PRESSURE EFFECTS, INFRA-RED STIMULATION AND QUENCHING ON THE LUMINESCENCE OF BLUE EMITTING ZnS:Cu PHOSPHORS*

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Detailed study of the emission and excitation spectra, hydrostatic pressure effects as well as infra-red stimulation and quenching show that blue copper centers are *not* truly localized centers such as Tl^+ in KCl, *not* conventional donor-acceptor centers, but have some kind of an intermediate character.

1. Introduction

The mechanism of the blue emission from copper-activated ZnS phosphors (B–Cu emission) is still controversial. Isolated substitutional Cu^{2+} ions produce the infra-red transitions [1, 2]. The green emission (*G*–Cu emission) is ascribed to a donor-acceptor type transition [3] between a deep donor, for instance Cl^- or Al^{3+}, and the copper acceptor level. Riehl and coworkers [4, 5] assume that the *B*–Cu emission from highly doped samples comes from more complex centers, created by the association of an interstitial copper ion with a substitutional one. Compensation of two substitutional copper ions by a neighbouring (S) vacancy has also been considered.

Now a direct transition from the bottom of the conduction band, or from a shallow donor level, to the T_2 level of the Cu^{2+} ion is allowed [6]: such a transition may result in a blue emission, in which the ground state may be the same as for the *G*–Cu emission [7]. More recently, Grasser et al. [8] have shown that an emission whose spectral characteristics (peak position, bandwidth and temperature shift) are identical with those of the *B*–Cu emission may be as well observed upon ultra-pure phosphors with an undetectable concentration of copper (in their experiments less than 2 p. p. m.). Such a result is not surprising if we consider that a Zn vacancy produces a ground state level whose energy

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on the classical valence band — conduction band scheme is not far different from that of the copper ion.

Most probably, several kinds of copper blue emissions can occur. The main condition for observing these blue emissions is a low concentration in deep donors: if the concentrations in deep donors and deep acceptors are about the same, then the conventional D–A emission turns out to be the most important one.

Let us remember that the *B*–Cu emission is easily separated from the self-activated (SA) blue emission in the following way:

(a) the SA bandwidth is larger, about 0.45 eV at room temperature (RT), while both the *B*–Cu and *G*–Cu bands have approximately the same width, i. e. about 0.33 eV at RT [9].

(b) for the *B*–Cu emission, the shift in the peak position of the band takes place towards higher energies when temperature is lowered; it occurs in the opposite direction for the SA emission.

Time-resolved spectroscopy [3] has shown that for both *G*–Cu and SA bands a shift is observed towards low photon energies for increasing decay times, in agreement with the D–A model, while no displacement has been found for the *B*–Cu emission. Similarly, no evidence has been given for a shift of the *B*–Cu band for increasing excitation intensities [3].

Polarization experiments do not lead to quite conclusive results [10–12]. A rather low symmetry type center is involved in the *B*–Cu emission, but the assumptions of C_{3v} and C_{2v} symmetries (perhaps also C_s) are both in agreement with the available experimental evidence. On the other hand, for the SA emission Shionoya and Koda found unambiguously that the emitting center is of the C_{3v} type [13].

2. Materials; emission and excitation spectra

We describe here mainly experiments which have been performed upon a blue ZnS: Cu, Cr, Cl crystal, which has been grown by the high-pressure method in the laboratory of Prof. Shionoya in Tokyo. This crystal is labelled "19" in what follows. The basic material was a powder phosphor ZnS: Cu 5×10^{-5}, Cr 5×10^{-6}, Cl 10^{-2}, which has been used previously for EPR studies in the laboratory of Prof. Kallmann in New–York.

Both the powder and the crystal show simultaneously the *B*–Cu and the *G*–Cu emissions; incidentally, the *B*–Cu emission is found to be relatively stronger in the crystal.

The peak position of this band is at 2.692 eV (460.5 nm) at RT and at 2.771 eV (447.5 nm) at 4.2 K. Such a shift occurs indeed in the right direction for *B*–Cu centers; the numerical values for the peak positions themselves correspond to a faulted cubic ZnS crystal.

The bandwidth $2W$ of the blue band, slightly corrected from the high energy tail of the green band, has been evaluated $2W \sim 0.305$ eV at room temperature. It follows rather accurately the simple formula:

$$W(T) = W(0\,\mathrm{K})\left[\coth\frac{h\nu_e}{2kT}\right]^{1/2} \tag{1}$$

(without any additional correction term), with the extrapolated value for low temperatures:

$$2\,W(0\text{ K}) = 0.233\text{ eV}.$$

Such a result gives some support to the use of the configurational model in the next paragraph. The vibrational frequency of the ligand ions coupled with the excited state of the center is:

$$\nu_e = 9 \times 10^{12}\text{ s}^{-1}.$$

Much smaller values have been found for other kinds of localized centers in Zinc sulphide, for instance:

$$\nu_e = 3\text{–}4 \times 10^{12}\text{ s}^{-1} \text{ for SA centers [14]}$$

$$\nu_e = 4.8 \times 10^{12}\text{ s}^{-1} \text{ for the red band of ZnS: Pb [15].}$$

On the contrary, for the D–A pairs involved in *G*–Cu emission, it is well known that ν_e is not far different from the frequency of the LO phonons, i. e. $11 \times 10^{12}\text{ s}^{-1}$.

We received slightly different values for the powder from which the crystal "19" has been prepared, but formula (1) still holds.

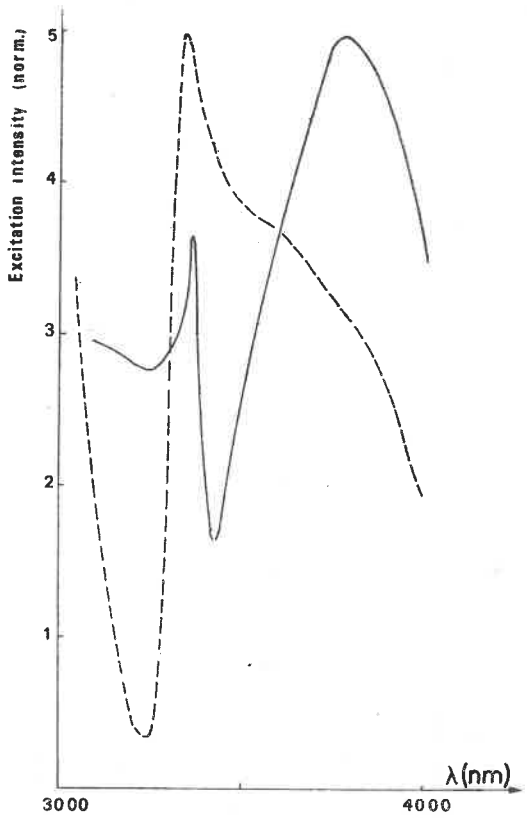

Fig. 1. Excitation spectrum of ZnS: Cu, Cr, Cl crystal "19". Solid line: 300 K, dashed line: 4.2 K

The excitation spectrum (Fig. 1) is more complex than the emission spectrum. A sharp maximum occurs near the band gap, which is due to excitonic excitation of the centres, followed by a lower energy excitation band peaked at 3.263 eV (380 nm) at RT. In agreement with Shionoya and co-workers [10, 13], we ascribe this band to direct excitation of the *B*–Cu centers, because such an excitation results in a higher polarization rate for the emitted radiation (when polarized radiation of course is used for exciting the sample).

For the calculations to be described below, we need the position of this band at low temperatures. It is seen on Fig. 1 that the bands are then not well resolved; if we assume that the temperature shift is the same for the excitation and the emission peaks, then we may accept 3.34 eV for the excitation energy at low temperatures, and this figure looks reasonable.

With other coactivators, i. e. Al^{3+} instead of Cl^{-}, the main features of the emission and excitation spectra are the same, but slightly different numerical values are obtained. Most probably, the nature of the coactivator is mainly involved in the excited state of the center rather than in the ground state, but no totally conclusive argument can be given at present.

3. Hydrostatic pressure experiments

Let us turn back to crystal "19". Fig. 2 shows the spectral shift of the emission band versus pressure. This shift has been found accurately linear in the whole range of pressures we could apply (from 1 bar to 8 Kilobars):

$$\frac{dE}{dP} = 6.2 \text{ meV/Kbar}. \tag{2}$$

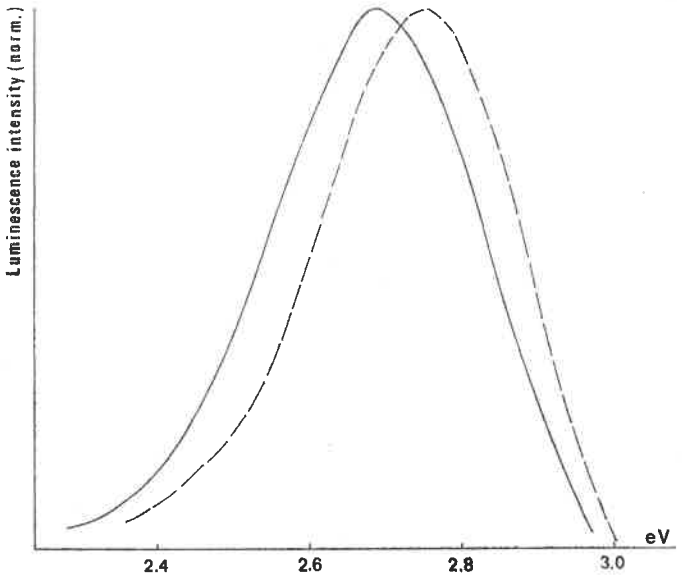

Fig. 2. Effect of hydrostatic pressure upon the emission spectrum of the ZnS: Cu, Cr, Cl crystal "19". Solid line: 1 bar, dashed line: 8.02 Kilobars

TABLE I

Summary of pressure effects on ZnS phosphors

SA blue	+8.3 meV/Kbar	[16]
	+10	[17]
B—Cu	+6.9	[16]
	+6.2	present work
G—Cu	+6.7	[16]
	+6.5	[17]
B—Ag	+4.7	[16]
	+7	[17]
Mn	−2.3	[16]
	−3.1	[18]
Pb green	0	[16]
	−1.6	[18]
Pb red	−1.38	[15]
Fe red	+7.9	[19]
absorption edge	+9	[17]

It may be seen in Table I that, except perhaps the fact that for SA centers the magnitude of the shift is approximately the same as for the gap, no straightforward conclusion can be obtained from these data. More specifically, the difference between the magnitude of the shift for the *B*–Cu band and the *G*–Cu band, if any, is smaller than the experimental errors. Thus some more detailed analysis appears to be necessary.

From the numerical value (2), and from the above data on emission and excitation spectra, we can derive the following results (the method for performing the calculations, on the basis of Alers and Dolecek's theory [20], is described in [15] and the notations here are the same as in this paper):

Stokes shift between excitation and emission peaks: 0.57 eV;

Displacement of the equilibrium position of the ligand ions between the excited state and the ground state: $X_0 = -0.07$ Å;

Ratio of the force constants K_e in the excited state and K_g in the ground state: $\alpha = K_e/K_g = 1.06$;

Ratio of the coupling constants of the center with pressure: $\beta = A_e/A_g = 1.026$;

Magnitude of these coupling constants:

$$A_e = 3970\,\text{Å}^2, \quad A_g = 3870\,\text{Å}^2.$$

It is perhaps more interesting to visualize these coupling constants as respective areas $A_e = \pi r_e^2$ and $A_g = \pi r_e^2$ and $A_g = \pi r_g^2$, in which r_e and r_g are expected to have approximately the same size as the center:

$$r_e = 35.5\,\text{Å}, \quad r_g = 35.1\,\text{Å}.$$

While performing these calculations, we assumed that the total mass of the vibrating ions is $4\,M_{Zn}$, and that no quadratic shift occurs.

TABLE II

Displacements of the ligand ions (assuming the configurational model to be valid)

B—Cu in ZnS: Cu, Cr, Cl	$X_0 \sim -0.07$ Å	present work
SA in ZnS: Cl	~ -0.3 Å	[21]
Pb red in ZnS	-0.21 Å	[15]
Tl^+ in KCl: Tl	-0.25 Å	[20]

The above results are quite unusual, first because of the small value of X_0 (see Table II), and moreover because of the very high values of the coupling constants. For a comparison, while studying the red emission band of ZnS: Pb^{2+}, one receives [15]:

$$A_e = 54\,\text{Å}^2, \quad A_g = 61\,\text{Å}^2,$$

$$r_e = 4.15\,\text{Å}, \quad r_g = 4.40\,\text{Å}.$$

4. Effects of infra-red irradiation

In a previous study, two of us [22] have measured the steady-state emission level reached when both UV excitation and IR irradiation ($\lambda > 1\mu$m) are applied on the sample: at liquid nitrogen temperature, the *G*–Cu band is enhanced while the *B*–Cu band was

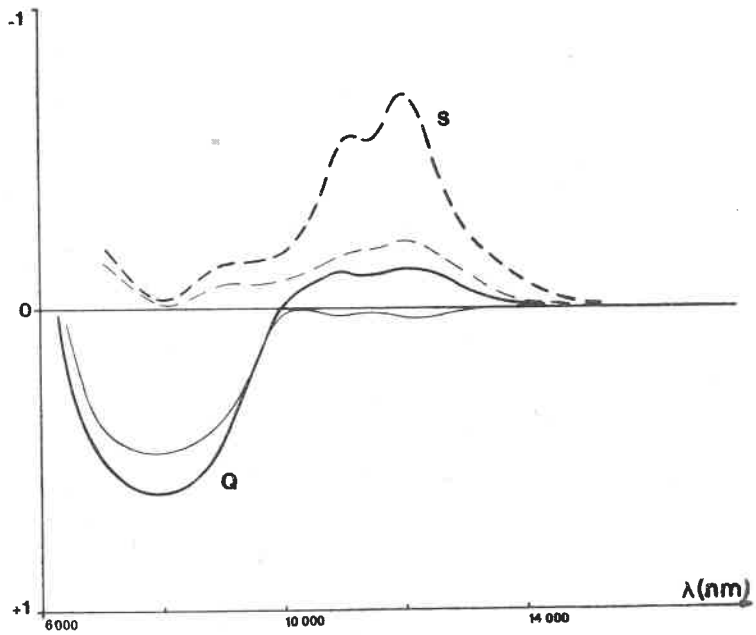

Fig. 3. Infra-red effects on powders ZnS: Cu, Cr, Cl versus the infra-red irradiation wavelength λ. Liquid nitrogen temperature. Solid lines: $Q = (I_{UV} - I_{UV+IR})/I_{UV}$ ($Q < 0$ permanent quenching, $Q > 0$ steady-state enhancement), dashed lines: maximum intensity S of transient stimulation. In both cases, the thick curve refers to the *G*–Cu band, the thin curve to the *B*–Cu band

unaffected. Similar experiments are described here on the powder ZnS: Cu, Cr, Cl from which the crystal "19" has been obtained (IR effects are stronger with the powder than upon the crystal sample). Higher intensities are used than in paper [22].

Fig. 3 shows that a slight quenching is observed indeed for the *B*–Cu emission, at liquid nitrogen temperature, when $\lambda > 1$ μm is used. For the *G*–Cu emission, the same enhancement is obtained as above. On the other hand a strong quenching effect is observed on both bands by means of 0.8μm irradiation. These results are in agreement with Kramer et al. [23] who worked upon analogous base materials; they received in addition the following result: at RT, the above effects can be reversed, the *B*–Cu band is either enhanced or less quenched than the *G*–Cu one by IR irradiation.

We observe also a general agreement with Shionoya's observations [24], performed upon the green band of ZnS: Cu, Al phosphors: according to the specific material upon study, and also to the excitation and irradiation conditions, we may observe either a steady--state enhancement or a permanent quenching, but both are maximum for the same IR wavelengths. We may extend this remark to the *B*–Cu band, and also the transient stimulation effects.

However, in our experiments two maxima occur in the $\lambda > 1$ μm region, the well-known one near 1.2 μm is due to copper and the 1.1 μm one to chromium.

We observed also that the *shape* of the *B*–Cu band remains unchanged by IR irradiation, while a shift is produced in the *G*–Cu band towards higher energies. This shift is correlated with the shifts obtained in time-resolved spectroscopy or while increasing the UV excitation intensity [3, 24].

As a conclusion, we cannot say that our experiments lead to a concrete model of the *B*–Cu center. It is well known that the D–A model does not work for this center; we observe from pressure effects that the conventional coordinate configuration model can be formally used, but leads to quite unusual results and more specifically to a considerable size of the center when compared with ordinary "localized" centers; furthermore the fact that transient stimulation as well as steady-state enhancement effects by IR are stronger for the green band proves that the *G*–Cu band is generally less sensitive than the *B*–Cu one to radiationless transitions: this is in agreement with the general idea that the *B*–Cu centers are more easily ionized than the *G*–Cu ones, and therefore they involve a shallower donor level as their emitting state.

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