

Energy Transfer between Inequivalent Eu^{2+} Ions

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The luminescence of $\text{Rb}_2\text{ZnBr}_4\text{-Eu}^{2+}$ is reported and discussed. Efficient energy transfer occurs between inequivalent Eu^{2+} ions ($R_c \approx 35 \text{ \AA}$). This phenomenon is compared with similar situations in other host lattices. © 1986 Academic Press, Inc.

Introduction

The luminescence of the Eu^{2+} ($4f^7$) ion is well known and has been widely discussed (1, 2). In many host lattices the emission is interconfigurational, i.e., $4f^65d \rightarrow 4f^7$. As a consequence the observed emission spectrum consists of a broad band with a peak position which depends strongly on the nature of the Eu^{2+} surroundings. Host lattices with Eu^{2+} ions on different crystallographic sites (here called inequivalent Eu^{2+} ions) show more than one emission band. Energy transfer between inequivalent Eu^{2+} ions has been reported for $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ (3), $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (4), and $\text{SrB}_6\text{O}_{10}$ (5). The aluminate is an efficient lamp phosphor. Here we add to this series Rb_2ZnBr_4 with two inequivalent Rb^+ sites. Further we present a more quantitative evaluation than in the earlier papers. Critical transfer distances of up to 35 \AA will be reported.

Experimental

Crystals of $\text{Rb}_2\text{ZnBr}_4\text{-Eu}^{2+}$ were grown using the Bridgman technique. For this pur-

pose RbBr , Zn metal, and Eu_2O_3 were dissolved in a concentrated HBr solution. The final solution was evaporated and the residue dried at 150°C . This residue was brought into an ampulla which was evacuated. The optical measurements were performed on a Perkin-Elmer MPF-3L spectrofluorometer equipped with an Oxford helium cryostat. Details have been given elsewhere (6). To reduce the influence of radiant energy transfer as much as possible, the measurements were performed on powdered crystals.

Results

The samples $\text{Rb}_2\text{ZnBr}_4\text{-Eu}^{2+}$ show a blue emission under ultraviolet excitation. For 0.1 at.% Eu^{2+} per formula unit, the emission spectrum contains two emission bands with maxima at 415 nm and 435 nm (see Fig. 1). Their intensity ratio is about 1 and does not depend on excitation wavelength nor on temperature. Obviously it is hard to excite one of these bands selectively. The luminescence output is independent of temperature up till 300 K.

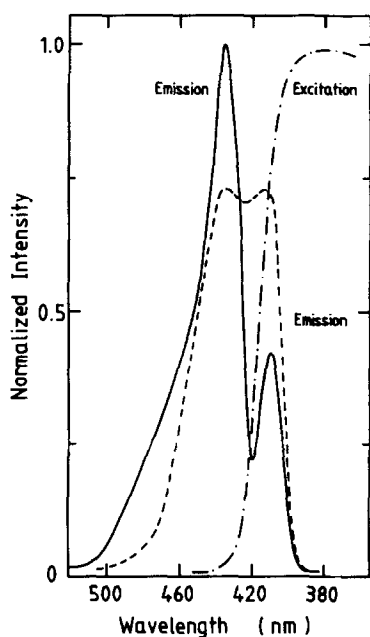


FIG. 1. Luminescence spectra of $\text{Rb}_2\text{ZnBr}_4\text{-Eu}^{2+}$ at 4.2 K. Full line: Emission spectrum of sample with 1 at.% Eu per formula unit (excitation 280 nm). Broken line: Emission spectrum of sample with 0.1 at.% Eu per formula unit (excitation 280 nm). Broken line with dots: excitation spectrum of the 440 nm emission of the 1 at.% Eu sample.

For a sample with 1 at.% Eu^{2+} per formula unit, the results are different. The 415-nm band decreases considerably in intensity relative to the 435-nm band (see Fig. 1). In addition we observed a longer wavelength shoulder. Note that the excitation spectrum of the 435-nm band overlaps the 415-nm emission band.

Unfortunately the excitation spectra of the emissions are broad and structureless, which restricts their use in a discussion of energy transfer considerably. The onset of these spectra was usually determined by the spectral filters applied.

These results, observed at 4.2 K, do not depend critically on excitation wavelength. However, the emission spectrum changes, if the temperature is increased. Above 75 K the shoulder disappears and the intensity of

the 435 nm decreases. Due to additional broadening we are left at 300 K with one broad emission band with considerably lower intensity and a maximum at about 430 nm.

Discussion

$\text{Rb}_2\text{ZnBr}_4\text{-Eu}^{2+}$

The bromide Rb_2ZnBr_4 has $\beta\text{-K}_2\text{SO}_4$ structure. For rubidium there are two crystallographic sites in equal amount, one with nine, the other with ten coordination. The two emission bands observed are assigned to Eu^{2+} on the two different sites. In view of their equal intensity in the dilute Eu^{2+} sample, there seems to be no outspoken preference for one of the two sites. It is hard to decide with certainty which emission band belongs to which site, especially because the exact excitation spectra are not known. None of the two emissions shows pronounced thermal quenching below room temperature.

In the higher concentration sample the 415-nm emission band is drastically reduced. This is ascribed to energy transfer from the 415-nm emitting center to the 435-nm emitting center, in analogy with the interpretation of earlier observations of a similar kind (3-5). Note in Fig. 1 the favorable spectral overlap of the 415-nm emission band and the 435-nm center excitation band. We return to this transfer below.

The shoulder in the emission spectrum is ascribed to another Eu^{2+} center. The nature of such a center is hard to unravel, but an associate of a Eu^{2+} ion with the defect that compensates its effective charge is an obvious possibility. The thermal quenching temperature of the emission of this additional Eu^{2+} center is lower than that of the Eu^{2+} ions on the Rb^+ sites in a regular surroundings.

The thermal quenching of the 435-nm emission at higher temperatures is ascribed to thermally stimulated energy transfer

among the 435-nm emitting centers, which will transport the excitation energy to killer centers (7). Note that the 415-nm emission in the 1% Eu^{2+} sample is not strongly thermally quenched. We explain these two phenomena as follows. At low temperatures the spectral overlap between the 415-nm emission band and the 435-nm excitation band is large. Thermal broadening or a shift of the bands will not influence the spectral overlap strongly, so that the probability for transfer from the 415-nm center to the 435-nm center is approximately temperature independent (8).

The spectral overlap related to transfer from a 435-nm center to another 435-nm center will vanish at liquid helium temperature, since no zero-phonon lines have been observed (9). However, at higher temperatures the bands will broaden and the spectral overlap will increase. Let us now turn to a more quantitative analysis.

Energy Transfer

Energy transfer has been treated quantitatively by Förster (10) and later by Dexter (8). Since we are dealing with allowed electric-dipole transitions in the case of Eu^{2+} , the value of the critical transfer distance (R_c) can be found from

$$R_c^6 = 0.63 \times 10^{28} \frac{4.8 \times 10^{-16} \cdot P}{E^4} \text{ S.O.}$$

Here P is the oscillator strength of the Eu^{2+} ion, E the energy of maximum spectral overlap, and S.O. the spectral overlap integral (7). For P we took the value 10^{-2} (7). The values of E and S.O. can be derived from the spectral data. For Rb_2ZnBr_4 the present data were used, for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ we estimated E and S.O. from the literature data (Refs. (4) and (2), respectively). Especially the S.O. values are rather inaccurate. Table I shows the results of our calculation of R_c for the energy transfer between inequivalent Eu^{2+}

TABLE I
PARAMETERS USED IN THE ENERGY TRANSFER
CALCULATIONS

Eu^{2+} in	S.O. (eV^{-1})	E (eV)	P	R_c (Å)
Rb_2ZnBr_4	5	3.0	10^{-2}	35
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$	4	3.0	10^{-2}	34
$\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$	0.1	2.8	10^{-2}	19

Note. S.O., spectral overlap; E , energy of maximal S.O.; P , oscillator strength of Eu^{2+} ; R_c , critical transfer distance.

ions in Rb_2ZnBr_4 , $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, and $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$. As a matter of fact these data relate to transfer from the higher energy emitting center to the lower energy emitting center.

The values of R_c obtained are very high. Especially in the case of Rb_2ZnBr_4 and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ the value of R_c points to very efficient transfer. In passing we note that the suitability of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ - Eu^{2+} as a lamp phosphor rests on the quenching of the higher energy emission by the center with the lower energy emission. The high value of R_c is due to the perfect spectral overlap in these two host lattices. In the apatite $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ the spectral overlap involved is considerably smaller. This is due to the large difference between the emission wavelengths of the two Eu^{2+} centers in this lattice (490 and 585 nm). The 490-nm emission band overlaps the 585-nm excitation band only partly, so that the spectral overlap is small and R_c less than in the other lattices of Table I.

As argued above, the values in Table I are not expected to be strongly temperature dependent. The data for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ were only reported at 300 K, so that the R_c value is also for 300 K. The data for Rb_2ZnBr_4 relate to 4.2 K.

Similar calculations were made for the 435-nm emitting center in Rb_2ZnBr_4 with itself. The spectral overlap is about 0.05. This yields $R_c = 16$ Å. This value is valid

TABLE II
ENERGY TRANSFER PARAMETERS FOR Eu^{2+}

	R_c (Å)	0.1% Eu^{2+}		1% Eu^{2+}	
		R_{av} (Å)	I	R_{av} (Å)	I
Rb_2ZnBr_4	35	80	0.5	38	0.85
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$	34	64	0.5	30	0.93
$\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$	19	46	0.2	22	0.8

Note. R_c , critical transfer distance; R_{av} , averaged Eu–Eu distance; I , amount of emission intensity from the lower-energy Eu^{2+} emission. Complete transfer implies $I = 1$, no transfer $I = \approx 0.5$. See also text.

for 100 K. It makes the energy migration suggested above quite possible.

It is hard to derive an experimental value for R_c from the experimental data. Not only are the data incomplete for this purpose, but also there may be a site preference and the number of sites is not necessarily equal (as in $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$). Therefore we calculated as a rough approximation an average distance between the Eu^{2+} ions using the crystallographic data of the lattices involved and the value of the Eu^{2+} concentration. This was done by calculating for every sample the amount of space available per Eu^{2+} ion. From this we derived the diameter of the sphere with the same volume. Although inaccurate, this diameter measures an average Eu^{2+} – Eu^{2+} distance (R_{av}) in the sample. If $R_{av} \gg R_c$, energy transfer will not be of any practical importance. If $R_{av} \leq R_c$, a considerable amount of energy transfer from the higher energy emitting center to the lower energy emitting center is to be expected.

Table II shows the results for samples with 0.1 and 1.0 at.% Eu^{2+} . Also given is a quantity I which gives the relative amount of emission intensity from the lower energy center. Complete transfer means $I = 1$, no transfer implies $I \leq 0.5$ (depending on how selective the excitation wavelength applied is). We note in this way a satisfying agreement between the experimental results and

the calculations. Here it should be realized that, due to the inaccuracy in the spectral overlap, the error in the calculated R_c values is at least 10%. Note that the lower R_c value for $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ is compensated by a higher density of sites that are available for occupation by Eu^{2+} . A 1% Eu^{2+} concentration in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ corresponds with 0.4% Eu^{2+} in $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$, i.e., these two samples show comparable R_{av} values (30 and 28 Å, respectively). The 0.4% apatite sample shows, however, $I = 0.5$. This indicates incomplete energy transfer, so that a comparison of the spectra of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ – Eu^{2+} and $\text{Sr}_5(\text{PO}_4)_2(\text{SiO}_4)$ – Eu^{2+} with equal Eu^{2+} density (i.e., equal R_{av}) shows immediately the difference between the R_c values.

It is interesting to compare the present R_c values with those obtained by Powell *et al.* (11) for RbMgF_3 – Eu^{2+} . Their R_c values amount only to some 8 Å. In RbMgF_3 , however, the Eu^{2+} emission is intraconfigurational, i.e., the spectra consist of narrow lines and the transitions are highly forbidden. As a consequence the value of the oscillator strength decreases several orders of magnitude relative to our value of 10^{-2} . This is the main factor responsible for the lower R_c values in RbMgF_3 .

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