CHARACTERIZATION OF STRESS FIELD AND ELECTRIC ACTIVITY OF DISLOCATIONS IN SEMICONDUCTORS

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CHARACTERIZATION OF STRESS FIELD AND ELECTRIC ACTIVITY OF DISLOCATIONS IN SEMICONDUCTORS

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Résumé - Les mesures optiques et photoélectriques peuvent être utilisées pour caractériser les dislocations dans les semiconducteurs. Nous avons ainsi interprété la biréfringence et la photoconductivité excitonique de cristaux de Cu_2O : les maxima anisotropes de photocourant sont dus à la dissociation des excitons par des champs électriques internes provenant d'arrangements de dislocations du type empilement.
Le rôle des dislocations peut être envisagé de la même manière dans d'autres composés semiconducteurs : CuCl et CuBr en particulier.

Abstract - Optical and photoelectrical measurements can be used to characterize dislocations in semiconductors. Birefringence and excitonic photoconductivity in Cu_2O crystals are interpreted : anisotropic photocurrent maxima are due to dissociation of excitons by internal electric fields resulting from specific arrangements of dislocations of pile-up type. The role of dislocations can be interpreted in the same way in other semiconducting compounds : CuCl and CuBr in particular.

INTRODUCTION

It is well established that electronic energy levels in crystals depend on the nature of atoms in the crystal and its symmetry. Dislocations, as linear structure defects, can then affect local intrinsic electronic states in semiconductors by their stress or electric fields which change the symmetry of the crystal.

Excitons[1], as intrinsic elementary excitation of non metallic solids, are very sensitive to imperfections or impurities in the crystal. They are affected by perturbations such as electric, stress (internal or external) and magnetic fields. The study of external perturbation effects on excitons is necessary to understand the nature of internal ones. These effects are studied in many materials [Cu_2O, CuX (X = Cl, Br, I), II-VI, III-V, Si, Ge ...][1].

The two particle nature (electron and hole) of excitons lead to different properties from material to another. Excitons, as neutral quasi-particles, cannot contribute, at low excitation densities, to photoconductivity at low temperature (4 K) without interaction with imperfections or impurities in the crystal. The photoconductivity measurements constitute then a very sensitive tool to study the effects of dislocations on excitons[2]. Such effects were also observed by light scattering, reflexion and luminescence spectra of excitons[3,4]. The comparison with the effects of external perturbation is very useful to characterize dislocations.

On the other hand, elastobirefringence revealed to be a good technique to characterize stress field of slip-bands[5,6] or individual dislocations in semiconductors[7]. Dark-field-illumination based on light scattering was also used to visualize dislocations[8]. In contrast with electron microscopy technique which is necessary to study detailed structure of dislocations, these optical methods are nondestructive and permit real structure investigations.

More complete informations are available by associating birefringence and excitonic photoconductivity measurements. We discuss here the results obtained in

Cu_2O crystals. We present then excitonic photoconductivity spectra in CuCl, CuBr which show similar behaviour as in Cu_2O.

I. BIREFRINGENCE AND STRUCTURAL DEFECTS IN Cu_2O CRYSTALS

Recently, we have studied the birefringence in different kinds of Cu_2O crystals[6]. We summarize here the principal results.

In as grown crystals, birefringent regions are generally localized near precipitations, called "teratoïdes". These birefringent regions depend on the direction of observation : they are cross shaped in [100] and [010] when [001] is the direction of observation as shown in figure 1. Principal axis of the crystal in these birefringent regions are [100] and [010]. Etch pits reveal particular arrangements of dislocations "pile-ups" in birefringent regions as shown in figure 2.

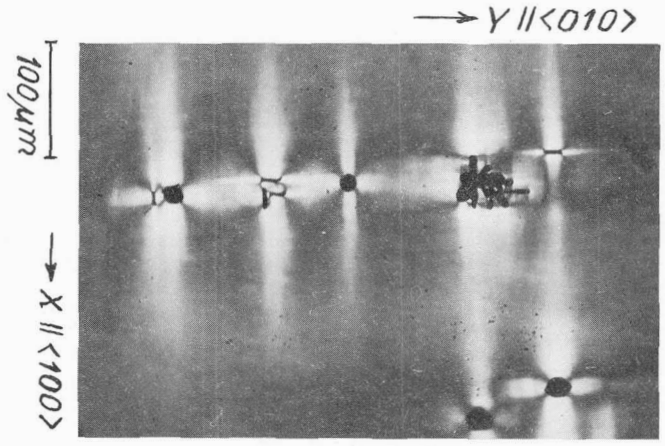

Figure 1. Cross shaped birefringent regions on an as-grown crystal of Cu_2O.

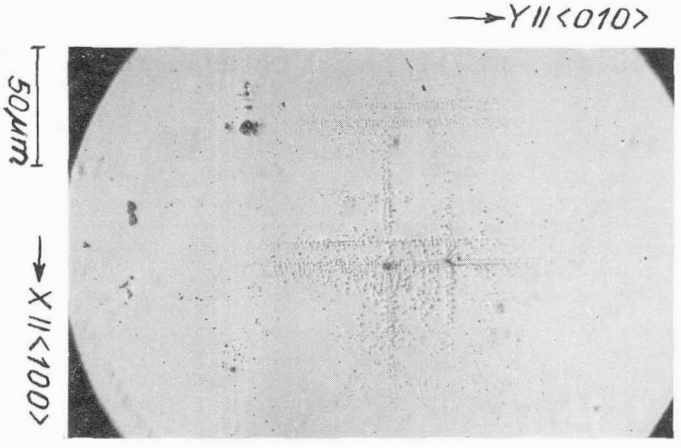

Figure 2. Etch pits on a [001] face of an as-grown crystal of Cu_2O.

These "pile-ups" are formed in crystallographic plans of the type (100) during crystals growth. The same birefringence was also observed in pile-ups regions in the absence of "teratoides".

Using a quarter wave plate[6], we have shown that the slow principal axis of the crystal in birefringent regions are parallel to "pile-ups" in these regions i.e. parallel to Burgers vector of dislocations.

On the other hand, plastic deformation and electron microscopy investigations[9,10] show that the majority of dislocations are of edge type with Burgers vector [100]. Two equivalent glide systems (100) [010] and (010) [100] are active in plastic deformation at high temperature (∿ 700°C) when the applied stress is in [110] direction. In such deformed crystals, similar birefringence with cross shaped slip regions in [100] and [010] directions is observed (see figure 3). Using a quarter wave plate, we also show that the slow principal axis of the crystal in birefringent regions are perpendicular to cross bars. It was concluded that "pile-ups" are formed in birefringent regions by plastic deformation. These "pile-ups" are perpendicular to cross bars as illustrated schematically in figure 4.

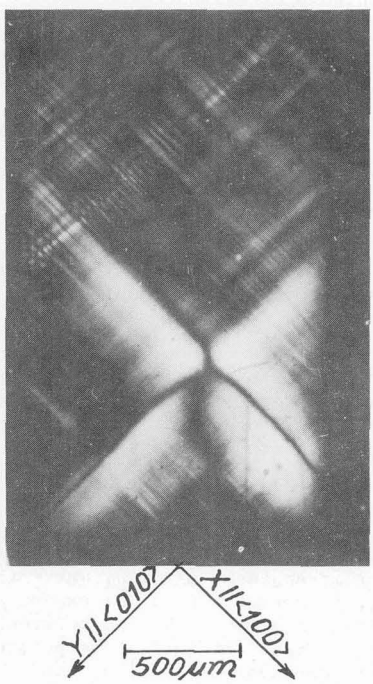

Figure 3. Birefringence of a deformed crystal of Cu_2O by an uniaxial stress along [110] direction.

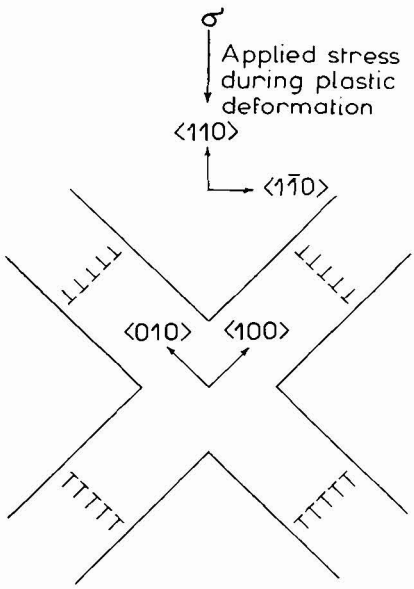

Figure 4. Arrangement of dislocation in cross bar regions.

II. EXCITONS IN Cu_2O CRYSTAL

Cuprous oxide crystallizes in cubic system with non symorphic symmetry group O_h^4 [11]. In the visible spectrum, allowed and forbidden excitonic transitions exist. They are known as yellow, green, blue and violet series refered to the region of visible spectrum where they take place[12].

The symmetry properties of possible optical transition were studied in such

crystal[13,14]. The first excitonic state in Cu_2O crystal, called ($1S_J$), corresponds to an optical quadrupolar transition at 6098Å. Experimental studies[18] show that it has the symmetry Γ_5^+ which is threefold degenerate. Because of the quadrupolar nature, the corresponding optical absorption depends on the direction and polarization of light with respect to crystallographic directions :

- $\vec{q}$ // C_4 : isotropic absorption
- $\vec{q}$ // C_3 : isotropic absorption
- $\vec{q}$ // C_2 : anisotropic absorption
  - $\vec{e}$ // C_4 the absorption take place.
  - $\vec{e}$ // C_2 no absorption.

where $\vec{q}$ and $\vec{e}$ is the wave vector and polarization of light respectively.

We choose to study the photoconductivity corresponding to this excitonic transition because of its low absorption coefficient ($\sim$ 1 cm^{-1}) and high binding energy of the corresponding quasi-particle ($\sim$ 0,14 eV). It follows that thermal ionization at low temperature (4 K) and surface effect can be neglected.

On the other hand, the effects of external perturbations (electric[21-24] and stress[14,24-27]) on the ($1S_J$) excitonic transition were already studied.

When the crystal is perturbed by electric field, the following effects are expected[14] :

- Broadening and displacement to smaller energies of the absorption line.
- Splitting and ignition of some forbidden components for certain polarization of light.

The experimental investigations[23] show the broadening, the displacement and the ignition of the absorption line. No splitting was observed even for applied electric field of 150 KV/cm.

When the crystal is perturbed by stress, one expect broadening and splitting of the absorption line[19] which is in agreement with experimental results[25,26]. Non-linear effect is observed at high applied stress[27].

It should be mentioned that the fundamental difference between these two perturbations is that the electric field does not conserve the parity of electronic states, therefore one observe the ignition of the absorption(i.e. dipolar character of the optical transition) in normally forbidden directions, which is not the case under applied stress. Also, displacement of the absorption line to smaller energies is observed only with applied electric field.

A) Excitonic photoconductivity[2,28-30]

We have investigated the photoconductivity in as-grown crystal corresponding to the $1S_J$ excitonic transition in the particular arrangement $\vec{q}$//[110] where the absorption is anisotropic in the absence of electric perturbation. The experimental arrangements were described elsewhere[2,30]. Figures 5 a)b) show the photocurrent and transmission spectra in the region of $1S_J$ excitonic transition at low temperature (4.2 K). Two different polarizations of light were considered : $\vec{e}$//[001] and $\vec{e}$//[1$\bar{1}$0] where the following point should be noticed :

i - Isotropic photocurrent which corresponds to anisotropic absorption.

ii - Spectral width of photocurrent response is higher than that of absorption line in allowed direction $\vec{e}$//[001].

iii - Photocurrent minima which corresponds to the absorption line in the allowed direction. The asymmetric shape of the photocurrent response indicates its displacement to lower energies relative to the absorption line.

We obtain this shape in most of the cases. However other shapes are available depending on the applied potential, on the sample, on the point of the sample

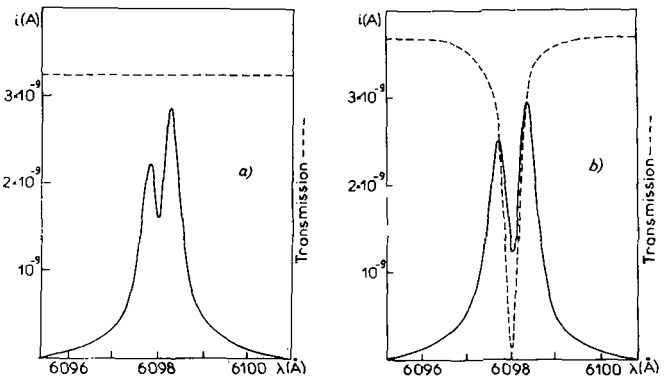

Figure 5. Photocurrent in the $1S_J$ absorption line for two polarizations a) $\vec{e}//[1\bar{1}0]$, b) $\vec{e}//[001]$. Transmission is drawn in interrupted line.

which is irradiated. Figure 6 summarizes three types of response curves :

a) The maximum of photocurrent is in the exact position of the line.

b) The maximum of photocurrent is on the low energy side of the line and the minimum at $h\nu_o$.

c) The maximum of photocurrent is on the high energy side of the line and the minimum also at $h\nu_o$.

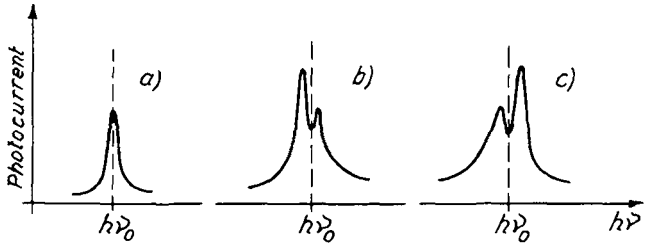

Figure 6. Types of photocurrent response curve in the $1S_J$ excitonic line of Cu_2O.

The photocurrent in the forbidden direction $e//[1\bar{1}0]$ indicates that excitonic absorption had taken place but, it is too small to be detectable by transmission measurement. This can only happen under electric field perturbation[14,23]. Applied potential being very small (2.5 V/cm) to perturbe the crystal, it follows that excitonic absorption for $e//[1\bar{1}0]$ is due to perturbed regions by internal electric fields.

Isotropic excitonic photoconductivity and anisotropic absorption indicates inhomogeneous efficiency of excitons in photoconductivity at low temperature : only excitons which are created in regions perturbed by internal electric fields can contribute to the creation of photocarriers.

This indicates also that ignition of excitonic absorption in perturbed regions occurs only in the polarization $\vec{e}//[1\bar{1}0]$. Comparison with the effect of external electric field on excitonic absorption in similar experimental conditions[23] indicates that internal electric field in perturbed regions should be in C_4 directions. It was shown in this case[23] that the absorption in the forbidden direction $\vec{e}//[1\bar{1}0]$ becomes equal to that in allowed direction $\vec{e}//[001]$ for applied electric field of about 30 KV/cm. It follows that internal electric field in photoconductive regions is of the same order.

The inhomogenous efficiency of excitons in photoconductivity is confirmed also by the shape of the photocurrent response cuvre which corresponds to excitonic absorption in non perturbed regions for "allowed" direction $\vec{e}//[001]$. The shape of photocurrent response could be explained by a simplified model[2] :

Suppose that ν_o and ν_p are the frequencies at which excitonic absorption take place in imperturbed and perturbed regions respectively. It should be remember that $\nu_p < \nu_o$ for electric field perturbation. The absorption coefficient corresponding to $1S_J$ excitonic transition could be considered as a Gaussian with respect to the frequency[31] :

$$K_o(\nu) = K_{o\,max} \exp\left[-\left\{\frac{2(\nu_o-\nu)}{\Delta\nu_o}\right\}^2 \ln 2\right] \qquad (1)$$

and we suppose that it has the same shape in perturbed regions :

$$K_p(\nu) = K_{p\,max} \exp\left[-\left\{\frac{2(\nu_p-\nu)}{\Delta\nu_p}\right\}^2 \ln 2\right] \qquad (2)$$

where :

$K_o(\nu)$ $\{K_p(\nu)\}$: is the absorption coefficient in unperturbed {perturbed} regions.

$K_{o\,max}$ $\{K_{p\,max}\}$: is the absorption coefficient at ν_o $\{\nu_p\}$ in unperturbed {perturbed} regions.

$\Delta\nu_o$ $\{\Delta\nu_p\}$: is the width of absorption line at $\frac{K_{o\,max}}{2}$ $\{\frac{K_{p\,max}}{2}\}$ in unperturbed {perturbed} regions.

Let us consider all perturbed regions as a fictive one with width X_p in the middle of the crystal along the direction of the incident light (see figure 7). The number of absorbed photons by unit time in this fictive retion is :

$$N_p = N\{1-\exp(-K_p X_p)\} \qquad (3)$$

where :

$$N = N_o \exp(-K_o X_o) \qquad (4)$$

N_o : is the number of incident photons on the crystal by unit time.

X_o : is the depth of fictive perturbed regions (see figure 7).

For small absorption coefficient and small thickness of the crystal, which is satisfied in our case, one can write :

$$\exp(-K_o X_o) = 1 - K_o X_o \qquad (5)$$

$$\exp(-K_p X_p) = 1 - K_p X_p \qquad (6)$$

Equation (3) takes then the following form :

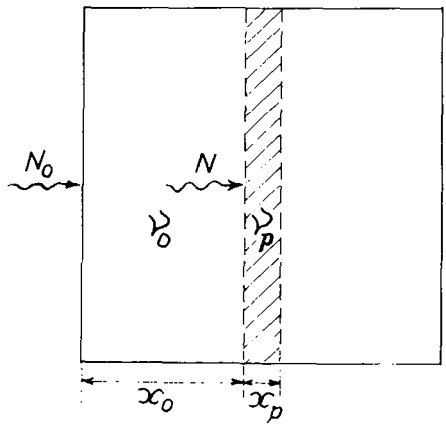

Figure 7. Absorption process in a simplified model of inhomogeneous crystal.

$$N_p = N_o K_{p\,max} X_p \left[1 - K_{o\,max} X_o \exp\left[-\left\{\frac{2(\nu_o-\nu)}{\Delta\nu_o}\right\}^2 \ln 2\right]\right]$$

$$\exp\left[-\left\{\frac{2(\nu_p-\nu)}{\Delta\nu_p}\right\}^2 \ln 2\right] \qquad (7)$$

The photocurrent is proportional to the number of excitons created in perturbed regions i.e. to the number of absorbed photons N_p in these regions.

Figure 8 shows the photocurrent response obtained by equation (7) which has the same form as in figure 5. We have considered $N_o K_{p\,max} X_p$ as unity and

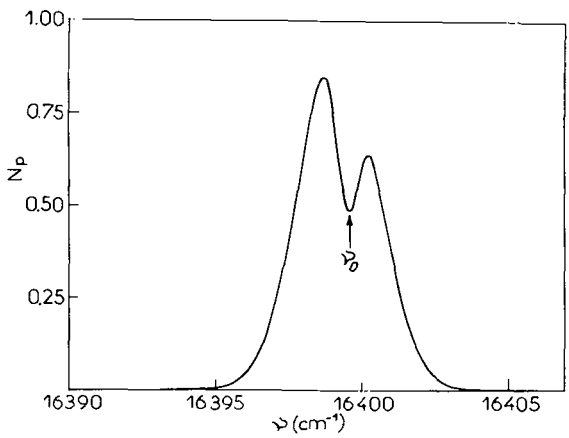

Figure 8. Calculated response curve of the photocurrent in the $1S_J$ excitonic line.

ν_o = 16399,5 cm^{-1}, ν_p = 16399,2 cm^{-1}, $\Delta\nu_o$ = 1 cm^{-1}, $\Delta\nu_p$ = 3 cm^{-1}, $K_{o\ max}$ = 5 cm^{-1}, X_o = 0.1 cm. $\Delta\nu_p$ = 3 cm^{-1} corresponds to regions perturbed by an electric field of about 30 KV/cm [23].

According to the existence of localized electric fields we have put in evidence, these shapes are very well interpreted :

Case a) : The localized electric fields are too weak to give rise to a shift of the line but high enough to drift the excitons towards retions where they can dissociate.

Case b) : The LEF are high enough to give rise to a shift. We know that a continuous electric field induces a decrease of the gap and a shift of the lines in the low energy side of the spectrum. A minimum should occur at $h\nu_o$ which corresponds to the formation of excitons in region of the crystal where no LEF exists.

Case c) : A shift of the photocurrent maximum towards high energy could be induced by electric field gradient. The quadrupolar character of the line give rise to specific interaction with the gradient of electric fields which can explain the shift.

In fact, one should know the exact distribution of perturbed regions to have quantitative interpretation of excitonic photocurrent response. We supposed that these regions are essentially the birefringent ones where an electric field could be formed by dislocations in "pile-ups". This is in agreement with photoconductivity measurements by optical scanning in plastically deformed crystals[2,32].

B) Excitonic photoconductivity by optical scanning

We have investigated the excitonic photoconductivity point by point in plastically deformed crystals because the birefringent regions are more localized, which permit us to compare photocurrent response in different regions. Experimental set-up was described elsewhere[2,32]. In these experiments, we have $\vec{q}//[001]$ where no anisotropic effect in $1S_J$ excitonic absorption is expected without electric field[14,23]. The crystal was scanned at wavelength λ = 6098 Å which corresponds to $1S_J$ excitonic absorption.

Figure 9 shows the birefringence (a), the excitonic photocurrent response for two polarizations, $\vec{e}//[100]$ (b) and $\vec{e}//[010]$ (c) in 5 % deformed crystal. Black regions in (b) and (c) correspond to a maximum of excitonic photoconductivity

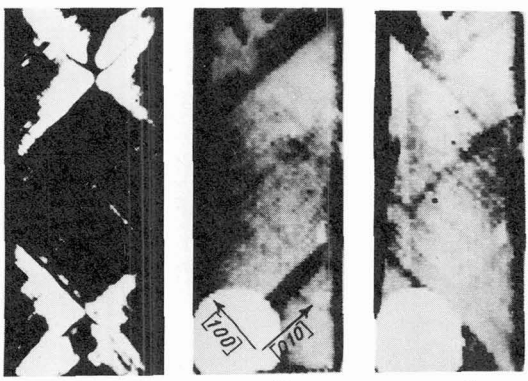

Figure 9. Birefringence (a) and scanned photoconductivity at 6098 Å (b and c) of a deformed crystal. Axes of crystal are given in (b).

relative to other regions. White round regions correspond to electric contact on the semi-transparent electrode on the surface of the crystal.

One can see that excitonic photoconductivity maxima correspond to birefringent cross bars which are perpendicular to the polarization of incident light. It should be mentioned that homogeneous photocurrent distribution is obtained when the crystal is scanned at wavelength outside the excitonic absorption[2]. These results confirm the inhomogeneous model of excitonic photoconductivity.

The anisotropic photocurrent maxima in birefringent regions could be interpreted by anisotropic excitonic absorption in these regions because of internal electric field perturbation. We have shown that internal electric field in perturbed regions should be in C_4 directions (§ A). We expect then the existence of internal electric field perpendicular to "pile-ups" in birefringent regions as represented schematically in figure 10.

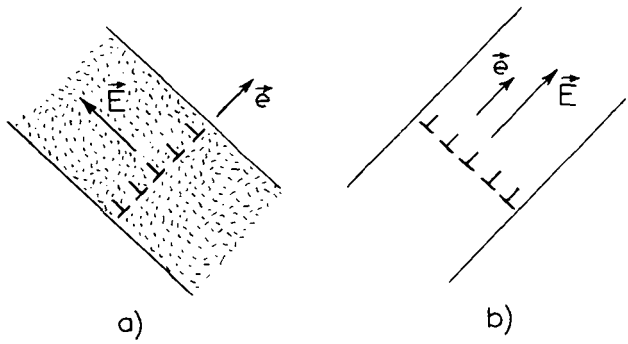

Figure 10. Relative efficiency of the photoconductivity at 6098 Å according to the direction of polarization vector with respect of the position of pile-ups in the cross bars of birefringence. Case a) corresponds to a maximum of photocurrent.

On the other hand, ignition of excitonic absorption is expected theoretically[14] and observed experimentally[23] when $\vec{q}//C_4 \perp \vec{E}$, and $\vec{E}$ is parallel to another C_4 direction, only for light polarization $\vec{e} \perp \vec{E}$. This ignition is represented schematically on figure 9 a) and can explain the anisotropic excitonic photoconductivity.

In fact, pile-ups could be considered as charged plans with surface charge density ρ. At a distance greater than that between two adjacent dislocations in the pile-up, the induced electric field perpendicular to the pile-up is given by :

$$E = \frac{\rho}{2\varepsilon_o \varepsilon} \qquad (8)$$

where :

ε_o : is the vacuum permitivity.

ε : is the dielectric constant of the crystal.

To evaluate charge density, one should know the exact structure of dislocations in pile-ups which is not available in Cu_2O.

III. DISLOCATIONS AND EXCITONIC PHOTOCONDUCTIVITY IN OTHER COMPOUNDS AND CONCLUSION

This analysis can be applied to other compounds already studied ten years ago[33,34]. Minima of photocurrent in the 1S lines in CuCl and CuBr (see figures 11 and 12) were interpreted in terms of surface effects : the recombination rate of

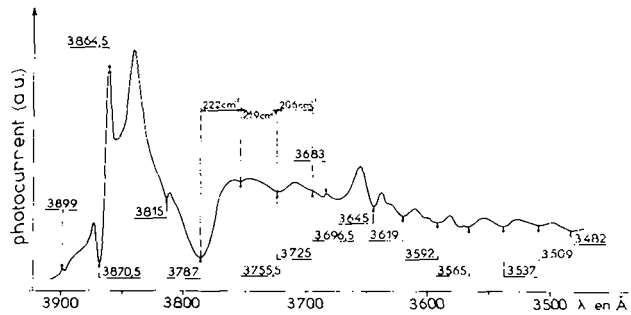

Figure 11. Photoconductivity spectrum of a crystal of CuCl at 4 K. Minima at 3870.5 Å and 3787 Å correspond to the position of ν_{1f} and ν_{1d} absorption lines respectively.

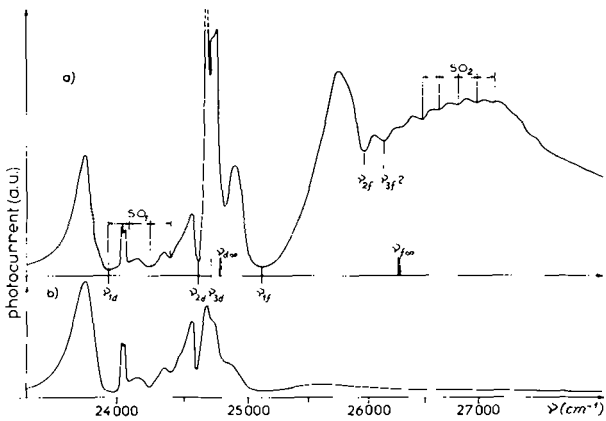

Figure 12. Photoconductivity spectrum of a CuBr crystal at 4 K for two different applied potentials : a) E = 20 V/cm, b) E = 2 kV/cm.

carriers was believed to increase near the surface. The schemes of figure 13 show how the maxima of photocurrent are shifted according to the absorption lines. Position of lines in an energy scale are ν^{+}_{1f}, ν^{-}_{1d} for CuCl, ν^{-}_{1d} and ν^{-}_{1f} for CuBr.

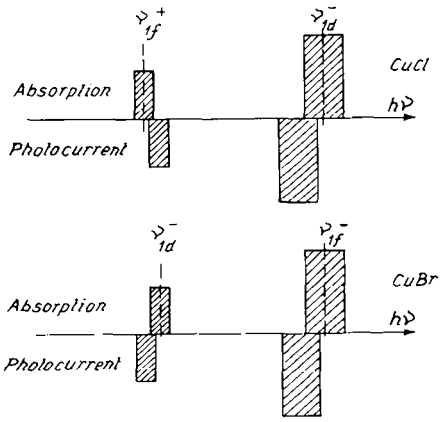

Figure 13. Schematic representation of the relative positions of the absorption lines and maxima of photocurrent of 1S excitons in CuCl and CuBr.

f and d are reported to two exciton series related to the degeneracy of the valence band of the two compounds. + or - indicates how the resonance line is shifted by the application of an electric field : towards high and low energy respectively.

It is clear that the maximum of photocurrent is shifted in the same way as the absorption line under application of an electric field. According to the dipolar nature of the optical transitions, no effect of an electric field gradient is to be expected. Furthermore, all the experiments on reference are made at low temperature ($\sim$ 4 K) where the thermal dissociation of excitons is negligible.

It results that the work we have done on Cu_2O permits a generalization of the physical interpretation of exciton dissociation in electric fields to at least two other compounds. In this later case (CuCl, CuBr), we have no proof of the direct role of dislocations : surface electric fields can also work in the exciton dissociation process. However, the recent data on CdS by Vyvenko et al.[3] show that the optical spectra of excitons are shifted near dislocation slip bands. Less recent data[35] have shown that the existence of minima of photocurrent in the exciton lines is a quite general phenomenon (especially in CdS) although irreproducible.

We have now an ensemble of experimental data which put in evidence the close relation between excitons and structural defects. We have seen that a good knowledge of the optical properties of a given crystal can help in the characterization of these defects.

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