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Electron Mobility and Luminescence Efficiency in Cadmium Sulfide

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The mobility of the photoelectrons produced in cadmium sulfide by pulsed ultraviolet and x-ray excitation has been determined through measurements of the incident radiation, the luminescence radiation, and the initial rates of rise and decay of the photocurrent. The mobility value as well as the efficiencies of the excitation and radiative recombination processes for the two types of excitation are obtained directly from these measurements by means of a general analysis which is independent of the details of the photoelectric mechanism. The following approximate numerical results are obtained: The electron mobility is 30 cm^2/volt-sec. Two percent of the conduction electrons radiate red light quanta upon recombining. Each 0.5A x-ray quantum produces about 2000 conduction electrons.

I. INTRODUCTION

PHOTOCONDUCTIVITY in the crystal phosphors is accompanied by the phenomenon of luminescence and is closely related to it. It is this relation which gives this class of crystals its importance in the development of solid state theory. That a given crystal of the class could profitably be investigated both for its photoconducting properties and its luminescence behavior seems to have been realized first by Lehfeldt[1] working with zinc sulfide. Later Kallman and Warminsky[2] and Frerichs[3] studied cadmium sulfide using the same approach.

Lehfeldt observed the decay of the current simultaneously with the decay of the luminescence, but only for low intensities of the exciting radiation and for long decay times. It occurred to the authors that perhaps a study of the simultaneously observed current and luminescence responses of such a crystal for high intensities of excitation and short times might give new insight into the above relation, and into the mechanism of photoconductivity. The introduction of fast and sensitive light detecting systems[4,5] had made it experimentally possible to do this.

The authors therefore devised a method of making the measurements and were able to record the simultaneous rise-and-decay curves of the current and of the luminescence for a crystal of cadmium sulfide, the time interval covered being about 10 milliseconds. The approximate magnitudes of the electron mobility and other parameters were deduced from these curves.[6] The full interpretation of the curves was not attempted and indeed cannot be given until further work is done, but the authors feel that certain deductions from a limited portion of the work are of sufficient interest to justify giving them now.

The aim of this paper is to describe the new method for the quantitative determination of the mobility of the conduction electrons in crystal phosphors and to say something about the efficiencies of the excitation and radiative recombination processes in cadmium sulfide.

II. THEORY

Although it is unnecessary to adopt a detailed model of a crystal phosphor in the development which follows, we shall use the Seitz-Johnson model[7] to make the analysis clearer. The theory develops logically if we specify only that when the crystal is excited, e.g., subjected to radiation of sufficient energy, as x-rays or ultraviolet light, electrons are raised to the conduction band and while there contribute to the conductivity of the crystal; and that after spending a few milliseconds in excited states (i.e. the conduction band and traps) the electrons fall down again (recombine) into lower energy levels, either with the emission of the characteristic luminescence quanta, or without (radiationless transitions). Further, whether the law describing the recombination is monomolecular or bimolecular does not have to be known.

The customary expression for the current density in the crystal is consistent with the above limited picture of the process

$$j = e\mu E\rho, \tag{1}$$

where e is the electron charge, μ is the electron mobility in the conduction band, E is the electric field intensity, and ρ is the density of conduction electrons. Since cadmium sulfide is an N-type conductor, a term for the hole-conductivity is not included.[3]

The main assumption in the development is that changes in the current density are determined entirely by changes in the density of conduction electrons. Thus, if ρ changes with time because of a time variation of the excitation intensity, the resulting variation in j is given by

$$dj/dt = e\mu E d\rho/dt. \tag{2}$$

Substitution of the measurable quantities i and V (the

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[1] W. Lehfeldt, Göttingen Nachr., Fachgruppe II, 3, 263 (1933).

[2] H. Kallman and R. Warminsky, Ann. Physik 4, 69 (1948).

[3] R. Frerichs, Phys. Rev. 76, 1871 (1949).

[4] R. J. Cashman, OSRD Report No. 5997 NDRC Div. 16.4 (1945), unpublished.

[5] L. Holland and W. Hole, OSRD Report No. 5298 NDRC Div. 16.4 (1945), unpublished.

[6] L. Gildart and A. Ewald, Phys. Rev. 78, 645 (1950).

[7] F. Seitz and R. Johnson, J. Appl. Phys. 8, 246 (1937).

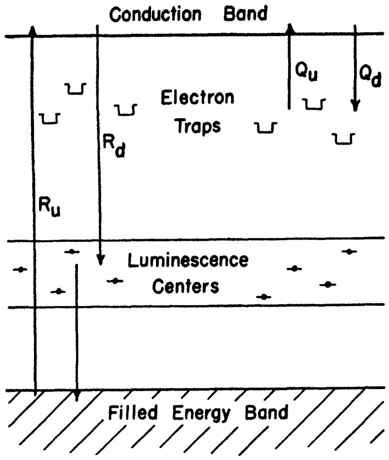

FIG. 1. Band scheme of cadmium sulfide defining the transitions explicitly considered in the analysis.

current and the voltage) for j and E gives

$$i/A=e\mu V\rho/L \tag{3}$$

and

$$di/dt=e\mu VA(d\rho/dt)/L, \tag{4}$$

where A is the cross section of the crystal and L is its length.[7a]

In Eq. (4) $d\rho/dt$ is the net rate of change of the conduction electron density in the crystal, i.e., the difference between the rate at which the density is increasing due to excitation and the rate at which the density is decreasing due to recombination. This relation applies to two cases which are of particular importance: case (a) The irradiation is suddenly blocked off from the crystal, the crystal having reached a steady state in the light, and case (b) The irradiation is suddenly allowed to fall on the crystal, the crystal having already reached a steady state in the dark. One of us has shown[8] that in these cases the magnitude of $d\rho/dt$ is given by the excitation rate. That this is so even for a many-process model can be seen from the following argument, applied to the Seitz-Johnson model (Fig. 1):

Let R_u be the rate at which electrons are raised from the centers to the conduction band, and R_d the reverse process. Let Q_u be the rate at which they are raised from the traps, and Q_d be the reverse process. If n is the population of electrons in the conduction band ($n=\rho AL$), then the rate at which it is changing at any instant is given by

$$dn/dt=R_u-R_d+Q_u-Q_d.$$

Suppose that the crystal has been receiving constant irradiation and equilibrium has been attained. The rate at which electrons are raised from the valence band into the conduction band (either by direct or indirect process) must equal the rate at which they return again to the valence band. Likewise, for any competing process, as, for instance, the exchange of electrons between the conduction band and the normally empty trapping centers, the rate at which electrons are raised into the conduction band must equal the rate at which they drop down again. Up until the instant at which the radiation is cut off, it is true that

$$R_u=R_d \quad \text{and} \quad Q_u=Q_d.$$

At the cut-off instant and for a moment afterward,[8a] say, from time (t) to time ($t+\epsilon$), it is true that

$$R_u=0,$$

while

$$Q_u=Q_d$$

still. Therefore, it follows that during the short interval of time, ϵ,

$$dn/dt=-R_d, \tag{5}$$

or the instantaneous rate of decrease of the number of electrons in the conduction band is equal to the rate at which electrons fall into the activating centers, e.g., the recombination rate. This is case (a) above.

Suppose the crystal has been in the dark long enough so that all rates of transfer of electrons, and the population of electrons in the conduction band, are not appreciably greater than zero, *viz.*:

$$R_u=R_d=Q_u=Q_d=0, \quad \text{and} \quad n=0.$$

If the crystal is suddenly illuminated, it will be true for a short interval of time, ϵ, thereafter, that

$$R_d=0=Q_u=Q_d$$

still, and therefore

$$dn/dt=+R_u, \tag{6}$$

or the instantaneous rate of increase of the number of electrons in the conduction band is equal to the excitation rate. This is case (b) above.

If the number of activating centers is large compared with the maximum value of n, then R_u is constant for a given excitation intensity and thus we can deduce from Eqs. (4), (5), and (6) that the initial rise slope of the current is equal to the initial decay slope of the current. This was found to be true within the limit of experimental error for several crystals studied. There were, however, some crystals for which, under the experimental conditions, this equality was not satisfied. These require further investigation before one can decide whether or not they do conform to this general model.

The luminescence process can be described in terms of the luminescence radiation by the equation

$$p_l=h\nu_l ALd\rho/dt, \tag{7}$$

where p_l is the luminescent light power emitted by the crystal and $h\nu_l$ is the energy of each luminescent light quantum. Equation (7) assumes that each conduction

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[7a] For simplicity these equations, and also those below describing the luminescence process, are written for the case of uniform charge and current densities. However, products of the type ρA and $(d\rho/dt)A$ can be replaced by integrals over the cross-sectional area without affecting our results.

[8] A. W. Ewald, Phys. Rev. 81, 607 (1951).

[8a] The time interval, ϵ, is taken as short compared with the lifetime of the electron in the conduction band.

electron emits one luminescence quantum when it falls from the conduction band. If, however, only a fraction α of the conduction electrons undergo such radiative recombinations, Eq. (7) must be written as

$$p_l=\alpha h\nu_l A L d\rho/dt. \tag{8}$$

Alternatively, the luminescence process can be described in terms of the excitation by

$$p_a=h\nu_a AL(d\rho/dt)/\beta, \tag{9}$$

where p_a is the excitation radiation power absorbed by the crystal, $h\nu_a$ is the energy per excitation quantum, and β is the number of electrons excited per absorbed quantum.

The photoconductive process and the luminescence process can be related, as previously mentioned, by eliminating $(d\rho/dt)$ between Eqs. (4) and (8) or between (4) and (9). All quantities in the resulting relations are experimentally measurable by the method described below, except α, β, and μ. If we assign β a value for one type of excitation, this value being based on other experimental evidence, then the electron mobility in a given crystal can be found, together with the remaining coefficients of the equations. As a check the value of μ so obtained can be put back into the same relation but for another type of excitation, and the β resulting from this solution can be compared with β from other experiments.

III. APPARATUS AND PROCEDURE

A. Ultraviolet Excitation

The light source for the ultraviolet excitation of the crystal was a high pressure mercury arc in quartz envelope operated at 65 volts.[9] Light from this source could be interrupted at 30 cps by a rotating chopper disk shown at position *I* in Fig. 2 and was sent through a glass ultraviolet filter and directed upon the crystal. The voltage developed across a 10,000-ohm load resistor connected in series with the crystal and a 45-volt battery was applied to an oscilloscope. The steady-state power of the ultraviolet light incident on the crystal was measured by means of a vacuum thermocouple calibrated against a Bureau of Standards lamp.

A known fraction of the luminescent light from the crystal was gathered by an *f*/1 optical system and focused on a photocell receiver, first passing through a No. 70 Wratten filter and a second 30-cps chopper (shown at position *II*). The detecting system consisted of a Cashman thallous sulfide cell[4] sensitive in the red, and a tuned amplifier based on the design of Holland and Hole.[5] This system was calibrated against a beam of red light of known intensity coming from the exit slit of a monochromator.

The initial slope of the current rise curve was found as follows: A chopper disk having a 15-degree aperture and driven by an 1800-rpm synchronous motor was used in the first modulation position, giving a dark time of 32-msec and an on-time of 1.4 msec. This ratio of dark time to on-time allowed the crystal studied to come to equilibrium in the dark once each cycle while still allowing time enough for the initial rise curve to have sufficient extent so that its slope could be measured easily. The curve appearing on the oscilloscope screen was recorded photographically. The initial slope of the current decay curve was found similarly, except that the chopper in the first modulation position had an aperture of 345 degrees, inverting the ratio of dark time to on time. The crystal now came to a steady state condition in the light once each cycle.

For the calculation of the present paper the steady-state luminescence power was the only luminescence measurement needed. Thus a chopper disk of 180-degree aperture driven by the 1800-rpm synchronous motor in the second modulation position was used to provide the modulation of the luminescence light required by the ac detecting system. During this measurement the first chopper was not operated. That the filter system was not allowing a false signal to get through to the detector was proved by substituting a nonluminescent diffuse reflector in the position of the crystal.

To get the entire rise-and-decay curve of the luminescence, previously described,[6] the 180-degree disk was replaced by one having a 5-degree aperture, and both this disk and one in the first modulation position were operated simultaneously. Any desired phase relation between the two choppers could be obtained by rotating one motor while both were operating which made possible pointwise scanning of the luminescence curve.

B. X-Ray Excitation

The source of x-rays was a copper target tube operated at 40 kv with 18-ma beam current. The target-to-crystal distance was 10 cm, and the components were arranged as in the ultraviolet experiment. Because the x-rays from the self-rectified tube were pulsed at 60 cps, it was necessary to use a 10-degree aperture disk in the first modulation position so as to pass only the middle portion (of nearly constant amplitude) of alternate x-ray pulses. The modulator was phased for maximum response while running, thus insuring that the middle portion of the x-ray pulse was

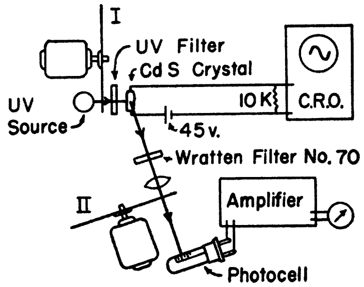

FIG. 2. Schematic diagram of apparatus arrangement.

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[9] W. W. Coblentz and R. Stair, J. Research Natl. Bur. Standards **16**, 83 (1936), RP 858.

TABLE I. Experimentally determined magnitudes.

	p_i	p_l	di/dt	i
Ultraviolet excitation	46 μw	0.23 μw	3.7×10^{-2} amp/sec	24 μa
X-ray excitation	52 μw	0.14 μw	2.1×10^{-2} amp/sec	42 μa

coming through. Although this procedure allowed ample time for the crystal to reach a steady-state condition in the dark between pulses, the pulse length was not sufficient to assure a steady state under irradiation. However, the fact that the initial slopes of the rise and decay curves obtained were equal is taken as evidence that the crystal reached an approximately steady state condition during each pulse.

To determine the x-ray power striking the crystal, the x-ray beam was chopped as described above, and the average power of this pulsed beam was found by measuring the heating of a lead target. The amplitude of these approximately rectangular pulses was then calculated from the average value. The heating of the target was measured by a thermocouple arrangement operated as a null system as follows: Two lead targets, made from layers of foil in which were embedded (a) thermocouples and (b) small heating coils, were constructed to be as nearly alike as possible. The thermocouples of the two targets were connected in series opposition through a galvanometer. One target was put in the x-ray beam. The heating of the absorbed x-rays produced a thermal emf which deflected the galvanometer. A small current was then sent through the heating coil of the dummy target which remained out of the beam. When the emf generated in this target balanced the emf produced by the x-ray heating, the galvanometer came to zero, and the electric power into the dummy target gave the average x-ray power absorbed.

C. General

The crystals used in these measurements were furnished the authors by Dr. Frerichs. No impurity was intentionally added, and the luminescence is attributed therefore to a stoichiometric excess of cadmium. The crystals were mounted upright on Lucite rods; and the electrodes were graphite-painted over the ends, to which fine copper wires were attached. The crystals contained a sufficient thickness of cadmium to stop at least 99 percent of the x-rays incident on them. All the results given below were obtained with one crystal and are typical of the data obtained with the crystals which satisfied the "equality of slopes" criterion. This crystal was approximately cylindrical, 5 mm long by 2.2 mm in diameter.

IV. EXPERIMENTAL RESULTS

A. Ultraviolet Excitation

From Eqs. (4) and (9) the mobility becomes

$$\mu=h\nu_aL^2(di/dt)/\beta ep_aV. \qquad (10)$$

To evaluate this from the ultraviolet data of Table I we set $h\nu_a=3.38$ ev (corresponding to an effective wavelength of 3650A for the filtered ultraviolet) and $\beta=1$. The assumption of this value for β is justified by the results of other experiments using ultraviolet excitation, and also because it leads to an entirely reasonable value of β for the x-ray case. The excitation power, p_a, which appears in Eq. (10) is smaller than the power incident on the crystal, p_i, because of surface reflection and small losses within the crystal. The total loss is probably between 30 and 50 percent. Setting $p_a=0.5p_i$ the mobility comes out to be

$$\mu=30 \text{ cm}^2/\text{volt sec.}$$

The uncertainties in β and in the loss factor mentioned above are at present the primary limiting factors on the accuracy of the results. It is estimated that this mobility value and the results found below are correct to within a factor of two.

Defining an over-all luminescence efficiency as p_l/p_a, we find from the table that

$$\text{efficiency}=p_l/p_a=0.01.$$

This, together with Eqs. (8) and (9), yields the radiative recombination coefficient, $\alpha=0.02$, or only one electron in fifty radiates upon recombining.

B. X-Ray Excitation

Taking the mobility to be constant, i.e., independent of the type of excitation, and $h\nu_a=2.47\times10^4$ ev (corresponding to an effective wavelength of 0.5A for the 40-kv x-rays),[10] we find from Eqs. (4) and (9),

$$\beta=h\nu_aL^2(di/dt)/\mu eVp_a=1850,$$

or there are 1850 electrons raised to the conduction band per absorbed x-ray quantum. If all the energy of a single x-ray quantum of effective wavelength 0.5A were spent in raising electrons through the 2.4-ev energy gap between the valence band and the conduction band of cadmium sulfide, then 10,000 electrons would be excited per absorbed x-ray quantum. Using our result for β, we see that the efficiency for this process is 18 percent.

The over-all efficiency of the present crystal for x-ray excitation is

$$\text{efficiency}=p_l/p_a=0.003,$$

giving for the radiative recombination coefficient the result, $\alpha=0.022$, in good agreement with the value found for the ultraviolet excitation. The over-all efficiency of 0.3 percent above is somewhat lower than the values of 0.5 to 20 percent reported as the over-all efficiency of phosphors for x-ray excitation.[11] However, the excitation efficiency for this crystal (18 percent) is

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[10] C. T. Ulrey, Phys. Rev. 11, 401 (1918).

[11] H. W. Leverenz, *Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), p. 316.

comparable with the over-all efficiency of the most efficient phosphors, indicating that its lower over-all efficiency is due to a small percentage of radiative recombinations.

C. General

While this work was in progress, two other papers reporting the evaluation of the electron mobility in cadmium sulfide by combined photometric and photoelectric measurements appeared.[12,13] In each of these the analysis depends upon the assumption of detailed models incorporating the bimolecular recombination law. By measuring the ac component of the photocurrent produced by modulated ultraviolet excitation, Fassbender and Lehmann found mobility values between 20 and 40 cm^2/volt-sec, for which they claim only an order-of-magnitude accuracy because of the approximate nature of the theoretical representation. An investigation of the complete current decay curve led Broser and Warminsky to conclude that the mobility is of the order 5 cm^2/volt-sec. Our method differs from these primarily in that it does not require a detailed model. The ultimate accuracy of the method is not limited by the validity of assumptions as to details of the mechanism or by the degree of approximation of the theoretical development.

The authors are grateful to Professor R. J. Cashman, Dr. R. Frerichs, and Professor A. J. F. Siegert of the Physics Department of Northwestern University, for help and advice.

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[12] J. Fassbender and H. Lehmann, Ann. Physik **6**, 214 (1949).

[13] I. Broser and R. Warminsky, Ann. Physik **7**, 289 (1950).

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Centrifugal Distortion in Asymmetric Top Molecules. I. Ordinary Formaldehyde, $H_2C^{12}O$*

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A semiclassical approach is used to develop a simple expression for the centrifugal distortion correction in asymmetric top molecules. The general expression for the shift of any given energy level involves five experimentally determined distortion coefficients and a knowledge of the dependence of the term value as a function of asymmetry. A useful simplified expression for the frequency correction in $\Delta J=0$ transitions involves only two effective rigid rotor parameters and four distortion coefficients. The method is applied to the microwave spectrum of $H_2C^{12}O$; the results show excellent internal consistency. The resulting rigid-rotor parameters are: $a=282{,}106$ Mc/sec, $b=38{,}834$ Mc/sec, and $c=34{,}004$ Mc/sec. The electric dipole moment is determined to be 2.31 ± 0.04 debye and the line breadth parameter as 97 ± 10 microns Hg per Mc/sec.

I. INTRODUCTION

THE problem of handling the effects of centrifugal distortion in rotational spectra is not one of theory, which has been extensively discussed by several authors; rather, it is one of finding convenient and direct means of relating the experimental data to the theoretical parameters. With the high precision now available through microwave spectroscopy this central problem has acquired renewed urgency. In a series of papers by various authors from this Laboratory it is proposed to develop and apply two simplified methods for calculating the frequency shifts due to centrifugal distortion.

The general theory of vibration-rotation energies was first formulated by Wilson and Howard,[1] and several other similar analyses[2] have since appeared. For our purposes the analysis given by Nielsen is the most convenient. His paper gives explicitly to second order the matrix elements for the hamiltonian of a general vibrating-rotating polyatomic molecule.[3] The analysis proceeds in conventional fashion; the matrix elements for the rotational energies are developed in terms of symmetric top wave functions which have the quantum numbers J, K, and M. The matrix has off-diagonal elements in K only, namely, $(K|H|K\pm2)$ and $(K|H|K\pm4)$. The elements are expressed in terms of the three equilibrium-molecule principal moments of inertia, the variation of these moments with vibrational state, and six centrifugal distortion coefficients which involve the equilibrium structure and the vibrational potential constants through cubic terms. When the

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† Now at National Research Corporation, Cambridge, Massachusetts.

[1] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

[2] A list of these publications, mostly dealing with specific molecular symmetries, is given in H. H. Nielsen, Phys. Rev. **60**, 794 (1941); **61**, 540 (1942).

[3] The treatment excludes molecules with internal rotation and those with tetrahedral symmetry. For accidental degeneracies see H. H. Nielsen, Phys. Rev. **68**, 181 (1945).