Saturation Effects in the Sensitized Fluorescence of CaF_2(Ce, Mn)

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The visible fluorescence of Ce^{3+} and Mn^{2+} impurities in crystals of CaF_2 has been investigated under conditions of intense uv irradiation. A change in the fluorescent quantum efficiencies for both impurities is observed at high intensities. In particular, the resonant energy transfer from a Ce^{3+} sensitizer to a neighboring Mn^{2+} begins to saturate. A simple model is postulated to explain this effect. From this model an estimate can be made of the number of sensitizable sites surrounding the Ce^{3+}. The rather large numbers obtained, about 150, may be due to some pairing of the Ce^{3+} and Mn^{2+} ions.

I. INTRODUCTION

THE sensitized fluorescence of impurities in solids is a fairly common effect[1] and has generated particular interest in recent times in connection with laser materials. An example of this type of process occurs in the nonphotoconducting phosphor CaF_2-(Ce, Mn) first investigated by Ginther[2] and Leach.[3] They showed that radiation in some uv absorption bands of Ce^{3+} produces a green Mn^{2+} emission ($^4G \rightarrow {}^6S$) in addition to the usual allowed blue Ce^{3+} emission ($^2D \rightarrow {}^2F$). This resonant transfer of energy from the Ce^{3+} sensitizer S to the Mn^{2+} activator A is thought to occur by a spin-exchange mechanism[4] and can occur with high efficiency.

The purpose of this present paper is to report on the properties of some single crystals of CaF_2(Ce, Mn) when irradiated with uv light sufficiently intense to significantly alter the A ground-state populations. It is shown here that, under these conditions, there is no longer a simple proportionality between the uv radiation and the S and A fluorescence. The relative quantum efficiency of sensitization decreases at the higher irradiation intensities apparently because an appreciable number of A ions are in the metastable excited state where transfer of energy from S is no longer possible. This effect leads to a saturation of the sensitization process which is accompanied by a perceptible increase in the S quantum efficiency. The A saturation emission is determined for several crystals. From these measurements an estimate is made of the number of lattice sites surrounding S which can be sensitized. The reason for the rather large numbers obtained by this method is briefly discussed.

II. SATURATION OF THE SENSITIZATION MECHANISM

The possible transitions for S and A are illustrated in a somewhat idealized manner in Fig. 1. The asterisks indicate excited states and wavy lines represent radiationless transitions from S^* and A^* to the ground state. For a unit volume of crystal under steady-state conditions $\dot{N}_s$ photons per sec absorbed by S will yield J_s and J_a emitted photons per sec from S and A, respectively. Relationships between these quantities will be developed in terms of a simple model. We consider a crystal with a solid solution of N_s sensitizer and N_a activator ions per unit volume and postulate that each S is surrounded by k sensitizable lattice sites such that if an A in the ground state occupies one of these sites, irreversible transfer of energy can occur with a certain probability. If an A is in its excited state, or does not lie on one of the k sites, the probability of energy transfer is zero. We will also work with S and A impurity concentrations which are sufficiently dilute that there is no appreciable overlap among the k sites and that the average number of A associated with each S, $\langle n_a \rangle$, is small compared with 1. Under these conditions we assume that, to a first approximation at least, the rate at which A^* is created, $\dot{N}_a{}^*$, may be related to $\dot{N}_s$ by a simple equation of the form

$$\dot{N}_a{}^* = \alpha \langle n_a{}^0 \rangle \dot{N}_s. \tag{1}$$

Here α is a constant and $\langle n_a{}^0 \rangle$ represents the average number of A in the ground state on the k sensitizable sites. Of course the sum of $\langle n_a{}^0 \rangle$ and $\langle n_a{}^* \rangle$, the corresponding number in the excited state, must equal $\langle n_a \rangle$. If the decay from A can occur by means of photon emission with lifetime τ_a or by a radiationless transition with lifetime τ_r, we may then write the following
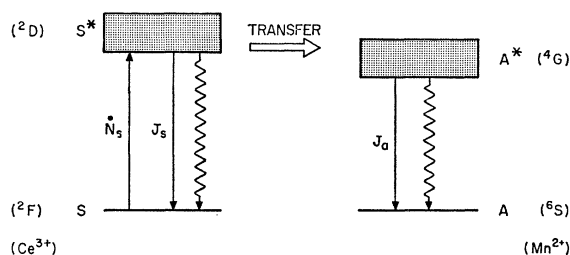

FIG. 1. Schematic energy-level diagram of possible transitions under steady-state conditions. $\dot{N}_s$ photons per sec are absorbed by the sensitizer producing J_s and J_a emitted photons per sec from the sensitizer and activator, respectively. Wavy lines indicate radiationless transitions.

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[1] For a review of the general subject, see D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963), Chap. 8.
[2] R. J. Ginther, J. Electrochem. Soc. **101**, 248 (1954).
[3] R. Leach, J. Electrochem. Soc. **105**, 27 (1958).
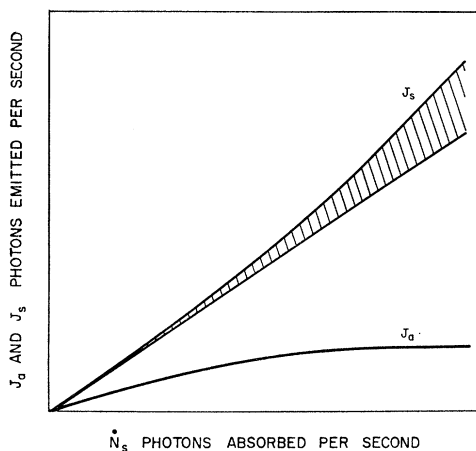[4] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

FIG. 2. Rate of emission by the activator J_a and sensitizer J_s as a function of the rate of sensitizer absorption $\dot{N}_s$. Shaded region indicates possible range of J_s as J_a saturates.

rate equation under equilibrium conditions:

$$J_a = \left[\frac{\alpha \langle n_a \rangle}{1 + \tau_a/\tau_r + \alpha \tau_a \dot{N}_s / N_s} \right] \dot{N}_s. \tag{2}$$

In the limit as $\dot{N}_s$ tends to zero, the quantity in brackets approaches a constant representing the usual definition of quantum efficiency. For sufficiently large $\dot{N}_s$, however, we have $1 + \tau_a/\tau_r \ll \alpha \tau_a \dot{N}_s / N_s$, and J_a will approach a limit corresponding to the case of all possible A in the excited state. This limit is defined as $(J_a)_{max}$ and is given by

$$(J_a)_{max} = N_s k x_a / \tau_a, \tag{3}$$

where we have put $\langle n_a \rangle = k x_a$ for our case of dilute impurity concentrations. Here x_a is the activator mole fraction. Equation (3) provides a basis for estimating k since the other quantities appearing in this relationship are easily measurable. A long lifetime τ_a is desirable for the observation of this saturation effect and this often occurs in cases of practical interest since the $A^* \rightarrow A$ transition can be forbidden.

In our model there are only three de-excitation channels available once a $S \rightarrow S^*$ transition has occurred. Therefore a decrease in sensitization efficiency must result in a corresponding increase either in the S quantum efficiency, or in the efficiency of S radiationless transitions, or both. There seems to be no *a priori* reason why one of these two exit channels should be favored over the other. These possibilities are illustrated in Fig. 2. The shaded region represents the allowable range of values of J_s as J_a becomes saturated. The limits of the shaded area are associated with a constant S quantum efficiency and a constant transfer-plus-S quantum efficiency, respectively. In the foregoing the possibility of induced transitions has not been considered.
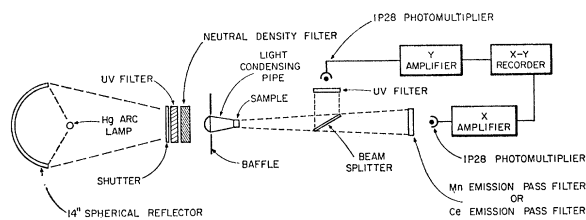

FIG. 3. Schematic diagram of the experimental apparatus.

As a matter of experimental convenience we will in the following section compare J_a and J_s to the irradiating intensity I_{uv} rather than to the rate of S absorption $\dot{N}_s$. In the experiments reported on here they are proportional to a good approximation since the ratio of the number of S^* to S is small. That is, due to the long A^* lifetime, an appreciable number of A^* can be obtained without seriously depleating the S ground state.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The Mn^{2+} and Ce^{3+} fluorescence from several crystals of $CaF_2(Ce, Mn)$ was recorded as a function of uv intensity with the apparatus shown in Fig. 3. A 2500-watt compact mercury arc lamp was used as the uv source. The uv filters consisted of a saturated solution of $NiSO_4$ and $CoSO_4$ along with Corning and Schott filters and were fairly transparent in a broad region around 0.31μ and 0.33μ in the Ce^{3+} absorption bands. Other radiation from the lamp was strongly absorbed. Crystals cut and polished to the dimensions 2 mm $\times 2$ mm $\times 1$ mm were bonded to the back of a crystal quartz light-condensing pipe.[5,6] These crystals were grown by the Bridgman method in an oxygen-free atmosphere.
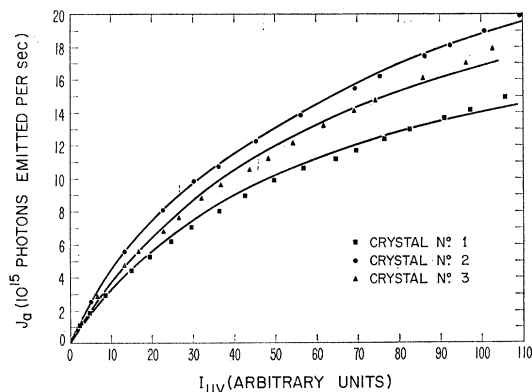

FIG. 4. The Mn^{2+} emission versus uv excitation for three different crystals. The solid lines represent the least-squares fit to Eq. (2).

[5] D. E. Williamson, J. Opt. Soc. Am. 42, 712 (1952).
[6] P. H. Peck, J. J. Redman, C. E. White, and R. E. DeKinder, Appl. Opt. 2, 827 (1954).
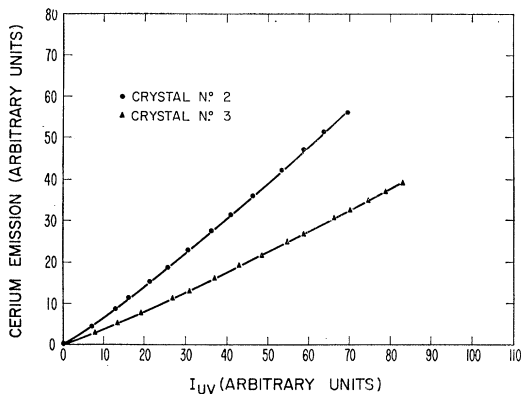
FIG. 5. The Ce^{3+} emission versus uv excitation for two crystals. The solid lines represent the best fit to the data.

In order to maintain the linearity of the photo-multiplier response[7] the ratio of the voltage-divider current to phototube current was kept at a value of at least 800.

Figure 4 shows the Mn^{2+} fluorescent response for various values of neutral density filter interposed in the uv beam. With a suitable narrow-band filter the Mn^{2+} band at 0.48 μ is easily separated from the other radiation present. The effective quantum efficiencies are proportional to the slopes shown in the figure. A relative decrease in the Mn^{2+} emission is clearly dis-cernable at the higher uv intensities (about 10^{19} photons per cm^2 per sec). The solid lines in the figure represent the least-squares fit to Eq. (2). The data seem to be in general accord with our model which predicts a bottleneck in the sensitization exit channel.

The Ce^{3+} response under the same conditions is shown in Fig. 5. This emission occurs in three bands at 0.32, 0.34, and 0.39 μ. Only the line at 0.39 μ can be isolated with a filter from the background uv radiation. This overlapping of the exciting radiation and emission bands prevents a quantitative determination of the increase in the Ce^{3+} quantum efficiency as the Mn^{2+}

fluorescence approaches saturation. Nevertheless, a very slight increase in Ce^{3+} emission can generally be observed at the higher uv intensities.

To determine k from Eqs. (2) and (3) it is necessary to measure the absolute rate of fluorescent emission J_a in terms of the number of A photons being emitted per second from the crystal. To do this the response of the photomultiplier for Mn^{2+} emission was calibrated by comparison to an Eppley Thermopile and corrections were made for refraction at the crystal surface and attenuation due to the beam splitter and filter. Table I summarizes the values of k obtained from these experi-ments for three crystals. Our measured values of τ_a were very nearly the same as those reported by Leach.[3] The impurity concentrations were determined by neutron-activation analysis.[8]

The values of k determined from this saturation effect correspond to an effective range for energy transfer of about 11 Å. This is somewhat larger than the maximum estimated by Dexter[4] for a spin-exchange mechanism. Also, from a method due to Schulman[9] and Botden,[10] Ginther[2] has estimated k at about 31 to 36 for various concentrations of powdered CaF_2-(Ce, Mn) phosphors. The values of k found by the present method in single crystals must be considered order-of-magnitude results due to limitations of our simplified model. Our most serious errors are probably associated with the assumption of a solid solution of impurities. Leach,[3] for example, has reported that Ce^{3+} and Mn^{2+} appear to form close associations in fluorite crystals. Pairing of this sort or a tendency for the impurities to concentrate near lattice imperfections during the process of crystal growth would increase the apparent values of k as determined by this method. It would be of interest to repeat this type of experiment on other crystal phosphors in which the S and A impurities have the same valence and about the same ionic radii as the host lattice. In this case the pairing effects would be minimized and a more meaningful value of k could possibly be obtained.

ACKNOWLEDGMENTS

TABLE I. Concentrations for the activator x_a and sensitizer x_s, and values for k, the number of sensitizable sites per Ce^{3+}.

Crystal	x_a	x_s	k
1	0.0025	0.000064	130
2	0.0024	0.000060	160
3	0.0022	0.000098	130

[7] R. W. Engstrom and E. Fischer, Rev. Sci. Instr. 28, 525 (1957).

[8] This analysis was performed by General Dynamics, General Atomic Division, Activation Analysis Service, San Diego, California.

[9] J. H. Schulman, R. J. Ginther, and C. C. Klick, J. Electro-chem. Soc. 97, 123 (1950).

[10] P. J. Botden, Philips Res. Rept. 7, 197 (1952).