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Energy Model for Edge Emission in Cadmium Sulfide

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The blue and green fluorescence emitted by CdS single crystals subjected to ultraviolet radiation at low temperatures has been examined in the temperature interval from 4.2°K to 77°K. The spectral position and relative intensity of certain lines found in this fluorescence have been measured as a function of temperature between 4.2°K and 77°K. The degree of polarization of the fluorescence has been investigated at 4.2°K. From this data an energy model is proposed which accounts for the transitions leading to the blue and green fluorescence at 4.2°K, the change in these transitions as the temperature increases from 4.2°K to 77°K, and the transitions leading to the blue and green fluorescence at 77°K.

I. INTRODUCTION

IN 1940 Kroger[1] first reported on the fluorescence observed in CdS crystals subjected to ultraviolet radiation at 93°K. Following this initial observation, other investigators[2–6] examined the fluorescence at 77°K and 4.2°K, and, as a result of their findings, a rather detailed picture of the edge emission spectrum of CdS now exists. The fluorescence is found to spread over a wavelength interval of 600A beginning near the fundamental absorption edge of the crystal (∼4850A) and extending at least as far as 5600A. At 4.2°K the fluorescence has been found to contain as many as twenty-three lines or bands with varying intensities, some of which are sharp and some of which are diffuse. The fluorescence observed in the wavelength interval 4850A–5020A contains lines which appear to be sharper and more intense than the series of bands observed in the wavelength interval from 5020A to 5600A.

Several energy models have been proposed to account for the luminescence in CdS. A model based essentially on the recombination between free electrons and trapped holes at impurity centers for CdS:Ag was suggested by Schön[7] and Klasens.[8] More recently a model for luminescence in CdS:Ag proposed by Lambe and Klick,[9] reversed the mode of interaction between electrons and holes and suggested that the luminescence results from the recombination between trapped electrons and free holes. In a later paper, Lambe, Klick, and Dexter[10] extended a similar interpretation to account for the green fluorescence observed in undoped CdS.

In order to account for the complex structure of the fluorescence observed at 4.2°K and the change in structure as the crystal is heated, a more extensive model based on the presence of additional centers is required. The purpose of this paper is to present experimental evidence which relates different parts of the fluorescence observed at 4.2°K to different centers, and to suggest an energy model using these centers to account for the transitions observed at 4.2°K and 77°K.

II. PREVIOUS RESULTS

Furlong and Ravilious[5] observed and measured twenty-one lines (or bands) in the fluorescence spectrum of CdS irradiated with ultraviolet light at 4.2°K. This fluorescence was divided into two parts. One part was made up of the bands found between 4853A and 5020A, eleven in all, which were labelled "blue bands"; the remaining ten bands located between 5020A and 5630A were labelled "green bands." This division into two nonoverlapping sets of bands was made on the basis of difference in sharpness, spacing, and intensity of the bands in the two wavelength regions, on the observed existence of an absorption line at 4867A, and on the dependence of various bands on the condition of the crystal surface.

More recently a different classification of this same fluorescence at 4.2°K has been suggested.[6] This classification has been based on the discovery that some CdS crystals show only fluorescence between 4853A and 5100A while other crystals show fluorescence between 4853A and 5600A. The crystals showing fluorescence over the wavelength region 4853A-5600A invariably contain those same lines contained in the fluorescence of crystals showing lines only between 4853A and 5100A. The difference in the fluorescence spectrum

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[1] F. A. Kroger, Physica **7**, 1 (1940).

[2] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

[3] L. R. Furlong, Phys. Rev. **95**, 1086 (1954).

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[5] L. R. Furlong and C. F. Ravilious, Phys. Rev. **98**, 954 (1955).

[6] L. S. Pedrotti and D. C. Reynolds, Phys. Rev. **119**, 1897 (1960).

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

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

[9] J. J. Lambe and C. C. Klick, Phys. Rev. **98**, 909 (1955).

[10] J. J. Lambe, C. C. Klick, and D. L. Dexter, Phys. Rev. **103**, 1715 (1956).

TABLE I. Classification by wavelength of blue and green fluorescence in cadmium sulfide at 4.2°K.

"Blue fluorescence" (A)	"Green fluorescence" (A)
4853 $-B_1^1$	4885 $-G_1$
4863 $-B_1^2$	4959 $-G_2$
4871 $-B_1^3$	5037 $-G_3$
	5129 $-G_4$
4913 $-B_2^1$	5179 $-G_5$
4925 $-B_2^2$	5211 $-G_6$
4938 $-B_2^3$	5254 $-G_7$
	5298 $-G_8$
4986 $-B_3^1$	5341 $-G_9$
5002 $-B_3^2$	5382 $-G_{10}$
5016 $-B_3^3$	5436 $-G_{11}$
5065 $-B_4^1$	
5082 $-B_4^2$	
5092 $-B_4^3$	

resulting from the two types of CdS crystals at 4.2°K and 77°K are shown in the four photographs of Fig. 1. Comparison of B and C has made possible the division of the twenty-three lines observed in the fluorescence spectrum into two classifications as detailed in Table I. The first classification is simply called "blue fluorescence" and includes lines $B_1^1-B_4^3$, a series of lines appearing to form four distinct triplets. The second classification, which includes line G_1-G_{11}, is called "green fluorescence" even though it contains some lines whose wavelengths are definitely in the blue region. It should be noted that this classification differs from the "blue band"-"green band" classification suggested by Furlong and Ravilious since considerable overlapping exists between the blue fluorescence and green fluorescence.

Although the fluorescence spectrum at 4.2°K contains twenty-three components, the observed equal spacing between some of these indicates possible phonon interaction. For example, the triplets B_2, B_3, and B_4 are separated by ~0.04 ev; in addition lines G_1, G_2, G_3, lines G_4, G_6, G_8, G_{10}, as well as lines G_5, G_7, G_9, and G_{11} are separated by approximately 0.04 ev. In each group the spacing between lines is very nearly equal to the longitudinal optical phonon energy of 0.038 ev.[11,12]

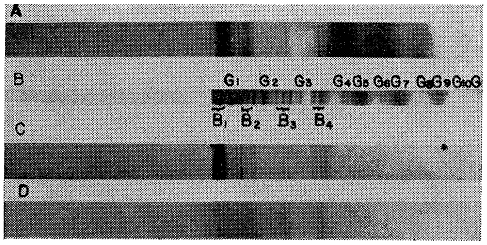

FIG. 1. "Blue" and "green" fluorescence observed in pure CdS platelets at 77°K and 4.2°K. A shows "blue green" at 77°K, B shows "blue green" at 4.2°K, C shows "blue only" at 4.2°K and D shows "blue only" at 77°K.

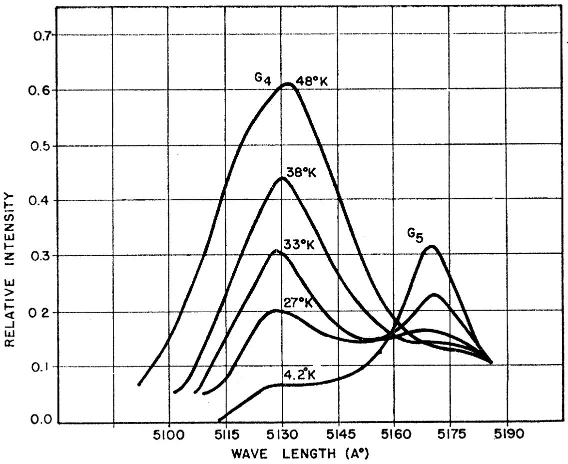

FIG. 2. Change in relative intensity of fluorescence lines G_4, G_5 as temperature increases above 4.2°K.

Photographs A and B or C and D in Fig. 1 illustrate the temperature shift of the edge emission between 4.2°K and 77°K as previously observed by others.[2,5,13] It has been shown[6] that it is possible to attribute the greater part of this apparent shift to a change in intensity of certain lines with temperature change. One observes in Fig. 2 that G_4, weak at 4.2°K, grows into the prominent emission band at 77°K with peak at 5130A, while G_5, prominent at 4.2°K, disappears at 77°K. Some actual shifting of position does occur and this has been attributed to the shift of the bands with temperature.

III. EXPERIMENTAL RESULTS

The evidence presented in the previous section indicates that (1) the fluorescence usually observed between 4850A–5600A in CdS crystals irradiated with ultraviolet light at low temperatures consists of two distinct parts, (2) the existence of certain lines in the spectrum can be attributed to phonon interaction, and (3) the apparent temperature shift of portions of the green fluorescence between 4.2°K and 77°K is due in large part to a change in intensity of lines with temperature and in small part to a shift of the forbidden energy gap with temperature.

It was felt that additional evidence, defining more completely the difference between the green and blue fluorescence, was needed before an energy model accounting for all the transitions could be postulated. To obtain this information two sets of experiments were performed. One set of experiments was designed to investigate in detail the change in intensity and position of transitions B_1, B_2, B_3, G_1, and G_2 with temperature between 4.2°K and 77°K; the other set of measurements was designed to examine the polarization of similar lines at 4.2°K.

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[11] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[12] R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).

[13] D. C. Reynolds, Phys. Rev. **118**, 478 (1960).

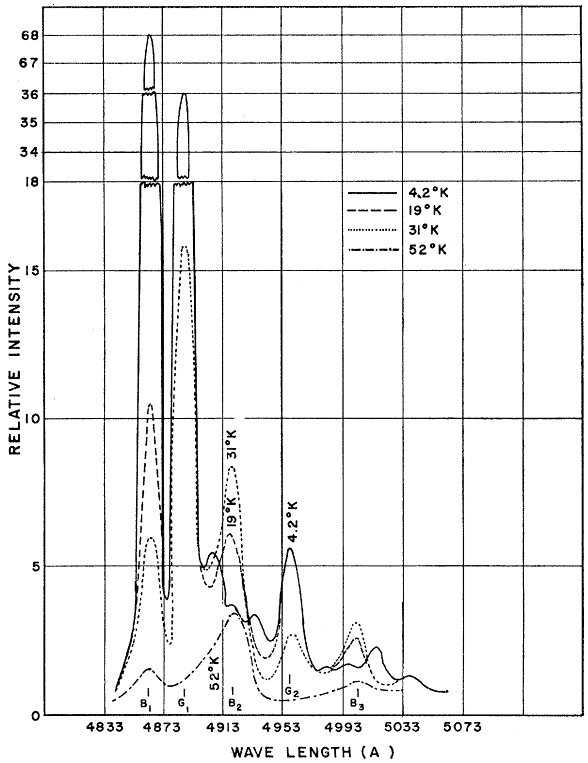

FIG. 3. Change in relative intensity of fluorescence lines B_1, B_2, B_3, G_1, G_2 as temperature increases above 4.2°K.

A. Change in Intensity and Position of Blue and Green Fluorescence with Temperature

The crystals used for these measurements consisted of CdS platelets grown from the vapor phase.[14] The crystals vary in thickness from $<1\mu$ to approximately 100μ and contain the "C" axis in the plane of the plate. The emission was measured on the as grown surface in all cases.

A CdS platelet (0.2 cm×1 cm×40μ), showing the complete "blue-green" fluorescence spectrum, was cemented with silver paint to an aluminum rod which was immersed in liquid helium, all of which was contained in the inner Dewar of a double Dewar arrangement. The crystal was irradiated with ultraviolet light from a 100 WSP4 lamp equipped with an ultraviolet filter. The experimental procedure consisted of using a Bausch and Lomb grating monochromater equipped with an IP28 photomultiplier tube to plot directly the intensity and position of a given spectral region as the temperature increased. The temperature was measured with a copper-constantan thermocouple imbedded in the aluminum rod adjacent to the crystal. The temperature rise between 4.2°K and 77°K occurred naturally as the liquid helium evaporated from the inner Dewar; no attempt was made to achieve temperature equilibrium. As a result a small temperature lag between the thermocouple reading and the crystal temperature may have existed. In addition, readings between 4.2°K and 12°K were not obtained due to the questionable reliability of the copper-constantan thermocouple in this temperature range.

Figure 3 shows the change in relative intensity and position of triplets B_1 (unresolved), B_2, B_3, and "green" lines G_1, G_2. One observes that B_1 decreases in intensity more repidly than G_1, that G_1 and G_2 vanish completely as the temperature increases, and that each triplet loses its indentification with temperature increase, such that at 19°K each triplet has changed into a band whose peak is centered about the middle line of the triplet.

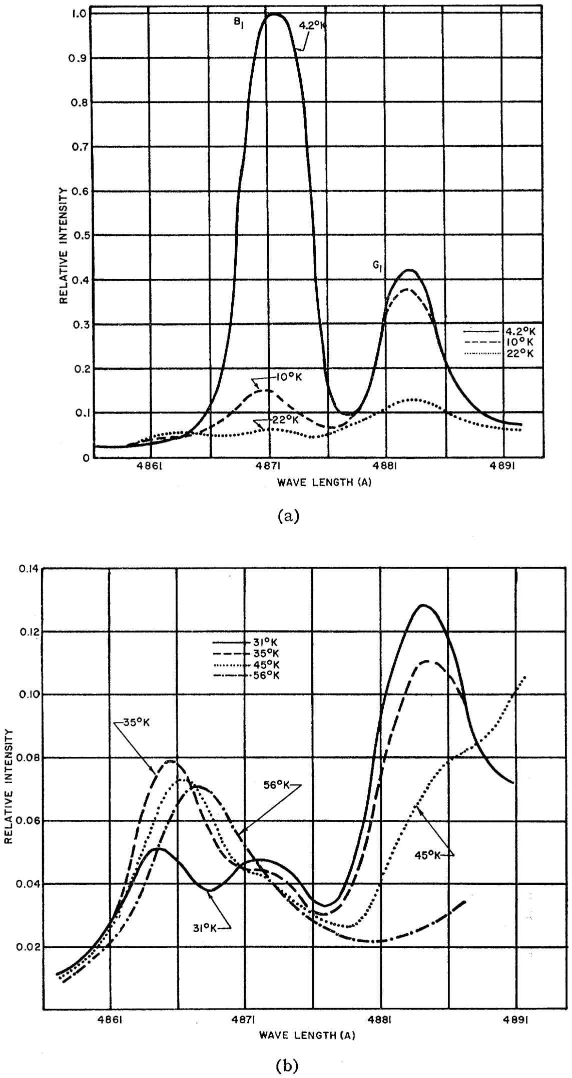

FIG. 4. Change in relative intensity of fluorescence lines B_1, G_1 as temperature increases above 4.2°K. (b) is a continuation of (a) after increasing the sensitivity of the photomultiplier tube.

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[14] D. C. Reynolds and L. C. Greene, *International Conference on Solid State Physics, Brussels, June, 1958* (Academic Press Inc., New York, 1960).

Figure 4(a) shows similar results in greater detail for triplet B_1 (unresolved), and line G_1. Both B_1 and G_1 decrease in intensity, B_1 more rapidly than G_1. Figure 4(b), plotted after increasing the photomultiplier tube voltage to obtain increased sensitivity, shows the details of the change in the structure of B_1 and G_1 between 31°K and 56°K. It is seen that at 31°K the intensity of B_1^3 has decreased sufficiently to allow resolution of the lines B_1^3 and B_1^2. At 45°K line B_1^3 has disappeared completely with B_1^2 remaining. Line B_1^1 was not intense enough to be detected with the photomultiplier.

B. Polarization of Blue Fluorescence at 4.2°K

For this set of measurements a CdS platelet, about 10μ thick showing only the blue fluorescence at 4.2°K was examined using a polarizer in conjunction with a Jarrel-Ash spectrograph having a linear dispersion of 7 A/mm. The crystals were irradiated with ultraviolet light as before. For each exposure taken, all experimental conditions with the exception of the position of the polarizer were held constant.

Figure 5 shows the relative intensity of triplets B_2 and B_3 at 4.2°K. The upper curves were obtained from the photographs taken with $E\|C$; the lower curves were obtained from the photographs with $E\perp C$, giving evidence of, at best, a slight polarization; however, no one component shows evidence of being strongly polarized.

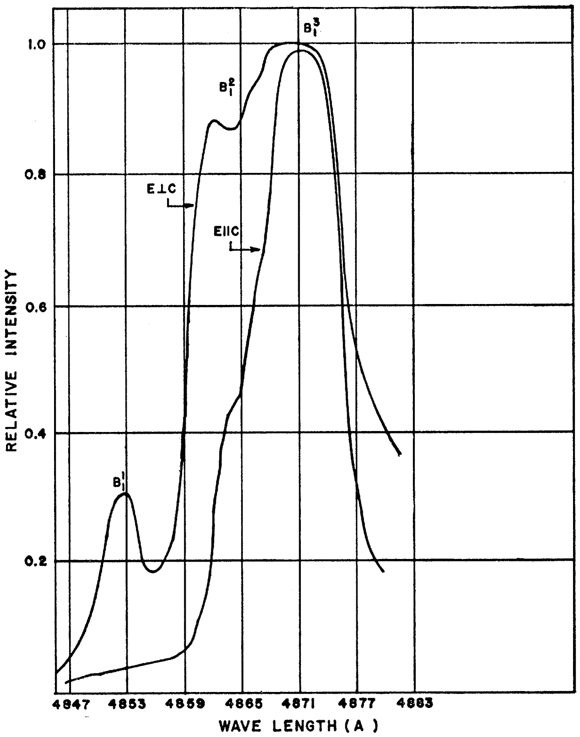

FIG. 6. Relative intensity of triplet B_1 at 4.2°K. One curve shows the fluorescence with $E\|C$, the other with $E\perp C$.

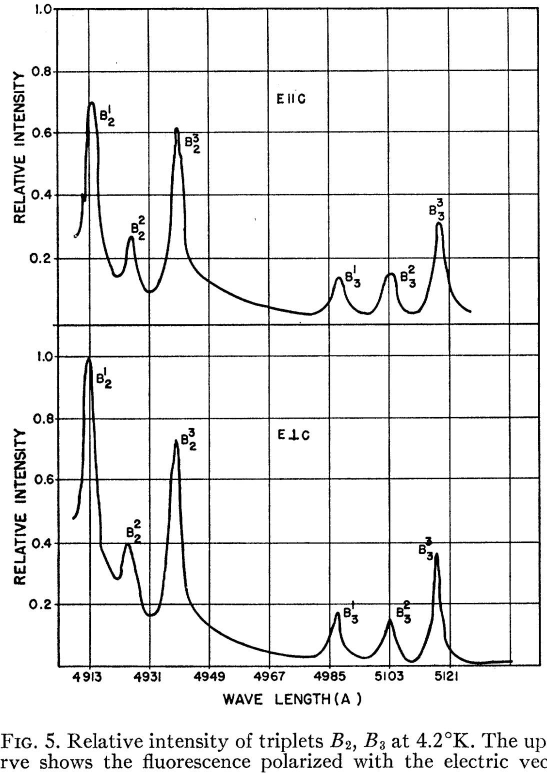

FIG. 5. Relative intensity of triplets B_2, B_3 at 4.2°K. The upper curve shows the fluorescence polarized with the electric vector parallel to the "C" axis of the CdS crystal; the lower curve with the electric vector perpendicular to the "C" axis.

On the other hand, as seen in Fig. 6, triplet B_1 (resolved in this densitometric trace) exhibits marked polarization effects. With $E\perp C$, B_1^1, B_1^2, B_1^3 are as shown. When the polarizer is rotated 90° placing $E\perp C$, B_1^1 vanishes completely, B_1^2 is reduced substantially, while B_1^3 remains practically unaffected.

IV. PROPOSED ENERGY MODEL

If a proposed energy model is to explain successfully the experimental observations, it must (1) distinguish clearly between the origins of the "blue" fluorescence and the "green" fluorescence (2) account for transitions B_1, B_2, G_1, G_4, and G_5 at 4.2°K, the remaining lines being attributed to phonon interaction (3) account for the transitions at 77°K and the changes in the transitions between 4.2°K and 77°K and (4) be consistent with the results obtained from the polarization measurements.

A. Energy Model for Green Fluorescence

It has already been shown by Kulp and Kelley[15] that the center for green "edge" emission (G_4, G_6, G_8, G_{10}) at 77°K is due to the sulfur interstitial atom. This center is located about 0.14 ev from the band edge. In order to account for the remaining green fluorescence

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[15] B. A. Kulp and R. H. Kelley, J. Appl. Phys. 31, 1057 (1960).

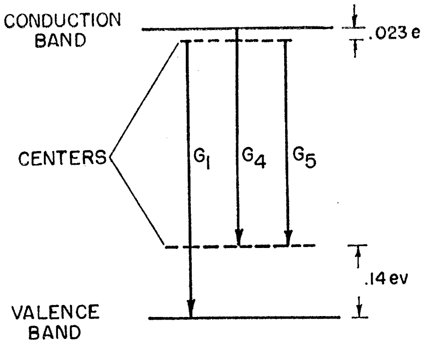

FIG. 7. Energy model for "green fluorescence" in CdS.

G_1, G_2, G_3, and G_5, G_7, G_9, G_{11}, it has been necessary to introduce a second center, 0.023 ev[16] below the conduction band. Figure 7 shows the proposed energy model. This model is consistent with the observed results, namely that G_1 and G_5 vanish as the crystal is heated from 4.2°K to 77°K and that G_4, while weak at 4.2°K, becomes the dominant transition at 77°K. At low temperatures the 0.023-ev center is sufficiently populated so that recombinations between the trapped electrons in this center with the trapped holes in the deeper center and free holes in the valence band can occur. As the temperature is increased, the 0.023-ev center becomes depopulated and recombinations occur between the conduction band and the lower center, which is sufficiently far removed from the valence band to remain populated. It should be noted that whereas the energy model chosen to explain the green fluorescence shows the shallow center near the conduction band and the deep center near the valence band, a mirror reflection of these centers about the middle of the forbidden energy gap would account for the transitions G_1, G_4, and G_5 equally well. The experimental evidence does not distinguish between these two choices.

Likewise the experiment of Lambe *et al.*[10] does not allow one to resolve uniquely the location of these two centers. In their experiment three possible recombination processes were assumed: (a) recombination of free electrons and holes, (b) recombination of free holes with trapped electrons, and (c) recombination of free electrons with trapped holes. The experiment consisted of first irradiating the crystal with ultraviolet light which was then removed. The emission then decayed rapidly while the photocurrent decayed much more slowly. The photocurrent from the crystal as well as the emission intensity was monitored while the crystal was irradiated with infrared light of quenching energy. As a result of the infrared light the photocurrent was quenched and green emission was stimulated by the release of holes. In all cases the photocurrent decayed more rapidly as a function of infrared radiation time than did the green emission. It was assumed that the photocurrent was directly proportional to the number of free electrons and that the number of free holes either remained constant or decreased as a function of time. The luminescent intensity is proportional in case (a) to the product of the number of free holes and electrons, in case (b) to the product of the number of free holes and trapped electrons and in case (c) to the product of the number of free electrons and trapped holes. Therefore in case (a) and case (c) the luminescent intensity should decay at least as fast as or faster than the photocurrent. Since this did not occur, case (b) was the only recombination process consistent with the experimental results.

According to our experimental results the recombination process at 4.2°K is actually one of a trapped electron with a trapped hole as shown in the model, Fig. 7. The luminescent intensity in this case is proportional to the product of the number of trapped electrons and trapped holes. Consequently, the luminescent intensity could well decay more slowly than the photocurrent, in conformity with the experimental results of Lambe *et al.*[10] Since the model from which their three recombination processes were derived did not include a second center, as our model must, their experimental results are not sufficient to decide explicitly on the position of the two centers relative to the bands. It is possible that one could uniquely resolve the positions of the centers if one were to repeat their measurements at a temperature above which the shallow center is rendered inactive.

B. Energy Model for Blue Fluorescence

In order to account for the triplet structure observed in the blue fluorescence at 4.2°K, an energy model based on the band structure calculations made by Balkanski and des Cloizeaux[17] has been adopted. The band structure calculations for the CdS point group originally made by Hopfield[18] and Birman[19] were extended to the $0K_x$, $0K_y$, and $0K_z$ axes in the Brillouin zone by Balkanski and des Cloizeaux. In this calculation the conduction band minima do not occur at $K=0$ along the $0K_x$ and $0K_y$ axes; likewise the two lower valence bands have maxima away from $K=0$ along the above two axes. The top valence band is degenerate at $K=0$ with the maxima occuring at $K=0$. The general feature of the calculation neglecting the two lower valence bands is shown for the $0K_x$ axis in Fig. 8. The Γ_7 symmetry of the conduction band at the center of the Brillouin zone goes into a $\Sigma_3+\Sigma_4$ symmetry along the $0K_x$ axis and the Γ_9 symmetry of the top valence band also goes into a $\Sigma_3+\Sigma_4$ symmetry along the same axis. The selection rules[20] permit $\Sigma_3 \rightleftarrows \Sigma_4$ transitions only when the "E" vector is polarized ⊥ to the "C" axis. The $\Sigma_3 \rightarrow \Sigma_3$ and $\Sigma_4 \rightarrow \Sigma_4$ transitions are allowed

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[16] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[17] M. Balkanski and J. des Cloizeaux, J. Phys. Chem. Solids (to be published).

[18] J. J. Hopfield, Bull. Am. Phys. Soc. **3**, 409 (1958).

[19] J. L. Birman, Phys. Rev. Letters **2**, 157, (1959).

[20] R. G. Wheeler (private communication).

for both the ⊥ and || modes of polarization. The same general features are true for the $0K_y$ axis. Along the $0K_z$ axis, the maxima in the valence bands and the minima in the conduction band occur at $K=0$.

To account for the "blue" fluorescence and dependence of this fluorescence on temperature two centers are required, as was the case in the model for "green" fluorescence. The proposed transitions responsible for the B_1 triplet are shown in Fig. 8(a). $B_1{}^1$ is a band-to-band transition occurring at the minima of the conduction band for $\Delta K=0$. The $B_1{}^2$ transition occurs with phonon cooperation from the minima in the conduction band to the maxima in the valence band. The $B_1{}^3$ transition occurs from the top of the valence band to a center 0.005-ev below the conduction band. $B_1{}^3$ is much more intense than $B_1{}^2$ or $B_1{}^1$. As the temperature is increased above 4.2°K, $B_1{}^3$ decreases in intensity very rapidly and has disappeared completely at 45°K as shown in Fig. 4. This would be expected from the model since this center would become depopulated rapidly as the temperature is increased. From the model one would expect $B_1{}^1$ to be strongly polarized since it is a $\Sigma_3 \rightleftarrows \Sigma_4$ transition; that this is the case is seen in Fig. 6. $B_1{}^2$ is less strongly polarized. Though it arises from pure states in the conduction band, the valence band will be made up of a mixture of states of Σ_3 and Σ_4 symmetry resulting in decreased polarization. The $B_1{}^3$ transition occurs from a center made up of mixed states of Σ_3 and Σ_4 symmetries to the valence band again made up of mixed states of Σ_3 and Σ_4 symmetries resulting in very little polarization as is observed. The B_2 triplet results from center to center and band to center transitions. In addition to the center 0.005 ev below the conduction band, another center 0.022-ev above the valence band is present. The transitions occur from the minima of the conduction band. It is reasonable to assume that the centers will reflect the symmetries of the bands and that the center near the valence band will reflect the splitting of the valence band.[21] The transitions for B_2 are shown in Fig. 8(b). $B_2{}^1$ and $B_2{}^3$ are center-to-center transitions. $B_2{}^2$ is a band-to-center transition. As the temperature is increased the center nearest the conduction band will become depopulated, which causes lines $B_2{}^1$ and $B_2{}^3$ to disappear as is observed in Fig. 3. The fluorescence builds up about line $B_2{}^2$, analogous to line G_4 in the green fluorescence. This behavior also occurs for the B_3 triplet providing further evidence that B_3 and B_4 result from phonon interaction. Since the centers are made up of mixtures of states of Σ_3 and Σ_4 symmetries one would not expect the lines to be very strongly polarized. That this is the case is seen in Fig. 5.

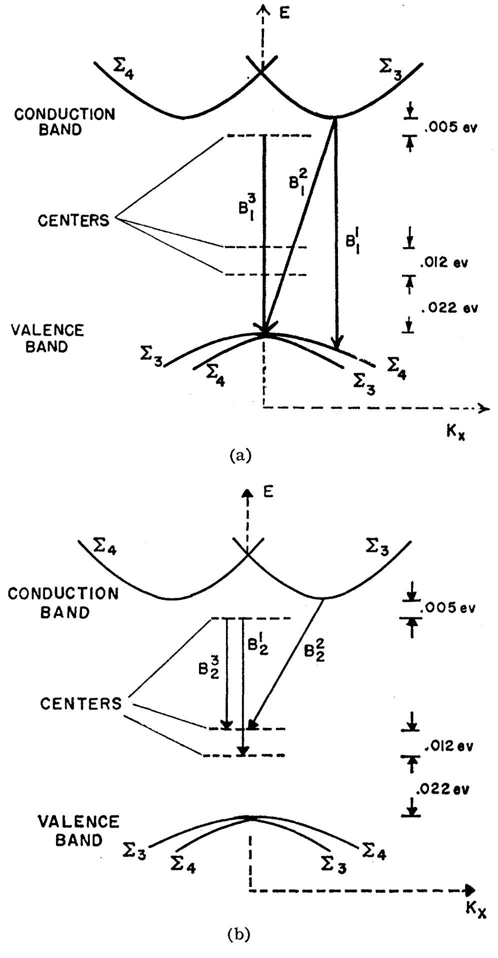

FIG. 8. Energy model for "blue fluorescence" in CdS. (a) accounts for triplet B_1; (b) accounts for triplet B_2.

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[21] R. J. Collins and J. J. Hopfield, Phys. Rev. **120**, 840 (1960).

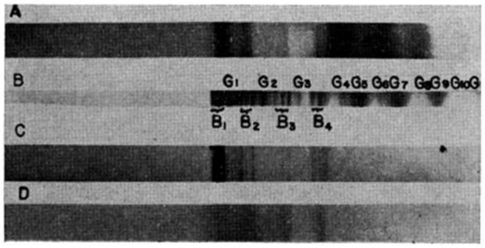

FIG. 1. "Blue" and "green" fluorescence observed in pure CdS platelets at 77°K and 4.2°K. *A* shows "blue green" at 77°K, *B* shows "blue green" at 4.2°K, *C* shows "blue only" at 4.2°K and *D* shows "blue only" at 77°K.