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Radiationless Recombination in Phosphors

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An Auger-type process is proposed for a possible means of nonradiative annihilation of free holes at electron traps in phosphors. A rough calculation is made of the cross section for the process, and some of the consequences are considered qualitatively.

I. INTRODUCTION

IT has been realized by a number of investigators[1–4] that to account for such phenomena as the marked decrease of photoluminescence efficiency at high temperatures and at the shorter wavelengths of ultraviolet excitation, it is necessary to postulate the existence of nonradiative recombination in phosphors. Using the energy-band model to approximate the crystal phosphor, a brief qualitative explanation for the decrease of photoluminescence efficiency will be given in what follows. The schematic energy diagram for the band model is shown in Fig. 1. The crystal phosphor is assumed to have impurities and defects so that there will exist deep traps (marked L in Fig. 1, and usually called activators) to which radiative transitions can take place. Moreover, there are also a large number of shallow traps (marked T in Fig. 1 and to be called electron traps hereafter) which can trap a free electron in the conduction band and later release it.

In the photoluminescent process an ultraviolet quantum can ionize an activator center (which is normally filled) so that there will remain an empty activator and a free conduction-band electron. This electron can then be captured by another empty activator by a radiative process which will give off a light quantum, or it can be captured by an electron trap (with presumably only the emission of phonons). It would appear that in most phosphors the latter process is more probable.

An electron held in an electron trap will fill an empty activator by either of two main processes. In the first process, the electron will be released from the trap (by thermal agitation) and may directly, or even after being retrapped several times, migrate to an ionized activator and be captured. This process will be a radiative one since the final capture (marked R in Fig. 1) will take place with the emission of a light quantum. In the second process, the empty activator is first filled by a thermally agitated electron jumping up from the valence band and thus creating a hole. This hole can migrate to one of the filled electron traps and annihilate the bound electron. It has been postulated[1,2] that this hole-annihilation process is a nonradiative one (marked N in Fig. 1).

It now becomes possible to explain the decrease in photoluminescent efficiency with increase of temperature already mentioned. Whether a trapped electron returns to a vacant activator by a radiative or by a nonradiative process will depend on the ratio of the rate of release of electrons in filled electron traps to the rate at which electrons in the valence band jump into empty activators. The greater this latter rate, the greater will be the proportion of nonradiative recombinations and the lower will be the efficiency. For most phosphors the trap levels and activator levels are such that, in general, an increase in the temperature will increase the jumping rate of the valence electrons much faster than it will increase the release rate of the electron traps, and will thus produce a decrease in the photoluminescent efficiency.

In a similar manner it is possible to explain the efficiency decrease at the shorter wavelengths of ultraviolet excitation. The efficiency will begin to drop when the excitation wavelength becomes short enough to create pairs as well as ionize activators. The holes from these pairs can theoretically be annihilated both at filled activator and at filled electron trap sites, but, in practice, the process at the trap sites seems to predominate. A hole annihilated at an electron trap will remove an electron in a nonradiative process which could eventually have been captured radiatively by an empty activator. This, then, would account for the observed decrease of photoluminescent efficiency.

The purpose in presenting the above brief review of the theory of photoluminescent efficiency was, first, to compile the very scattered background information on nonradiative transitions in phosphors and, second, to

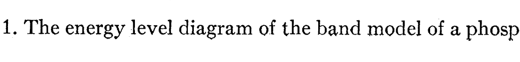

FIG. 1. The energy level diagram of the band model of a phosphor.

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[1] M. Schön, Z. Physik **119**, 470 (1941).
[2] H. A. Klasens, Nature **158**, 306 (1946).
[3] H. A. Klasens and M. E. Wise, J. Opt. Soc. Am. **38**, 226 (1948).
[4] G. F. J. Garlick and A. F. Gibson, J. Opt. Soc. Am. **39**, 935 (1949).

illustrate the importance of the process involving the nonradiative annihilation of a hole at a filled electron trap site. The purpose of this paper is to propose and study a possible detailed mechanism for this recombination process.[5] The nature of this mechanism and the procedure for calculating its cross section will be very similar to those of the radiationless recombination scheme proposed by the author in a previous work.[6]

The proposed mechanism is again an Auger-type process resembling the process corresponding to σ_{1h} in (I). An additional assumption which must be made here is that a single electron trap can trap more than one electron. Thus, in the process to be described here, both electrons will be trapped initially instead of one of them being free as in the σ_{1h} process. The process will then consist of a free hole moving with thermal velocity and approaching an electron trap containing two or more electrons. It will then be possible for one of the electrons and the free hole to annihilate each other with the excess energy absorbed by the other electron, which will be ejected into the conduction band to become an energetic free electron. Just as in (I), the energetic electron will rapidly lose most of its kinetic energy through various types of collisions so that excess energy will ultimately be turned into heat.

In order to obtain an estimate of the probability of the process and how it will depend on various physical parameters, the cross section, σ_{th}, for the hole annihilation described above will be calculated in the same manner and under the same three main assumptions as in (I). In the calculation which will follow it will be assumed that the electron trap at the annihilation site contains just two electrons. To estimate roughly the cross section for an electron trap containing more than two electrons, it is only necessary to multiply the derived cross section σ_{th} by the factor $(N-1)$, where N is the number of electrons in the trap.

II. CROSS-SECTION CALCULATION

As mentioned above, the calculation for σ_{th} will closely resemble that for σ_{1h} in (I).[7] One difference, however, is that $\Psi_b(\mathbf{r},t)$ [in Eq. set (5) of (I)] must be substituted for $\Psi_n(\mathbf{r},t)$. The justification for this is that the model for an electron trap to be used here is to be a structure similar to the parahelium atom in atomic physics. However, instead of using the complicated 1S wave functions for the helium atom, both of the electron wave functions are assumed to have the relatively simple form of the 1s hydrogen wave function. Physically, this is equivalent to deriving the wave function for one electron by assuming the other electron to be always at the position of the nucleus. The "trap radius," a_t, can then be given by Eq. (6) of (I). Since, as in (I), all that is desired here is a rough order-of-magnitude calculation, this type of simplification is felt to be justified.

Moreover, the form of $\Psi_h(\mathbf{r},t)$ (i.e., the wave function for the hole) must be altered to include the interaction of the hole with neutral trap. This was not necessary in (I) because the wave function will be significantly changed only in the volume region of the order of a_t^3 around the trap, and the matrix element integral obtained most of its contributions in a volume region of the order of L_D^3 (which is much larger than a_t^3). Thus, the alteration in wave function would not greatly affect the result. However, as will be seen later, in the present case the matrix element integral will receive its significant contributions from a volume region of the order of $\frac{1}{8}a_t^3$, so that the alteration in $\Psi_h(\mathbf{r},t)$ due to trap interaction will be very important.

In accord with the previous treatment of these problems, it will be assumed that the interaction potential of the hole and the neutral trap will be of the form $[2e^2/\epsilon_t r]\exp[-2r/a_t]$. where r is the distance of the hole to the trap nucleus and $\epsilon_t \equiv a_t/a_H$. The wave function $\Psi_h(\mathbf{r},t)$ can thus be shown to take the following form:

$$\Psi_h(\mathbf{r},t)=[B(\mathbf{b}_0)G(p_0,r)/L^{\frac{3}{2}}]\exp\{(i/\hbar c)\times[\mathbf{b}_0\cdot\mathbf{r}-(E_0-\Delta E/2)t]+(i/\hbar c)\times[\mathbf{p}_0\cdot\mathbf{r}-p_0^2t/2m^*c^2]\}. \quad (1)$$

The factor $G(p_0,r)$ can be approximately evaluated by the WKB method and for small values of p_0 can be shown to approximate the following form:

$$G(p_0,r)\cong G_0(r)$$

$$=\exp\left\{-\left[\frac{(4me^2a_t/\epsilon_t)^{\frac{1}{2}}}{\hbar}\right]\int_{r/a_t}^{\infty}du\left[\frac{\exp(-2u)}{u}\right]^{\frac{1}{2}}\right\}$$

$$=\exp\{-2(\pi)^{\frac{1}{2}}[1-\mathrm{erf}((r/a_t)^{\frac{1}{2}})]\}. \quad (2)$$

Since $p^2/2m^*c^2>E_T$, it is justifiable to use a plane wave for the wave function of $\Psi_f(\mathbf{r},t)$ just as in (I).

Another difference in the calculation is that instead of Eq. (7) in (I) H_i can now be given by

$$H_i=e^2/(\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|). \quad (3)$$

Since interaction between electrons at a large distance will be unimportant in this process, the Debye "cutoff" need not be used.

When one makes the proper substitutions in Eq. (3) of (I) and carries out the indicated integration, the

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[5] Incidentally, from the fact that in the succeeding sections no mention is made of other types of nonradiative recombination processes, it is not to be inferred that the position has been taken that these do not exist. The Auger-type process is presented here as one possible answer, but not necessarily the entire one, to the problem of radiationless recombination in phosphors. Other possible processes are not treated primarily because they fall outside the main interest of this paper.

[6] Leon Bess, Phys. Rev. **105**, 1469 (1957). This work will hereafter be referred to as (I).

[7] Moreover, the notation which will be adopted here will be that of (I).

result for the matrix element will be[8]:

$$(b,b|H_i|f,h)=2\pi(e^2/\epsilon_0)(a_t/L)^3\{F^2(\tfrac{1}{2}pa_t)[1+9F(pa_t)] \\ -(16/81)F^2(\tfrac{1}{3}pa_t)[2+(25/4)F(\tfrac{1}{2}pa_t)]\}[1\pm1], \quad (4)$$

where $F(x)\equiv[1+(x/\hbar c)^2]^{-1}$.

Upon using the result of Eq. (4) with Eqs. (1) and (2) of (I), performing the $d\Omega_p$ integration, and averaging over spin directions as in (I), the result for the cross section σ_{th} becomes

$$\sigma_{th}(\bar{p}_0)=4\pi(a_t^2/a_H)^2(\bar{p}m^*/\epsilon_0^2\bar{p}_0m) \\ \times\{F^2(\bar{p}a_t/2)[1+9F(\bar{p}a_t)]-(16/81)F^2(pa_t/3) \\ \times[2+(25/4)F(pa_t/2)]\}^2. \quad (5)$$

Instead of Eq. (10) of (I), the energy relation which must be satisfied here is

$$p_0^2/2m^*c^2-2(E_c-E_T)+\Delta E=p^2/2m^*c^2. \quad (6)$$

To obtain an estimate of the magnitude of the cross section σ_{th}, a substitution in Eq. (5) will be made using the following typical values at 300°K for the various physical parameters: $\Delta E=3$ ev; $E_c-E_T=0.5$ ev; $m^*/m=1$; $a_t=2.5\times10^{-8}$ cm; $\hbar c/\bar{p}_0=1.2\times10^{-7}$ cm; $\hbar c/\bar{p}=1.3\times10^{-8}$ cm; and $\epsilon_0=8$. The result of the calculation is that $\bar{\sigma}_{th}\cong2\times10^{-15}$ cm^2.

III. GENERAL REMARKS

If the numerical values of the various physical parameters in the previous section are substituted in Eq. (19) of (I) for the radiative capture of a hole, it is found that the radiative capture cross section, $\bar{\sigma}_{rh}$, has the value of about 10^{-19} cm^2. Thus, the most significant result of this treatment seems to be that the cross section for nonradiative hole capture is very much larger (a factor of 10^4) than that for the radiative capture.

In addition to the multiply occupied electron traps spoken of above, it seems probable that there should exist singly occupied electron traps (i.e., traps able to capture a maximum of one electron). Unless there exists another type of radiationless process, these would not be able to nonradiatively annihilate a hole and would in a sense protect the electron (since the radiative process would have a very small cross section). Thus, it would appear, high ratios of singly occupied traps to multiply occupied traps might work toward high photoluminescent efficiencies.

It should be pointed out that the type of radiationless recombination processes considered in (I) probably does not play a large role in phosphors (at least not in the bulk). This is because all of the cross sections of these processes are proportional to one of the mobile carrier concentrations which are generally very small in phosphors. It was the inadequacy of these processes to explain nonradiative phosphor recombination that led to the present investigation.

It is now accepted that nonradiative recombination plays an important role also in cathodoluminescence[9] where their main effect seems to be to limit the efficiency. It is suggested that exactly the same type of hole annihilation process postulated above for photoluminescence should also operate for cathodoluminescence.

ACKNOWLEDGMENTS

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APPENDIX A

Just as in Eq. (1A) in (I), it can be shown that

$$(b,b|H_i|f,h)=(e^2/\epsilon_0)(\pi a_t^3L^3)^{-1} \\ \times[I(r_1/a_t;\,p_0r_1|r_2/a_t;\,pr_2)][1\pm1], \quad (1A)$$

where

$$I(r_1/a_t;\,p_0r_1|r_2/a_t;\,pr_2)\equiv\int\frac{d^3r_1d^3r_2}{|\mathbf{r}_1-\mathbf{r}_2|}G_0(r_1) \\ \times\exp[(1/\hbar c)(i\mathbf{p}_0\cdot\mathbf{r}_1-i\mathbf{p}\cdot\mathbf{r}_2-r_1/a_t-r_2/a_t)]. \quad (2A)$$

In Eq. (1A) use has been made of the identity

$$I(r_1/a_t;\,p_0r_1|r_2/a_t;\,pr_2)\equiv I(r_1/a_t;\,p_0r_2|r_2/a_t;\,pr_1). \quad (3A)$$

The only problem now remaining is the evaluation of $I(r_1/a_t;\,p_0r_1|r_2/a_t;\,pr_2)$. To simplify the calculations it will be noted that, in the temperature range and the trap depths of interest, $\hbar c/\bar{p}_0\gg a_t$. Thus over the range of volume from which most of the contributions to the integral of (2A) arise, the factor $\exp(i\mathbf{p}_0\cdot\mathbf{r}_1/\hbar c)$ will be nearly unity, and the assumption can be made in the following that the factor is unity over the whole range of integration. Moreover, to simplify the calculation without falling out of the adopted limits of accuracy, the following empirical approximation will be made for the function $G_0(r_1)$:

$$G_0(r_1)\simeq G_1(r_1)=1-\exp(-r_1/a_t). \quad (4A)$$

It will be found that $G_1(r_1)$ does not deviate from $G_0(r_1)$ by more than 15% over the whole range $0<r_1<\infty$.

Thus, after the following substitutions have been made:

$$\mathbf{r}_1/\hbar c=\mathbf{x},\quad \mathbf{r}_2/\hbar c=\mathbf{y},\quad\text{and}\quad 1/a_t=\alpha. \quad (5A)$$

Equation (2A) will become

$$I=(\hbar c)^5\int\int\frac{d^3xd^3y}{|\mathbf{x}-\mathbf{y}|}G_1(x)\,\exp[-\alpha x-\alpha y-i\mathbf{p}\cdot\mathbf{y}], \quad (6A)$$

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[8] See Appendix A for the details of the matrix element integration. Just as in (I), the variations resulting from the factor $|B(\mathbf{b}_0)|^2$ being different from unity have been neglected.

[9] See, for example, G. F. J. Garlick, Proc. Inst. Radio Engrs. **43**, 1907 (1955).

$$I=2\pi(\hbar c)^5\int_0^\infty\int_{-1}^1 dyd\mu_0 y^2\exp[-\alpha y-ipy\mu_0][I_x(\alpha;y)-I_x(2\alpha;y)],\quad(7A)$$

where

$$I_x(\alpha;y)\equiv 2\pi\int_0^\infty x^2dxe^{-\alpha x}\int_{-1}^1 d\mu[x^2+y^2-2xy\mu]^{-\frac{1}{2}}.\quad(8A)$$

In writing the results of the μ integration in Eq. (8A), they must be arranged so that the factor $(x-y)$ will always be greater than zero since $|\mathbf{x}-\mathbf{y}|>0$. Thus it can be shown that

$$I_x(\alpha;y)=4\pi\left[\left(\frac{1}{y}\right)\int_0^y x^2e^{-\alpha x}dx+\int_y^\infty xe^{-\alpha x}dx\right],\quad(9A)$$

$$I_x(\alpha;y)=(4\pi/y)[2/\alpha^3-(y/\alpha^2)e^{-\alpha y}-(2/\alpha^3)e^{-\alpha y}].\quad(10A)$$

Upon substituting Eq. (10A) in Eq. (7A) and performing the μ_0 integration, the result will be

$$I=\left[\frac{(4\pi)^2(\hbar c)^5}{\alpha^2 p}\right]\int_0^\infty dy\,\sin py e^{-\alpha y}\left\{\left[\frac{2}{\alpha}ye^{-\alpha y}-\frac{2}{\alpha}e^{-\alpha y}\right]-\left[\frac{1}{\alpha}ye^{-2\alpha y}-\frac{1}{\alpha}e^{-2\alpha y}\right]\right\}.\quad(11A)$$

When the y integration in Eq. (11A) has been performed, I will take the explicit form

$$I=\left[\frac{2(4\pi)^2(\hbar c)^5}{\alpha}\right]\left[\frac{p^2+10\alpha^2}{(p^2+\alpha^2)(p^2+4\alpha^2)^2}-\frac{2p^2+33\alpha^2}{(p^2+4\alpha^2)(p^2+9\alpha^2)^2}\right].\quad(12A)$$

Upon using the results of Eq. (12A) and the substitutions of Eq. (5A) in Eq. (1A), the result can be brought into the form of Eq. (4) of the text.

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Superconducting Transition in Aluminum*

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Further results on the superconducting properties of aluminum are given which supplement those previously reported. The critical field curve for pure Al has been measured by using a paramagnetic salt as a thermometer. Except for a region very near T_c, our data are accurately represented by the parabolic relation, $H_c=H_0[1-(T/T_c)^2]$, where $T_c=1.196\pm0.005$°K and H_c is about 99±1 gauss. The excellent reproducibility of the *S-N* transition in Al suggests that it may serve as a useful secondary thermometric standard near 1°K. Further observations are reported on the broadening tendency of magnetically measured transitions in single-crystal specimens near T_c. It is also found that polycrystalline specimens of the same material do not show the broadening effect. A semiquantitative theory of the intermediate state is applied to explain the observation that the magnetic transition is sharper than predicted on the basis of specimen geometry at temperatures well below T_c. The difference in sharpness can be explained as a contribution of the interphase free energy whose order of magnitude has been estimated with fair success from the observed shape of the magnetic transition.

I. INTRODUCTION

IN a previous article[1] (to be referred to herafter as I) a cryostat was described for investigating the superconducting transition in metals having critical temperatures down to about 0.8°K. Although the cryostat was found to be very satisfactory for studying the properties of the transition at constant temperature, a carbon resistor was used as a thermometer and our experience indicated that the resistance-temperature relationship for such resistors could not be reliably extrapolated to temperatures below our calibration range of 1.5–4.2°K. Because of the lack of a reliable thermometric element, it was decided to redesign the inner helium container of the cryostat described in I so as to incorporate into it a paramagnetic salt pill. The use of this modified cryostat to measure the temperature dependence of the critical field in pure aluminum is reported herein.

The attempt in the present work has been to obtain precise information about the critical-field curve of pure Al. Previous study of the superconducting transition under isothermal conditions has shown that the *S-N* transition in pure aluminum is very reproducible from specimen to specimen. Thus accurate measurements of the critical field curve, in addition to yielding information about the properties of Al, may also provide a practical secondary thermometric standard for a range in which absolute temperature determinations are difficult.

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[1] Cochran, Mapother, and Mould, Phys. Rev. **103**, 1657 (1956).