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ON THE NATURE OF THE LONG-TERM DEGRADATION OF "CADMIUM SULFIDE" SOLAR CELLS

T. Peterson and J. Washburn

February 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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SUBJECT CLASSIFICATION: 14.3; 16; 22.4.1

On The Nature of The Long-Term Degradation of "Cadmium Sulfide" Solar Cells

T. Peterson and J. Washburn

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, California 94720.

ABSTRACT

The spectral response of the Cu_xS/CdS (x = 2, 1.95) heterojunction is calculated using a simple model; and a comparison with published data is made. This comparison suggests that there is a degradation of the djurleite cell (x = 1.95) besides that due to the fact that djurleite has a smaller optical absorption constant than chalcocite. It is shown that the dislocation array necessary to accommodate the lattice mismatch between the djurleite and the cadmium sulfide could be a contributing factor in this degradation.

RÉSUMÉ

Nous avons calculé la réponse spectrale de l'hétérojonction Cu_xS/CdS (x = 2; 1,95) à l'aide d'un modèle simple; et nous avons comparé ces calculs avec les données publiées. Cette comparaison suggère qu'il y a une dégradation de la cellule de djurleite (x = 1,95) outre le fait que la djurleite ait une constante d'absorption optique plus faible que la chalcocite. Nous avons montré que le réseau de dislocations nécessaire à l'ajustement de la différence de paramètre des mailles de la djurleite et du cadmium sulfuré peut être une cause de cette dégradation.

I. INTRODUCTION

In recent years it has come to be generally acknowledged that the principal production center of carrier pairs in so-called "cadmium sulfide" solar cells is, in fact, the thin layer of a copper sulfide phase which forms a p-n heterojunction with the CdS. Several workers [1,2] have noted that the properties of this "Cu_xS"/CdS heterojunction are very sensitive to the stoichiometry of the copper phase--the closer x approaches 2 (chalcocite), the higher the cell's efficiency. This phenomenon is usually dispatched with the observation that the copper sulfide phases of higher copper content exhibit greater absorption; therefore, one would expect diminishing efficiency with decreasing x. However, it will be shown that the observed changes in absorption are not sufficient to account for the observed changes in cell properties. Furthermore, it will be shown that the changes in lattice parameter which accompany changes in x could be a contributing factor to the decreased efficiency of cells with copper sulfides of lower copper concentration.

II. SIMPLE ONE-DIMENSIONAL THEORY OF THE PHOTO-CURRENT

Consider the structure illustrated in Figure 1. The illumination is incident from the left, so the photon flux Φ at point z, between wavelengths λ and $\lambda + d\lambda$ is given by

$$\Phi(z,\lambda)d\lambda = \Phi(0,\lambda)e^{-K(\lambda)z}\, d\lambda \quad (0 \leq z \leq w) \tag{1}$$

where $K(\lambda)$ is the absorption constant of the Cu_xS at wavelength λ and is assumed to be independent of z. The rate of photon absorption between z and z + dz is given by

$$R(z)dz = [\int_0^\infty K(\lambda)\Phi(z,\lambda)d\lambda]dz. \tag{2}$$

In order to find an expression for the rate of carrier production it is necessary to distinguish that part of $K(\lambda)$ due to interband transitions (pair creation) $K_{pc}(\lambda)$ from the part due to other processes such as intraband transitions (free carrier absorption) $K_{fc}(\lambda)$:

$$K(\lambda) = K_{pc}(\lambda) + K_{fc}(\lambda).$$

Then the minority carrier production rate between z and z + dz is given by

$$\dot{n}(z)dz = [\int_0^\infty K_{pc}(\lambda)\Phi(0,\lambda)e^{-K(\lambda)z}d\lambda]dz \tag{2a}$$

If the probability $P(z)$ of the arrival of a minority carrier at $z = w$ (where w = depletion region boundary ≅ metallurgical boundary) before recombination is taken as $\exp[(z - w)/L]$ where L is the minority carrier diffusion length, the rate of arrival of minority carriers at $z = w$ is given by

$$\dot{N} = \int_0^w P(z)\dot{n}(z)dz = \int_0^\infty \int_0^w K_{pc}(\lambda)\Phi(0,\lambda)e^{-K(\lambda)z}e^{(z-w)/L}\,dzd\lambda$$

$$= \int_0^\infty [\Phi(0,\lambda)\frac{K_{pc}(\lambda)L}{K(\lambda)L-1}(e^{-w/L}-e^{-K(\lambda)w})]d\lambda$$

Then, when $\Phi(0,\lambda) = \delta(\lambda-\lambda')$ where $\delta(\lambda-\lambda')$ is the dirac delta function, the spectral quantum efficiency $Q(\lambda)$ is proportional to $\dot{N}$:

$$Q(\lambda) = \eta\,\frac{K_{pc}(\lambda)L}{K(\lambda)L-1}\,(e^{-w/L} - e^{-K(\lambda)w}) \tag{3}$$

where η is a constant (<1) which allows for loss mechanisms other than bulk recombination,* e.g., recombination at interfacial states.

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* A more exact calculation which included surface recombination effects was made using the one-dimensional diffusion equation with no drift field. The resulting $Q(\lambda)$ reduces to equation (3) when the surface recombination velocity s equals the bulk minority carrier diffusion length divided by the bulk minority carrier lifetime, i.e. $st/L = 1$.

III. CALCULATION OF SPECTRAL RESPONSE

B. J. Mulder[3] has measured the absorption constants of the various copper sulfide phases in the optical region. He found that the imaginary part (2nk) of the dielectric constant ($[n-ik]^2$) can be well approximated by an expression of the form

$$2nk = \frac{P}{1+\exp[S(H-E)]} + \frac{p}{1+\exp[s(h-E)]} + \frac{f}{E^3} \qquad (4)$$

where E is the incident photon energy ($h\nu$) and the other letters represent empirical constants. He interpreted the three terms of the R.H.S. of (4) as absorption by direct interband transitions, indirect interband transitions, and free carriers respectively. In order to obtain $K(\lambda)$ from 2nk, one must know (or estimate) the index of refraction n as a function of wavelength, since

$$K(\lambda) = (2\pi/\lambda n)\ (2nk).$$

Mulder shows plots of n(E) for the various copper sulfides in which n is seen to increase roughly proportional to E until it reaches a maximum which occurs at about 2.5 eV for both chalcocite and djurleite. Therefore, one can approximate $n(\lambda)$ as follows:

$$n(\lambda) \simeq n(2.5\text{eV}) - \left\langle \frac{dn}{de} \right\rangle \left| E - 2.5 \right|$$

$$= n(2.5\text{eV}) - \left\langle \frac{dn}{de} \right\rangle \left| \frac{1.24}{\lambda(\mu m)} - 2.5 \right| \qquad (6)$$

Although this approximation is admittedly crude, it should be satisfactory since the even cruder estimate n = constant was found to give substantially the same results; which means that the exponential behaviour of 2nk dominates $K(\lambda)$.

Finally, to obtain the spectral response under constant intensity illumination rather than constant photon flux, equation (3) must be

multiplied by a factor proportional to λ to account for the fact that the number of photons per unit wavelength increases proportional to λ in a constant energy spectrum.

Then equations (3) - (6) yield

$$j_{sc}(\lambda) \propto q\eta\lambda I_0 \frac{K_{pc}(\lambda)L}{K(\lambda)L-1} (e^{-w/L} - e^{-K(\lambda)w}) \qquad (7)$$

where $j_{sc}(\lambda)$ is the short-circuit current density, q is the carrier charge, I_0 is the incident light intensity, and $K_{pc}(\lambda)$ is derived from (5) and the first two terms of the R.H.S. of (4) while $K(\lambda)$ includes all three terms of (4).

Equation (7) was plotted using values of w from .3 to 1.0 micron, L from .03 to .4 microns, and the appropriate constants in equation (4) as determined by Mulder*. Figure 2 shows a typical calculated spectral response of a chalcosite layer and a djurleite layer which differ only in their absorption constants $k(\lambda)$. (See Sec. VII for discussion of the assumptions implied here.) Also shown are the experimental responses of actual cells reproduced from Palz et al. [1]. It can be seen that the ratio of chalcocite to djurleite response currents is larger for the experimental curves in spite of the fact that the series resistance effects were neglected in the calculated curves. None of the combinations of w and L used to calculate response curves gave as high a short-circuit current ratio as the experimental curves show. This would indicate that there is another loss mechanism in the djurleite cell.

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* It should be noted that Mulder's data extend only down to about .45μm. Therefore, the shorter wavelength calculations are of doubtful validity. Also, these calculations do not include the effects of series resistance; some of which would be a "flattening-out" of the response peaks at high illumination levels and a non-linear dependence of $j_{sc}(\lambda)$ on I_0, both due to forward biasing of the junction.

IV. MINORITY CARRIER DIFFUSION LENGTH

Upon observing the rather sensitive dependence of the response curves on the minority carrier diffusion length shown in Fig. (3) one might be tempted to postulate a decrease in L to accompany the chalcocite to djurleite transformation. Several attempts have been made to measure the minority carrier diffusion length in cuprous sulfide. Gill and Bube[4] succeeded in placing an upper bound of about .4μm on L; however, they made no attempt to ascertain which phase of Cu_xS they investigated. More recently, Mulder[5] reported that the diffusion length in chalcocite (in equilibrium with djurleite) is about 300Å for diffusion perpendicular to the c-axis; while L in djurleite is 50Å or less. If this factor of six change were real, it would more than account for the remaining difference in the spectral sensitivities of chalcocite and djurleite cells. However, there is a compelling reason to not accept Mulder's result: The calculated quantum efficiency (using an expression derived in the same manner as the expression used by Mulder) of a Cu_2S/CdS heterojunction does not exceed 5% over the entire spectrum if the ratio w/L = 10 (i.e. w = .3μm; L = 300Å). Since the observed <u>power</u> efficiency of such devices with w ≃ .3 m is as high as 7%, (implying quantum efficiences higher than 7%) it seems clear that L must be much larger than 300Å. Furthermore, as Gill and Bube[4] point out, even a diffusion length of several thousands of angstroms puts an upper limit of about 10^{-9} sec. on the minority carrier lifetime τ_n. Hence, if L is no more than a few hundred angstroms, $\tau_n \lesssim 10^{-11}$ sec; and in djurleite $\tau_n \sim 10^{-12} - 10^{-13}$ sec; unless the electron diffusivity $D_n \ll 1 cm^2/sec$. It seems likely that there is an error in Mulder's result.

V. DISLOCATION ARRAY MODEL

Oldham and Milnes[6] have shown that the dislocations necessary to accommodate the lattice mismatch at a heterojunction can have a pronounced effect on the junction's current-voltage relation. Assuming that the number of dislocations is equal to that required by the lattice mismatch, and that a regular array is formed, they derived an expression relating the dislocation spacing h to the degree of mismatch:

$$h = M \frac{a_1 a_2^2}{a_2^2 - a_1^2}$$

where a_1, a_2 are the smaller and larger lattice parameters and M is a constant determined by geometric factors, such as the crystallographic plane of the array and the angle between the dislocation lines and their burgers vectors. The imperfect material (i.e. "dangling bonds") in the cores of these dislocations acts as a multitude of carrier trapping and recombination sites. It is apparent that the more closely spaced these dislocations are, the more likely a free carrier is to be trapped or to recombine while attempting to traverse the array. Thus, the array can be assigned a "transmission coefficient" equal to the probability that a free carrier will successfully pass through it. McKelvey and Longini[7] have derived an expression for the transmission coefficient T of a planar array of parallel dislocations of capture diameter g and inter-dislocation spacing h:

$$T = \frac{2}{\pi} \left[\cos^{-1}(g/h) - g/h \ \mathrm{sech}^{-1}(g/h)\right] \qquad (10)$$

Then for a (111) plane with three sets of parallel dislocations*

$$T = \left(\frac{2}{\pi}\right)^3 \left[\cos^{-1}(g/h) - g/h \operatorname{sech}^{-1}(g/h)\right]^3. \qquad (11)$$

This expression is valid if there is a driving force on the carriers such that they each make a single pass through the array; for example, in the depletion region of a pn device where the built-in electric field supplies the force. If, however, the only "driving force" for the carriers is a concentration gradient so that each carrier is executing a (nearly) random walk; equation (11) is not valid because the carriers will, on average, traverse the array many times. McKelvey[8] considered this case and algebraic manipulation of his equations(29) yields an effective transmission coefficient τ:

$$\tau = \frac{T(1-B)}{1-R(B+B') - BB'(T^2-R^2)} \qquad (12)$$

where R is the probability of reflection from the array, B is the probability that a carrier having passed through the array will be reflected back to the array before it is collected by the junction or before it recombines via some bulk mechanism; and B' is the probability that a carrier starting from the array, moving "upstream", will not recombine before it returns to the array. The value of B depends on the proximity of the array to the edge of the depletion region. If it is very far away $B \to (1-\varepsilon)/(1+\varepsilon) \simeq 1$, where $\varepsilon \equiv {}^{2D}/v_{th} L$ and D, L, v_{th} are the carrier diffusivity, thermal speed and diffusion length, respectively [8].

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* Here the assumption of Oldham and Milnes (op. cit.) that T for i sets of non-parallel dislocations can be approximated by T^i is used.

However, as the array approaches the junction, B approaches zero. If $R \approx 0$ and $B' \approx 1$, equation (12) reduces to Oldham and Milnes'[6] equation (16):

$$\tau \approx \frac{T(1-B)}{1-BT^2} \tag{13}$$

Equation (13) is plotted vs. $^g/h$ in Fig. 4 for an array on a (111) plane and several values of B. [Notice that $\tau(B=0) = T$.]

VI. APPLICATION TO Cu_xS/CdS HETEROJUNCTION

High efficiency "cadmium sulfide" solar cells are made by conversion of a thin layer (typically less than one micron thick) of n-CdS to cuprous sulfide (chalcocite), forming a p-n heterojunction. This is usually accomplished by dipping the CdS in a hot (80-90°C), aqueous Cu^+ solution for a time of about 10 sec. to one minute. Even in the case of chalcocite which has about 4.5% misfit with CdS there will be a considerable number of misfit-accommodation dislocations, h(111) ≈ 100Å. However, since these dislocations best relieve the lattice strain if they are in the region of high copper concentration gradient (i.e. the depletion region), that is where they should be found, similar to the case of misfit dislocations in boron-diffused silicon[9]. Therefore, since the array is in the field of the depletion region, the corresponding transmission coefficient is T (equation 11). Assuming a capture diameter of 2Å (approximately the largest value found experimentally by McKelvey[8] in Ge), $^g/h \approx .02$ and $T \approx .8$ (from Fig. 4). This value assumes, also, that the dislocations all lie on one plane; however, that is almost certainly not the case. Washburn, Thomas, and Queisser[10]. found that the dislocations induced by diffusion of phosphorous into Si

formed several arrays stacked one atop another with parallel dislocations on different levels tending to be aligned in planes perpendicular to the diffusion front. This configuration is quite reasonable if one considers the interaction forces between two identical edge dislocations on different, parallel glide planes. They are in stable equilibrium when lined up perpendicular to their glide planes (see Fig. 5). The net effect of this stacking is likely to be a slight increase in T.*

It is found that exposure to the atmosphere is irreversibly deleterious to the cell's efficiency over long terms, expecially if the cell is heated to 60°C or higher[1, 11, 12]. It has also been noted that exposure to air causes a spontaneous conversion of chalcocite to lower copper concentration sulfides[13]. This, together with the fact that the heat treated cells show the same shift in spectral sensitivity as those converted to djurleite by electro-oxidation of the chalcocite layer (cf. Fig. 1 of [11] and Fig. 12 of[1]), leads one to suspect that the degradation (whether rapid, as in the heat treatments, or over the long term, in actual use) is accomplished by the diffusion of copper to the surface with the formation of a thin layer of CuO or Cu_2O no more than about 100Å thick. If this is the case, as the copper diffusion proceeds, a layer of djurleite should form at the surface and grow in at the expense of the chalcocite Especially at lower

* This is because of the ordering of the arrays, i.e., they are no longer independent; therefore, the approximation $T(i) = [T(1)]^i$ is not applicable. This ordering will cause the "windows" in the arrays to be larger on average than a random stacking would give. Note that this is only true for an array in an electric field where the electrons are not undergoing a random walk; in other cases the effect of the stacking is negligible.

temperatures one should expect the djurleite phase to nucleate at the surface rather than at the junction, where there is of course also loss of copper via diffusion into the CdS, because twice as many dislocations would be required--one array at the djurleite-chalcocite boundary plus an equal number added to the existing array at the junction. At first this layer will be strained to match the chalcocite lattice; but when it becomes more than several tens of lattice constants thick, the dislocated interface becomes energetically favored[14]. Thus, a second dislocation array moves inward as the djurleite layer grows. The misfit between djurleite and chalcocite is about 0.5%, so depending on how many planes the array is spread over, the interdislocation spacing will be greater than or equal to about 800Å. When this second array approaches the first to within a distance comparable with its own interdislocation spacing, it will be retarded by the repulsive climb force interaction between stacked edge dislocations as in Fig. 5. Therefore, the final configuration will consist almost entirely of djurleite and contain two arrays separated by a thin ($\lesssim$ 1000Å) strained layer of djurleite* as shown in Fig. 6. The response of this cell is then essentially the djurleite cell response times the transmission coefficient of the second array.

The transmission coefficient of this array will be given by equation (13) since it is in a field-free region. Thus, the second array is much more effective recombination/trapping center than the first

* Perhaps it would be better to describe this layer as "non-equilibrium chalcocite" containing an abnormal copper deficit.

array, which is in the high electric field of the depletion region. (Taking g = 2Å again; g/h ≃ .0025 and, if B ≥ .95, τ ≲ .42)

VII. DISCUSSION

A simple calculation of the spectral response of a Cu_xS/CdS heterojunction solar cell has been performed and has demonstrated that the differences in absorption are unlikely to be the only cause of the radically differing efficiencies of cells made of chalcocite and djurleite. In the worst case investigated (w = 1μm; L = 1μm) the calculated response peaks differ by only about a factor of four compared to a measured ratio of more than eight[1]. Further, the calculated ratios are very likely over estimated because of the neglect of the junction's forward bias current (see footnote, Sec. III).

It was argued that although a change in minority carrier diffusion length could be responsible for the balance of the difference between chalcocite and djurleite cells there is little evidence of such a change.

Although there are, indeed, changes in other properties which might lead to significant changes in sensitivity between chalcocite and djurleite cells; comparison of the optical absorption curves presented in [3 (p. 87)] lends much credibility to the "rigid band" model as discussed by Mulder in [15]. In that scheme djurleite is regarded, as far as electrical properties are concerned, as very highly doped "chalcocite" in which the indirect (i.e., $k \neq 0$) valence band maximum is nearly depleted of carriers. Hence the probability of the indirect transition of 1.2 eV is much diminished and the change in Fermi level gives rise to a slight increase in the direct band gap which shows up as a

shift of the onset of strong absorption between chalcocite and djurleite to shorter wavelengths.

Finally, it was shown to be possible for that part of the decrease in short circuit current not due to absorption changes to be due to the presence of a dislocation array located within the cuprous sulfide. This array, unlike the array at the interface in the depletion region, acts as a very effective trapping-recombination center for the photo-generated carriers; and, therefore, reduces the sensitivity of the cell.

ACKNOWLEDGMENTS

The authors wish to thank Professor W. G. Oldham for several very helpful discussions and for his critical reading of the manuscript. We are also grateful for the support of the United States Atomic Energy Commission through Inorganic Materials Research Division of Lawrence Berkeley Laboratory.

REFERENCES

1. W. Palz, J. Besson, T. Nguyen Duy, and J. Vedal, Conference Record of the 9th Photovoltaic Specialists' Conference, Silver Spring, Md., 1972, Catalog No 72CHO 613-0, I.E.E.E. (p. 91).

2. K. Bogus and S. Mattes, Conference Record of the 9th Photovoltaic Specialists' Conference, Silver Spring, Md., 1973, Catalog No 72CHO 613-0, I.E.E.E. (p. 106).

3. B. J. Mulder, phys. stat. sol. (a) 13, 79 (1972).

4. W. D. Gill & R. H. Bube, J. appl. Phys. 41, 1694 (1970).

5. B. J. Mulder, phys. stat. sol. (a) 13, 569 (1972).

6. W. G. Oldham and A. G. Milnes, Sol. State Electronics 7, 153 (1964).

7. J.P. McKelvey & R. L. Longini, Phys. Rev. 99, 1227 (1955).

8. J. P. McKelvey, Phys. Rev. 106, 910 (1957).

9. E. Levine, J. Washburn, and G. Thomas, J. appl. Phys. 38, 81 (1967).

10. J. Washburn, G. Thomas, and H. J. Queisser, J. appl. Phys. 35, 6 (1964).

11. K. Bogus, H. Fisher, S. Mattes, and N. Peters, Solar Cells, Proc. Internat. Colloq. organized by Europ. Coop. Space Environment Comm., Toulouse 1970, Gordon & Breach, New York/London 1971 (p. 121).

12. R. J. Mytton, L. Clark, R. W. Gale, and K. Moore, Conference Record of the 9th Photovoltaic Specialists' Conference, Silver Spring, Md., 1972, Catalog No 72CHO 613-0, I.E.E.E. (p. 133).

13. W. R. Cook Jr., L. Shiozawa, and F. Augustine, J. appl. Phys. 41, 3058 (1970).

14. J. H. van der Merwe, J. appl. Phys. 34, 123 (1963).

15. B. J. Mulder, phys. stat. sol. (a), 18, 633 (1973).

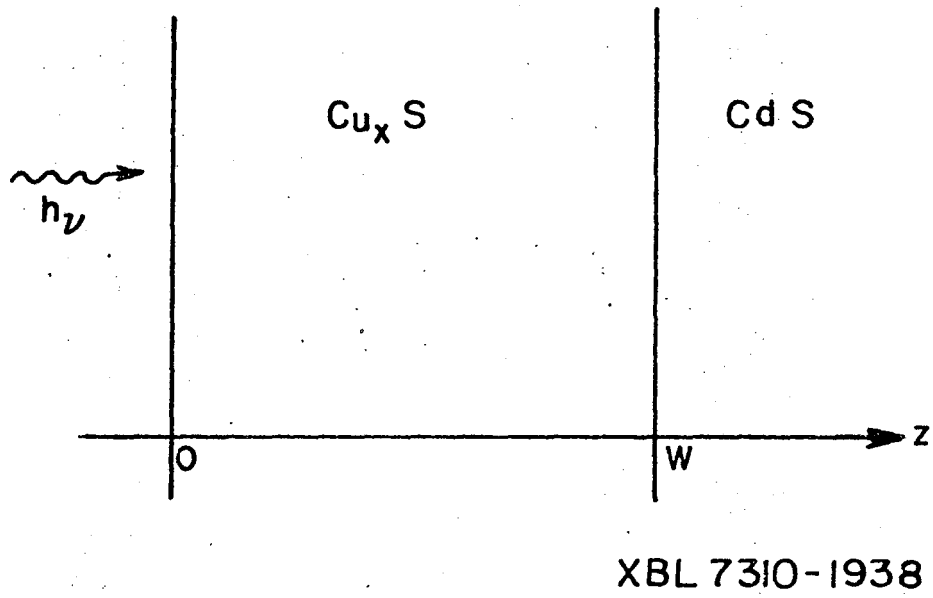

Fig. 1. Structure considered in calculation of spectral sensitivity. Metallurgical boundary z = w is assumed to coincide with edge of depletion region; and absorption in CdS is neglected.

Fig. 2. Comparison of calculated spectral response with data of Palz *et al.* (ref. 1) for chalcocite and djurleite active layers. The peak on the experimental djurleite curve at .53μm is probably due to CdS absorption which was not considered in the calculations.

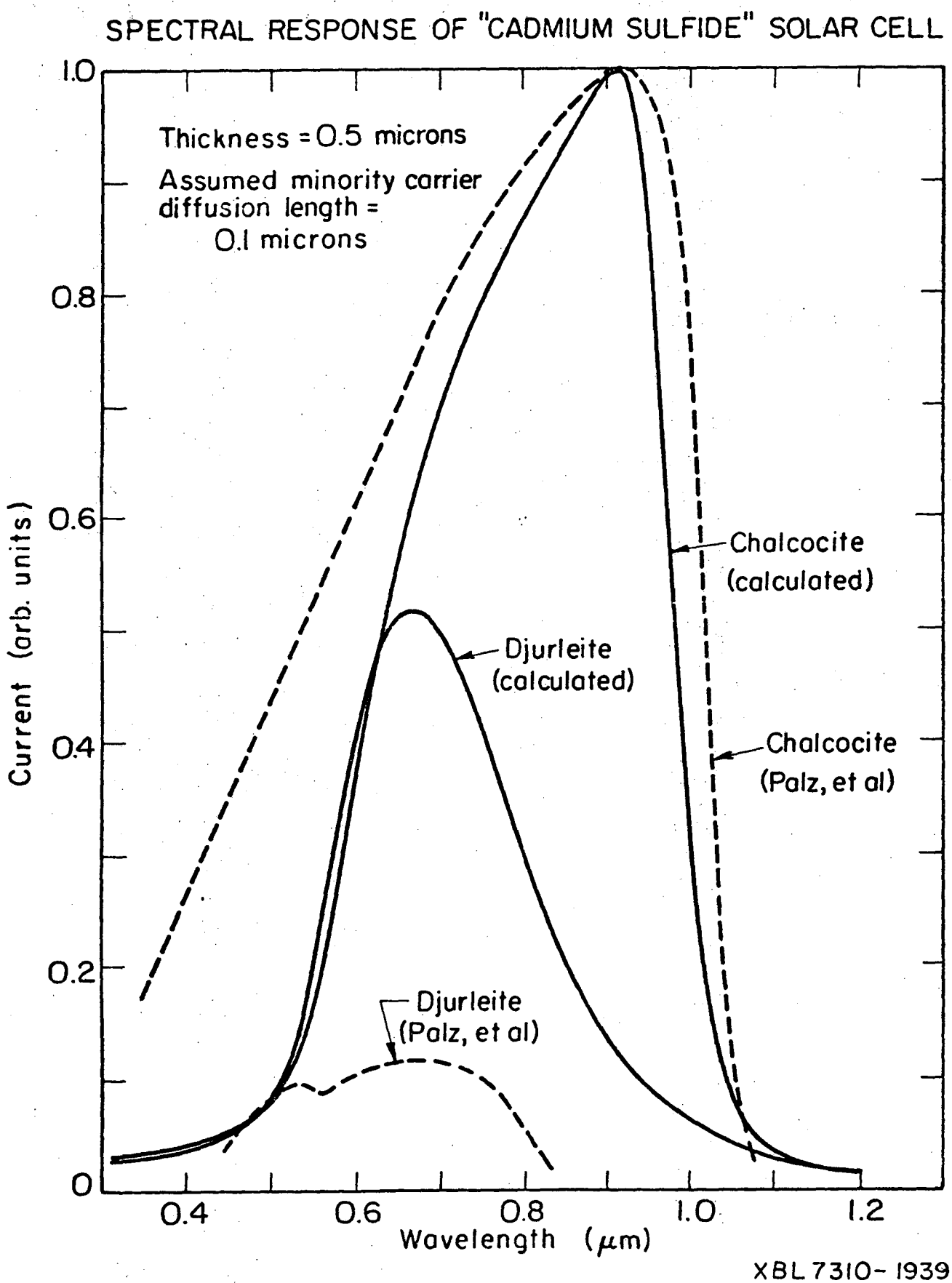
SPECTRAL RESPONSE OF "CADMIUM SULFIDE" SOLAR CELL
Thickness = 0.5 microns
Assumed minority carrier diffusion length = 0.1 microns
Chalcocite (calculated)
Djurleite (calculated)
Chalcocite (Palz, et al)
Djurleite (Palz, et al)
Current (arb. units)
Wavelength (μm)
1.0
0.8
0.6
0.4
0.2
0
0.4
0.6
0.8
1.0
1.2
XBL 7310-1939

Fig. 2

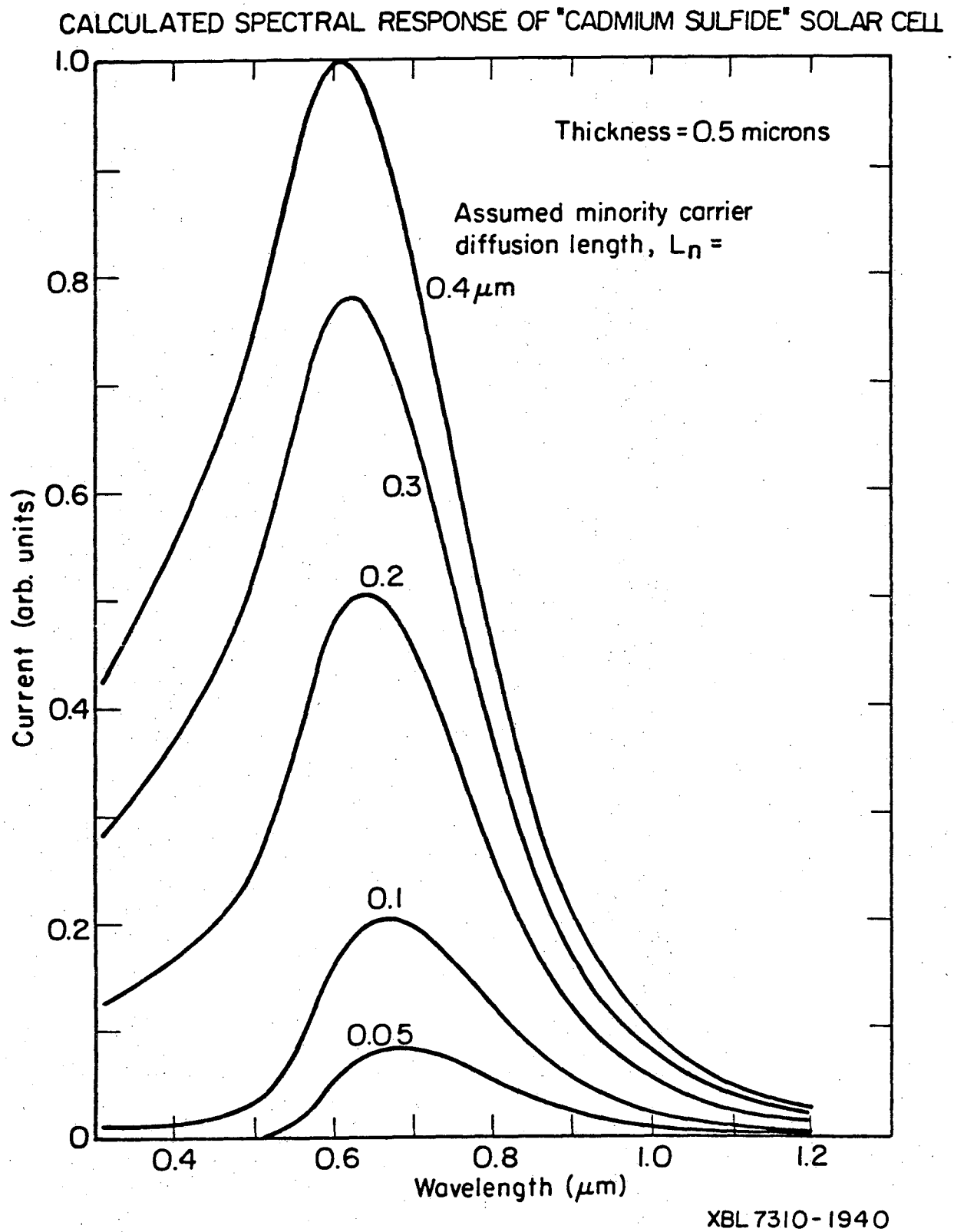

Fig. 3. Spectral response of a djurleite layer with the minority carrier diffusion length as a parameter.

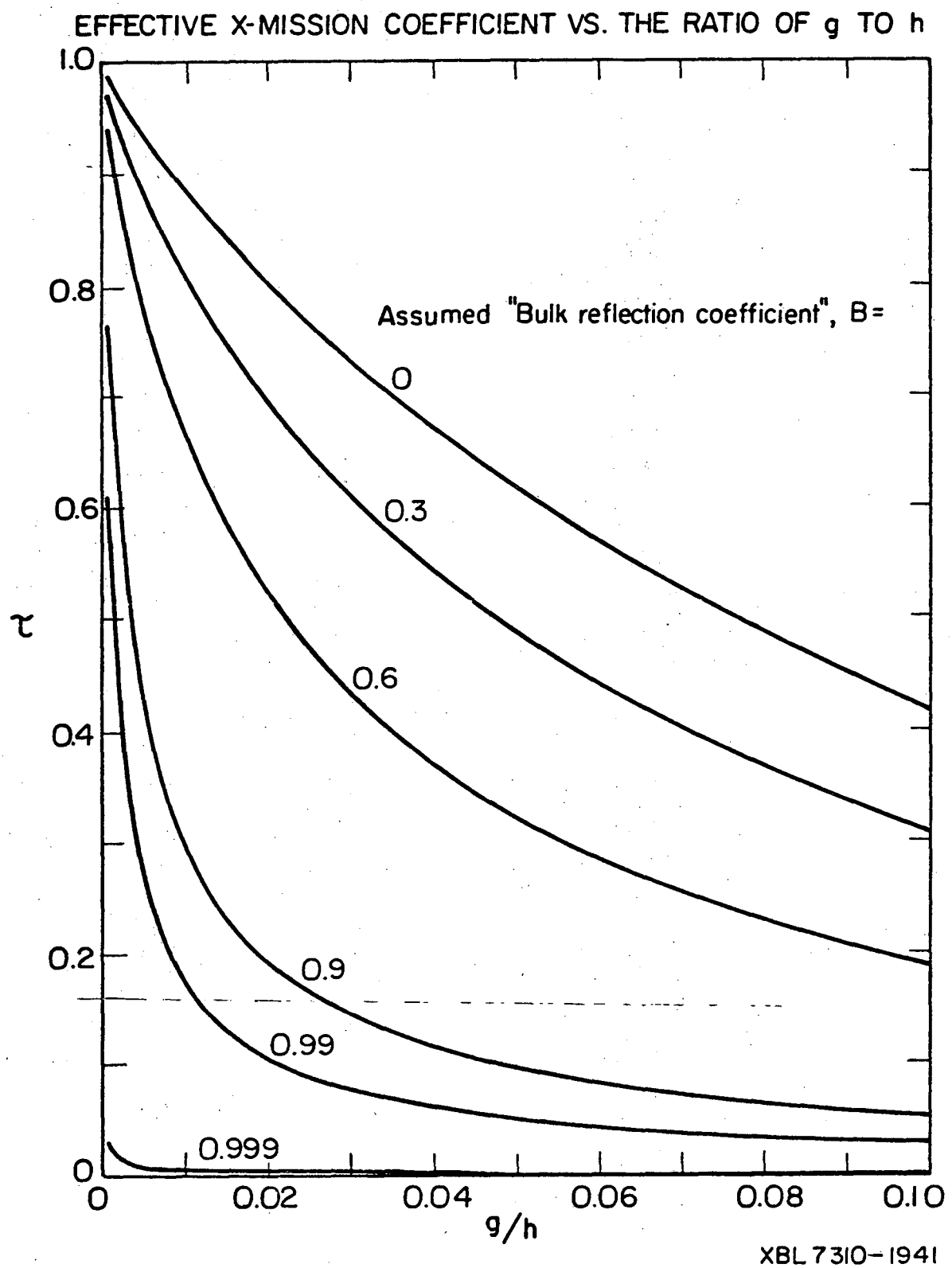

Fig. 4. Effective transmission coefficient of a single-layer dislocation array with the bulk reflection coefficient as a parameter.

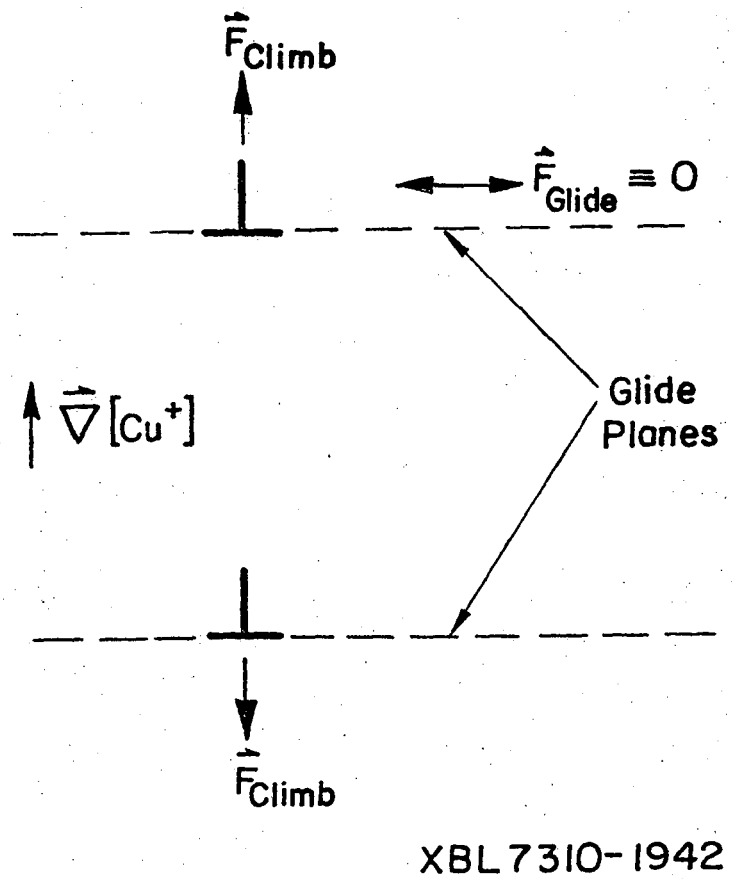

Fig. 5. Stacking of two parallel dislocations of identical burgers vector on different glide planes.

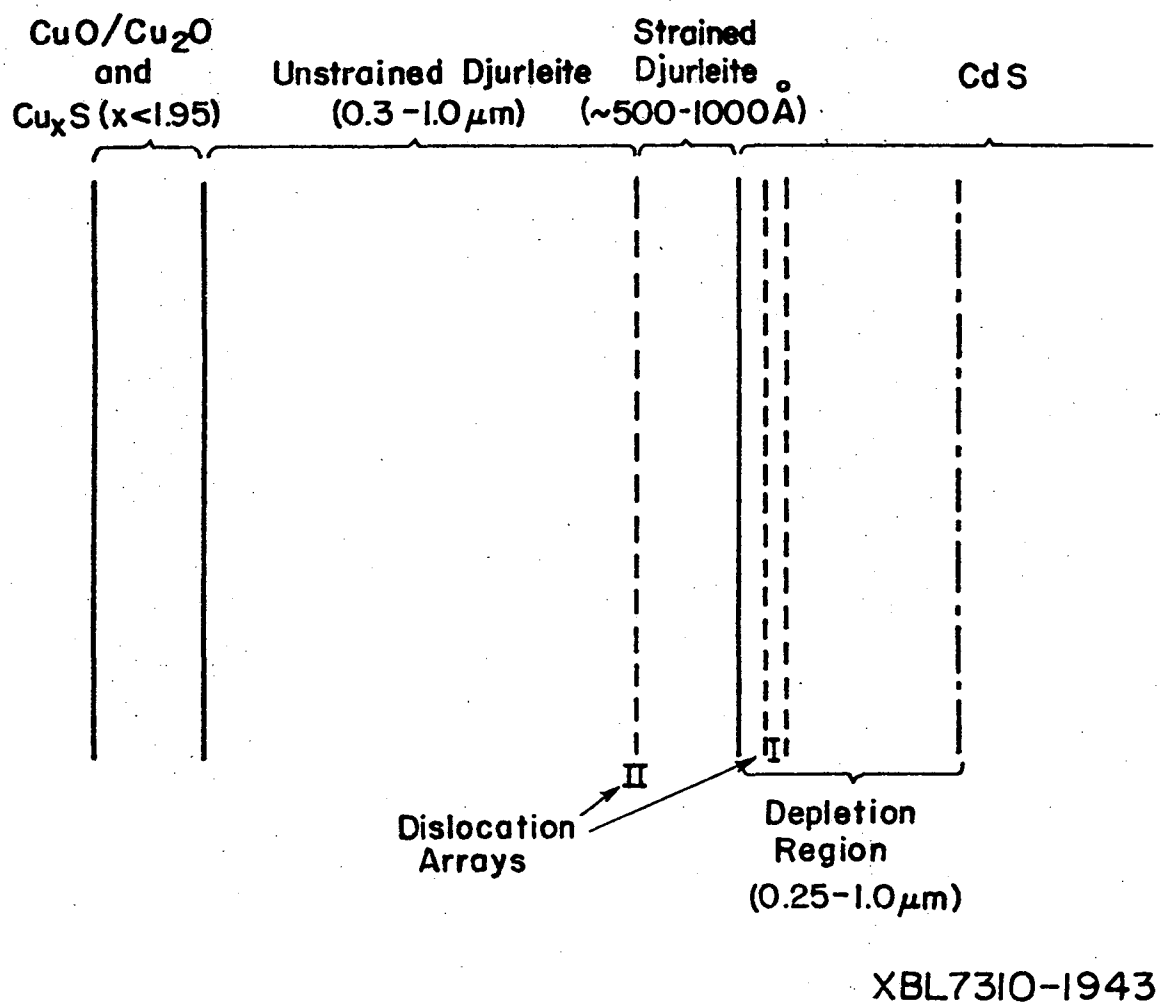

Fig. 6. Configuration of degraded "cadmium sulfide" cell.

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