

How Far Are Luminescence Properties Predictable?

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Our knowledge of the luminescence of isolators has increased considerably during the past decade. As a consequence it has become possible to understand the luminescence of technically important phosphors and even to predict efficient luminescent materials. We first illustrate how emission spectra of a given activator can be varied by changing the host lattice. Second we consider the factors influencing the luminescent efficiency. Using a single-configurational coordinate model, we have performed calculations on a model system. These illustrate which factors are important for efficiency. Some clear results are reported. Finally, we discuss the mobility of excitation energy. In some phosphors the excitation is highly mobile even at low temperatures. As a consequence emission originates from centers which trap the excitation energy. In other phosphors this mobility is low, and at low temperatures emission occurs from the regular luminescence centers. At higher temperatures the excitation energy can become mobile because of thermal activation.

Introduction

Luminescence is nowadays a well-known phenomenon the applications of which are used almost universally. Luminescent materials have been studied for many decades. During the last decade the answers to the questions "How can we regulate the luminescence color by the choice of the host lattice?" and "How can we control the luminescence efficiency?" have been found, assuming that one is satisfied, for the time being, with a qualitative and rough picture. These questions are typical materials science problems and belong as such to the field of solid-state chemistry. We restrict ourselves to the case of isolating materials.

Emission Color

Here we give one example of the influence of the host lattice on the emission of a luminescent ion. Consider the Pr^{3+} ion with $4f^2$ configuration. Its energy level scheme is

shown in Fig. 1. Depending on the host lattice in which it is incorporated this ion may give a number of different emissions, viz., red (from the 1D_2 level), green (from 3P_0), blue (from 1S_0), and ultraviolet (from the $4f5d$ state). The position of the excited $4f5d$ state determines which of the emissions is to be expected.

In some fluorides the lowest component of the $4f5d$ state is situated above the 1S_0 level. Short-wavelength ultraviolet excitation or cathode rays excite the Pr^{3+} ion from the 3H_4 ground state to the $4f5d$ state, whence it decays radiationlessly to the 1S_0 level. From the 1S_0 level the Pr^{3+} ion returns to the ground state by two-photon luminescence: emission occurs in the blue and in the green and red parts of the visible spectrum. The green and red emissions are ascribed to emission from 3P_0 , the blue emission to $^1S_0 \rightarrow ^3P_2$ or 1I_6 transitions.

If the $4f5d$ state lies below the 1S_0 level, two-photon luminescence is no longer

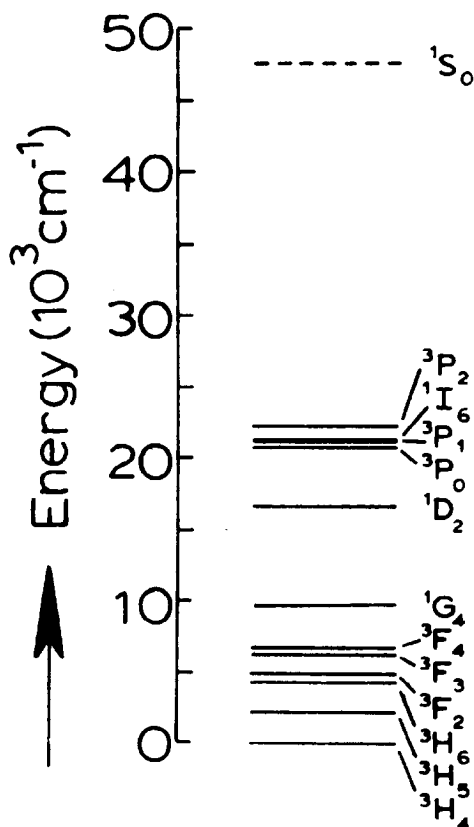


FIG. 1. Energy level scheme of Pr^{3+} . The $4f5d$ excited state is variable and has been omitted.

observed. In some host lattices emission from the $4f5d$ state is observed; in others the $4f5d$ state is emptied into the 3P_0 level (see Fig. 2), followed by emission from this level. In many oxides, however, only the red 1D_2 emission of Pr^{3+} is observed. Effective ${}^3P_0 \rightarrow {}^1D_2$ relaxation may be imagined via the $4f5d$ state in the same way as that shown in Fig. 2 for relaxation to the ${}^3P_{2,0}$ levels, if this state is at energies lower than those in Fig. 2.

This relaxation shows the drastic influence of the $4f5d$ state of the Pr^{3+} ion on its emission characteristics. Since we have a relatively good model for understanding where the position of this level is situated, we can also make a prediction of the emission of the Pr^{3+} ion in a given host lattice. For

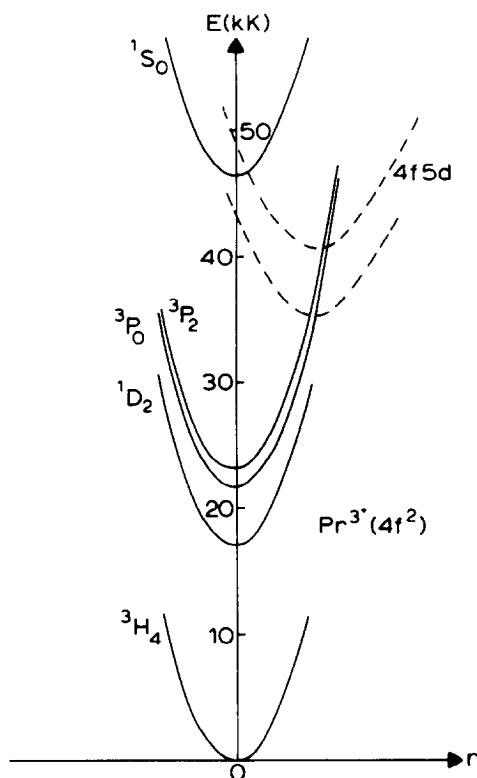


FIG. 2. Configurational coordinate diagram for Pr^{3+} . Only some of the $4f^2$ levels have been drawn. Two possible $4f5d$ states have been indicated (broken lines). Excitation into these states results in occupation of the 3P_0 level.

further details the reader is referred to Ref. (1). For many other ions or groups of ions, some of which were dealt with during a recent summer school (2), the situation is comparable.

Luminescence Efficiency

An even more difficult question is the prediction of host lattices in which ions will show efficient luminescence. The efficiency of luminescence depends on the ratio of the probabilities of radiative and nonradiative transitions in the luminescent center. These transitions can be most easily studied in the configurational coordinate model (see, e.g.,

(3)). The ground state and the emitting state are presented by parabolas which have been shifted relative to each other (Fig. 3). It is clear that the larger the offset of the two parabolas, the larger the nonradiative transition probability and the lower the luminescence efficiency and the thermal quenching temperature of the emission (1).

Struck and Fonger (4) have indicated a method for calculating the temperature dependence of these nonradiative processes. Here we will not describe their procedure, but report some results of calculations performed by Bleijenberg in this laboratory. In his calculations the parameters in the configurational coordinate model are varied, so that their influence on the luminescence efficiency becomes clear (5). The starting point is a luminescent center with a two-parabola level scheme which emits in the red. The vibrational frequency in the parabolas is

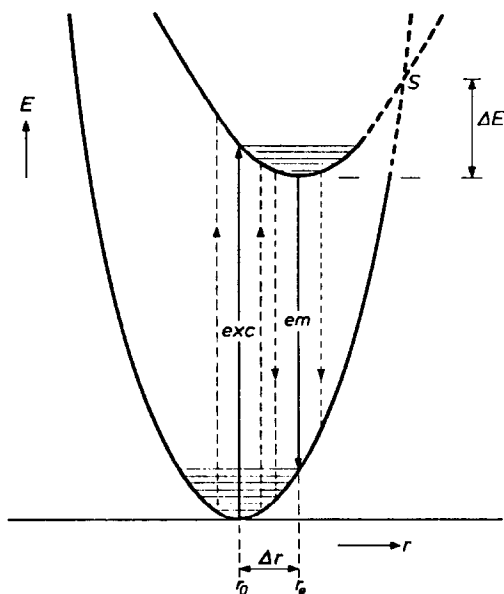


FIG. 3. Schematic configurational coordinate diagram. Excitation and emission transitions have been indicated. The emission is at lower energy than the absorption (excitation). Nonradiative return from the upper to the lower parabola is possible via the region around S (Mott-Seitz model).

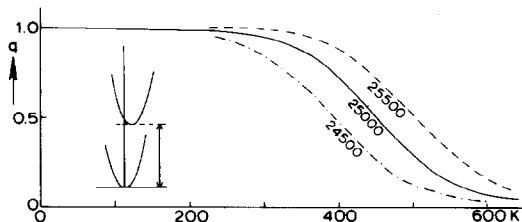


FIG. 4. Calculated quantum efficiency as a function of temperature. The energy difference between the two parabolas has been varied (see inset and values at the curves; these are in cm^{-1}). All other parameters remain the same.

taken as 500 cm^{-1} . The dimensionless parameter a_{uv} , measuring the offset (4), is taken to be 7.746. It should be stressed that it is not the absolute values of these quantities which interest us, but the influence of their variations on the luminescence efficiency.

Figure 4 shows the luminescence efficiency as a function of temperature for this case. The energy difference between the parabolas in the standard case is 25000 cm^{-1} . Figure 4 also contains curves for a larger and a smaller value of the energy difference between the parabolas. The larger this energy difference, the higher the quenching temperature of the luminescence. The figure suggests a linear relation between this energy difference and the quenching temperature if all other parameters remain unchanged. This was suggested years ago by an experimental study on the luminescence of the octahedral niobate group (6).

In Fig. 5 the offset between the parabolas has been varied, which has a drastic effect on the luminescence. The variation is some 7%, corresponding in practical cases to a

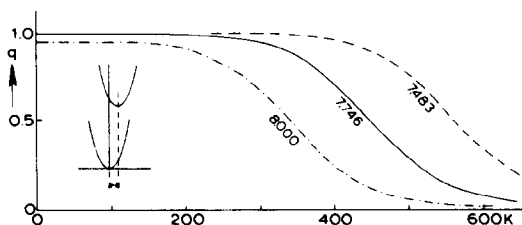


FIG. 5. As Fig. 4. The offset has been varied.

difference of about 0.015 \AA . Such small variations in the offset between the two parabolas can easily be the result of using different host lattices. This effect was predicted qualitatively earlier (2), and a number of examples were given. A striking example is the luminescence of the U^{6+} ion in ordered perovskites (7). The quenching temperature of the U^{6+} emission in this lattice depends on the nature of the cations which are behind the oxygen ions surrounding the uranium ion. If they are small, they will restrict the expansion of the uranate group after excitation; i.e., the offset will be relatively small. In fact it was observed experimentally that the smaller these surrounding cations, the higher the quenching temperature. There is a considerable amount of experimental evidence for the fact that efficient phosphors require a small offset and that this offset can be realized by using strongly bound surroundings around the luminescent ion.

One may ask why alkali halides with bonding much weaker than that in oxides are often successful host lattices for luminescent ions. Figure 6 gives the answer. Here the vibrational frequency is varied, which has a dramatic influence. Low vibrational frequencies (as in the alkali halides) are to be preferred over host lattices for efficient phosphors. Here we encounter difficulties: The frequency used in the calculation is an averaged, effective frequency, because the host lattice has many frequencies available; at present, quantitative calculations are only feasible with one frequency. This is one of

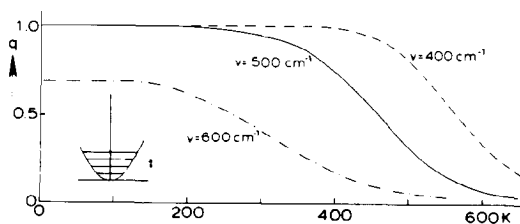


FIG. 6. As Fig. 4. The vibrational frequency has been varied.

the topics of current research, and we will not discuss it here.

Although the approach is rough, the results can be used to get an approximate idea of which host lattices will be suitable for preparing efficient luminescence: the offset should be small, which can be realized by strongly bound surroundings; the effective vibrational frequency should be low. In a sense these rules are contradictory, but it is not very clear what the effective vibrational frequency is. High-frequency internal modes are often not very effective in radiationless transitions.

The problem indicated above probably prevents further progress in predicting suitable host lattices. In practice, however, working with these rules is not unsatisfactory at the moment (2).

Energy Migration

Up to now it has been assumed that the excitation energy remains at the emitting center after excitation. This, however, is not necessarily true, and the excitation energy can become mobile, so that it migrates through the lattice. In fact this is only possible for fairly short distances between the luminescent ions, i.e., for concentrated systems. This requirement is not sufficient for migration of excitation energy.

In Fig. 7 we have drawn two different configurational coordinate diagrams. On the left-hand side the offset is very small, so that emission and absorption overlap, whereas on the right-hand side the offset is large, so that emission and absorption are shifted relative to each other. After excitation strong relaxation occurs and the system is out of resonance with the other centers, which hampers energy migration; whereas on the left-hand side energy may become mobile, even at low temperatures. This situation is shown schematically in Fig. 8. After excitation the energy migrates through the lattice until it is trapped at an ion with a slightly

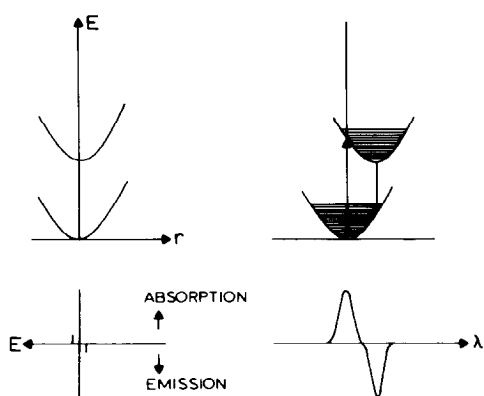


FIG. 7. Small offset parabolas (left-hand side) and large offset parabolas (right-hand side) with the relevant absorption and emission spectra (schematic).

lower energy level, possibly because this ion is situated near a defect or impurity. This ion shows emission which is different from the absorption (in the intrinsic luminescent ions). The energy can also be trapped by killer sites so that luminescence is absent. Let us consider some examples.

a. MnF₂ (8). After excitation into the Mn²⁺ ions, the emission does not originate from the Mn²⁺ ions which were excited, but from Mn²⁺ ions that have impurity Mg²⁺ ions as nearest neighbors in the lattice. The Mg²⁺ concentration is only about 1 ppm. The Mn²⁺ ions have a small offset which makes efficient energy transport to the Mn²⁺ ions next to Mg²⁺ possible. At higher temperatures the traps (with depth ΔE in Fig. 8) are emptied thermally, and all the excitation energy migrates to killer sites.

b. Ba₂CaUO₆ (9). The offset in the case of U⁶⁺ ions is also small. Rapid energy migration is observed, and the emission is due to

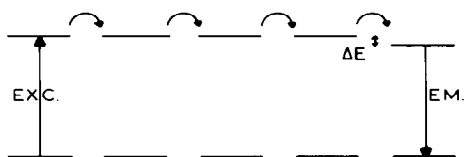


FIG. 8. Rapid energy migration through the lattice after excitation. The trap is on the right-hand side.

U⁶⁺ ions next to defects. Several of these trapping U⁶⁺ ions have been observed. These traps are emptied above 20°K when all excitation energy is transferred to killer sites (Fig. 9).

c. Tb₃Al₅O₁₂ (10). At 4°K, 90% of the excitation energy reaches killer sites (Fe²⁺ and Ni²⁺ impurities). The remaining 10% is emitted: 2% from intrinsic Tb³⁺ ions and 8% from Tb³⁺ next to impurities (probably Si_{A1} and Ca_{Tb}). At 20°K 99% of the excitation energy reaches the killer sites.

d. YVO₄-Eu (2, 11). Here the situation is completely different, because the VO₄ group is a center with a large offset. At low temperatures the excitation energy is not mobile. Excitation into the vanadate group results mainly in vanadate emission at low temperatures, because the Eu³⁺ ions cannot be reached.

At higher temperatures, however, energy migration among vanadate groups becomes possible by thermal activation. At room temperature excitation into the vanadate group results in efficient Eu³⁺ luminescence. The Eu³⁺ ion serves as a (luminescent) trap for the vanadate excitation energy.

For practical applications the lesson from these concentrated systems seems to be to avoid high concentrations of luminescent centers. This is correct. A large advantage of high concentrations, however, is that a high absorption strength can be reached. This is a requirement for phosphors with high light output under photoexcitation. The high Eu³⁺

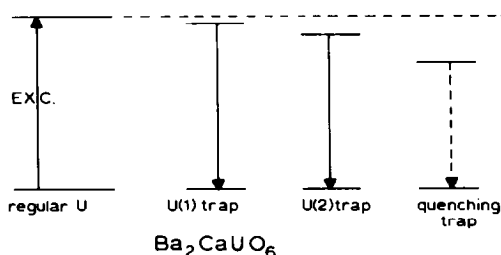


FIG. 9. Schematic figure for the situation in Ba₂CaUO₆. Excitation energy can be trapped at different U⁶⁺ ions or at killer sites.

light output of $\text{YVO}_4\text{-Eu}$ at room temperature is due to the high absorption strength of the vanadate groups. But often high concentrations are disadvantageous, because the excitation energy is then transferred to killer sites. A careful consideration of the offset of the parabolas of the centre involved can help us to predict whether energy migration will occur or not.

Acknowledgment

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