

Ambiguities in the Analysis of Non-Radiative Energy Transfer Data in Solid-State Laser Materials

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Abstract. We apply a recently developed model for non-radiative energy transfer in correlated systems to recently published data on energy transfer in garnets. We show that even in well-studied materials in which the analysis of the data appears straightforward, subtle deviations from theory and difficulty in quantitatively evaluating interaction parameters may be due to a non-random distribution of donors and acceptors in the crystal.

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One of the most exciting developments in solid-state laser research has been the increased efficiency of materials codoped with donors (to absorb pump energy) and acceptors (to lase at the desired wavelength). Indeed, Nd:Cr:GSGG ($\text{Gd}_3\text{Sc}_{1.8}\text{Ga}_{3.2}\text{O}_{12}$ codoped with Nd^{+3} and Cr^{+3}) has a significantly increased efficiency over the very popular Nd:YAG laser in both steady state [1] and pulse-mode [2]; the Cr^{+3} absorbs the pump light while the Nd^{+3} ion lases. Soviet [3], American [4], and Israeli [5, 6] researchers, among others, have been considering the possibilities which doping crystals opens up for new luminescent materials.

The mechanism by which a donor transfer its energy to an acceptor is, in general, non-radiative in nature through the exchange of a virtual photon. The theory for this type of transfer has been developed extensively beginning with papers by Foerster and Dexter [7]. The time dependencies for the excited states of the donor and acceptor have been calculated by Inokuti and Hirayama [8].

The original paper by Inokuti et al. on multipole and exchange interaction considered the case where the acceptors and donors were randomly distributed through the crystal and positionally uncorrelated with each other. Blumen et al. [9] and Rotman and Hartmann [10] have extended the multipole analysis

to the case where there is either an enhanced or an excluded volume surrounding the donor in which the probability of an acceptor being found is either enhanced or diminished, respectively. A dramatic example of correlation has been found in Eu:Mn:RbMgF₃ and Eu:Mn:NaCl by Shinn et al. [11] and Rubio et al. [12], respectively. It was estimated that 30–80% of the Eu^{+2} and Mn^{+2} ions form pairs in Eu:Mn:RbMgF₃ and 99% in Eu:Mn:NaCl.

In this paper, we consider the cases of two common laser materials, Nd:Cr:GSGG and Nd:Ce:YAG. We show in GSGG that a small discrepancy in the rate of energy transfer in GSGG from that predicted by the standard Inokuti theory can be explained by assuming an enhanced volume around the chromium ions. Similarly, we show that an exact calculation of the strength of the interaction between cerium and neodymium in Nd:Ce:YAG is made more difficult when the possibility of correlation is included.

1. Theory

One assumption in the generally successful Foerster-Dexter theory, as developed by Inokuti et al. [8] is that the distribution of donors and acceptors in a crystal is uniform and independent of each other's location. In

this specific case, the time-dependent excited donor concentration $N_D(t)$ is

$$N_D(t) = N_D(0) \exp[-t/\tau_D - \Gamma(1 - 3/s)c/c_0(t/\tau_D)^{3/s}], \quad (1)$$

where $N_D(0)$ is the initial concentration of excited donors at time $t=0$, c is the acceptor dopant concentration, Γ is the gamma function, and τ_D is the decay rate of the donors without the presence of acceptors. The critical distance R_0 is that distance at which the energy transfer rate between donor and acceptor and the natural donor decay rate are equal; the critical concentration c_0 is that concentration of acceptors for which the average donor-acceptor separation equals the critical distance R_0 . s determines the particular multipole interaction being modeled; for dipole-dipole interaction, $s=6$ and the decay rate contains an exponential $t^{1/2}$ factor.

In a recent paper [10], we have extended the model to include the case in which the donors and acceptors are correlated with each other, i.e., the location of a donor in a particular site is influenced by the presence of nearby acceptors.

The radial distribution for an ideal excluded-volume correlated placement is shown in Fig. 1a. The

solution for the excited-state donor concentration is (for the free parameter R_1)

$$N_D(t) = N_D(0) \exp\{-t/\tau_D - cV_1[1 + \Phi(Z_1)/\exp(Z_1)]\}, \quad (2)$$

where Z_1 is obtained by replacing R with R_1 in the expression

$$Z = (R_0/R)^6(t/\tau_D). \quad (3)$$

R_1 and V_1 are the radius and volume of the excluded volume, respectively. $\Phi(1, 1 - 3/s; Z_1)$ is the degenerate hypergeometric function [abbreviated in (2) as $\Phi(Z_1)$ for the case $s=6$]. For $s=6$, $\Phi(Z_1)$ is given as

$$\Phi(Z_1) = \sum_{i=0}^{\infty} \frac{(2Z_1)^i}{(2i-1)!!}. \quad (4)$$

Figure 1b shows a more practical distribution for actual solid-state crystals; $2R_D$ is the average distance between donors while R_1 and A are free parameters. B is given by

$$AR_1^3 + B(R_D^3 - R_1^2) = R_D^3. \quad (5)$$

R_1 is the radius of the inner volume V_1 ; A and B are the magnitude of the radial probability distributions in the inner and outer volume, respectively. The resulting

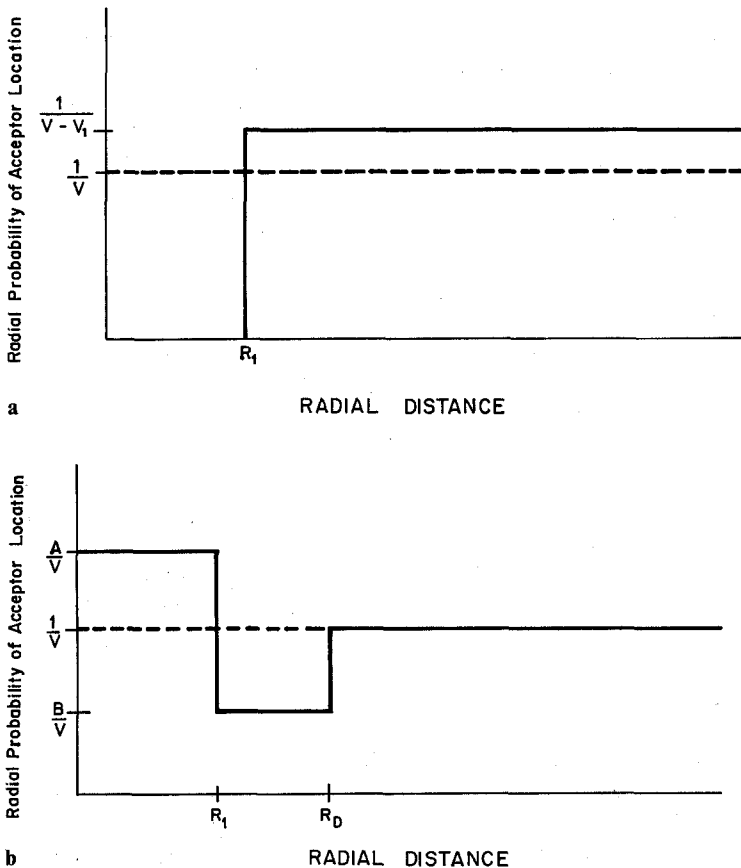


Fig. 1. **a** Excluded-volume, donor-acceptor radial-distance probability distribution. R_1 and V_1 are the radius and volume of the excluded volume, respectively. **b** More complicated distribution for the donor-acceptor radial-distance probability. R_1 is the radius of the inner volume. R_D is one-half the average distance between donors. A is the magnitude of the radial probability in the inner volume; B is determined by (5)

excited-state donor concentration is

$$N_D(t) = N_D(0) \exp[-t/\tau_0 - A\sqrt{\pi c/c_0}(t/\tau_D)^{1/2} - (B-A)\Phi(Z_1)/\exp(Z_1) - (1-B)\Phi(Z_D)/\exp(Z_D)], \quad (6)$$

where Z_1 and Z_D are defined by (3) for R replaced by R_1 and R_D , respectively. Note that this distribution assumes that the presence of a donor influences the distribution of acceptors only within half the average distance between donors. In a distance greater than that, any possible influences to cause non-uniform distributions are washed out by the effects of other donors. $A > 1$ corresponds to an enhanced volume in Fig. 1b, while $A < 1$ would correspond to an excluded volume.

The concentration of excited acceptors $N_A(t)$ is given both in the standard Inokuti analysis and in this model by

$$N_A(t) = \exp(-t/\tau_A) \int_0^t \exp(t'/\tau_A) \times \left(- \left[\frac{N_D(t')}{\tau_D} - \frac{dN_D(t')}{dt'} \right] \right) dt', \quad (7)$$

where τ_A and τ_D are the time constants for the acceptors and donors, respectively.

2. Correlation Effects in GSGG Codoped with Nd^{+3} and Cr^{+3}

Zharikov et al. [13] have analyzed the neodymium-chromium energy transfer rates in GSGG. They note a small discrepancy between the experimental observation and the theoretical calculations of the Nd emission (Fig. 2); the transfer rate observed in the initial rising region is faster than theory predicts. They suggested that a fit to the data can be made if one assumes that any chromium with a neodymium as a nearest neighbor or next-nearest neighbor will in-

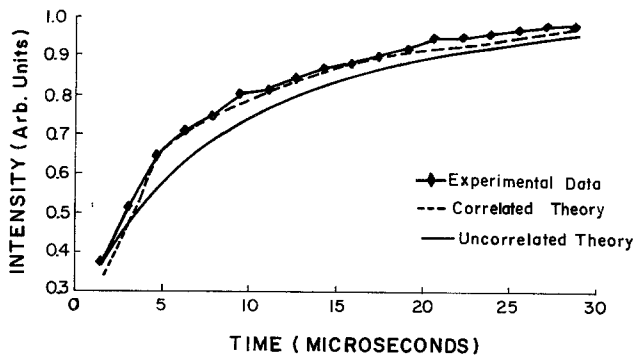


Fig. 2. Comparison of uncorrelated and correlated theory with experiment for the excited Nd^{+3} concentration in Nd:Cr:GSGG. Details of fit are given in Table 1

Table 1. Parameters for GSGG simulations based on the distributions in Fig. 1b

Parameters	Correlated values	Uncorrelated values
R_A/R_D	0.79	0.79
R_0/R_D	0.54	0.54
τ_A	270	270
τ_D	120	120
R_1/R_D	0.43	-
A	1.26	1

Table 2. Sizes of trivalent ions in garnets (Oct.: Octahedral site; Dod.: Dodecahedral site)

Ion	Size (A)	Site	Ref.
Y^{+3}	1.02	Dod.	[14]
Nd^{+3}	1.12	Dod.	[14]
Cr^{+3}	0.61	Oct.	[18]
Sc^{+3}	0.81	Oct.	[19]
Ga^{+3}	0.62	Oct.	[19]
Gd^{+3}	1.05	Dod.	[20]
Al^{+3}	0.53	Oct.	[20]
Ce^{+3}	1.14	Dod.	[14]

stantaneously transfer its energy [13]. One possible mechanism for this would be the exchange interaction with its enhanced short range effects, although this has been questioned by Mares et al. [14].

Since there is no evidence of a role for the exchange interaction in other garnets such as YAG, and to improve upon the assumption of an instantaneous exchange of energy between next-nearest neighbors, we suggest an alternative explanation. Assuming that the strength of the interaction is constant, but that the chromium ions are positionally correlated with respect to the neodymium ions, we can analyze the results. Figure 2 shows the fit to the excited acceptor ion concentration using the new model described in Sect. 1, Fig. 1b. The parameters used for this fit are shown in Table 1. The data for τ_A , τ_D , R_A/R_D , and R_0/R_D are taken from [13].

$2R_A$ is the average distance between acceptors; the other terms have already been defined.

It should be emphasized that there is a physically reasonable explanation as to why neodymium and chromium would be correlated in GSGG. The replacement of the native constituents of a garnet by neodymium or chromium ions may affect the neighboring ionic sites in the crystal. The data in Table 2 show that the neodymium ion is considerably larger than the other species it replaces in the dodecahedral sites in garnets (typically yttrium or gadolinium ions). On the other hand, no such blanket statement can be made for

Table 3. Analysis of Ce:Nd:YAG data. D: dipole, Q: quadrupole

Crystal	Interaction	R_D (nm)	R_A (nm)	R_0/R_D (nm)	R_1/R_D (nm)	A
1	D-Q	8.32	1.33	0.12	0.13	0.11
1	D-Q	8.32	1.33	0.23	0.14	0.10
2	D-D	4.42	1.25	0.12	0.20	0.05
2	D-Q	4.42	1.25	0.23	0.26	0.09

the chromium ion; chromium ions are larger than aluminum ions, roughly the same size as gallium ions, and considerably smaller than scandium ions. Since it is known that chromium ions enter the octahedral sites in these garnets, the strain in a GSGG crystal will be relieved by their locating next to neodymium ions,

It should be noted that similar neodymium-chromium correlation appears to occur in GGG ($Gd_3Ga_5O_{12}$). Here size constraints alone are not adequate to explain correlation; we are currently undertaking theoretical research into the causes of correlation to better understand this phenomena.

3. Correlation Effects in YAG Codoped with Ce^{+3} and Nd^{+3}

An alternative to chromium as a sensitizer for neodymium-doped garnet crystals is cerium. Extensive studies have been reported by Kvapil et al. [15, 16] of Ce:Nd:YAG crystals; the nature of the transfer has been found to be due to both radiative and non-radiative transfer [14, 17].

It was concluded in [14] that the nature of the non-radiative transfer is not immediately clear. It could be due to either dipole-dipole or dipole-quadrupole coupling. Close fits to either model for two samples of Ce:Nd:YAG have been shown in [Ref. 14, Figs. 7-10]. For dipole-dipole interaction, the critical distance R_0 was found to be approximately 1 nm while for quadrupole-dipole interaction it was approximately 1.2 nm for both Ce:Nd:YAG samples.

We have digitized the initial experimental data given in [Ref. 14, Fig. 2]. We have relaxed Mares' [14] assumption of uniform doping and done a best fit analysis to the data. We shall refer to the lightly doped crystal investigated by Mares as Crystal 1 ($[Ce^{+3}] = 0.003\%$; $[Nd^{+3}] = 0.73\%$) and the heavily doped crystal as Crystal 2 ($[Ce^{+3}] = 0.02\%$; $[Nd^{+3}] = 0.88\%$). The lifetimes for cerium and neodymium are 60 ns and 260 μs , respectively.

The results are given in Table 3. For Crystal 1, a good dipole-dipole fit was indeed found for $R_0 \cong 1$ nm ($R_0/R_D \cong 0.12$). However, with this critical distance (representing the strength of the interaction), a better

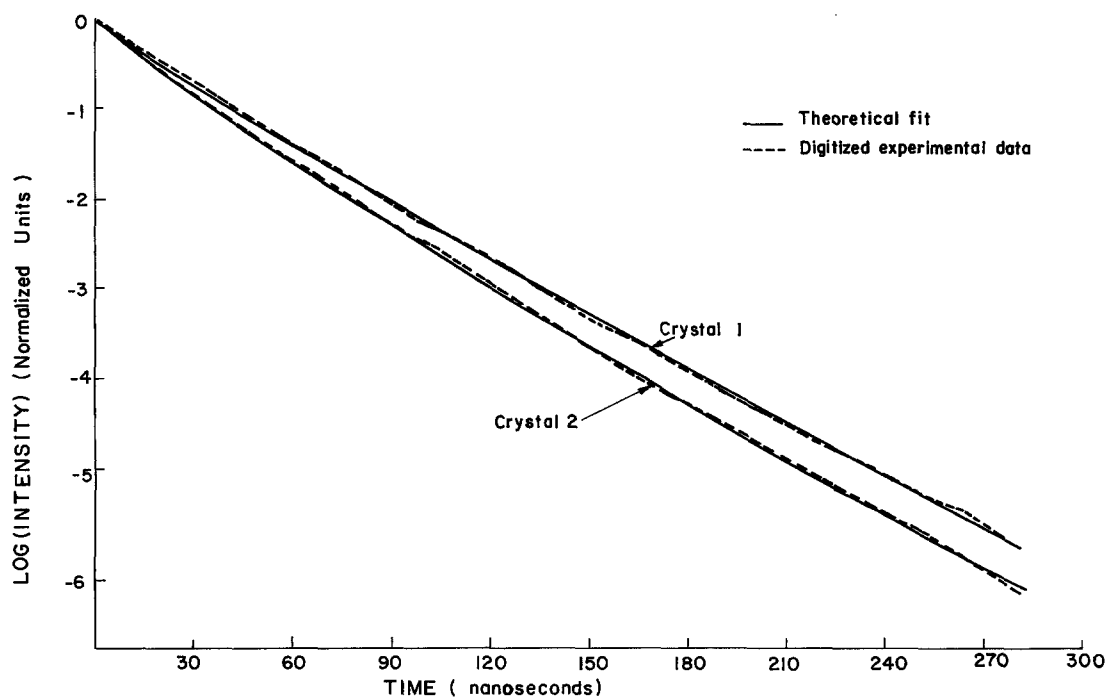


Fig. 3. Theoretical and experimental excited Ce^{+3} decay curves assuming a dipole-dipole interaction for Ce-Nd energy transfer in Crystals 1 and 2. Parameters are given in Table 3. \log_e of fluorescence intensity is shown

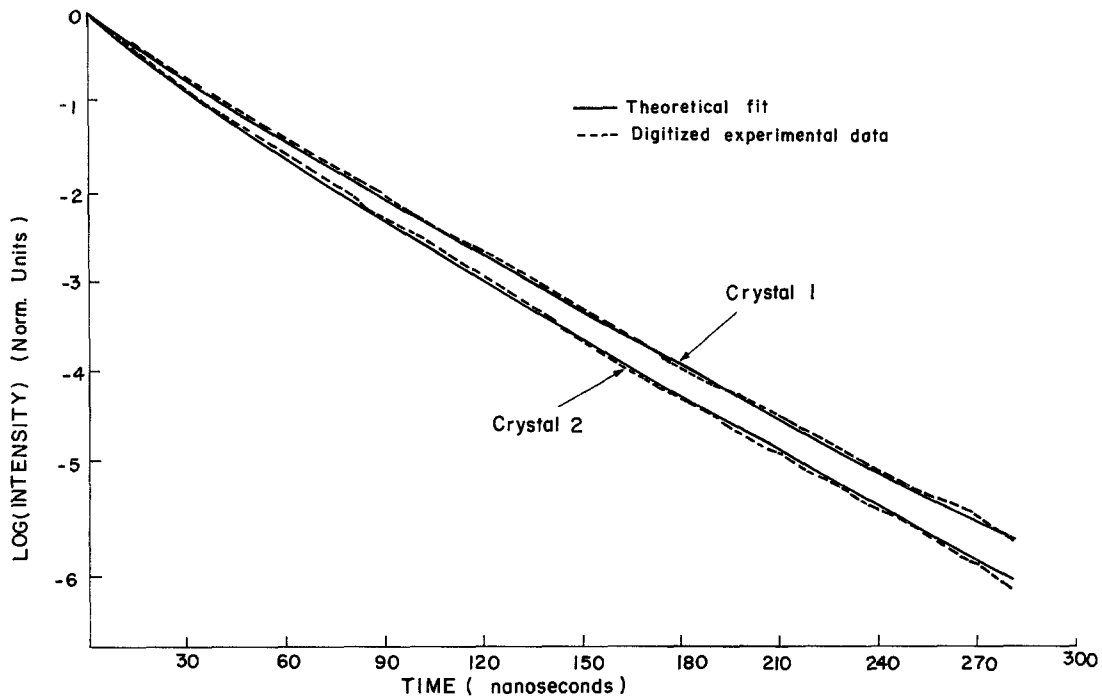


Fig. 4. Theoretical and experimental excited Ce^{+3} decay curves assuming a dipole-quadrupole interaction for Ce-Nd energy transfer in Crystals 1 and 2. Parameters are given in Table 3. Log_e of fluorescence intensity is shown

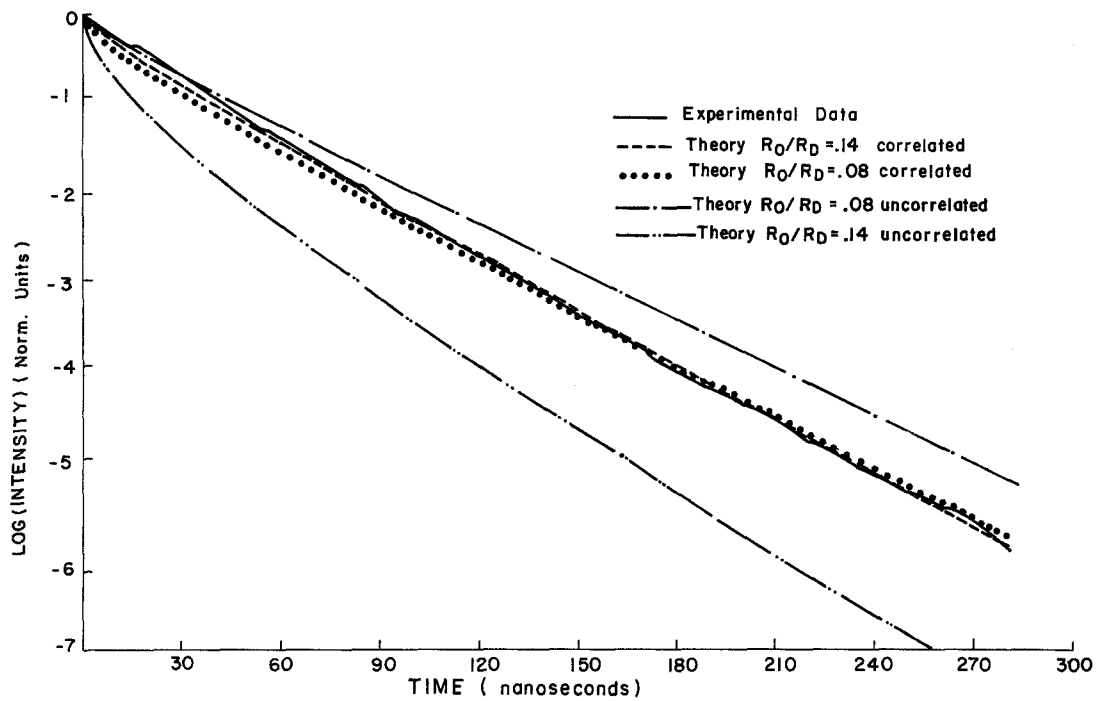


Fig. 5. Fits of the excited Ce^{+3} decay curves for different possible values of R_0/R_D . Parameters are given in Table 4. Log_e of fluorescence intensity is shown

Table 4. Alternative fits to Ce:Nd:YAG data

Crystal	Interaction	R_D (nm)	R_A (nm)	R_0/R_A (nm)	R_1/R_D (nm)	A
1	D-D	8.32	1.33	0.14	0.24	0.21
1	D-D	8.32	1.33	0.08	0.29	2.28

fit could be obtained if one postulated an excluded volume of approximately 1.1 nm ($R_1/R_D \cong 0.13$) with a value of A (from Fig. 1b) of 0.02. A fit of this data to the model is shown in Fig. 3. Similar results for the other cases were obtained (Figs. 3 and 4). Since this data was digitized based on published data, the accuracy of the digitized process must be taken into consideration; we hesitate to come to any conclusions vis-à-vis the question of whether the nature of the interaction is dipole-dipole or dipole-quadrupole.

Of equal interest is the fact that excellent fits can be made to the Crystal 1 data with dipole-dipole interaction with $R_0 \cong 1.2$ nm ($R_0/R_D \cong 0.14$) if an excluded volume of greater distance is postulated. Similarly $R_0 \cong 0.65$ nm ($R_0/R_D \cong 0.08$) fits the data if an enhanced volume is assumed to occur (Fig. 5 and Table 4). While these changes in critical distance are small, it should be remembered that the strength for the interaction is proportional to $(R_0)^s$ where $s=6$ for dipole-dipole coupling and $s=8$ for dipole-quadrupole coupling. Thus, R_0 is a very sensitive parameter for measuring the interaction strength. It appears that from donor decay measurements alone, one cannot determine the exact quantitative value of R_0 .

It is actually quite reasonable that an excluded volume would form for Nd:Cr:YAG. Both Nd^{+3} and Ce^{+3} are approximately 10% larger than the Y^{+3} ion they replace and hence should logically repel each other. Thus, unlike in Nd:Cr:GSGG, Nd:Ce:YAG may tend to be an example of codoped crystal with an excluded volume.

4. Conclusions

Data from Nd:Cr:GSGG and Nd:Ce:YAG has been reexamined using a new model for non-radiative transfer in cases of coordinated placement of donors and acceptors. A deviation in the Nd:Cr:GSGG data first noted by Zharikov et al. [13] can be explained by

assuming an enhanced volume for acceptor location around the donor. A careful examination of the Ce:Nd:YAG data shows a possible excluded volume around the donors. The actual qualitative measurement of R_0 can be complicated by the presence of these correlative effects.

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