



Fig. 2. Fluorescent emission energies in the Zn(S, Se, Te) system (as measured at 77°K).

1% of the ZnS by ZnSe causes a strong green emission band (peak ~ 2.46 eV) besides the blue, and both bands can then be followed through the entire range up to ZnSe:Ag, Cl. Hence, the 2.76 eV band (blue) of ZnS:Ag, Cl corresponds to a band at ~ 2.61 eV (blue-green) in ZnSe:Ag, Cl, while the 2.22 eV band of ZnSe:Ag, Cl (yellow) corresponds to the (ordinarily almost or completely absent) green emission band of ZnS:Ag, Cl located at ~ 2.46 eV. A similar appearance of a new emission band is to be observed if some of the ZnSe is replaced by ZnTe (also shown in Fig. 1).

This behavior with a variation of the host lattice from ZnS over ZnSe to ZnTe may vary considerably depending on the particular defect or impurity producing the emission. For instance, the complex "A₂-emission" near the optical adsorption edge of ZnSe is no direct continuation of the, also complex, near-edge emission of ZnS, and the two well-known Cu-emission bands in ZnS (blue and green) exhibit a distinct "jump" toward lower quantum energies if only a few per cent of the ZnS are replaced by ZnSe. Except for these irregularities, however, all peak positions vary considerably less than the band gap does over the same variation of the host lattice composition. Hence, if Fig. 4 by Halsted, Aven and Coghill is redrawn in a way as to correspond to experimental evidence in between ZnS and ZnSe, and in between ZnSe and Te, one obtains Fig. 2 here which clearly shows that a simple interpolation can be dangerous.

R. E. Halsted, M. Aven, and H. D. Coghill: W. Lehmann's 77°K results on ZnSSe:Ag provide a worthwhile addition to the literature. They appear to be in accord with the cited 300°K data of Leverenz and of Klasens. The recent analysis of these data by W. H. Fonger³³ is also relevant. The "jumps" apparent in the ZnSSe:Cu data of Lehmann are not evident in the work of Morehead. The jump in his edge emission data is particularly striking, if confirmed. Lehmann's results do indeed suggest that estimates of the positions of spectra derived by simple extrapolation from "analogous" end points may be invalid in ZnSSe:Ag, and perhaps more generally. This would appear to be an important point meriting further study. Our paper was motivated in part by the desire to raise this very question. We clearly distinguish between experimental data and possible implications of the data.

It should be noted, however, that the problem of sample preparation and emission band identification in

³³ W. H. Fonger, *Phys. Rev.*, 137, A1038 (1965).

such investigations is not simple. Trace impurities can exert a profound influence. It is interesting that Bundel's results on self-activated ZnSSe phosphors coincide closely with Morehead's data on the ZnSSe:Cu system. No evidence for the 2.46 eV ZnS:Ag band cited by Lehmann has been found at this laboratory in Cu-free material. We are impressed by Lehmann's conviction that the ZnS edge emission exhibits a 0.8 eV shift with small Se additions. We hope that additional experimental data on the ternary compounds may soon resolve these questions.

Hydrogen Evolution at a Solid Indium Electrode

J. N. Butler and M. Dienst (pp. 226-232, Vol. 112, No. 2)

R. Piontelli and B. Mazza³⁴: The reference given by the authors to the work done in our Laboratory³⁵ on the cathode behavior of indium, completely overshadows the main result, which may deserve to be recalled also in view of the study of the hydrogen discharge on indium. This consists in the abrupt increase of the cathode overvoltage (in the order of: 0.4-0.5v), encountered when plating indium from some concentrated baths, and long before attaining the "limit current conditions" (for instance at current densities in the order of 10 amp/m²).

This phenomenon is typical for: sulfate, sulfamate, perchlorate baths, while in chloride, or by adding adequate chloride amounts to the baths above, the insurgence of this "cathodic passivity" effect is very much displaced toward high values of the current density.

This phenomenon has been successively recognized by Kangro and Weingärtner,³⁶ who appear to consider it to be correlated with the participation of In⁺ to the cathode processes.

In spite of the very extensive work carried out in this laboratory on this matter, some important aspects remain still unexplained, and they will require supplementary effort.

In any case, our results indicate the essential part taken by the hydrogen interference in the electrode processes, and suggest the indium behavior toward hydrogen to be largely different from the mercury one.

Once more the explicit and thorough consideration of the structural properties of the metallic phase and of its surface appears to be an indispensable step to make the kinetic theories some thing more than a formalistic game.

J. N. Butler and M. Dienst: Drs. Piontelli and Mazza have pointed out the importance of the hydrogen evolution reaction in the electrodeposition of indium from solution. Although there may be complex interactions between the hydrogen evolution and indium deposition reactions, we hope that studies of each of these processes, under conditions where the other does not occur, will further the understanding of those phenomena observed in practical situations.

Kinetics of the Silicon-Silicontetrachloride Reaction in a Flow System

Ole Alstrup and C. O. Thomas (pp. 319-323, Vol. 112, No. 3)

S. E. Craig, Jr.³⁷: The interesting and timely work of Alstrup and Thomas conclusively proves that Mon-

³⁴ Institute for Electrochemistry, Physical Chemistry and Metallurgy, Milan Polytechnic, Milan, Italy.

³⁵ R. Piontelli and M. Simonetta, *Gazz. Chim. Ital.*, 79, 716 (1949); R. Piontelli and G. Poli, Proc. 2nd Meeting C.I.T.C.E., Milan 1950, p. 136, Tamburini, Milan (1951); R. Piontelli, G. Poli, and G. Serravalle, *Rend. 1st Lomb. Sci. Lett. (A)*, 93, 301 (1959); G. Serravalle, *ibid.*, 93, 653 (1959); G. Serravalle and B. Mazza, *Electrochim. Acta*, 8, 313 (1963).

³⁶ W. Kangro and F. Weingärtner, *Z. Elektrochem.*, 58, 505 (1954).

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