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DYNAMICS OF ENERGY TRANSFER FROM 3d TO 4f ELECTRONS IN $\text{LaAlO}_3:\text{Cr}^{3+}\text{Nd}^{3+}$

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In a recent publication,¹ transfer of energy was reported between the 3d levels of Cr^{3+} and the 4f levels of Nd^{3+} in LaAlO_3 . The energy transfer was observed by studying the excitation spectrum of powder samples of LaAlO_3 doped with varying amounts of the transition-metal (Cr_2O_3) and rare-earth (Nd_2O_3) oxides. From the experimental evidence it was shown that nonradiative energy transfer involving a resonance process takes place from the Cr^{3+} to the Nd^{3+} ion. Moreover, it was concluded that the energy transfer takes place from the 4T_2 state of the Cr^{3+} ion (Fig. 1) to some level of the Nd^{3+} ion, and that energy transfer from the 2E state of Cr^{3+} is not important.

In the past year we have also studied the energy-transfer mechanisms between 3d electrons of transition metals and 4f electrons of rare earths and, in particular, the dynamics of the energy-transfer mechanism from Cr^{3+} to Nd^{3+} was investigated in detail in single crystals of LaAlO_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAlG). In this Letter we would like to describe the energy-transfer rates for the $\text{LaAlO}_3:\text{Cr}^{3+}\text{Nd}^{3+}$ system, and present evidence that the energy transfer takes place entirely from the 2E metastable level of Cr^{3+} to the Nd^{3+} system, contrary to the conclusions of reference 1. Consequently, we suggest that the transfer rate is of the order of 10^{-3} second, as opposed to transfer rates of 10^{-8} second implied in reference 1.

The energy levels of Cr^{3+} and Nd^{3+} in LaAlO_3 are shown in Fig. 1. Both impurity ions enter substitutionally the Al and La sites, respectively, and the Cr^{3+} in the octahedral Al site has the familiar energy-level scheme of ruby.² The 2E state is about $13\,600\text{ cm}^{-1}$ above the ground 4A_2 state, and it is split in the near-cubic field by 5.6 cm^{-1} , giving the characteristic separation of the two R lines. The broad intense absorption bands corresponding to the ${}^4A_2 - {}^4T_2$ and ${}^4A_2 - {}^4T_1$ transitions peak at $18\,000\text{ cm}^{-1}$ and $24\,000\text{ cm}^{-1}$, respectively.

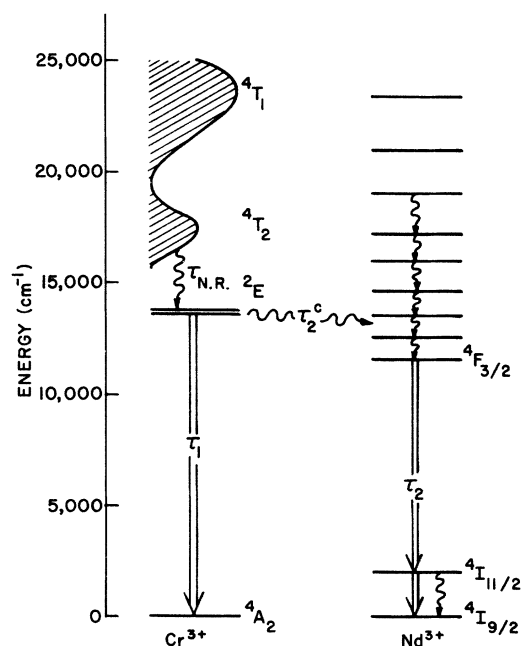


FIG. 1. Energy-level diagram of Cr^{3+} and Nd^{3+} in LaAlO_3 .

The gross energy-level scheme of Nd^{3+} was established by Dieke and Crosswhite.³ The strong fluorescence at $11\,000\text{ cm}^{-1}$ is due to the ${}^4F_{3/2} - {}^4I_{9/2}$ transition, and the emission in the $9\,500\text{-cm}^{-1}$ region arises from the ${}^4F_{3/2} - {}^4I_{11/2}$ transition.⁴ The fact that the Nd^{3+} emission is excited by the light absorbed in the 4T_2 and 4T_1 bands of Cr^{3+} is illustrated in Fig. 2 of reference 1. To understand the mechanism of energy transfer, we have undertaken to measure the lifetimes τ_1 , τ_2 , and τ_2^c , as indicated on Fig. 1, in single crystals of LaAlO_3 doped with Cr^{3+} alone, doped with Nd^{3+} alone, and various concentrations of $\text{Cr}^{3+};\text{Nd}^{3+}$ double doped. The lifetimes were measured by observing the fluorescence through a Bausch and Lomb monochromator with a resolution of 10 \AA using a cooled RCA No. 7102 photomultiplier

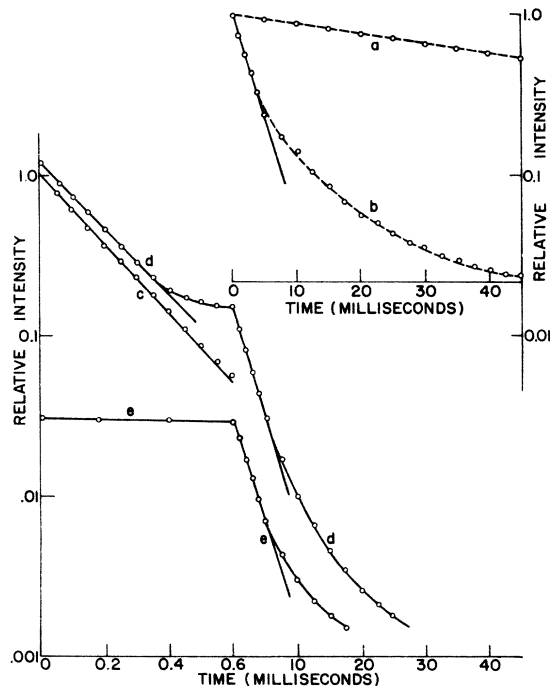


FIG. 2. Time dependence of fluorescent decay plotted on semilog scale ($T = 78^\circ\text{K}$). (a) ${}^2E \rightarrow {}^4A_2$ transition (τ_1) of 0.3% Cr^{3+} in LaAlO_3 . (b) ${}^2E \rightarrow {}^4A_2$ transition of 0.3% Cr^{3+} and 3% Nd^{3+} in LaAlO_3 . (c) ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition (τ_2) of 3% Nd^{3+} in LaAlO_3 . (d) ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition (τ_2) of 0.3% Cr^{3+} -3% Nd^{3+} in LaAlO_3 . (e) ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of 0.3% Cr^{3+} + 3% Nd^{3+} in LaAlO_3 , when the system is excited only in 4T_1 band of Cr^{3+} (τ_2^C).

with an S-1 photoemitter. The pulsed excitation was accomplished with a 500-watt Hg lamp, with a total pulse duration of 2 microseconds. The exciting light was focused on the crystals through a second monochromator having a resolution of 60 Å. With this arrangement we could isolate both in excitation and in emission the various components of both the Cr^{3+} and Nd^{3+} spectra. The time dependence of the observed lifetimes is illustrated in Fig. 2, and the vari-

ous lifetimes are summarized in Table I.⁷

The radiative lifetime, τ_1 , of Cr^{3+} is 76 msec at 78°K , and it is clearly an exponential decay. However, superimposed on this long decay, characteristic of the Cr^{3+} R lines ($\lambda = 7338 \text{ \AA}$), there is a faster rate observed if the R lines are not isolated completely. This fast rate has a lifetime $\tau_1^P = 2.5$ msec, and its intensity is strongly concentration dependent. It begins to appear at a fairly low Cr^{3+} concentration of $\sim 0.2\%$, and it originates from Cr^{3+} pairs.² The strongest component of the pair lines is at 7480 \AA .⁴ Ignoring the behavior of the pair lines for the moment, the $\tau_1 = 76$ -msec lifetime for the pure 0.2% Cr^{3+} shortens appreciably in the double-doped system [Figs. 2(a) and 2(b)]. On the semilog plot the straight line corresponding to an exponential decay of the pure Cr-doped sample 2(a) changes into a curve 2(b) for the doubly doped specimen representing the effect of multiple exponentials, the fastest of which has a lifetime $\tau_1^C = 3.5$ msec, and the slowest $\tau = \sim 40$ msec.

The lifetime τ_2 of the pure Nd^{3+} -doped LaAlO_3 for low-concentration Nd^{3+} ($>0.5\%$) is $\tau_2 = 460 \mu\text{sec}$. However, this lifetime begins to shorten already at 1% Nd^{3+} concentration, and at 3% Nd concentration $\tau_2 = 220 \mu\text{sec}$ [Fig. 2(c)]. In the double-doped crystal, the time dependence of the Nd^{3+} fluorescence consists of two parts [Fig. 2(d)], a fast part $\tau_2 = 220 \mu\text{sec}$, as in the pure Nd-doped specimen, and a slow part which is a composite of a number of exponentials, where the leading slow exponential is $\tau_2^C = 3.5$ msec.

We suggest that the shortening of τ_1 in going from the pure Cr-doped to the doubly doped specimen, and the appearance of the long component of τ_2 with the same lifetime, proves conclusively the energy transfer from the 2E level of Cr^{3+} to levels of Nd^{3+} . The long component of the Nd^{3+} emission τ_2^C is a direct mea-

Table I. Observed lifetimes of ${}^2E \rightarrow {}^4A_2$ transition of Cr^{3+} and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} in LaAlO_3 (milliseconds).

Dopant	78°K			300°K		
	τ_1	τ_2	τ_2^C	τ_1	τ_2	τ_2^C
3% Nd^{3+}		0.220			0.195	
0.5% Nd^{3+}		0.460			0.430	
0.3% Cr	76			44		
0.3% Cr + 3% Nd	3.5 → 40	0.22 → ~20	3.5 → ~20	2.0 → 30	0.19 → ~10	2.0 → ~10

sure of the resonance-energy-transfer rate, and since it is much longer than the radiative lifetime, τ_2 , of Nd, this cross-transfer rate controls the time dependence of the Nd fluorescence. The lack of a single exponential cross-transfer rate can be understood if the cross-transfer rate depends on the Cr-Nd separation, and the different rates correspond to different possible Cr-Nd locations. This interpretation was confirmed qualitatively by the fact that the shortest cross-pumping rate $\tau_2^C = 3.5$ msec predominates more and more as the product of the Cr and Nd concentration is increased.

The question remains, does all the energy transfer take place from the 2E state? We know that the nonradiative relaxation rate from the 4T_2 band to the 2E state in ruby is very fast,⁵ of the order of 10^{-8} sec. We do not exactly know what it is in $\text{LaAlO}_3:\text{Cr}^{3+}$, but it is faster than $\tau_{\text{NR}} < 10^{-6}$ sec (the time resolution of our equipment), since no rise time could be observed on the fluorescent time dependence of the R lines. If any efficient energy transfer were to take place from the 4T_2 band to Nd^{3+} , it would have to be faster than τ_{NR} . The efficiency of transfer from the 2E state is $\sim 95\%$ for the fastest τ_2^C , and absolute energy measurements indicate that this accounts for all the energy transfer. But the final evidence to indicate that there is no energy transfer from the 4T_2 band is shown in Fig. 2(e). When the Nd^{3+} is pumped in Cr^{3+} , 4T_1 band only, there is no fast component to the Nd^{3+} fluorescence, indicating that there is no faster cross-transfer rate than that observed from the 2E state.

The above study implies that the cross-transfer rates between transition-metal and rare-earth ions are of the order of 10^{-3} sec, and for these resonance transfers to occur, the

transition metal has to have a fairly long-lived metastable level ($\tau \sim 10^{-3}$ sec). This was qualitatively confirmed by the study of some other $3d-4f$ systems, where, e.g., in $\text{Mn}^{3+}-\text{Nd}^{3+}$ systems no energy transfer was observed. Cross-pumping scheme of $\text{Cr}^{3+}-\text{Nd}^{3+}$ system in YAlG has been utilized to build an improved, more efficient laser system.⁶

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