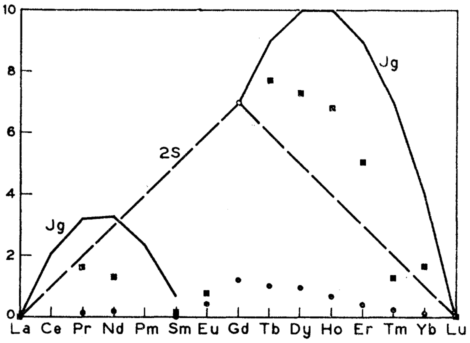

FIG. 5. Observed 0°K (■) and 298°K (●) values of the average moments of the rare-earth ions compared with the theoretical *Jg* and spin-only values.

have been discussed elsewhere[3]; it will be noted that all contributions of these ions are lower than the spin-only values, although that of Pr is close to the spin-only value of 2 μ_B. The behavior of the Eu ion has been interpreted by Wolf and Van Vleck.[16] The average contribution of the Tm ion is lower than that of the spin-only value and the contributions of the other heavier ions, Tb, Dy, Ho, Er, and Yb lie between the spin-only and *Jg* values. At least partly, this is the result of the canting of the moments of these ions relative to the easy direction.

The behavior of the contributions to the spontaneous moments by the heavier rare-earth ions at higher temperatures differs from that at 0°K. At room temperature (see Fig. 5), they decrease monotonically from Gd to Lu.

ACKNOWLEDGMENT

We wish to thank L. R. Walker for helpful discussions.

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[16] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

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Nearest-Neighbor Splitting of the Luminescence Levels of ZnS_xSe_{1-x}†

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The gradual shift of ZnS_xSe_{1-x} luminescence levels toward the valence band with decreasing x is attributed to replacement of S by Se in the activator surround. If the center wave function is confined mainly to the four anions surrounding the activator, the center level should split into five levels corresponding to centers with surrounds containing j S atoms and $4-j$ Se atoms. These five j levels are not inconsistent with the gradual level shift toward the valence band. If the five levels are fitted to this shift, emissions from different j levels are not resolved and combine to form a composite broadened band that shifts gradually with x. The broadening of the composite band agrees with that observed for the green bands for Ag, Cu, and self-activation. It also accounts for band crossovers through the terminal ZnSe band and for sliding sidewise emission shifts with quenching reported for Ag activation. The Ag blue band is narrower than calculated for five j levels. Possible explanations are that the blue-center wave function extends to additional anions beyond the nearest neighbors or that the blue emission is partly absorbed at green centers.

INTRODUCTION

In a mixed crystal such as ZnS_xSe_{1-x}, the anion sublattice is not unique, and impurity levels should be split according to their different anion surrounds. Monovalent cation impurities are incorporated substitutionally at Zn sites and form deep acceptor centers. Insofar as the center wave function is confined mainly to the four anions surrounding the impurity, the center level should be split into five levels corresponding to centers with surrounds containing j S atoms and $4-j$ Se atoms. It is shown that this splitting accounts for certain fetures of ZnS_xSe_{1-x} emission spectra.

The review of ZnS phosphors given by Klasens[1] is excellent for the purposes here, although the covalent nature of the binding could have been emphasized more; see the discussion by Prener and Williams.[2] Emission commonly occurs in broad bands. These bands are more characteristic of the host lattice than of the particular activating impurity. For example, the emission bands of Cu-, Ag-, and self-activated ZnS all have about the same shape and width, all peak in the range from 2.3 to 2.8 eV, and all shift gradually to lower $h\nu$ with decreasing x in $Zn_xCd_{1-x}S$ and ZnS_xSe_{1-x}. These behaviors are possible because the deep acceptor state that is the luminescence center is formed mainly from host-crystal anions surrounding the activator. The activator perturbs the anions to form this state.

Figure 1 shows the positioning in the forbidden gap

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† Research sponsored by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. AF19(628)-3866.

[1] H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953).

[2] J. S. Prener and F. E. Williams, J. Electrochem. Soc. **103**, 342 (1956).

of the "green" and "blue" levels of $Zn_xCd_{1-x}S$ and ZnS_xSe_{1-x}.[3] In $Zn_xCd_{1-x}S$, all levels displace parallel to the valence band with decreasing x, and the emissions shift to lower $h\nu$ at the same rate as the bandgap. In ZnS_xSe_{1-x}, all levels displace gradually closer to the valence band, and the emissions shift to lower $h\nu$ at a lower rate than the bandgap. For Cu activation, either the green band or the blue band can be made prominent at any x. For Ag and self-activation, only the blue band is prominent in $Zn_xCd_{1-x}S$, and, as x is decreased in ZnS_xSe_{1-x}, the blue band decreases, and the green band becomes dominant.

This conversion from blue-band to green-band dominance in ZnS_xSe_{1-x} was attributed by Klasens[1] and by Leverenz[3] to conversion of blue centers to green centers by replacement of S by Se in the activator surround. This view seems to have been accepted in the literature.[4,5] Although one would expect similar conversions to new centers in Cu-activated materials, these are not observed. Klasens[1] was puzzled by this anomaly and considered the absence of new Cu bands in ZnS_xSe_{1-x} a leading drawback to the model. Moreover, since the green levels shift gradually closer to the valence band with decreasing x, this model requires that initial substitution of Se into the activator surround should *increase* level depth in one jump (blue-to-green conversion) while further Se substitution should *decrease* level depth gradually. This behavior is unlikely.

We believe that replacement of S by Se in the activator surround causes instead the *gradual* shift of levels closer to the valence band. This gradual shift is observed for the green and blue levels separately of *all* activators; see Fig. 1. This shift requires such an explanation. In $Zn_xCd_{1-x}S$ where the anions do not change with x, the levels do not shift closer to the valence band.[6] A potential difficulty with this interpretation is that one does not expect a gradual shift. Insofar as the center wave function is confined mainly to the four anions surrounding the activator, one expects five levels due to centers with activator surrounds containing $j=0$, 1, 2, 3, and 4 S atoms and $4-j$ Se atoms, and one expects structure in the emission because of these five levels.

In the work here, it is assumed that five j levels do exist, and the consequences of this assumption are investigated. The difficulty cited does not materialize. Emission structure resulting from five j levels is very subdued. When the five levels are fitted to the gradual level shift toward the valence band, individual j emissions are not resolved and combine to form a composite band. The composite band shifts gradually with x in the same manner as observed bands. The composite band has the nominal appearance of a single band. It is merely somewhat broadened compared with its component j bands and, in particular, compared with the single terminal bands in ZnS and ZnSe.

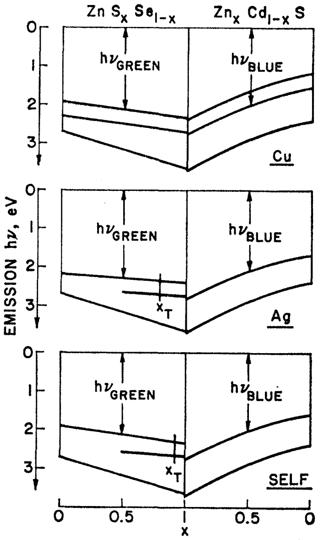

FIG. 1. Positioning in the forbidden gap of the green and blue levels of cubic ZnS_xSe_{1-x} and hex $Zn_xCd_{1-x}S$. The level positions were determined mainly from emission spectra reported by Leverenz; see Discussion. The transitions from blue-band to green-band dominance in Ag- and self-activated ZnS_xSe_{1-x} occur near x_T.

The broadening of the composite band calculated for five j levels is consistent with that observed for the green bands for Ag, Cu, and self-activation. For the favorable Ag case, it also accounts for band crossovers through the terminal ZnSe band reported by Leverenz[3] and for "sliding sidewise[7]" emission shifts with quenching reported by Klasens.[1] We conclude that nearest-neighbor splitting of the green levels does occur and is responsible for the shift of these levels toward the valence band. The Ag blue band is narrower than calculated. This fact is attributed either to absorption of the high-$h\nu$ side of the blue band at green centers or to extension of the blue-center wave function to additional anions beyond the nearest neighbors. In the latter case, the gradual level shift toward the valence band is still attributed to replacement of S by Se in the activator surround, but the effect is caused in part by replacements at sites more distant than nearest neighbors.

In the present work, no attempt is made to explain the difference between the green and blue centers. The existence of both centers is accepted simply as empirical fact. While incorporation of Se into the lattice promotes the green centers, the green center is something other than a blue center with one or more Se-for-S substitutions in the activator surround. Both centers cannot consist of the same Zn-substituted activator in an otherwise perfect lattice. At least one center must involve additional impurities.

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[3] H. W. Leverenz, *An Introduction to the Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950), pp. 194–217.

[4] C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 150.

[5] W. Hoogenstraaten, Philips Res. Rept. **13**, 521 (1958).

[6] Lattice dilation with decreasing x cannot be used to explain the gradual shift. This dilation is larger for $Zn_xCd_{1-x}S$.

[7] I. J. Hegyi, S. Larach, and R. E. Shrader, J. Electrochem. Soc. **104**, 717 (1957).

THE FIVE-LEVEL MODEL

In this section, it is assumed that the center wave function is confined mainly to the four anions surrounding the activator and, therefore, that the level shift toward the valence bands results from replacement of S nearest neighbors by Se. Thus, five j levels are assumed.

Several authors[8–10] have shown that simple ZnS emission bands are Gaussian against photon $h\nu$. Figure 2 shows the appearance of two adjacent Gaussian bands as a function of the ratio of their separation Δ to their half-widths θ. The existence of two bands is readily recognized for $\Delta/\theta=1.2$; would probably be recognized for $\Delta/\theta=0.9$; but is not readily recognized for $\Delta/\theta=0.6$. The separations between the green and blue bands of $\text{ZnS}_x\text{Se}_{1-x}$ lie typically near $\Delta/\theta=1.2$, and the existence of these distinct bands has long been recognized.[1,3] The separations between adjacent j bands lie typically near $\Delta/\theta=0.6$, and the existence of distinct j bands is not readily recognized. The procedure followed here is to assign reasonable characteristics to individual j bands, to sum the j emissions, and to compare the composite emission with observed emissions.

Individual j bands are assumed to be Gaussian against photon $h\nu$. In $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ where the anions do not change with x, levels shift parallel to the valence band, emissions shift to lower $h\nu$ at the same rate as the bandgap, and band half-widths (in eV) do not change.[10,11] These same behaviors are assumed for centers with fixed anion surrounds in $\text{ZnS}_x\text{Se}_{1-x}$. These are centers with fixed index j. The assumptions concerning the j levels are illustrated in Fig. 3. The j levels displace parallel to the valence band. The level depths D_4 and D_0 are determined empirically from observed emissions in ZnS and ZnSe, respectively. The depths D_3, D_2, and D_1 are interpolated linearly. The half-widths θ_4 and θ_0 are determined empirically from observed bandwidths in ZnS and ZnSe. θ_3, θ_2, and θ_1 are interpolated linearly. Following the results of Larach, Shrader, and Stocker,[12] the $\text{ZnS}_x\text{Se}_{1-x}$ bandgap is taken to vary linearly with x. The assumption that j levels displace parallel to the valence band is the most severe that can be made. Any departure from this behavior would be in the direction that individual j levels displace somewhat closer to the valence band with decreasing x. Adjacent j levels would then be closer together, and the gradual level shift toward the valence band would be all the more easily explained.

In the absence of quenching or of some selective excitation of centers, the amplitudes of component j emissions are taken proportional to the number of j centers. If S and Se atoms were placed randomly at anion sites, the fraction of j centers would be

$$P_j(x)=[4!/j!(4-j)!]x^j(1-x)^{4-j}. \qquad (1)$$

If this distribution of j centers is used, the calculated composite bands prove to be somewhat broader than observed bands. The explanation is the following: S and Se atoms are not placed randomly. Centers with surrounds of low strain energy are favored. If ϵ_j is the strain energy associated with surround j, the fraction of j centers is given by

$$P_j(x,\epsilon_j/kT)=A\Gamma^j e^{-\epsilon_j/kT}P_j(x). \qquad (2)$$

This result is derived in the Appendix. A is a normalization constant such that the P_j's sum to unity. Γ is a normalization constant such that the fraction of sulfur atoms in activator surrounds averages to x. $P_j(x,\epsilon_j/kT)$ reduces to $P_j(x)$ if the ϵ_j's are equal.

We assume that ϵ_j has the parabolic form

$$\epsilon_j=4\epsilon(\tfrac{1}{4}j-x)^2. \qquad (3)$$

This is a simple form that favors surrounds whose sulfur fractions $j/4$ lie near x. The parameter ϵ determines the sharpness of the parabola. If ϵ is large, centers with $j/4$ far from x occur infrequently, and the width of the composite band is reduced. However, for reasonable values of ϵ, the width of the composite band is reduced

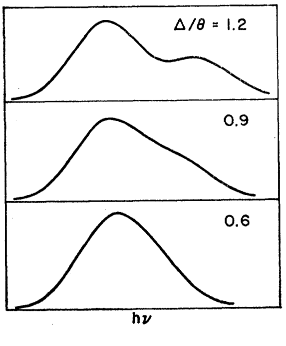

FIG. 2. Appearance of two adjacent Gaussian bands with fixed half-widths θ and different separations Δ. The amplitudes of the two bands differ by a factor of 2.

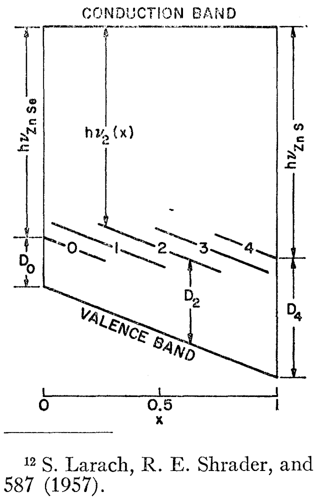

FIG. 3. Positioning in the forbidden gap of the j levels of the Ag green center in $\text{ZnS}_x\text{Se}_{1-x}$. The Ag blue levels would lie 0.36 eV below their corresponding green levels. Each j level is drawn across the restricted x range where the fractional number of j centers P_j is greater than 10% (for $4\epsilon/kT=20$).

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[8] S. T. Henderson, Proc. Roy. Soc. (London) **A173**, 323 (1939).

[9] H. Brinkman and C. C. Vlam, Physica **14**, 650 (1949).

[10] W. Lehmann, J. Electrochem. Soc. **110**, 754 (1963).

[11] H. W. Leverenz, Ref. 3. The half-widths (in eV) of Leverenz's $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ bands are independent of x, although this property was not cited.

[12] S. Larach, R. E. Shrader, and C. F. Stocker, Phys. Rev. **108**, 587 (1957).

only moderately. It is shown below that a good fit to observed green bandwidths is obtaind for $4\epsilon/kT$ of the order of 20. For such values, the composite band is composed mainly of the two or three j bands nearest the parabola minimum. See Fig. 3 and Table I. If T is taken to be the phosphor firing temperature (≈ 1100°K), ϵ is of the order of 0.5 eV.

The spacing between adjacent j levels is sufficiently large (≈ 0.15 eV) that j levels can be divided into three groups: (1) deeper unquenched levels whose emission amplitudes in relative units can be taken equal to P_j; (2) shallower quenched levels whose emission amplitudes are zero; and (3) one, at most, intermediate partly quenched level whose emission amplitude lies between 0 and P_j. Quenching can be either thermal or optical. A partial excitation similar to that obtained in quenching can also be obtained through selective excitation of the deeper levels.

Figure 4 shows some component and composite bands calculated for the Ag green center. This figure illustrates how the composite band is broadened somewhat and how it shifts gradually with x. As x is decreased, individual j bands shift to lower $h\nu$ at the same rate as the bandgap. However, the j-band amplitudes P_j shift continuously with x, and the composite band transfers gradually to centers of lower j and shifts to lower $h\nu$ at a much lower rate than the bandgap.

Figure 5 shows root-ln plots of composite bands calculated for the Ag green center. This plot is a variation of that used by Lehmann[10] and others.[13,14] The quantity $y=\pm(\ln I_0/I)^{1/2}$ is plotted against photon $h\nu$, where I is the emission at $h\nu$ and I_0 is the peak emission. The $+$ sign is used on the high-$h\nu$ side of the band, the $-$ sign on the low-$h\nu$ side. The root-ln plot converts a band Gaussian against $h\nu$ into a straight line whose slope is inversely proportional to the bandwidth. Band maximum lies at the intersection of the band line and the $h\nu$ axis. For the Ag green center, the band maximum shifts smoothly from 2.40 eV in ZnS to 2.18 eV in ZnSe. The bands are confined to such a small $h\nu$ range because the composite band shifts to lower $h\nu$ at a much lower rate than the bandgap.

TABLE I. Values of $P_j(x)$ and of $P_j(x,\epsilon_j/kT)$ for $4\epsilon/kT=20$ (latter values in parentheses). Values for $x<0.5$ may be found from the relation $P_j(x,\epsilon_j/kT)=P_{4-j}(1-x,\ \epsilon_{4-j}/kT)$.

x	P_4	P_3	P_2	P_1	P_0
1	1	0	0	0	0
	(1)	(0)	(0)	(0)	(0)
0.9	0.6561	0.2916	0.0486	0.0036	0.0001
	(0.6075)	(0.3850)	(0.0075)	(0.0000)	(0.0000)
0.8	0.4096	0.4096	0.1536	0.0256	0.0016
	(0.2568)	(0.6865)	(0.0565)	(0.0002)	(0.0000)
0.7	0.2401	0.4116	0.2646	0.0756	0.0081
	(0.0580)	(0.6874)	(0.2513)	(0.0034)	(0.0000)
0.6	0.1296	0.3456	0.3456	0.1536	0.0256
	(0.0093)	(0.4095)	(0.5538)	(0.0274)	(0.0000)
0.5	0.0625	0.2500	0.3750	0.2500	0.0625
	(0.0005)	(0.1381)	(0.7229)	(0.1381)	(0.0005)

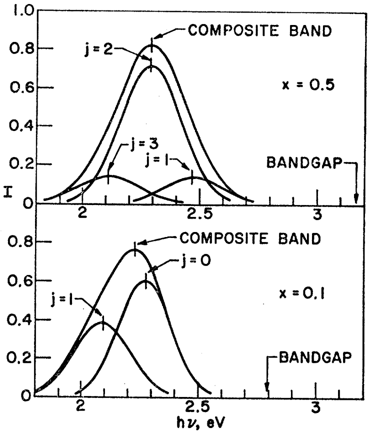

FIG. 4. Some component and composite bands calculated for the Ag green center. The component-band amplitudes have been taken equal to P_j for $4\epsilon/kT=20$.

The outstanding feature shown in Fig. 5 is the absence of any structure in the composite bands due to component j bands. The composite bands are only somewhat broadened compared to the single terminal bands for ZnS and ZnSe. This differential broadening manifests itself through a lowering of the slopes of the band lines for $0<x<1$; it distinguishes emission calculated for five j levels from emission due to a single band displacing gradually from 2.40 eV in ZnS to 2.18 eV in ZnSe. The differential broadening causes band crossovers through the $x=0$ band for $x<0.7$ and through the $x=1$ band for $x>0.7$. The specific origin of these crossovers is illustrated in Fig. 3. For example, for x near 0.25, the component $j=2$ band peaks at lower $h\nu$ than the terminal $x=0$ band. This $j=2$ band causes the composite band near $x=0.25$ to extend to lower $h\nu$ than the terminal $x=0$ band. The crossovers shown in Fig. 5 are more pronounced through the $x=0$ band than through the $x=1$ band because the half-width θ_0 is smaller than the half-width θ_4.

Composite bands exhibit a characteristic displacement with quenching. Figure 6 shows the Ag green

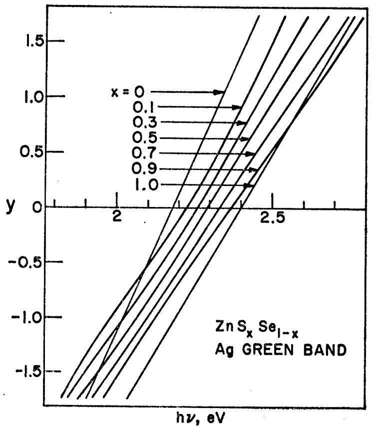

FIG. 5. Root-ln plots of Ag green bands of ZnS_xSe_{1-x}. These are composite bands calculated for $4\epsilon/kT=20$, all levels unquenched. The terminal bands for $x=0$, 1 are single and are Gaussian (straight lines) by assumption.

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[13] D. C. Patterson and C. C.Klick, Phys. Rev. **105**, 401 (1957).

[14] H. Treptow, Czech. J. Phys. **13**, 115 (1963).

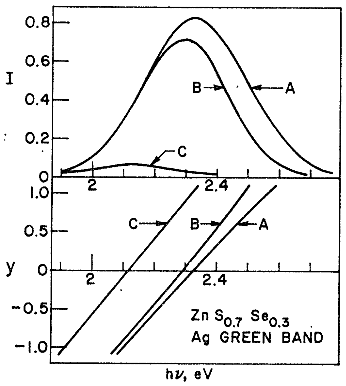

FIG. 6. Normal and root-ln plots of the Ag green band in various stages of quenching. A, unquenched; B, $j\leqq 2$ emission quenched; C, $j\leqq 3$ emission quenched. The curves are calculated for $x=0.7$, $4\epsilon/kT=20$.

band calculated for $x=0.7$ in different stages of quenching. As the quenching is increased, component bands of successively lower $h\nu$ are quenched, and the composite band shifts gradually to lower $h\nu$. This shift is just another example of the Schön-Klasens[15,16] shift of emission to lower $h\nu$ with quenching. The particular gradual shift here that results because the component emissions are not resolved has been called "sliding sidewise" displacement by Shrader.[7]

THE *N*-LEVEL MODEL

In contradistinction to the assumptions of the preceding section, it is assumed here that the center wave function extends over a number of anions smaller or larger than four and that the level shift toward the valence band is due to replacement of S by Se in this surround. At one limit, the center wave function is confined to a single anion, and emission is characteristic of either the S anion or the Se anion. At the other limit, the center wave function extends to many anions, and emission is insensitive to the identity of any single anion. The five-level model above is an intermediate case. If the center wave function involves $N-1$ anions, there are N levels due to activator surrounds with $j=0, 1, 2, \cdots, N-1$ S atoms and $(N-1)-j$ Se atoms, and these levels are further split if j S atoms and $(N-1)-j$ Se atoms can be arranged in physically different ways. To obtain a simple model, we neglect the latter splitting and assume that the j levels exhibit the ordering, spacing, and shift with x illustrated for the five-level model in Fig. 3. The five-level model can then be taken over bodily except that the index j now runs to $N-1$ and the number 4 in Eqs. (1) and (3) is replaced by $N-1$.

Figure 7 shows one composite band calculated for different assumed values of N. For each N case, the levels have been positioned to account for the level shift toward the valence band observed for the Ag green center. The level positions relative to the valence band are shown in the figure insert. The width of the composite band decreases with increasing N. For $N=3$, the composite band is sufficiently wide that component j bands can be distinguished. At the opposite extreme, for $N=\infty$, the composite band has the same width as component j bands. In this case, the emission shift with x is the same as that of a single unbroadened band displacing steadily from 2.40 eV in ZnS to 2.18 eV in ZnSe.

These results have been derived for a particular model. Nevertheless, similar results can be argued for other models: If the center wave function extends over a large number of anions, most activator surrounds differ very little from the most probable surround, the composite band is only slightly broadened, and the emission approaches that of a single unbroadened band displacing steadily with x. In this case, the gradual level shift toward the valence band is all the more easily accounted for by the model. It is shown below that this case may be realized for the Ag blue center. In the opposite direction, if the center wave function is confined to a small number of anions, emissions from the different j levels are rather different and are resolved, and the level shift toward the valence band is not gradual. This case is not observed.

COMPARISON WITH EXPERIMENT

The comparison with experiment, carried out in following sections, is concerned with two points: (1) Is the five-level model consistent with the gradual shift of levels closer to the valence band? (2) Is the band broadening (and associated phenomena such as band crossovers and sliding sidewise displacements) predicted by the model confirmed in observed spectra? It will be evident that the answer to the first question is yes. Thus, our attention reduces mainly to the band broadening.

A number of adjustments are needed to fit the model to observed spectra. The terminal bands in ZnS and ZnSe must be fitted empirically. Green and blue emissions commonly occur together, and the ratio of green to blue centers must be chosen. The level separating quenched and unquenched levels must be chosen. The strain-energy parameter ϵ determining the distribution of j centers must be chosen. These numerous adjustments tend to give the impression that the model can

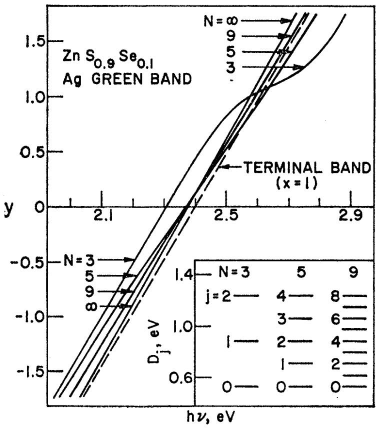

FIG. 7. The Ag green band calculated for N mixed-anion-split levels where $N=3$, 5, 9, and ∞. The curves are calculated for $x=0.9$, $\epsilon/kT=5$, no quenching. The dotted curve shows the terminal band in ZnS.

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[15] M. Schön, Z. Physik **119**, 463 (1942).

[16] H. A. Klasens, Nature **158**, 306 (1946).

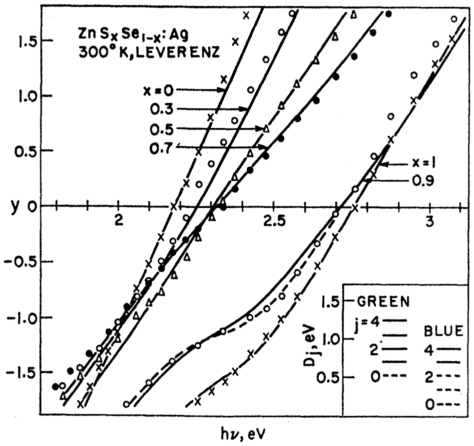

FIG. 8. Observed and calculated emission spectra for ZnS_xSe_{1-x}:Ag. Observed spectra reported by Leverenz for cathode-ray excitation at room temperature.

be fitted to any set of spectra. However, this is not so. In spite of the numerous adjustments, it is still possible to ascertain whether the calculated band broadening is or is not observed.

In the comparison with experiment, observed spectra are fitted using five-level models of both the green and blue centers. This choice of five levels should be regarded as a trial subject to modification as guided by the fit. If an observed band is broader (or narrower) than calculated for five levels, a N-level model with N smaller (or greater) than five is suggested. The observed bands prove never to be broader than calculated. They are sometimes narrower. In the latter cases, the band can always be fitted using an N-level model with $N>5$. This fitting is not done, however, since the predictions of the model then become insensitive to N, and this number cannot be determined accurately. Moreover, it is possible that the five-level model still applies and that the reduced broadening has an alternative explanation. For all calculated bands except one expressly noted, the the value of the parameter $4\epsilon/kT$ was taken to be 20. Values of P_j for this choice are listed in Table I.

ZnS_xSe_{1-x}:Ag

Figure 8 shows observed and fitted spectra for ZnS_xSe_{1-x}:Ag. The observed spectra were taken from Leverenz,[3] and I/I_0 versus λ plots of these may be seen in his Fig. 39. The fitted curves were calculated for the level scheme shown in the insert; levels that were temperature quenched under Leverenz's conditions are shown dotted. The D_4, D_0, θ_4, and θ_0 values used are listed in Table II. These values were chosen principally for good fit to the terminal bands for $x=0$ and 1. The ratio of blue to green centers was taken to be 12, 4, and 1 for $x=1$, 0.9, and 0.5, respectively. These ratios were chosen arbitrarily for good fit. For $x<0.4$, blue emission is completely quenched.

The calculated bands account well for the smaller-than-bandgap shift of emission bands with x. The bandgap shifts 0.94 eV from ZnS to ZnSe. The green and blue bands shift only 0.22 eV. The difference between these is made up by a 0.72-eV shift of emission from the $j=4$ level in ZnS to the $j=0$ level in ZnSe. The green band dominates the emission for $x<0.8$. In this range, the agreement between observed and calculated band broadening is good, and the band crossovers through the terminal band in ZnSe are matched well. The origin of these crossovers was discussed in connection with Fig. 5.

The band for $x=0.7$ is unusually broad and, on its low-$h\nu$ side, crosses through all bands for $x<0.7$. A possible explanation is the following: For $x=0.7$, blue emission is partially quenched. Blue emission which is not quenched is merged into the dominant green band and has the effect of broadening the high-$h\nu$ side of this band. Moreover, this blue emission lies above the threshold for excitation of green $j=4$ centers (see below) and can be absorbed and re-emitted at green $j=4$ centers. This absorbed and re-emitted light has the effect of broadening the low-$h\nu$ side of the green band. Thus, the total emission has the appearance of a symmetrically broadened green band similar to that which would obtain for green emission alone if the strain-energy parameter ϵ were very small. To match this behavior, the fitted curve for $x=0.7$ has been calculated for green emission alone with $\epsilon=0$.

The blue band dominates the emission for $x>0.8$. For $x=0.9$, the fitted curve above 2.5 eV where the blue band dominates has a lower slope than the observed emission. Two explanations are possible. First, the wave function of the blue center may extend to additional anions beyond the nearest neighbors so that the broadening of the blue band is reduced. See Fig. 7 for $N>5$ where, for example, the crossover of the $x=0.9$ band through the terminal $x=1$ band is eliminated. Second, blue emission above 2.7 eV may be absorbed and re-emitted at green $j=4$ centers. The dotted curve shows the limiting form of the fitted curve below 2.7 eV if such re-emitted light dominates the green band. The

TABLE II. D_4, D_0, θ_4, and θ_0 values (in eV) used to fit observed ZnS_xSe_{1-x} emission spectra. The band-gap values used were 3.64 eV for ZnS and 2.70 for ZnSe at room temperature, 3.70 and 2.76 eV near 77°K. Measurements near 77°K are indicated by an asterisk.

Worker	Center	D_4	D_0	θ_4	θ_0
Leverenz	Ag Gr	1.24	0.52	0.34	0.26
	Ag Bl	0.88	0.16	0.34	0.26
Klasens	Ag Gr	1.22	0.50	0.29	0.21
	Ag Bl	0.92	0.20	0.29	0.21
Leverenz	Cu Gr	1.30	0.78	0.30	0.26
	Cu Bl	0.92	0.40	0.30	0.26
Morehead	Cu Gr*	1.25	0.79	0.26	0.20
	Cu Bl*	0.97	0.47	0.26	0.20
Leverenz	Self Gr	1.29	0.79	0.40	0.30
	Self Bl	0.96	0.24	0.40	0.30
Bundel'	Self Gr*	1.39	0.87	0.31	0.23
	Self Bl*	1.10	0.38	0.31	0.23

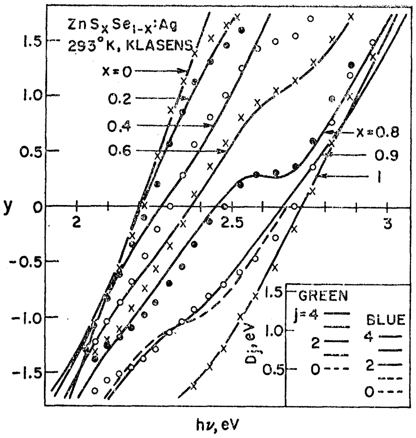

FIG. 9. Observed and calculated spectra for ZnS$_x$Se$_{1-x}$:Ag. Observed spectra reported by Klasens for excitation by 3.40-eV light at room temperature. The fitted curves were calculated for D_4, D_0, θ_4, and θ_0 values listed in Table II and for the ratio of blue to green centers 17, 3.3, 1.05, 0.28, and 0 for $x=1$, 0.9, 0.8, 0.6, and <0.5, respectively.

dotted curve is not extended above 2.7 eV for lack of detailed absorption-versus-$h\nu$ data. Qualitatively, absorption above 2.7 eV would increase the slope of the fitted curve and bring it into better agreement with the observed emission.

Figure 9 shows a similar fit to ZnS$_x$Se$_{1-x}$:Ag spectra reported by Klasens.[1] The level scheme used for the fit is shown in the insert. The transfer from blue- to green-band dominance near $x=0.8$ and the smaller-than-bandgap shift of bands with x are the same as shown by Leverenz's spectra. The fit to the observed spectra is poorer in the present case. Klasens' green bands come together near 2 eV, but they do not cross the terminal $x=0$ band. Also, for $x=0.6$ and 0.4, his green-band slopes are greater than those of the fitted spectra. For $x=0.9$, the observed blue band is again narrower than the fitted band, neglecting absorption of blue light at green $j=4$ centers (solid curve). One or both of the explanations above are needed to explain this discrepancy. Klasens shows somewhat resolved blue emissions for $x<0.5$. These could be due to blue $j=0$ and 1 emissions. However, emission from such shallow levels makes no sense at room temperature, and these emissions are not matched by the fitted curves.

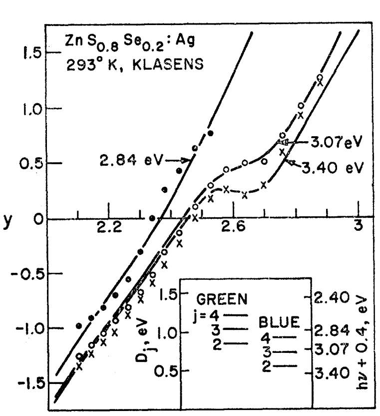

FIG. 10. Observed and calculated spectra of ZnS$_{0.8}$Se$_{0.2}$:Ag for excitation by 3.40-, 3.07-, and 2.84-eV light at room temperature.

Klasens[1] gives interesting examples of emission shifts with excitation conditions. Figure 10 shows emission shifts with excitation $h\nu$, while Fig. 11 shows emission shifts with the temperature of the phosphor. The fitted curves were calculated for the same D_j and θ_j values and blue-to-green ratios used previously for Fig. 9. For the cases here ($x=0.8$), the populated j levels are the $j=4$, 3, and 2 levels of both centers. See Table I for $4\epsilon/kT=20$. The positions of these six levels are shown in the figure inserts. The low slope of the observed band at 433°K in Fig. 11 is due to temperature broadening of j bands. This effect was not taken into account in the calculated curves.

The j-band amplitudes used to fit the spectra in Figs. 10 and 11 are listed in Table III. An explanation of these amplitudes is suggested by the $h\nu$ and T scales in the figure inserts. The Fig. 10 scale gives emission $h\nu$ plus 0.4 eV. The threshold for optical excitation of a given j center lies approximately 0.4 eV above the peak of its emission band. Thus, the threshold for excitation of green $j=3$ emission lies near 2.84 eV, that for blue $j=3$ emission near 3.07 eV, and that for blue $j=2$ emission below 3.40 eV. The Fig. 11 scale gives the Kelvin temperature of the phosphor during excitation. The Kelvin temperature necessary to quench emission from level j is approximately proportional to D_j. Thus, for the excitation conditions used, the quenching temperature for green $j=3$ emission lies near 433°K, that for blue $j=3$ emission near 293°K, and that for blue $j=2$ emission above 90°K.

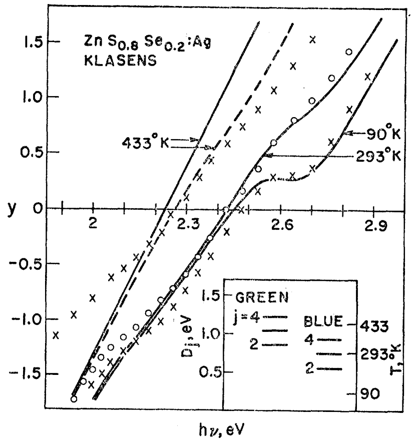

FIG. 11. Observed and calculated spectra of ZnS$_{0.8}$Se$_{0.2}$:Ag excited by 3.40-eV light at different temperatures.

Interestingly, these emission shifts cannot be accounted for by adjusting the amplitudes of two single bands, that is, single green and blue bands. The single blue band would have to be placed with its peak near

2.68 eV to account for the secondary band observed when both bands are excited. The single green band would have to be placed with its peak near 2.35 eV in Fig. 10 and near 2.26 eV in Fig. 11 to account for the emission observed when only green emission is excited. In either case, the resolution between these single bands would be far greater than that exhibited by the observed emissions. At least one other band must be used to fit the data. In the model here, two sets of three j levels are used, and the emission shifts result from sliding sidewise displacements through these six levels.

ZnS_xSe_{1-x}:Cu

Figure 12 shows a similar fit to ZnS_xSe_{1-x}:Cu spectra reported by Leverenz.[3] I/I_0 versus λ plots of the observed spectra may be seen in his Fig. 40. The green band dominates the spectra for all x, and the ratio of blue to green centers is insensitive to x. Both bands exhibit the smaller-than-bandgap shift with x. Since the level shift toward the valence band is smaller than in the Ag case (the spacing between adjacent j levels is 0.13 eV compared to 0.18 eV for the Ag case), the bands shift to lower $h\nu$ at a slightly greater rate with decreasing x, band broadening is reduced, and band crossovers through the terminal bands are suppressed. The dominant green band is broadened for $0<x<1$, and the calculated and observed broadening agree.

TABLE III. Emission amplitudes I_j of bands used to fit the spectra of Figs. 10 and 11. The amplitudes are given in units of $P_j(x,\epsilon_j/kT)$.

	Green bands			Blue bands		
Curve	I_4	I_3	I_2	I_4	I_3	I_2
3.40 eV	1	1	1	1	1	1
3.07 eV	1	1	1	1	0.75	0
2.84 eV	1	0.6	0	0	0	0
90°K	1	1	1	1	1	1
293°K	1	1	1	1	0.35	0
433°K (dotted)	1	0.16	0	0	0	0
433°K (solid)	1	0	0	0	0	0

Absorption of blue emission at green centers has been neglected in the fitted curves. Insofar as this does occur, blue emission is partly absorbed, and the ratio of blue to green centers is larger than stated. The effect on the green band is small. For $x=0.8$ or 0.6, if half of the blue emission had been absorbed and re-emitted at green centers, the green band would be shifted approximately 0.015 eV to lower $h\nu$ with little change in slope.

Figure 13 shows a similar fit to ZnS_xSe_{1-x}:Cu spectra reported by Morehead.[17] Morehead's phosphors were prepared under conditions that favor the blue centers, and his spectra were taken at 80°K where blue emission is not quenched. Blue emission persists down to $x=0$, and the ratio of blue to green centers is insensitive to x throughout this range.

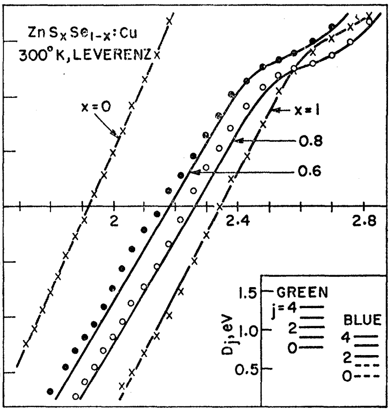

FIG. 12. Observed and calculated spectra for ZnS_xSe_{1-x}:Cu. Observed spectra reported by Leverenz for cathode-ray excitation at room temperature. The fitted curves were calculated for D_4, D_0, θ_4, and θ_0 values listed in Table II and for the ratio of blue to green centers 0.07, 0.16, and 0.14 for $x=1$, 0.8, and 0.6, respectively.

A difficulty exists with Morehead's spectra associated with the bandgap variation with x. Morehead's bandgap variation differs from that reported by Larach *et al.*[12] and used here. If Morehead's variation had been used, the calculated bands for $0<x<1$ would both be shifted to lower $h\nu$ by more than 0.1 eV. Morehead's phosphors may undergo a hex to cubic transition with decreasing x. At any rate, an uncertainty exists in band positioning along the $h\nu$ axis. Despite this uncertainty, Morehead's spectra do exhibit band broadening for $0<x<1$. This is shown by the fact that the spectra for $0<x<1$ extend over a larger $h\nu$ range than the terminal spectra and yet exhibit a poorer resolution between their green and blue components. This same behavior is shown by the calculated spectra.

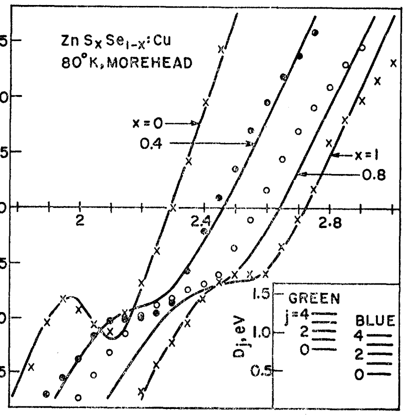

FIG. 13. Observed and calculated spectra for ZnS_xSe_{1-x}:Cu. Observed spectra reported by Morehead for optical excitation near the bandgap at 80°K. The fitted curves were calculated for D_4, D_0, θ_4, and θ_0 values listed in Table II and for the ratio of blue to green centers 1.7, 2.2, 2.7, and 2.0 for $x=1$, 0.8, 0.4, and 0, respectively.

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[17] F. F. Morehead, Phys. Chem. Solids 24, 37 (1963).

SELF-ACTIVATED ZnS_xSe_{1-x}

Figure 14 shows a similar fit to self-activated ZnS_xSe_{1-x} spectra reported by Leverenz.[3] I/I_0 versus λ plots of the observed spectra may be seen in his Fig. 38. The self-activated centers resemble the Ag centers in that the ratio of blue to green centers decreases with decreasing x. The transition between blue- and green-band dominance occurs near $x=0.92$. Blue emission is completely quenched for $x<0.4$. Just as in Leverenz's Ag and Cu cases, the level separating quenched and unquenched levels lies approximately 0.60 eV above the valence band. The location of this level is confirmed by the emission efficiencies that Leverenz reports. Both bands exhibit the smaller-than-bandgap shift with x. The agreement between calculated and observed band broadening is good, although, as in the Cu case, the effect is small due to the small ratio of level splitting to the half-widths θ_j.

Figure 15 shows a similar fit to self-activated ZnS_xSe_{1-x} spectra reported by Bundel', Guretskaya, and Noskova.[18] These spectra were taken at 77°K where blue emission is not quenched. Appreciable blue emission persists to the lowest x value reported. As in Leverenz's self-activated case, the level shift toward the valence band is somewhat greater for the blue centers, and the separation between the blue and green emission peaks increases with decreasing x. The self-activated bands shift anomalously to lower $h\nu$ with decreasing temperature. This was reported for the blue band in ZnS by Larach and Shrader[19] and has been extended by Bundel' *et al.*[18] to both bands throughout the ZnS_xSe_{1-x} range they investigated. Thus, the D_j values used to fit the spectra (see Table II) are larger for the 77°K case.

COMPLEMENTARY CASE IN $Zn_xCd_{1-x}S$

The complement of mixed-anion splitting of acceptor levels in ZnS_xSe_{1-x} is mixed-cation splitting of donor levels in $Zn_xCd_{1-x}S$. This donor case adds useful perspective to the problem. Discussion here is based on Hoogenstraaten's glow-curve studies of ZnS electron traps.[5,20] As x is decreased in $Zn_xCd_{1-x}S$, electron trapping levels near the conduction band displace gradually closer to the conduction band. In some cases, new trapping levels appear, and these too displace gradually closer to the conduction band. This behavior parallels that described previously for luminescence levels in ZnS_xSe_{1-x}. As x is decreased, these acceptor levels displace gradually closer to the valence band, and new levels appear in some cases which also displace closer to the valence band.

Following Klasens' interpretation[1] of the new luminescence levels in ZnS_xSe_{1-x}, Klasens[1] and Hoogenstraaten[5,20] attributed the new electron trapping levels in $Zn_xCd_{1-x}S$ to the replacement of Zn by Cd in the trap surround. We believe that this replacement causes instead the gradual shift of the trapping levels toward the conduction band. However, this gradual shift is sufficiently rapid that, if there were only five j levels due to traps with j Zn nearest neighbors and $4-j$ Cd nearest neighbors, distinct j peaks would be observed in the glow curves. These are not observed; the glow peaks in the mixed crystals are single.

The situation in CdS is clear: The traps are only about 0.03 eV below the conduction band,[21] and their

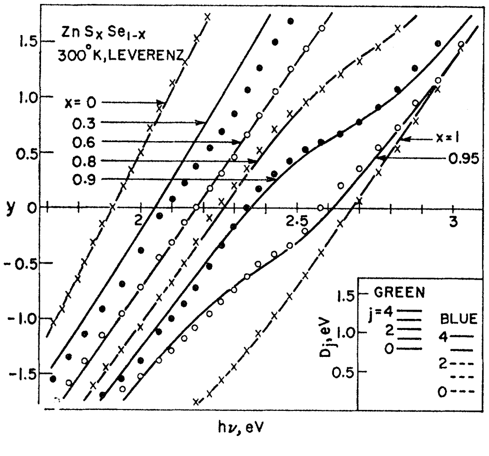

FIG. 14. Observed and calculated spectra for self-activated ZnS_xSe_{1-x}. Observed spectra reported by Leverenz for cathode-ray excitation at room temperature. The fitted curves were calculated for D_4, D_0, θ_4, and θ_0 values listed in Table II and for the ratio of blue to green centers 20, 1.92, 0.59, 0.15, and 0.06 for $x=1$, 0.95, 0.9, 0.8, and 0.6, respectively.

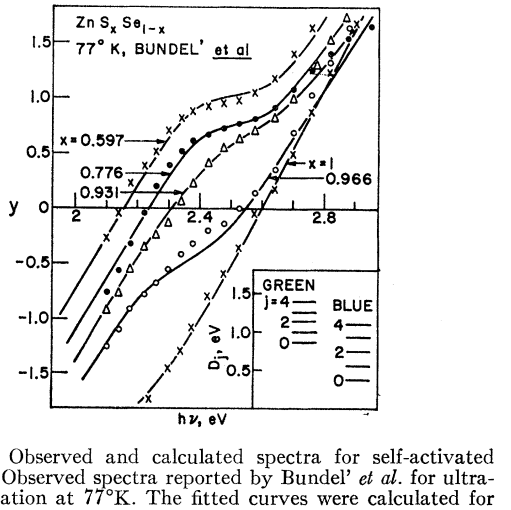

FIG. 15. Observed and calculated spectra for self-activated ZnS_xSe_{1-x}. Observed spectra reported by Bundel' *et al.* for ultraviolet excitation at 77°K. The fitted curves were calculated for D_4, D_0, θ_4, and θ_0 values listed in Table II and for the ratio of blue-to-green centers 22, 1.54, 0.60, 0.56, and 0.40 for $x=1$, 0.966, 0.931, 0.776, and 0.597, respectively.

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[18] A. A. Bundel', Z. I. Guretskaya, and M. N. Noskova, Opt. i Spektroskopiya **11**, 656 (1961) [English transl.: Opt. Spectry. USSR **11**, 352 (1961)].

[19] S. Larach and R. E. Shrader, Phys. Rev. **103**, 1899 (1956).

[20] W. Hoogenstraaten, J. Electrochem. Soc. **100**, 356 (1953).

[21] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), pp. 158–71.

wave functions must be large hydrogen-like states extending over many host-crystal atoms. The corresponding traps in ZnS are deeper (up to 0.5 eV below the conduction band[5]), and their wave functions must be much more confined. However, we take the lack of structure in $Zn_xCd_{1-x}S$ glow peaks, even for traps up to 0.5 eV below the conduction band, to mean that, throughout the mixed system and including ZnS, the trap wave functions extend to cations beyond the nearest neighbors. If a trap wave function extends over many mixed cations, most trap surrounds will differ very little from the most probable surround, the glow peak will be broadened only slightly and the glow will approach that which would result from a single trapping level displacing gradually closer to the conduction band. This appears to be the case realized.

Since trap wave functions extend over many atoms, there need be little qualitative difference between traps caused by Column III and VII impurities which substitute at different lattice sites. The glow curves associated with these impurities are in fact not qualitatively different.[5,20] The origin of the new trapping levels is not explained. Insofar as they are new levels and not just old levels displaced to the energy range accessible to the glow-curve method used, they are new arrangements of impurities promoted by Cd in the lattice. However, according to the model, they are not just old trapping states with one or more Cd-for-Zn substitutions in the trap surround. Electron trapping levels in ZnS_xSe_{1-x} also shift closer to the conduction band with decreasing x, but at a much lower rate than in $Zn_xCd_{1-x}S$. This behavior parallels that of luminescence levels in $Zn_xCd_{1-x}S$ which displace very little toward the valence band.

DISCUSSION

If the number of mixed-anion split j levels were two or three, individual j emissions would be resolved. These resolved emissions are not observed, and such splittings must be excluded. For example, the splitting into two levels suggested for ZnS_xSe_{1-x}: Cu by Bube[22] is excluded. If the number of j levels were near five, individual j emissions would not be resolved and would combine to form a composite, broadened emission. Such a broadened band is observed for the green centers of ZnS_xSe_{1-x}. In the favorable Ag case, this broadening accounts for band crossovers through the unbroadened $x=0$ band and also for sliding sidewise emission shifts with quenching.

If the number of j levels were larger than five such as would obtain if the center wave function extended to additional anions beyond the nearest neighbors, the emission would be broadened very little and would approach that of a single level displacing gradually closer to the valence band. This case may explain the narrowness of the ZnS_xSe_{1-x}:Ag blue band. It likely explains the narrowness of glow peaks associated with electron trapping levels in $Zn_xCd_{1-x}S$. An alternative explanation of the narrowness of the Ag blue band is that emission on the high-$h\nu$ side of the blue band is absorbed and re-emitted at green centers. This explanation requires green-center absorption constants of the order of 10^2 cm^{-1}; it also suggests that "sliding inward" emission shifts with quenching should be observed in some cases.

Prener and Williams[23] have proposed that the equivalent of the monovalent cation for self-activated emission is a Zn vacancy plus one nearest-neighbor halogen. For recent evidence, see the work of Koda and Shionoya[24] and references therein. In this event, nearest-neighbor mixed-anion splitting would produce only four j levels. However, for self-activated emission fitted with four j levels, individual green j bands are still not resolved, and the fit to observed spectra is not very different from that given in Figs. 14 and 15 using five levels.

The ZnS_xSe_{1-x} luminescence levels shown in Fig. 1 were constructed from the data in Table II. The $Zn_xCd_{1-x}S$ levels were constructed, for $x>0.5$, from the results of Leverenz[3] and, for $x<0.5$, from those of Grillot,[25] van Gool,[26] and Drozd and Levshin[27] for Cu, Ag, and self-activation, respectively. The $Zn_xCd_{1-x}S$ levels have been studied by many workers; see the review by Curie[28] and references therein. The $Zn_xCd_{1-x}S$ levels in Fig. 1 agree with those given by Curie. However, they are not the only levels associated with these activators. Van Gool[26] has shown a violet level in $Zn_xCd_{1-x}S$:Ag midway between the blue level and the valence band. Drozd and Levshin[27] have shown a similar level in self-activated $Zn_xCd_{1-x}S$. Henderson *et al.*,[29] Payen de la Garanderie,[30] and Grillot[25] have reported a small green band in Ag-activated ZnS, $Zn_xCd_{1-x}S$, and CdS, respectively.

All of these levels are distinguished by resolvable emissions spaced by 0.3 eV or more. Levels spaced by less than 0.2 eV undoubtedly occur, and emissions from these levels will form composite, broadened emissions similar to those discussed above for mixed-anion-split levels. Mixed-anion splitting is superimposed on these levels, and actual ZnS_xSe_{1-x} emission is probably more complicated than that described above by five simple j levels.

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[22] R. H. Bube, Stanford University, Department of Materials Science Report No. 63-16, 1963 (unpublished).

[23] J. S. Prener and F. E. Williams, J. Chem. Phys. **25**, 361 (1956).

[24] T. Koda and S. Shionoya, Phys. Rev. **136**, A541 (1964).

[25] E. Grillot, J. Phys. Radium **17**, 624 (1956).

[26] W. van Gool, Philips Res. Rept. **13**, 157 (1958). Van Gool's violet band lies at higher $h\nu$ than the green and blue bands studied in this paper. This band is not evident in the spectra reported by Leverenz (Fig. 8) and Klasens (Fig. 9) because (a) their phosphors were prepared in the presence of excess coactivator and (b) their spectra were taken at room temperature.

[27] L. Drozd and V. L. Levshin, Opt. i Spektroskopiya **10**, 773 (1961) [English transl.: Opt. Spectry. USSR **10**, 408 (1961)].

[28] D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963), Chap. V.

[29] S. T. Henderson, P. W. Ranby, and M. B. Halstead, J. Electrochem. Soc. **106**, 27 (1959).

[30] M. H. Payen de la Garanderie, J. Phys. Radium **22**, 423 (1961).

SUMMARY

ZnS_xSe_{1-x} luminescence levels shift gradually closer to the valence band with decreasing x. This shift is attributed to replacement of S by Se in the activator surround. If the center wave function is confined mainly to the four anions surrounding the activator, the center level should split into five levels corresponding to centers with surrounds containing j S atoms and $4-j$ Se atoms. These five levels are not inconsistent with the gradual level shift toward the valence band. If five j levels are fitted to this shift, emissions from different j levels are not resolved and combine to form a composite broadened emission band. The composite band shifts gradually with x in the same manner as observed bands.

The broadening of the composite band calculated for five j levels agrees with that observed for the green bands for Ag, Cu, and self-activation. In the favorable Ag case, it also accounts for band crossovers through the terminal ZnSe band reported by Leverenz and for sliding sidewise emission shifts with quenching reported by Klasens. The Ag blue band is narrower than calculated for five j levels. This is attributed either to absorption of the high-$h\nu$ side of the blue band at green centers or to a larger size for the blue center. If the center wave function extends to additional anions beyond the nearest neighbors, the number of j levels is increased, most j centers differ very little from the most probable center, and the broadening of the composite band is reduced.

The gradual shift of electron trapping levels toward the conduction band in $Zn_xCd_{1-x}S$ is similarly attributed to replacement of Zn by Cd in the trap surround. The lack of j-level structure in the glow peaks associated with these trapping levels is attributed to the extension of the center wave function to cations beyond the nearest neighbors.

ACKNOWLEDGMENTS

The writer is grateful to Dr. R. E. Shrader and Dr. C. W. Struck for helpful discussions. Dr. Shrader has independently arrived at some conclusions similar to those presented here.

APPENDIX: DERIVATION OF Eq. (2)

The derivation, including the notation, follows that for Boltzmann systems given in Mayer and Mayer.[31] Let $j=0$, 1, 2, 3, or 4 be the number of S atoms in the activator surround, $4-j$ the number of Se atoms, x the mole fraction of ZnS, and $1-x$ the mole fraction of ZnSe. Consider some definite arrangement of activator surrounds where N_j activators have the surround j. The probability of this definite arrangement is

$$P(N_j)=\prod_j\left[x^j(1-x)^{4-j}\right]^{N_j}. \tag{4}$$

The number of definite arrangements of this kind which keep the N_j's fixed is

$$F(N_j)=\frac{N!}{\prod_j N_j!}\prod_j\left[\frac{4!}{j!(4-j)!}\right]^{N_j}. \tag{5}$$

Thus, the weight Ω attached to the arrangement is

$$\Omega=P(N_j)F(N_j)=N!\prod_j\frac{(C_j)^{N_j}}{N_j!}, \tag{6}$$

where

$$C_j=[4!/j!(4-j)!]x^j(1-x)^{4-j}. \tag{7}$$

The three additional conditions are

$$N=\sum_j N_j, \tag{8}$$

$$E=\sum_j N_j\epsilon_j, \tag{9}$$

$$4Nx=\sum_j N_j j. \tag{10}$$

The values of the variables N_j at the maximum must fulfill the conditions

$$\frac{\partial}{\partial N_j}\left[\ln\Omega-\alpha\sum_j N_j-\beta\sum_j N_j\epsilon_j-\gamma\sum_j N_j j\right]=0. \tag{11}$$

The result is

$$N_j/C_j=e^{-\alpha-\beta\epsilon_j-\gamma j}. \tag{12}$$

Equation (2) is Eq. (12) with the substitutions $P_j(x,\epsilon_j/kT)=N_j/N$, $A=e^{-\alpha}/N$, $\Gamma=e^{-\gamma}$, $\beta=1/kT$, and $P_j(x)=C_j$. Equations (2), (8), and (10) may be combined to show that Γ is a root of the equation

$$\sum_j(j-4x)P_j(x)e^{-\epsilon_j/kT}\Gamma^j=0. \tag{13}$$

After Γ is found from Eq. (13), the normalization constant A is found from Eq. (8).

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[31] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), pp. 111–4.