

Electronic Structure of the Centers in ZnS

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A model of the common sulfide luminescent centers is proposed. The mutual perturbation of crystal eigenstates and transition-metal (activator) d eigenstates is assumed to give rise to the excited and unexcited eigenstates of the center. For substitutional $\text{Cu}^+(d^{10})$ in zincblende, zeroth order crystal field theory predicts that two sets of occupied center ground-state levels (T_2 and E) originating from d^{10} will exist. Additional level splittings result from (a) the spin-orbit effect, and (b) axial crystal field splittings in wurtzite. Experiments on visible and infrared, excitation and emission, are used to make tentative assignments of magnitude of level splittings.

THE chemical constitution and electronic structure of the centers (luminescent and "killer") in ZnS have been discussed for some time.¹ The models which have been proposed for these centers describe the origin of the eigenstates of the center; the relationship of center states and band structure; the absorption, excitation, emission, quenching, and stimulation effects in diverse fashion. The polarization of luminescence,² the relationship of luminescence and photoconductivity,³ the mechanisms of energy transfer⁴ (e.g., between "blue" and "green" centers), and the electron and hole capture cross sections of excited and unexcited centers⁵ involve elaborations of the basic model.

"Band" models¹ identify the eigenstates of the center as perturbed states of the valence band, or conduction band. Owing to failure of the effective-mass theory for such deep states,⁶ it has not proven possible to put these models on a quantitative basis. Hydrogen-like,³ and associated donor-acceptor⁷ models place emphasis on screened Coulomb effects arising from (effectively structureless) point charges embedded in the lattice. These models ignore the activator atom/ion except insofar as it perturbs the lattice.

Here, we propose a model considering the eigenstates

of the center (which arise from the mutual perturbation of host and transition metal activator states) within the framework of crystal field theory⁸ modified by relevant aspects of band theory. Consider the green center in cubic ZnS:Cu, which we take as arising when Cu^+ is substituted⁹ for Zn^{++} . The $\text{Cu}^+(d^{10})$ is at a site of symmetry T_d . In the resultant crystal field, the d electrons are split into two groups: $d(T_2)$ and $d(E)$, with the six T_2 levels higher⁸ in energy than the four E levels by $10Dq$. The assumed order of states is shown in Fig. 1(a). (Note that we place the E levels slightly above the upper valence edge: It is possible that the E levels are ~ 0.2 eV below valence edge, in which case the change in Dq postulated below after excitation will not be needed. Only a detailed calculation, or additional experimental results, can settle this question.) Excitation¹⁰ by $0.339\text{-}\mu$ or $0.420\text{-}\mu$ light raises a T_2 or E , electron, respectively, to one of the center's excited states, close to the conduction band edge. After excitation and ionization the Cu^{++} center (d^9 with the hole in the T_2 levels) suffers a rearrangement: (a) Increased Coulomb attraction between Cu^{++} and S^- decreases the four Cu-S distances symmetrically (A_1 distortion); (b) Jahn-Teller effect may produce an asymmetrical (T_2 or E) distortion. The A_1 distortion will raise the Madelung potential (V_M), and the potential energy (eV_M) of the average d electron. We have estimated the increase in potential energy as ~ 0.60 eV. The total change in environment (a) and (b) of the Cu^{++} also may manifest itself in an increased $E-T_2$ splitting: ($10D'q'$). Green ($0.52\text{-}\mu$) emission occurs when an electron falls from one of the excited states of the center to the T_2 level; and the center then returns to its initial configuration. [See Fig. 1(b).] From infrared absorption, emission, quenching, and stimulation experi-

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¹ H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953); C. C. Klick and J. H. Schulman, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 5. Both articles review the literature and "band" models.

² A. Lempicki, Phys. Rev. Letters **2**, 155 (1959); J. Electrochem. Soc. **107**, 404 (1960); J. L. Birman, Phys. Rev. Letters **2**, 157 (1959); J. Electrochem. Soc. **107**, 409 (1960).

³ I. Broser and R. Broser-Warminsky, Z. Elektrochem. **61**, 209 (1957).

⁴ N. T. Melamed, J. Phys. Chem. Solids **7**, 146 (1958).

⁵ W. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958), especially p. 529, line below Eq. (2.11), and pp. 624-628.

⁶ W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 5, reviews the conditions under which effective-mass theory may apply quantitatively. For deep states, the center eigenfunctions must involve admixture of states from valence and conduction bands, for many k in the zone, in order to create a localized function.

⁷ The experimental evidence favoring association for the common, halide coactivated green, blue, and "orange-red" centers in ZnS seems questionable. The theory proposed by F. Williams, J. Phys. Chem. Solids **12**, 265 (1960) is essentially in the effective-mass framework (see footnote 6 above) but does not include enough states to be quantitatively accurate.

⁸ Crystal field theory is reviewed by D. W. McClure, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9. We use here McClure's notation for the irreducible representations of T_d , and crystal field parameters.

⁹ R. Bowers and N. T. Melamed, Phys. Rev. **99**, 1781 (1955) discuss the evidence that the green center is due to substitutional Cu^+ sites; and that at least one blue center is due to Zn^{++} vacancies.

¹⁰ S. P. Keller and G. D. Pettit, Phys. Rev. **115**, 526 (1959); A. Halperin and H. Arbell, Phys. Rev. **113**, 1216 (1959).

ments,¹¹ we provisionally assign¹² $Dq(=0.073 \text{ eV})=590 \text{ cm}^{-1}$ and $D'q'(=0.091 \text{ eV})=740 \text{ cm}^{-1}$.

We take the excited states of the center as arising from 4s-like conduction states of the 12 second neighbor Zn^{++} ions. This twelvefold degeneracy is split by the T_d field, giving for the excited states:

$$\psi^{\text{ex}} = S_{\text{Zn}}(A_1) + S_{\text{Zn}}(E) + S_{\text{Zn}}(T_1) + 2S_{\text{Zn}}(T_2). \quad (1)$$

where, e.g., $S_{\text{Zn}}(A_1)$ is a linear combination of the twelve Zn^{++} 4s states possessing the indicated symmetry. To include covalency effects in the center eigenfunction, we consider the 12-dimensional representation generated by the three 3p-like valence states on each of the four first neighbor S^- . We find, on reducing this representation,

$$\psi^{\text{cov}} = P_s(A_1) + P_s(E) + P_s(T_1) + 2P_s(T_2), \quad (2)$$

and the P are linear combinations with the indicated symmetry. Hence, for the eigenfunctions of the two states of the center we take

$$\psi(T_2) = d(T_2) + \alpha P_s(T_2), \quad (3)$$

$$\psi(E) = d(E) + \beta P_s(E), \quad (4)$$

where α and β are mixing (covalency) coefficients, which are probably small, but need to be determined.

To the extent possible, a theory of the centers based on this model, must concern itself with the calculation of: the local crystal field at the center (particularly, V_M , and V_4 , respectively, the Madelung and "octohedral" potentials); the $\psi(T_2) - \psi(E)$, $\psi(T_2) - \psi^{\text{ex}}$ energy separations and optical transition probabilities.

We propose that the blue, green and "red" luminescent centers in ZnS all arise from a common source: the perturbed d^{10} configuration of either Cu^+ or Zn^{++} . These ions may be located at different sites in the lattice or, in the case of the "self-activated" blue center (believed caused by Zn^{++} vacancies)⁹ perturbed by the absence of a second neighbor cation. The green and blue luminescence [separation in energy of the $\psi(T_2)$ and ψ^{ex} states] reflects largely the V_M at the center; the infrared effects [energy separation of $\psi(T_2)$ and $\psi(E)$ states] reflect largely the value of V_4 .¹³ Analogous arguments hold for the corresponding centers in hexagonal ZnS and CdS, when lower center site symmetry is considered. The eigenstates of "killer" centers Fe, Co, Ni can be treated in the same framework of perturbed d^n electron states with admixture of covalency [Eqs. (3) and (4)] and excited transfer states¹⁴ [Eq. (1)]. In the sense that the

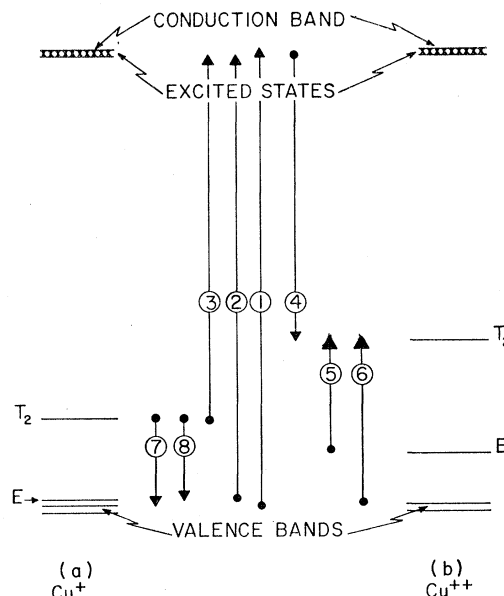


Fig. 1. Electronic structure of the green center in cubic ZnS:Cu; Cu^+ substituting for Zn^{++} . (a): The center (Cu^+) before excitation— T_2 levels contain 6 electrons, E levels contain 4. (b): The center (Cu^{++}) after excitation and ionization— T_2 levels contain 5 electrons, E levels contain 4. We assume that after ionization the T_2 — E separation has increased, and both levels have moved away from the valence band. Processes indicated are (1) band-band absorption,¹⁴ $\sim 0.331 \mu = 3.75 \text{ eV}$; (2) green center excitation,¹⁰ $\sim 0.339 \mu = 3.66 \text{ eV}$; (3) green center excitation,¹⁰ $\sim 0.420 \mu = 2.95 \text{ eV}$; (4) green emission peak, $\sim 0.522 \mu = 2.38 \text{ eV}$; (5) infrared absorption,¹¹ $\sim 1.30 \mu = 0.95 \text{ eV}$; (6) infrared absorption,¹¹ $\sim 0.95 \mu = 1.3 \text{ eV}$; (7) infrared emission,¹¹ $\sim 1.55 \mu = 0.80 \text{ eV}$; (8) infrared emission,¹¹ $\sim 1.67 \mu = 0.74 \text{ eV}$. The initial electron state in (1)–(8) is indicated by a dot. Data are numerically inconsistent as (7) and (8) are taken at 90°K , while (1)–(6) are for room temperature. Also, data on hexagonal ZnS:Cu have been used as there are no comparable data on cubic ZnS:Cu. Thus, axial splittings and polarization of absorption and emission in hexagonal structure, as well as spin-orbit effect are neglected. As indicated in the text, it is possible that the E — T_2 separation does not change after excitation, in which case the E levels in (a) are below the valence band, and processes (7) and (8) are from valence bands to the T_2 levels.

center levels are close to the valence band, that valence band states (3p-like functions of S^-) are admixed into the center eigenfunctions, and that a "free" electron recombines with a bound hole to produce luminescence, this model resembles the familiar Schoen-Klasens model.^{1,15} Our model of the origin of the center levels is, however, quite different, and, we believe, offers more possibility of quantitative elaboration.

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some 5–8 eV lower than the lowest excited state ($\text{Fe}^{++}4p$) which they consider, their analysis and conclusions require re-examination.

¹⁵ Recent work on the polarization of luminescence and band structure in CdS and ZnS single crystals: A Lempicki, J. Birman, H. Samelson, G. Neumark (to be presented at the International Conference on Semiconductors, Prague 1960, and published in the Proceedings) seems to indicate the failure of the Lambe-Klick model for long wavelength emission.

¹¹ Reviewed by E. F. Apple and J. S. Prener, J. Phys. Chem. Solids **13**, 81 (1960).

¹² The spin-orbit effect, which may be large in Cu^{++} , has been neglected here.

¹³ For the red center, believed due to interstitial Cu^+ in ZnS (see reference 9), it is most reasonable to place the Cu^+ at an interstitial site whose symmetry is approximately O_h (sixfold coordination). The order of T_2 and E levels is then inverted from that shown in Fig. 1, and the separations may be greater.

¹⁴ W. Low and M. Weger, Phys. Rev. **118**, 1119 (1960), have studied optical and PMR absorption in ZnS:Fe. In their analysis, covalency and transfer effects are ignored. Since the transfer-excited states [our Eq. (1)], e.g., conduction band, of ZnS are