[15] E. R. Ilmas and T. I. Savikhina, J. Lumin. **1&2**, 703 (1970).

[16] 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).

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

[18] S. P. Keller and G. D. Petit, Phys. Rev. **115**, 526 (1959).

[19] I. Broser, H. Maier, and H. J. Schultz, Phys. Rev. **140**, A2136 (1965); I. Broser, K. H. Franke, and H. J. Schultz, in *II-VI Semiconducting Compounds,* edited by D. G. Thomas (Benjamin, New York, 1967), p. 81.

[20] S. Shionoya, T. Koda, K. Era, and H. Fujiwara, J. Phys. Soc. Jpn. **19**, 1157 (1964).

[21] S. Narita and S. Sugiyama, J. Phys. Soc. Jpn. **20**, 153 (1965).

[22] For review of the models, see J. L. Birman, in *Proceedings of the International Conference on Luminescence,* edited by G. Szigeti (Hungarian Academy of Sciences, Budapest, 1966), p. 919.

[23] D. Curie, *Luminescence in Crystals* (Wiley, New York, 1963),

p. 114.

[24] F. A. Kroger, *The Chemistry of Imperfect Crystals* (North-Holland, New York, 1964).

[25] For example, an interstitial site for the Cu-B center was proposed in the following works: H. Blicks, N. Riehl, and R. Sizmann, Z. Phys. **163**, 594 (1961); J. Knolebich, N. Riehl, and R. Sizmann, *ibid.* **171**, 505 (1963).

[26] W. Walter and J. L. Birman, in *II-VI Semiconducting Compounds* (Ref. 19), p. 89.

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

[28] R. Dingle, Phys. Rev. Lett. **23**, 579 (1969).

[29] J. Schneider, in *II-VI Semiconducting Compounds* (Ref. 19), p. 40.

[30] The authors in Ref. 14 discussed the problem of the lack of an EPR signal from a divalent copper center in ZnS and seemed to favor the idea of a rapidly relaxing paramagnetic center near the divalent copper ion being responsible. However, it should be noted that an EPR signal has been observed for Cu^{2+} at 1–2 K [W. C. Halton, M. DeWit, and R. K. Watts, J. Phys. Chem. Solids **30**, 963 (1969), with $g=2.2$ In many ways, the Cu^{2+} center in ZnS behaves similarly to that in ZnO reported in Refs. 27 and 28].

[31] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1951).

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

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

[34] M. H. Sukkar, H. L. Tuller, and K. H. Johnson, in *Grain Boundaries,* edited by H. J. Leamy, G. E. Pike, and C. H. Seager (North-Holland, New York, 1982).

[35] J. A. Tossel, Phys. Chem. Miner. **2**, 225 (1978).

[36] X. Zeng and M. Huang, J. Lumin. **40&41**, 913 (1988), F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *Semiconducting Compounds,* edited by D. G. Thomas (Benjamin, New York, 1967), p. 503.

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