LUMINESCENT TRANSITIONS ASSOCIATED WITH DIVALENT COPPER IMPURITIES AND THE GREEN EMISSION FROM SEMICONDUCTING ZINC OXIDE

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Luminescent transitions at divalent copper impurities in ZnO give rise to a closespaced, no-phonon doublet at ~ 2.8590 eV, as well as a broad multiphonon side band. The transition is found to be an optical charge transfer between a highly shielded localized level of the copper impurity and a level which is strongly perturbed by the valence-band states of the crystal. The analysis provides information about the role of deep acceptor states in electronic processes in covalent solids.

In this Letter we describe the transition, and identify the center, responsible for the well-known^{1,2} but hitherto not understood green emission from zinc oxide.

Zinc oxide crystallizes in the hexagonal wurtzite structure. The crystals used here were large, perfectly formed, transparent hexagonal rods with *n*-type conductivities in the range σ = 0.1-1.0 Ω^{-1} cm⁻¹. Spectrographically determined impurities are copper (4±2 ppm), aluminum (<2 ppm), iron, magnesium, silicon, boron, and indium. The emission was excited by a pulsed nitrogen laser ($h\nu$ = 3.678 eV, above the band gap) or by a 200-W high-pressure mercury lamp ($h\nu \simeq 3.4$ eV, below the band gap but into the absorption band of the green center). Experiments were conducted on crystals held at 20.4°K and below.

Figure 1 shows the broad-band emission seen at 1.6 °K. At low temperatures the band decays exponentially, $\tau = 440 \pm 10$ nsec. Sampling small (5 Å wide) regions of the band demonstrates that the whole system decays with the same lifetime, a fact that is confirmed by time-resolved spec-



FIG. 1. Broad green band emission from ZnO at 1.6°K. The enlarged portion shows details of phonon cooperation in the region of the no-phonon lines.

troscopy.³ The short lifetime indicates that the transition is moderately allowed.

In the no-phonon region there are two sharp lines separated by ~0.1 meV, Fig. 2. The ratio of the intensities of the two lines (called A and B herafter), and indeed the absolute intensity of the two lines, remains constant over the range $1.6-20.4^{\circ}$ K. The former quantity is $A/B = 2.25 \pm 0.05$ and is not dependent upon crystal origin.

We have completed experiments that describe the behavior of these lines and/or the band as a function of temperature, uniaxial stress, ap-



FIG. 2. High-resolution spectra in the region of the A and B no-phonon lines near 2.8590 eV. The intensity ratio $A/B = 2.25 \pm 0.05$ does not vary in the range 1.6-20.4°K.

plied magnetic fields, and polarization. Radiative lifetimes and time-resolved spectra have also been obtained. Although all are necessary for a complete description⁴ of the emission, here we consider only the details of the experiments in applied magnetic fields. These results are sufficient to allow a detailed discussion of the transition mechanism, and when they are considered with earlier EPR^{5,6} and optical absorption⁵ studies, the center at which the transitions occur is identified. This is the first <u>direct</u> coupling of EPR and visible emission to give a positive identification of a luminescence center in a Π -VI semiconductor.

When the applied magnetic field *H* is parallel to the crystal *c* axis, each zero-field line splits into four symmetrically disposed components. There is no evidence of any interaction between the components of the *A* and *B* lines and the splitting patterns are linear in applied field strength. As θ , the angle between the crystal *c* axis and *H*, is varied in the range $0^{\circ} \le \theta \le 90^{\circ}$, the set of four lines derived from *A* behaves in the same manner as does the set arising from *B* (Fig. 3). Furthermore, each component of *A* maintains a constant intensity ratio to the equivalent component in set *B*.

We believe that the two lines A and B arise from identical electronic processes taking place at similar, but separate, sites. These sites are associated with different nuclear isotopes of the same foreign impurity atom. In the absence of energy transfer, the ratio of the emission intensity at the lines A and B must correspond to the natural abundance of these isotopes; the A/Bratio (Fig. 2) is in excellent agreement with the Cu^{63}/Cu^{65} ratio of 2.24. This observation, taken together with the absence of thermalization between the AB lines in zero field, the invariance of the A/B ratio from crystal to crystal, the known presence of copper in our samples, and the identical Zeeman patterns generated by the A and B lines gives strong support to this isotope explanation⁷ of the AB pair.

Dietz, Kamimura, Sturge, and Yariv⁵ and Dewit and Estle⁶ have reported g factors for the ground state of divalent copper on a zinc site in copper-doped ZnO. From EPR experiments they find

 $g_{\parallel} = +0.7383 \pm 0.0003$ and $g_{\perp} = +1.5237 \pm 0.003$.

Analysis of our Zeeman data (Fig. 3) generates the following g factors⁸ (since both patterns are the same, we no longer distinguish between the



FIG. 3. Complete Zeeman pattern for the A/B lines as a function of applied field strength and θ , the angle between the applied field and the crystal c axis. At the maximum field strength (30.4 kG) there are several accidental degeneracies. The deviation from the simple pattern at intermediate values of θ is not discussed in this Letter.

A and B lines):

 $g_{\parallel}' = 0.73 \pm 0.05, \quad g_{\perp}' = 1.48 \pm 0.05;$ $g_{\text{isotropic}}'' = -2.36 \pm 0.1.$

The single-primed g factors are very distinctive. They correspond so closely to those derived from EPR that the association of the green emission with a <u>divalent</u> copper ion on a zinc lattice site must be considered established.

Because of the short optical lifetime of the excited state, $\tau \sim 4 \times 10^{-7}$ sec, thermalization between the magnetic substates has not been observed at low temperatures (i.e., between 1.6 and 4.2°K). Presumably, the spin-lattice relaxation time of the excited state is long compared with the radiative lifetime. Thermalization has been observed between 4.2 and 20.4°K (where the spin-lattice relaxation time is much shorter). The results prove that the isolated Cu⁺⁺ ion is the ground state of the green emission. Both ground and excited states transform like Γ_4 of C_{3V} .

In terms of the band theory of solids, as usually applied to semiconductors, Cu^{++} (electronic configuration $\cdots 3d^9$) on a zinc site is a neutral acceptor. A plot of the green emission intensity versus excitation intensity is a straight line with slope +1, indicating that the ground state of the green emission is present in the unexcited crystal. Evidently the acceptor binding energy is large enough, and the Fermi level low enough, for the hole to be stable in the copper 3d shell. Since the crystals are *n* type, the acceptor

ground state must lie above the shallow donor levels ($E_D \sim 100$ meV), leading to an acceptor binding energy of ≥ 3.3 eV. Dietz et al.⁵ have constructed detailed wave functions for the Cu^{++} ground state. To this information we now add a binding energy, and for the first time the ground-state wave function and binding energy of a very non-effective-mass-like deep center are available, and should prove invaluable in the discussion⁴ of the origin of the binding energy of deep centers. Finally, we propose to extend the usual⁹ symbolic representation of neutral and ionized impurities to include more specifically an acceptor with a tightly bound hole in the 3d shell. Thus we write the ground state (and excited d states) of the neutral copper acceptor as [+-].

In our model of the excited state the copper 3*d* shell is filled. A hole exists in the vicinity of the copper site (the excited state g factor is -2.36), although it is no longer in the highly shielded, localized level of the copper atom. From the energy of the transition (2.86 eV) and the lower limit of E_A (~3.3 eV) the excited state of the green emission lies ~450 meV above the valence band maximum, and in the effectivemass approximation¹⁰ it will have a Bohr radius of ~ 2.4 Å. The hole is thus guite localized, even in the excited state. The latter is quite like the ground state of a simple neutral acceptor, i.e., no d shell holes but with a hole moving in the vicinity of the impurity. Hence this state may be represented by the usual neutral acceptor symbol, \bigcirc^+ . A tight-binding^{5,11} description would associate the excited-state hole with the four oxygen atoms surrounding the copper impurity (the average Zn-O band length is ~1.99 Å). The luminescence process is thus the transfer of a hole from an orbital encompassing these oxygen

atoms to a highly shielded, localized level of the copper atom.

This is the first detailed study of a transition between a highly shielded, localized level of an impurity and a level which is strongly perturbed by charge-transfer (valence band) states in a crystal. As such it provides new and important information about the detailed role of copper, and presumably other deep acceptors, in electronic processes in covalent semiconducting solids.

The author wishes to acknowledge valuable discussions with R. E. Dietz, P. J. Dean, and R. A. Faulkner.

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⁷Attempts to prove this point, using isotopically enriched crystals, have not yet been successful. This is attributed to strain broadening of the no-phonon pair.

⁸The g factors recently reported [R. Dingle, Bull. Am. Phys. Soc. 13, 1476 (1968)] require revision.

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ELECTRON SPIN RESONANCE IN AMORPHOUS SILICON, GERMANIUM, AND SILICON CARBIDE

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The g values, line shapes, and linewidths of the ESR signals from within the bulk of amorphous silicon, germanium, and silicon carbide are found to be similar to those of the electron states observed in the surface regions of the corresponding crystalline forms. Discussion is given in terms of a microcrystalline model.

We report the measurement and identification of the ESR signals in thin films of amorphous silicon, germanium, and silicon carbide. The gvalues, line shapes, and linewidths of the spinresonance signals are found to be similar to those of the electron states observed in the surface regions of the corresponding crystalline forms. However, in the amorphous films, the