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The Critical Concentration for Quenching of the Eu^{3+} Luminescence in Some Gd^{3+} : Eu^{3+} Systems

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The critical concentration for quenching of the Eu^{3+} luminescence is calculated theoretically for several Gd^{3+} : Eu^{3+} systems. A comparison is made with the experimental values. The results are discussed in terms of energy migration.

In the course of our investigations on energy migration in anisotropic systems, we reported recently on the energy migration properties of some two-dimensional compounds: $NaEuTiO_4$ (*1*), $Eu_2O_2SO_4$ (*2*), and EuOCl (*3*). It was shown that for these compounds concentration quenching occurs down to 1.2 K. The decay characteristics of the Eu^{3+} emission point to two-dimensional energy migration among the Eu^{3+} ions to quenching centers for the case of $NaEuTiO_4$ and $Eu_2O_2SO_4$. This two-dimensional energy migration behavior can be explained by the fact that the Eu^{3+} ions form double layers perpendicular to the *c* axis in these compounds. Although a similar type of double layer occurs in EuOCl, the decay characteristics of this compound cannot be explained by purely two-dimensional energy migration, but point to a more isotropic migration. It was shown, that the interaction between the Eu^{3+} ions in these compounds is, at least partly, exchange in character (*4*).

In order to study concentration quenching effects we prepared samples which were diluted wih gadolinium: $NaGd_{1-x}Eu_xTiO_4$, $(Gd_{1-x}Eu_x)_2O_2SO_4$, and $Gd_{1-x}Eu_xOCl$ $(0 < x \leq 1)$. For the former two compounds concentration quenching occurs above $x \simeq 0.25$. However, for the latter concentration quenching becomes obvious above $x \simeq 0.1$. The dependence of the energy migration probability on the concentration of the luminescent ions is closely related to the problem of percolation (*5, 6*). The so-called critical concentration (x_c) for lattice percolation depends strongly on the lattice structure. If the concentration quenching is due to energy migration to killer centers, this x_c should equal the concentration for which concentration quenching occurs (*7*).

Although x_c has been calculated for several types of lattice structures, it is not known for the three systems under consideration. However, it has been shown that an estimate of x_c can easily be obtained as follows (*8*). For $x = x_c$ each Gd^{3+} ion has roughly two Gd^{3+} neighbors to which it is connected by transfer, otherwise migration through the Gd^{3+} sublattice becomes impossible. Let the total number of crystallo-

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TABLE I

EXPERIMENTAL AND THEORETICAL VALUES OF THE CRITICAL CONCENTRATION FOR SEVERAL $Gd^{3+} : Eu^{3+}$ SYSTEMS

	x_{exp}	N_n	x_c	$N_n + N_a$	x_c'
$NaGd_{1-x}Eu_xTiO_4$	0.25	8	0.25	12	0.16
$(Gd_{1-x}Eu_x)_2O_2SO_4$	0.25	8	0.25	8	0.25
$Gd_{1-x}Eu_xOCl$	0.1	8	0.25	16	0.12
$Gd_{1-x}Eu_xAl_3B_4O_{12}$	0.3	6	0.33	6	0.33
$Gd_{1-x}Eu_xMgB_5O_{10}$	0.85	2	1	2	1

graphic sites available for these two Gd^{3+} ions be N, then we have the approximate relation

$$x_c = \frac{2}{N}, \tag{1}$$

where N is the number of neighboring positions on the sublattice through which the excitation energy migrates. Although this expression is not accurate, it is useful for our consideration, since the experimental error in the concentration for which concentration quenching starts is considerable (10 to 20%).

With the use of Eq. (1) it is possible to calculate x_c for the three systems. Table I shows the values of N_n, the number of nearest neighbor sites according to crystallographic data, and the corresponding values of x_c. The agreement between x_c and the experimentally determined value x_{exp} is surprisingly good, except for the oxychloride. It is interesting to note that x_{exp} is strikingly different for the systems $(Gd_{1-x}Eu_x)_2O_2SO_4$ and $Gd_{1-x}Eu_xOCl$, although the EuO layers are crystallographically equivalent.

In view of the fact that the energy transfer between Eu^{3+} ions can occur by superexchange (*4*), a number of additional nearest neighbor sites N_a, defined as sites which are not nearest neighbors, but which are connected to the central site by one anion, should be taken into account. $N_n + N_a$ yield now the number of sites involved in the Eu^{3+}–Eu^{3+} transfer. The corresponding values of x_c' are tabulated in Table I. There is good agreement with the value of x_{exp}. In case of the oxychlorides the value of N_a is due to contacts via the Cl^- ions. From the crystal structure it is also clear that the Cl^- ions connect the (Gd, Eu)O layers (*9*), so that this makes clear why the migration is three-dimensional.

The value of $(N_n + N_a)$ for $NaGd_{1-x}Eu_xTiO_4$ seems to be rather high, but it should be realized that this value holds for the undistorted Sr_2TiO_4 structure. It is known that the ordered variant $NaEuTiO_4$ is strongly distorted, which may lower $N_n + N_a$ (*1*).

The present arguments should be dimensionality independent. That this is the case, is shown by $Gd_{1-x}Eu_xAl_3B_4O_{12}$ (*7*) and $Gd_{1-x}Eu_xMgB_5O_{10}$ (*10*). These systems have a three- and a one-dimensional Eu^{3+} subsystem, respectively. The one-dimensional system clearly shows the limitations of Eq. (1).

It is interesting to note that in $Gd_{1-x}Tb_xOCl$ the value for which concentration quenching occurs is about 0.2 (*11*). This implies a lower value for N_a. We have to conclude that superexchange via the Cl^- ions is of much more importance for Eu^{3+} than for Tb^{3+} (see also Ref. (*9*)).

Van Uitert (*12*) has given a complete different approach to calculate the value of x_c. His starting point was that trimers of Eu^{3+} ions do not show luminescence due to cross relaxation. According to his statistics,

$$x_c = \frac{1}{1 + Z}, \tag{2}$$

where Z is a certain number of nearest neighbors. Actually, this formula worked very well, although we know now that the physical model involved is completely incorrect. If one compares, however, Eqs. (1)

and (2) it is clear that for high values of Z and N they yield values of x_c which are experimentally not easy discernable. Also the way in which Van Uitert counted the number of contacts yields values of Z which are lower than ours (90° interactions were counted half). This explains why the incorrect approach of Van Uitert yielded acceptable results.

In conclusion we have found that the crystal structure determines the value of the critical concentration for quenching of the luminescence and that it is possible to make quantitative evaluations. A more elaborate study on Gd^{3+} compounds yields similar results (*8*).

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