

al, but their values are smaller by an order of

magnitude than in, for example, TmAl_3 .

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As a check on our computer programs some of the calculations have been repeated starting from a crystal-field Hamiltonian with the quantization axis parallel to [111].

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Cooperative Energy Transfer from Yb^{3+} to Tb^{3+} in YF_3

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The transfer of energy from $\text{Yb}^{2F_{5/2}}$ to Tb^{5D_4} by the cooperative action of two Yb^{3+} ions has been observed in YF_3 . The correlation between the Tb^{5D_4} intensity and the $\text{Yb}^{2F_{5/2}}$ and Tb^{5D_4} lifetimes as a function of Tb concentration supports the conclusion that cooperative transfer has taken place. At an exciting (9300 Å) intensity of 1 W cm^{-2} the emitted Tb^{5D_4} (4900, 5460, 5850, and 6200 Å) power from a thin layer of powdered material was $0.8 \times 10^{-6} \text{ W cm}^{-2}$.

Emission of radiation from the Tb^{5D_4} manifold in YF_3 doped with Yb^{3+} and Tb^{3+} has been observed under 9300-Å excitation. Our experiments indicate this is due to two excited Yb ions cooperatively transferring their energy to one Tb ion exciting it from the ground state to the $5D_4$ manifold.

Figure 1 shows the emission spectrum of $\text{Y}_{0.3}\text{Tb}_{0.5}\text{F}_3$. The lines at 4900, 5460, 5850, and 6200 Å agree with emissions from Tb^{5D_4} to $7F_6$,

$7F_5$, $7F_4$, and $7F_3$, respectively. The intensities of these lines vary as the second power of the excitation intensity as shown in Fig. 2 for the 5460-Å line. This indicates that the absorption of two photons by the phosphor is required to raise one Tb ion to the $5D_4$ manifold.

As the effect is quite weak, in order to have sufficient excitation intensity and to be sure no shorter wavelengths are present which could excite Tb^{5D_4} directly, we placed the material

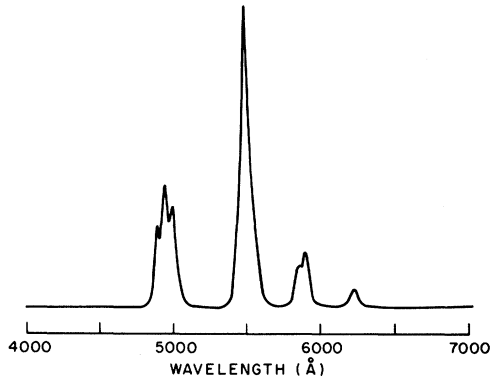


FIG. 1. Emission spectrum of Y_{0.3}Yb_{0.5}Tb_{0.2}F₃ under 9300-Å excitation.

on a GaAs:Si diode (Texas Instruments OSX 1610). This diode emits 21 mW in a band approximately 450 Å wide centered at 9300 Å and nothing at shorter wavelengths. Although 9300 Å is slightly lower than the maximum absorption of Yb in YF₃ it is well within the absorption band.

That the most likely explanation for the emission from Tb ⁵D₄ is the cooperative transfer from two Yb ions to one Tb ion can be seen from the energy-level diagram ¹ in Fig. 3. In order for the transfer to be stepwise (rather than simultaneous) the first transfer would have to be from Yb ²F_{5/2} to Tb ⁷F₀ which involves an excess energy of approximately 4200 cm⁻¹. This is a very large energy to have to give up to the lattice by multiphonon emission, and makes the transfer quite unlikely. The second transfer from Yb ²F_{5/2} exciting the Tb ion from ⁷F₀ to ⁵D₄ is even more unlikely as it requires the multiphonon absorption of 4200 cm⁻¹. Furthermore, the Tb ⁷F₀

level is undoubtedly extremely short lived due to the small energy gap (250 cm⁻¹) to the next lower level. These reasons combined with the fact that the Tb ⁵D₄ energy is exactly twice the Yb ²F_{5/2} energy make the cooperative transfer by far the most likely process.

Two arguments may be given against the possibility that the transfer might be accomplished by a small quantity of an impurity such as Tm³⁺, Er³⁺, or Ho³⁺. First, no lines characteristic of these elements are visible in the emission spectrum. Second, the intensity of the emission from Tb ⁵D₄ has been correlated with the Yb ²F_{5/2} and Tb ⁵D₄ lifetimes in the series Y_{0.5-x}Yb_{0.5}Tb_xF₃.

The lifetimes versus Tb concentration are shown in Fig. 4. The decrease of the Yb ²F_{5/2} lifetime with increasing Tb concentration is probably due to the quenching of Yb by transfer to excited manifolds of the ⁷F multiplet of two Tb ions. The decrease of the Tb lifetime is due to the self-quenching of Tb by the same process.

The rate equations for this cooperative transfer are

$$\frac{dn_2^{Yb}}{dt} = \sigma n_1^{Yb} F - \frac{n_2^{Yb}}{\tau_{Yb}} - \chi (n_2^{Yb})^2 n_1^{Tb} + \chi' n_2^{Tb} (n_1^{Yb})^2 = 0 \quad (1)$$

$$\text{and} \quad \frac{dn_2^{Tb}}{dt} = -\frac{n_2^{Tb}}{\tau_{Tb}} + \chi (n_2^{Yb})^2 n_1^{Tb} = 0, \quad (2)$$

where n_1^{Yb} , n_2^{Yb} , n_1^{Tb} , and n_2^{Tb} are the number densities of ions in the Yb ²F_{7/2}, Yb ²F_{5/2}, Tb ⁷F₆, and Tb ⁵D₄ manifolds, respectively, σ is the cross section for the Yb ²F_{7/2} → Yb ²F_{5/2} transition, F is the exciting photon flux, τ_{Yb} and τ_{Tb} are the total lifetimes of the Yb ²F_{5/2} and Tb ⁵D₄ manifolds, respectively, and χ and χ' are the probabilities for cooperative transfer and back transfer, respectively. The back-transfer term has been included in τ_{Tb} in Eq. (2), since it contributes to the observed total lifetime of Tb ⁵D₄. Since the effect is weak, we neglect the transfer terms in Eq. (1). Also, n_1^{Yb} and n_1^{Tb} will be very close to the Yb concentration n_{Yb} and the Tb concentration n_{Tb} , respectively. Solving for n_2^{Tb} we obtain

$$n_2^{Tb} = \chi (\sigma n_{Yb} F)^2 \tau_{Tb} \tau_{Yb}^2 n_{Tb}.$$

The intensity of emitted light is proportional to n_2^{Tb} . Therefore, at constant Yb concentration, the intensity should be proportional to $\tau_{Tb} \tau_{Yb}^2 n_{Tb}$ or $\tau_{Tb} \tau_{Yb}^2 \chi$.

In Fig. 5 we show the measured intensity together with the quantity $\tau_{Tb} \tau_{Yb}^2 \chi$ normalized to

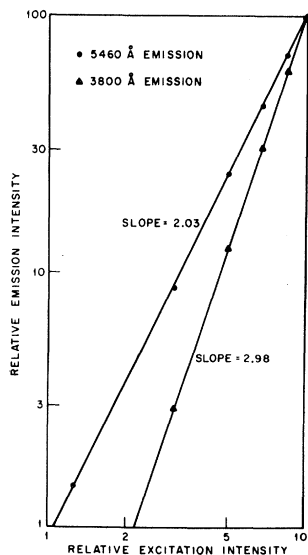


FIG. 2. Power dependence of emission from the Tb ⁵D₄ (5460 Å) and Tb ⁵D₃ (3800 Å) manifolds.

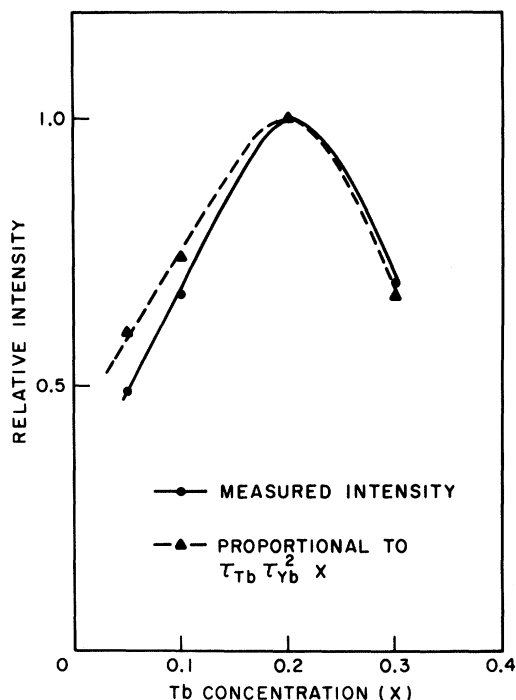


FIG. 5. Comparison of the measured intensity with the quantity $\tau_{\text{Tb}}\tau_{\text{Yb}}^2x$ as a function of Tb concentration in the series $\text{Y}_{0.5-x}\text{Yb}_{0.5}\text{Tb}_x\text{F}_3$.

at the photon energy ($10\,800\text{ cm}^{-1}$) above 5D_4 . The 5D_3 manifold is strongly quenched by Tb-Tb interactions² and the emissions from it do not appear at higher Tb concentrations (5% and greater).

A sample doped with Yb^{3+} , Tb^{3+} , and Eu^{3+} ($\text{Y}_{0.2}\text{Yb}_{0.5}\text{Tb}_{0.2}\text{Eu}_{0.1}\text{F}_3$) has also been studied and emission observed from $\text{Eu } ^5D_0$ in addition to $\text{Tb } ^5D_4$. The Eu is excited by transfer from $\text{Tb } ^5D_4$ to $\text{Eu } ^5D_0$.³ Since no emission is observed from $\text{Eu } ^5D_0$ in a sample without Tb present, the direct cooperative transfer from Yb to Eu is very much weaker due to the large energy mismatch of approximately 1000 cm^{-1} .

While this work was in progress we received a preprint by Miyakawa and Dexter⁴ in which they propose the Yb-Tb system as a good one in which to look for cooperative transfer. They estimate that the excitation intensity required to produce the same light output by cooperative transfer from Yb to Tb as by stepwise transfer from Yb to Er would be approximately 10^5 times higher at the same activator concentration.

To test this estimate we have measured the power per unit source area emitted from the $\text{Tb } ^5D_4$ manifold in $\text{Y}_{0.3}\text{Yb}_{0.5}\text{Tb}_{0.2}\text{F}_3$ and found it to be approximately $0.8 \times 10^{-6}\text{ W cm}^{-2}$ at an excitation intensity of 1 W cm^{-2} . For YF_3 doped

with Yb and Er, the best material ($\text{Y}_{0.79}\text{Yb}_{0.2}\text{Er}_{0.01}\text{F}_3$) produced so far has yielded approximately $0.7 \times 10^{-3}\text{ W cm}^{-2}$ at the same excitation intensity.⁵ To correct for the difference in activator concentration we should multiply the Er intensity by a factor of 20. From these numbers the ratio of excitation intensities required to produce the same light output at the same activator concentration is

$$\{ [(0.7 \times 10^{-3})(20)] / 0.8 \times 10^{-6} \}^{1/2} \approx 130.$$

The large difference between this number and Miyakawa and Dexter's estimate may be due to their neglect of the superexchange interaction.² Their calculation was based on multipolar interactions among the ions, having ruled out the direct-exchange interaction from the small values of the overlap integrals between 4f wave functions of rare-earth ions at interatomic distances. Their neglect of superexchange is not as convincing and since the transfer probability appears to be larger than their estimate we feel that superexchange may be important.

Another indication that superexchange may be important is that we have looked for and failed to find the effect in $\text{Y}_3\text{Al}_2(\text{AlO}_4)_3$ (YAG).⁶ A possible difference is that a cation in YAG is in superexchange contact with only four other cations while for YF_3 the contact number is 12.

The observation of cooperative transfer from Yb^{3+} to Tb^{3+} in CaF_2 and SrF_2 in the recent work of Livanova, Saitkulov, and Stolov⁷ came to our attention as this paper was being submitted. They observed that the $\text{Tb } ^5D_4$ lifetime was shorter and the fluorescence spectrum different under cooperative excitation ($0.98\text{ }\mu$) than under direct excitation ($0.49\text{ }\mu$). This indicates that centers with Tb^{3+} ions strongly interacting with one or two Yb^{3+} ions are responsible for the cooperative effect, supporting the conclusion that superexchange is involved. They do not give any indication of the efficiency of the transfer, but from the fact that the maximum concentration of Yb in these materials is limited (their material contained 7% Yb and 3% Tb), we believe YF_3 to be more efficient.

Although Ovsyankin and Feofilov⁸ proposed cooperative transfer from $\text{Yb } ^2F_{5/2}$ to $\text{Tm } ^1G_4$ in BaF_2 to explain the quadratic dependence of the $\text{Tm } ^1G_4$ intensity on the excitation intensity, Hewes and Sarver⁹ have demonstrated Auzel's¹⁰ conjecture that the transfer can be a successive three-step process with some saturation. It should be noted that cooperative transfer is the inverse of cooperative quenching as observed in the emission from $\text{Eu } ^5D_0$ ² and is similar to the inverse of cooperative photon absorption observed by Varsanyi and Dieke¹¹ and discussed by Dexter.¹² It is also

quite similar to triplet-triplet annihilation in anthracene.¹³

We wish to thank J. E. Geusic and J. P. van der Ziel for useful comments.

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