Criterion for the Occurrence of Luminescence*

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A mechanism is suggested for the nonradiative quenching of excited states of simple impurity centers, namely a crossover to the ground electronic state of the center immediately after excitation and before thermal equilibrium has had time to come about. It is proposed that this mechanism is responsible for the absence of strong luminescence in some impurity and color centers, e.g., the F-center in alkali-halide crystals. The quenching process proposed here is applicable only for certain geometries of the configuration coordinate diagram, which are discussed with a view to a criterion for strong luminescence. The quenching mechanism is consistent with known configuration coordinate curves, and leads to a prediction which is experimentally verified, to the effect that the wavelength of emitted radiation is not more than twice that of the light absorbed by the center. The same mechanism shows the possibility of photoconductivity arising from absorption in discrete lines even at low temperatures.

IN a simple impurity center the absorption of light in the center raises it to a bound excited state from which it returns to the ground state either by a radiationless transition or by a luminescent transition. Although a large number of luminescent and nonluminescent systems has been investigated experimentally, the properties which determine whether or not a particular system luminesces have not been well understood.

This problem has become of special interest recently in connection with the luminescence of the F-center in alkali halides. Huang and Rhys[1] have predicted that a multiphonon radiationless transition in the F-center would have a negligible probability at low temperatures and Pekar[2] has indicated that a variety of alkali halides should have their F-center emission near 10 000 A. However, an experimental investigation by Klick[3] from 2500 to 25 000 A indicated no emission from the F-center with a quantum efficiency larger than three percent over most of this range. Botden, Van Doorn, and Haven[4] have recently reported emission from colored alkali halides quenched from elevated temperatures to liquid nitrogen temperature, but the efficiency of this emission is reported to be only of the order of one percent. These authors tentatively suggest that this emission arises from the F-center. In any case the large majority of F-centers return to their ground state by processes which do not involve radiation.

Markham[5] and Meyer[6] have suggested that more refined calculations on the multiphonon transitions could show that these transition probabilities were underestimated by Huang and Rhys; detailed calculations have not as yet appeared. Since, however, an increase in the transition probability of at least several dozen powers of ten would be necessary to account for the experimental results in a typical case, it is believed that other mechanisms might account for the radiationless transition.

One alternative mechanism has been suggested by Seitz[7] for the case of excitons. If the lattice relaxation is sufficiently great, the minimum of the excited state curve will fall outside of the ground-state curve. (See Fig. 1.) Efficient luminescence would then be impossible because the transition to the ground-state curve would occur either as the system approached its new equilibrium after absorption or by a thermal activation after reaching equilibrium at point A. Using experimental data on the F-band absorption, Russell has computed the configuration coordinate curves for the F-center in KCl, as shown in Fig. 2(a).[8] These curves indicate that Seitz's mechanism probably does not apply in the case of the F-center.

In the past, treatments of transitions from the excited electronic state have all been implicitly based on the assumption that the system is in thermal equilibrium (except for the quantum of electronic excitation energy). Consequently, the population of the highly excited vibrational states is assumed negligible in the computation of transition probabilities from the excited elec-
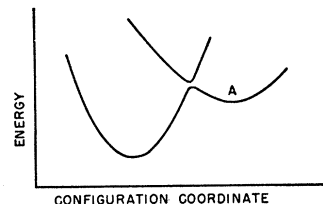
* Research supported in part by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.
[1] K. Huang and A. Rhys, Proc Roy. Soc. (London) **A204**, 406 (1950).
[2] S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 510 (1950); **22**, 641 (1952).
[3] C. C. Klick, Phys. Rev. **94**, 1541 (1954).
[4] Botden, Van Doorn, and Haven, Philips Research Repts. **9**, 469 (1954).
[5] J. J. Markham, Phys. Rev. **94**, 1395 (1954).
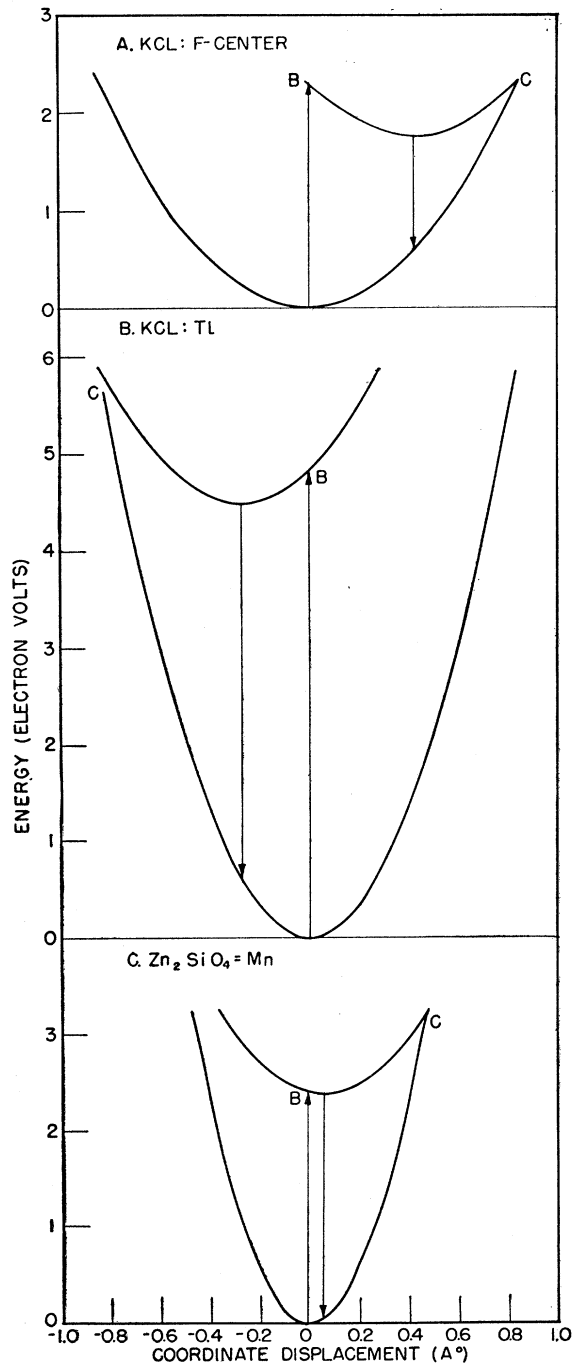[6] H. J. G. Meyer, Physica **20**, 181 (1954).

Fig. 1. An arrangement of configuration coordinate curves proposed by Seitz which would lead to radiationless transitions.

[7] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).
[8] G. A. Russell (to be published).

FIG. 2. Configuration coordinate curves for the F-center in KCl, KCl:Tl, and Zn_2SiO_4:Mn. In each case the coordinate is the displacement of the nearest neighbor ions from their ground-state equilibrium positions.

tronic state. In a Huang-Rhys-Lax[9] type of calculation, the initial wave function for the system in an excited electronic state thus contains very few or no phonons at low temperature. When pictured on a configurational

[9] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

coordinate diagram, the system is assumed to be in the vicinity of A on Fig. 3.

In the present note it is pointed out that the system, initially excited to the vicinity of B by the absorption of a quantum of light $\hbar\omega$, may never reach the equilibrium position A because an alternative mechanism for non-radiative transitions may occur before the system comes to equilibrium, and that this alternative mechanism may be the basis of a criterion for luminescence in simple systems.

When the system is first excited by the absorption of $\hbar\omega$, the system is in the Nth vibrational state, characteristic of the energy E_B-E_A. This energy will be radiated away in the form of phonons in a time long compared with 10^{-13} sec, if N is large. During this time, the configurational coordinates of the system will undergo violent oscillations, characteristic of the high local temperature. As the center "cools," the state of the system passes through the point with energy E_C and configurational coordinates X_C. At this point the energies of ground and excited electronic states are essentially the same, so that no activation energy is required for a redistribution of the electronic wave function, that is, for a transition to the ground electronic state. Thus before the system comes to its equilibrium position from B, it has the opportunity to change its electronic state at C; if the system once reaches A, however, it must await the unlikely occurrence of a statistical fluctuation in the local temperature to that characteristic of E_C, or must simultaneously emit a large number of phonons (to reach the point D), in order to change its electronic state by nonradiative transitions.

On the other hand, if the energy configuration is such that the intersection C occurs at an energy higher than that of B, as would occur if the two minima in Fig. 3 were laterally displaced only a short distance (small relaxation energy E_B-E_A), then during cooling the intersection point C would not be reached, and the system would reach A, where at not too high a temperature, it would stay long enough to luminesce. Thus a sufficient condition for luminescence at low temperatures is that E_C be greater than E_B; if the crossover at C occurs with high probability, the condition $E_C>E_B$ is also a necessary condition. We propose that this is sometimes the case.
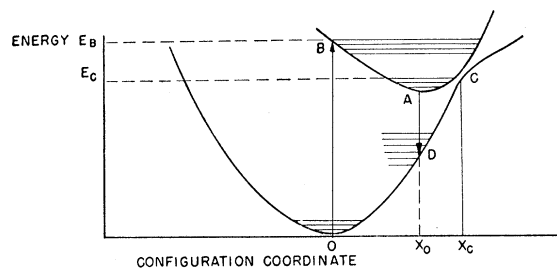

FIG. 3. Configuration coordinate curves leading
to radiationless transitions.

In Fig. 2 are given the three systems for which configuration coordinate curves have been determined.[10] In the case of $KCl:Tl$[11] and $Zn_2SiO_4:Mn$[12] the centers are luminescent with high efficiency and the intersection of the curves (C) is well above the region to which optical transitions are made (B). In the case of the F-center, work of Russell [see Fig. (2a)], indicates that (C) is at least no higher than (B) in agreement with the low efficiency of luminescence in the F-center.

The criterion proposed above is not only in agreement with the experimental facts for the three known systems, but from it may also be derived a relationship between absorption and emission wavelengths which may be checked in a large number of systems for which the configurational coordinate curves have not been determined. On the basis of the criterion proposed here it is possible to determine the smallest value of the emitted energy in relation to the absorbed energy. The smallest emission energy occurs when C is at the same energy as B, since for C lower than B it is postulated that no emission occurs. Under these conditions the position of the minimum of the excited state curve on the coordinate axis falls halfway between the minimum of the ground-state curve and the intersection point. Then if the configurational coordinate curves are parabolic, and if $E_B = E_C$, the energy of the peak of the absorption band is

$$E_{abs} = \tfrac{1}{2}k_g(2X_0)^2, \tag{1}$$

where k_g is the force constant in the ground state and X_0 the lateral displacement of the two minima in Fig. 3. The energy of emission is given by

$$E_{emis} = E_B - \tfrac{1}{2}k_g X_0^2 - \tfrac{1}{2}k_e X_0^2, \tag{2}$$

where k_e is the force constant in the excited state. The values of k_g and k_e are not known in most cases but it is generally agreed that $k_e \leqslant k_g$. The minimum value of E_{emis} would occur if $k_e = k_g$. Thus we obtain

$$E_{emis} \geqslant E_{abs}/2, \tag{3}$$

or, in terms of wavelength,

$$\lambda_{emis}/\lambda_{abs} \leqslant 2. \tag{4}$$

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[10] Configuration coordinate curves for $CaWO_4$ have been given by H. F. Hameka and C. C. Vlam [Physica 19, 943 (1953)] and by C. C. Vlam [Brit. J. Appl. Phys. 5, 443 (1954)] using a vibrational frequency obtained from Raman spectra in the determination of the curves. The resulting curves predict an absorption band at 3700 A which is not observed experimentally. For this reason the $CaWO_4$ data have not been included here although they do not disagree with the present criterion.
[11] F. E. Williams, J. Phys. Chem. 57, 780 (1953).
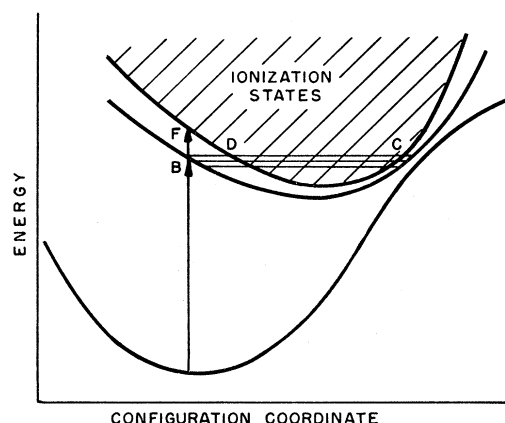[12] C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. 42, 910 (1952).

FIG. 4. An arrangement of configuration coordinate curves which might lead to photoconductivity without direct transitions to the conduction band. The upper curve represents the lowest energy ionization states of the center.

This inequality is strengthened further if one takes into account the deviations from the parabolic shapes, i.e., the increased curvatures, which are to be expected at large distances from the minima.

This upper limit for the wavelength ratio applies to a simple single center in which both the absorption and emission acts involve the same levels. A literature search reveals no such case where the relationship of Eq. (4) is violated. The general validity of the relationship of Eq. (4) gives added support to the mechanism of radiationless transitions from which it was derived.

There appears, then, to be a simple explanation for the low efficiency of luminescence of the F-center on the basis of configuration coordinate curves. The radiationless transition mechanism described here may be of general applicability for the case where absorption and emission transitions are localized at a center.

Another possible consequence of this mechanism might be the ionization of the center, that is, the removal of the electron, by absorption of a quantum of light appreciably less energetic than that predicted to be necessary by the Franck-Condon principle. If the ionization states dip below the point B at their minimum energy, a transition might also occur to them while the center is cooling. This possibility is indicated in Fig. 4, where the crossover might occur, energy-wise, at any configuration between X_C and X_D during the cooling process, although a direct Franck-Condon transition from the ground electronic state would require a photon of energy E_F, which may be appreciably larger than E_B. Thus photoconductivity might arise even at the lowest temperatures upon irradiating into discrete absorption lines as well as into bands associated with transitions directly into the conduction band.