Infrared luminescence of ZnO:Cu^{2+}(d^9)

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The $^2E(D) \rightarrow {}^2T_2(D)$ emission of substitutional Cu^{2+} in ZnO has been observed in the 3700–5800-cm^{-1} spectral range under 50-keV electron-beam excitation at cryogenic temperatures. The excitation mechanisms of this cathodoluminescence are discussed and compared with concurrent photoluminescence experiments.

Substitutional copper enters the lattice of ZnO as Cu^{2+}($3d^9$) on a zinc site, i.e., in tetrahedral coordination to first order.[1] Its cubic crystal-field splitting is manifested by the corresponding $^2E(D) \leftarrow {}^2T_2(D)$ absorption[2–5] characterized by a no-phonon-line (NPL) doublet at 5820 and 5780 cm^{-1} (vacuum wave numbers after Ref. 6) indicating the (higher) Γ_4 and (lower) Γ_5, Γ_6 components of the ^2E excited state split under the trigonal symmetry (point group C_{3v}; labeling after Ref. 7) of the hexagonal ZnO host. The absorption was positively identified as Cu^{2+} internal transition when a Cu isotope splitting and Zeeman g factors agreeing with electron paramagnetic resonance (EPR) findings were measured.[8]

While in the homologous compounds ZnS and CdS the respective absorptions are related to emission spectra featuring coincident NPL transitions,[9] no inverse $^2E(D) \rightarrow {}^2T_2(D)$ luminescence could be detected with ZnO. An emission spectrum displayed by most ZnO:Cu samples starts with a NPL at 6886 cm^{-1} and extends into the region of the Cu^{2+} absorption near 5800 cm^{-1}, but its spectral peculiarities, including the g factors, contradicted its interpretation as the missing inverse Cu^{2+} transition.[10,11] A proposal to assign this spectrum to a Cu^{3+}($3d^8$) internal emission embraced much of the then-known experimental evidence.[12] This description was overruled recently, however, when more detailed Zeeman data initiated an assignment to V^{3+}($3d^2$) transitions[13] akin to those studied earlier with ZnS.[14] Vanadium was thus proven to be a ubiquitous impurity in ZnO.

In the present paper, excitation of the formerly missing internal Cu^{2+} emission by medium-energy electrons is reported. Experiments were carried out with an electron-optical bench,[15] the utilized version providing a two-stage imaging by electromagnetic lenses. The samples were irradiated by an electron current of 20 μA at 50 keV, chopped with 80 Hz. They were attached by an indium solder to the cold finger of a commercial liquid-helium cryostat. The cathodoluminescence was analyzed by a grating monochromator of 25 cm focal length with a 1:3.5 aperture ratio and detected by means of a Peltier-cooled PbS detector and conventional lock-in electronics.

The measured spectrum (Fig. 1) displays a striking similarity to the known emissions[9] of ZnS:Cu and CdS:Cu, suggesting the same general mechanism of vib-

ronic coupling. A NPL at 5782 cm^{-1} (vacuum wave number) represents the lower-energy component of the doublet known from the absorption. No preferential polarization of this line was found, but the given setup is not particularly suited to polarization studies. A full width at half height (FWH) of approximately 40 cm^{-1} is recorded at $T \simeq 10$ K, the temperature being determined by an equilibrium between He cooling and heating under the electron beam. While the first satellite at a distance of 100 cm^{-1} from the NPL indicates TO(Γ) coupling (cf. Table IV of Ref. 12), the ensuing subsidiary maxima and shoulders are not related to host lattice modes in a straightforward manner. The dominating peak at 4510 cm^{-1} displays a shift of 1272 cm^{-1} versus the NPL and is thus neither a plausibly derivable phonon-assisted transition nor a representative of spin-orbit splitting in the
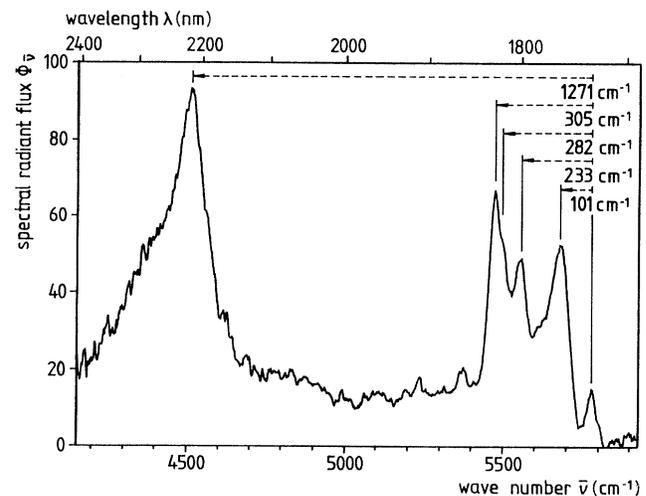

FIG. 1. Cathodoluminescence spectrum of ZnO:Cu crystal. Corrected for grating efficiency, transmission curve of the optical path, and spectral response of the detector by reference to an 800 °C black-body source. Not included in this rectification is the transmittance of the infrasil cryostat window and reflectance of two front-surface mirrors. Excitation by 50-keV electrons. $T \simeq 10$ K. Spectral slit width: $\Delta\lambda \simeq 10$ nm; diameter of electron probe: 1 mm.

$^2T_2(D)$ ground multiplet, which is much smaller even for the free Cu^{2+} ion. Probably a situation comparable to ZnS:Cu is met here where only dynamic Jahn-Teller coupling can account for the fine structure of the luminescence spectrum.[16-18] Very similar spectra are obtained from several vapor-grown ZnO:Cu crystals from different sources. The samples contain traces of vanadium, but the mentioned V^{3+} emission is extremely weak under cathode-ray excitation.

A faint Cu^{2+} emission is also measured under broad-band excitation with light within the range 23 000–33 000 cm^{-1}. A photoluminescence experiment carried out recently by a group at the Berlin Technical University[19] by means of a Ge detector yields the emission NPL at 5781 cm^{-1} with a FWH of 8 cm^{-1} and the first satellite at 5687 cm^{-1}, under nearly monochromatic excitation at 6850 cm^{-1}. It thus becomes clear that the electron-beam source employed is an effective but not the only means to excite the studied Cu^{2+} emission.

Under excitation with electron pulses of 5-μs duration, the decay of luminescence at $T \simeq 10$ K has an approximate time constant $\tau \simeq 0.2$ μs, measured with an InSb detector and a transient recorder. This τ value is about one-fifth of those of the Cu^{2+} emissions[20] in ZnS and CdS, the same order of magnitude indicating a comparable oscillator strength.

Excitation of the Cu^{2+} ir emission by the medium-energy electrons utilized in our experiment becomes feasible by generation of electron-hole pairs (generation energy E_g, the band gap of ZnO). The quasineutral oxidation state Cu^{2+}, whose presence in the used crystals is confirmed by their transmission spectra, is assumed to be the initial charge state of the luminescent center (cf. Ref. 1). The most plausible sequence of electronic processes leading to the observed internal Cu^{2+} emission $h\nu_{ir}$ is

$$E_g \rightarrow e_{CB}^- + e_{VB}^+ , \tag{1}$$

$$Cu^{2+}(d^9) + e_{CB}^- \rightarrow Cu^+(d^{10}) + E^{9,10}(t_2) , \tag{2}$$

$$Cu^+(d^{10}) + e_{VB}^+ \rightarrow [Cu^{2+}(d^9)]^* + E_{9,10}(e) , \tag{3}$$

$$[Cu^{2+}(d^9)]^* \rightarrow Cu^{2+}(d^9) + h\nu_{ir} . \tag{4}$$
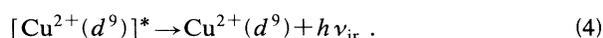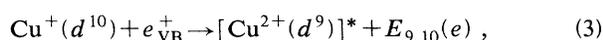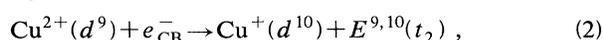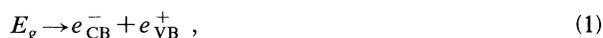
The intermediate charge state Cu^+ is known to occur in ZnO; the transition energy $E^{9,10}(t_2) \simeq 1500$ cm^{-1} is likely

to be dissipated in nonradiative processes while $E_{9,10}(e) \simeq 21\,000$ cm^{-1} could be related to a yellow emission observed with our crystals. For a visualization of reactions (1)–(4) see Fig. 8 of Ref. 12.

Should the hole e_{VB}^+ generated in process (1) recombine with the copper center sooner than the electron e_{CB}^-, processes (2) and (3) would be replaced by

$$Cu^{2+}(d^9) + e_{VB}^+ \rightarrow [Cu^3(d^8)]^* + E_{8,9}(e) , \tag{5}$$

$$[Cu^{3+}(d^8)]^* + e_{CB}^- \rightarrow [Cu^{2+}(d^9)]^* + E^{8,9}(t_2) , \tag{6}$$
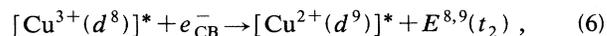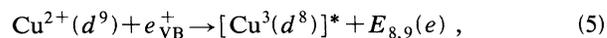
followed again by the radiative process (4). Although the sequence (1), (5), (6), (4) could yield a possible excitation channel, its realization is, at the very least, questionable since $Cu^{3+}(d^8)$ is now merely a hypothetical charge state.

Finally, a direct excitation of Cu centers through impact ionization by the impinging electrons is conceivable, although these processes are evidently rare because of the low concentration of impurities (10^{-5} mole Cu/mole ZnO estimated):

$$Cu^{2+}(d^9) + E_{9,10}(t_2) \rightarrow Cu^+(d^{10}) + e_{VB}^+ , \tag{7}$$

$$Cu^{2+}(d^9) + E^{8,9}(e) \rightarrow [Cu^{3+}(d^8)]^* + e_{CB}^- . \tag{8}$$
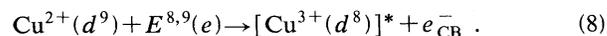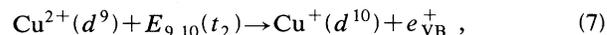
Both reactions could, in principle, initiate the radiative process (4), viz., via (3) or (6), respectively. Regarding (8), the reservations put forward concerning Cu^{3+} would hold. At any rate, reaction (7) is likely to take place under light irradiation. It would provide a means to excite the Cu^{2+} emission by visible light. In addition, the internal Cu^{2+} absorption, i.e., the inverse of process (4), would also produce an effective mode of excitation.

In conclusion, the experiments presented demonstrate the debated occurrence of the internal d^9 emission of Cu^{2+} substituting for Zn in ZnO, under suitable conditions of excitation. Coincidence of the emission NPL with one of the two NPL known from absorption spectra and its vibronic contour identify this luminescence. The scheme of electron transitions involving the significant Cu impurity in this semiconducting material is thus consolidated.

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