

Evidence for Exchange of Excitation Energy Between Impurities in KZnF_3

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A peculiar temperature behaviour of the emission from KZnF_3 containing Cu^{2+} and Mn^{2+} impurities is described, as well as the temperature dependence of the decay time of the emission from the $\text{Cu}^{2+} - \text{Mn}^{2+}$ pairs. A model that allows energy transfer between different kinds of impurities is suggested, and formulae are given which explain qualitatively the observed phenomena.

The application of a scanning dye laser in excitation spectroscopy has resulted in an improvement of the signal to noise ratio which permits a selective detection of the emitted light. The usual problems in emission spectroscopy of stating which species are emitting should therefore be overcome to a great extent, as long as excitation in one ion results in only little or no emission from other impurities.

This technique has been applied to KZnF_3 doped with Cu^{2+} and Mn^{2+} , and which contained a trace of Ni^{2+} .

The region of excitation was around the ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4T_{2g}$ absorption of the Mn^{2+} ion, where the $\text{Cu}^{2+} - \text{Mn}^{2+}$ pair is also absorbing.^{1–6} The emission from these systems is very weak, and the emission from one species due to excitation in the other is very low, if not absent. This paper reports on the intensity of a still unidentified species and on the decay time of the $\text{Cu}^{2+} - \text{Mn}^{2+}$ pairs. Both show peculiar temperature dependence, which have not yet been explained. The different species in KZnF_3 are generally believed to be independent of each other, and the experiments apparently confirmed this. It has, however, not been possible to find any satisfactory explanation of the observed temperature dependence considering only intra-

molecular transitions, and it is the primary purpose of this paper to prove that the observed phenomena are consistent with a very simple model that involves transfer of excitation energy between different species. Contrary to transitions between different electronic states of isolated species, where a Boltzmann distribution is considered to be established in an extremely short time, the intermolecular processes of the model have a finite time constant.

Transfer between only two species cannot explain the phenomena. However, because the case of three impurities requires many parameters for its description, the results are bound to be qualitative. It is, furthermore, outside the scope of this work to consider what mechanism could cause the energy transfer.

The formalism of the model is similar to that of Refs. 7 and 8, except that these works deal with transfer of excitation energy in molecular crystals between impurity perturbed molecules and the exciton band.

EXPERIMENTAL

The samples were those used in Ref. 5 and they were cooled by the same equipment. Excitation was made by a Molelectron DL 200 scanning dye laser driven by a Molelectron UV 1000 nitrogen laser. The emitted light was dispersed by a Spex double monochromator and time resolution was obtained by a PAR boxcar integrator.

EXPERIMENTAL RESULTS

The most prominent spectral features are shown in Fig. 1. Here the first spectrum shows the excitation spectrum, and the next three spectra

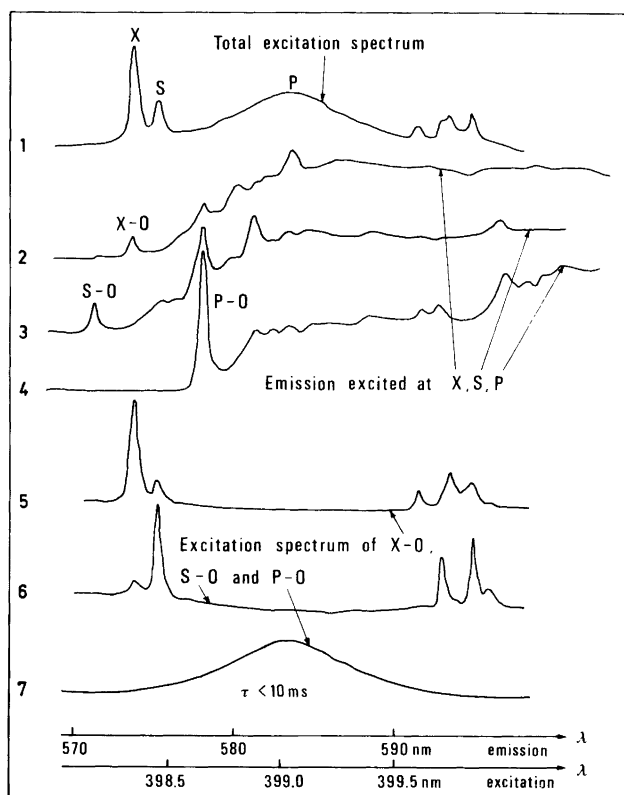


Fig. 1. Spectra from $\text{KZnF}_3 + \text{Cu}^{2+} + \text{Mn}^{2+}$. Top shows an ordinary excitation spectrum excited from 398.0 to 400 nm. Next is shown the emission spectra for excitation at wavelengths at X, at S and at P. (Upper wavelength scale.) The three last spectra are the excitation spectra obtained for detecting at X-O, S-O and P-O. For the last spectrum, light with decay time longer than 10 ms had to be excluded. Temperature below 10 K.

show the emission when exciting at the wavelength labelled P, S and X. The two next spectra are the selectively detected excitation spectra of the X and P species and the last that of the P system. The decay time was $65 \text{ mS} \pm 10\%$ for both the X and the S system at 5.5 K, while that of the P-system was $2 \text{ mS} \pm 10\%$ at that temperature. This difference was used to separate the last spectrum. Further, the X and P systems showed remains of a decay time of $3.5 \text{ mS} \pm 0.5 \text{ mS}$. The emission was very weak, and as no hypothesis of the mechanisms was available at the time of measurement, no emphasis was put on obtaining all components of the decays for the X and S systems. For the P system, however, the decay time is shown as function of temperature in Fig. 2. This decay could not be described by a simple expression like

$$1/\tau = a + b \exp(-\epsilon/kT)$$

but a good fit was obtained with one more exponential:

$$1 \text{ ms}/\tau = 0.45 + 0.48 \exp(-62 \text{ cm}^{-1}/kT) + 616 \exp(-570 \text{ cm}^{-1}/kT)$$

The temperature dependence of the intensity of the S and P systems was very small in the temperature range investigated. This was, however, not the case for the X system, for which the intensity measured as the amplitude of the plateau, is plotted *versus* the temperature in Fig. 3. This curve shows a hump around 10 K and a very steep rise in intensity towards lower temperatures. The P system was identified as the copper-manganese magnetically coupled pair.⁶

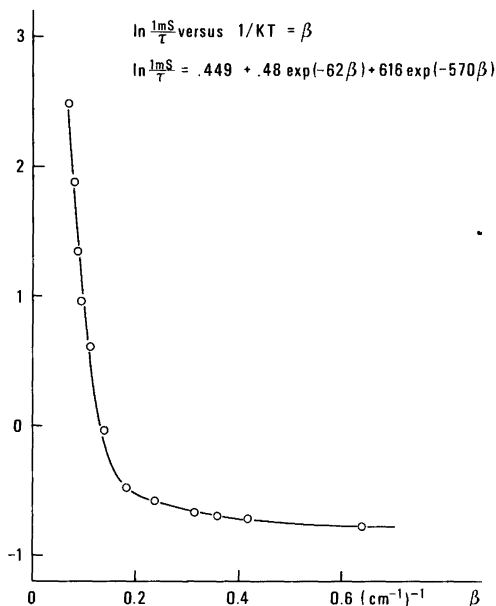


Fig. 2. Temperature dependence of the decay time for the Cu-Mn pair shown as $\ln(1 \text{ mS}/\tau)$ versus $kT/1 \text{ cm}^{-1}$. The curve joining the points is $1/\tau = 0.45 + 0.48 \exp(-62 \text{ cm}^{-1}/kT) + 616 \exp(-570 \text{ cm}^{-1}/kT)$.

The peak to the left of Fig. 1, spectrum 4, is the transition from the state $\text{Mn}^{2+*} = {}^4A_{1g}$, and the band of spectrum 7 is the absorption to the $\text{Mn}^{2+*} - \text{Cu}^{2+}$ with $\text{Mn}^{2+*} = {}^4A_{1g}, {}^4E_g^a$. The S system is the single ion Mn^{2+} reported in Refs. 1 and 2, but the value for the O-O band position of

the transition from the ${}^4A_{1g}(\Gamma_8)$ is 17842 cm^{-1} , while the energy obtained in Ref. 1 was 17373 cm^{-1} as seen on Fig. 1, spectrum 3.

Disregarding the rest of spectrum 5, the peaks of spectrum 6, Fig. 1, are from the left, the transitions to the $\Gamma({}^4A_{1g})$, and to Γ_6, Γ_7 and Γ_8 all from the ${}^4E_g^a$ according to Ref. 2.

The X system has not been detected before. It is very similar to the S system, only displaced by 70 cm^{-1} towards lower energies in the emission spectrum and approximately 6 cm^{-1} in the opposite way in the excitation (absorption) spectrum. In the three emission spectra of Fig. 1 the non-labelled peaks are assigned to phonon side bands.

The X system is absent in samples without copper.

A feature with very weak emission and spectra very similar to those of Mn^{2+} was detected at 17827 cm^{-1} . Its absorption was displaced 50 cm^{-1} towards higher energies than that of Mn^{2+} . Furthermore, an emission peak at 17808 cm^{-1} was excited in a broad band centered at 25065 cm^{-1} .

THE MODEL

The internal conversion is considered to take place within such a short time that the species, during excitation, can be considered totally isolated. The model can, therefore, treat the excitation as though the pumping were taking place to the lowest excited electronic state only. As the excitation light is monochromatic, only one species is excited at a time.

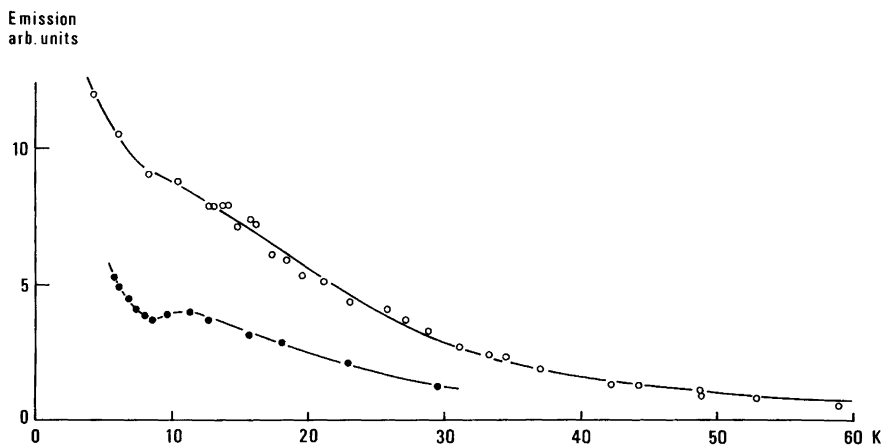


Fig. 3. Temperature dependence of the band showing an abnormal temperature behaviour.

The simplest possible model that can explain the temperature dependence observed involves three impurity levels. If the pumping rate to species p is K_p , and the number of excited species of type q is N_q , a set of equations can be established:

$$\frac{dN_p}{dt} = K_p + \sum a_{pq}N_q$$

where the a_{pq} 's are dependent on the differences of the energies of the lowest excited states, the temperature and the rate constants for transfer between the different species and between each species and its ground state. For three levels, the equations are

$$\frac{dN_1}{dt} = a_{11}N_1 + a_{12}N_2 + a_{13}N_3 + K_1 \text{ and two analogs. (1)}$$

The coefficients a_{pq} are:

$$\begin{aligned} a_{11} &= -(n_2\lambda_{12} + n_3\lambda_{13} + \lambda_1) = -(\lambda_1 + a_{21} + a_{31}) \\ a_{12} &= n_1\lambda_{12} \exp(-\varepsilon_2/kT) \\ a_{13} &= n_1\lambda_{13} \exp(-\varepsilon_3/kT) \\ a_{21} &= n_2\lambda_{12} \\ a_{22} &= -(n_1\lambda_{12} \exp(-\varepsilon_3/kT) + n_3\lambda_{23} + \lambda_2) \\ &= -(\lambda_2 + a_{12} + a_{32}) \\ a_{23} &= n_2\lambda_{23} \exp((-\varepsilon_3 + \varepsilon_2)/kT) \\ a_{31} &= n_3\lambda_{13} \\ a_{32} &= n_3\lambda_{23} \\ a_{33} &= -(n_1\lambda_{13} \exp(-\varepsilon_3/kT) + n_2\lambda_{12} \times \\ &\quad \exp((-\varepsilon_3 + \varepsilon_2)/kT) + \lambda_3) = -(\lambda_3 + a_{23} + a_{13}) \end{aligned}$$

λ_n is the sum of the emitting and non-emitting rate constants from level n out of the levels considered. The ε 's are the positive energy differences from the highest level, level 1. λ_{pq} is the rate constant between the level p and q . We assume this to be temperature independent.

$$a_{pq} \geq 0 \text{ for } p \neq q \text{ and } a_{qq} < 0$$

THE MODEL FOR THE STEADY STATE CASE

Here the dN/dt 's are zero. Further, only one K is different from zero, as the pumping was made by monochromatic light. Letting $N_p(q)$ denote the population of level p when exciting in q only, one obtains

$$\begin{aligned} N_1(1) &= \begin{vmatrix} -K_1 & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & a_{32} & a_{33} \end{vmatrix} / D \\ N_3(3) &= \begin{vmatrix} a_{11} & a_{12} & 0 \\ a_{21} & a_{22} & 0 \\ a_{31} & a_{32} & -K_3 \end{vmatrix} / D \end{aligned}$$

D is the determinant of a_{nn} . The solutions are

$$\begin{aligned} \frac{K_1}{N_1(1)} &= a_{11} \\ &- \frac{a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{32}a_{22}a_{13} - a_{33}a_{21}a_{12}}{a_{22}a_{33} - a_{32}a_{23}} \end{aligned}$$

$$= -a_{11} - R_1$$

$$\frac{K_3}{N_3(3)} = -a_{33}$$

$$\begin{aligned} &- \frac{a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{31}a_{22}a_{13} - a_{11}a_{32}a_{23}}{a_{11}a_{22} - a_{12}a_{21}} \\ &= -a_{33} - R_3 \end{aligned}$$

In the case of dominating diagonal elements, R_1 and R_3 are neglected, and the first order expressions are:

$$(N_1(1))^{-1} = K_1^{-1}(n_2\lambda_{12} + n_3\lambda_{13} + \lambda_1),$$

which is temperature independent, and

$$(N_3(3))^{-1} = K_3^{-1}(n_1\lambda_{13} \exp(-\varepsilon_3/kT) + n_2\lambda_{12} \times \exp((-\varepsilon_3 + \varepsilon_2)/kT) + \lambda_3)$$

As $\varepsilon_3 > \varepsilon_2$, the slope of this curve cannot change sign, and the first approximation can, therefore, not explain the observed hump. By evaluating R_3 and subtracting, however, one obtains

$$N_3 = N_0(1 + \exp((-\varepsilon_3 + \varepsilon_2)/kT)) \cdot \frac{C_2X^2 + C_1X + C_3^{-1}}{X + C_4} \quad (2)$$

where

$$X = \exp(-\varepsilon_2/kT) \text{ and } N_0 = K_3/\lambda_3$$

The four C 's are temperature independent constants that depend on the n 's and λ 's. The requirement for selectively detecting the species 1 and 3 are that the ratios

$$\frac{\lambda_E(1) N_1(1)}{\lambda_E(3) N_1(3)} = C \frac{a_{22}a_{33} - a_{32}a_{23}}{a_{12}a_{23} - a_{22}a_{13}} \quad (3)$$

and

$$\frac{\lambda_E(3) N_3(3)}{\lambda_E(1) N_3(1)} = \frac{1}{C} \frac{a_{11}a_{22} - a_{21}a_{12}}{a_{21}a_{32} - a_{31}a_{22}}$$

are higher than the experimental limit or at least ≈ 10 . Here $\lambda_E(p)$ is the rate constant for radiative decay of species p and

$$C = \lambda_E(1)/\lambda_E(3)$$

These conditions are fulfilled if for example a_{33}/C is large.

THE MODEL IN THE TIME DEPENDENT CASE

Time constants are here determined by measuring the quantity:

$$S \equiv d/\ln F \quad (4)$$

neglecting the derivative of S . F is the intensity which is considered proportional to the population. In the general case

$$F = \sum C_n \exp(s_n T) \quad (5)$$

C_n being constants and $s_n < 0$. dS/dt can, however, only vanish if $s_n = s_{n'}$ for all n and n' where C_n and $C_{n'}$ are different from 0.

In eqn. (1) we now put $K_1 = K_2 = K_3 = 0$ and Laplace-transform. By solving the equations we obtain the transform of N_3 , n_3 with the new variable s :

$$n_3 = -N_3(0+) \frac{(a_{22}-s)(a_{33}-s) - a_{12}a_{21}}{D(s)}$$

$N_3(0+)$ is the population in level 3 at time $t=0$, and $D(s)$ is the determinant D with s subtracted from each diagonal element. We get

$$D(s) = D - s^3 + s^2 T - sd$$

where

$$\begin{aligned} T &= a_{11} + a_{22} + a_{33} \\ d &= d_{12} + d_{23} + d_{13} \\ d_{pq} &= a_{pp}a_{qq} - a_{pq}a_{qp} \end{aligned}$$

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n_3 can be decomposed on the form

$$\frac{n_3}{N(0+)} = \frac{C_1}{s-s_2} + \frac{C_2}{s-s_2} + \frac{C_3}{s-s_3}$$

The inverse Laplace-transform in the case where s_1, s_2 and s_3 are all different gives eqn. (5). s_1, s_2 and s_3 are the roots in the equation $D(s)=0$. One root, s_1 , will always be real, and C_1 is therefore real. If $\text{Im}(s_3) \neq 0$, $s_3 = s_2^*$ and $C_2 = C_3^*$.

The equation is solved by a standard procedure. Transforming first $s = x + \frac{1}{3} T$ gives

$$x^3 + 3px + 2q = 0$$

with

$$p = \frac{1}{3}(d - \frac{1}{3} T^2) \text{ and } q = \frac{1}{27} dT - D - \frac{2}{27} T^3$$

As p can be rewritten:

$$\begin{aligned} p &= -\frac{1}{18} ((a_{11} - a_{22})^2 + (a_{11} - a_{33})^2 + (a_{22} - a_{33})^2) \\ &\quad - \frac{1}{3} (a_{12}a_{21} + a_{13}a_{31} + a_{23}a_{32}) \end{aligned}$$

it is always negative. All three roots can, therefore, not be equal and it is seen that the decay cannot be exactly exponential. If all diagonal terms are also equal, q is negative, and three different roots are obtained.

The coefficients are

$$\begin{aligned} C_1 &= \frac{(a_{11} - s_1)(a_{22} - s_1) - a_{12}a_{21}}{(s_1 - s_2)(s_1 - s_3)} \\ &= \frac{d_{12} + s_2 - s_1(a_{11} + a_{22})}{(s_1 - s_2)(s_1 - s_3)} \end{aligned}$$

and analogous equations for C_2 and C_3 . If $p^3 + q^2 = 0$, $s_2 = s_3$ and the inverse transform becomes

$$\begin{aligned} N_3/N_3(0) &= \frac{(a_{11} - s_1)(a_{22} - s_1) - a_{12}a_{21}}{(s_1 - s_2)^2} \exp(s_1 t) \\ &\quad + \frac{(a_{11} - s_2)(a_{22} - s_2) - a_{12}a_{21}}{s_2 - s_1} t \exp(s_2 t) \end{aligned}$$

This appears in the case where one diagonal element dominates the others.

With $\sqrt{-p} \approx \frac{1}{3}(-a_a + \frac{1}{2}(a_b + a_c))$, where a_a is the dominating diagonal element, and a_b and a_c the other diagonal elements, we get for $a_a \neq a_{33}$

$$N_3/N_3(0) \approx -a_a t \exp(\frac{1}{2} a_{33} t) \text{ and } S = \frac{1}{t} + \frac{1}{2} a_{33};$$

for $a_a = a_{33}$ we obtain

$$N_3/N_3(0) \approx \exp(a_{33} t) \text{ and } S = a_{33}$$

In the first case S becomes constant after some time. If on the contrary, all diagonal elements are of the same order of magnitude, p becomes very small and all three roots approach the value $\frac{1}{3} T$. $N_3/N_3(0)$ will then be proportional to

$$t^2 \exp(\frac{1}{3} T t) \text{ giving } S = \frac{2}{t} + \frac{1}{3}(a_{11} + a_{22} + a_{33})$$

In all of these cases, however, we obtain

$$1/\tau = A_1 + A_2 \exp(-\varepsilon_3 + \varepsilon_2)/kT + A_3 \exp(-\varepsilon_3/kT)$$

where the A 's are temperature independent constants. In the intermediate case the weights of the different contributions may change with temperature. In this case, however, the logarithmic plot will probably deviate too much from a straight line to allow a determination of S .

APPLICATION OF THE MODEL AND DISCUSSION

By applying the formula (2) the curves of Fig. 3 are obtained with the following values

$$\varepsilon_3 = 70 \text{ cm}^{-1} \text{ and } \varepsilon_2 = 62 \text{ cm}^{-1}$$

upper curve: $N_0 = 13.9$ arb. units.

$$C_1 = 1.74; C_2 = 76.6; C_3 = 8.36 \times 10^{-5} \text{ and } C_4 = 3.82 \times 10^{-5}$$

lower curve: $N_0 = 13.81$ arb. units

$$C = 6.03; C_2 = 157.3; C_3 = 7.33 \times 10^{-4} \text{ and } C_4 = 6.33 \times 10^{-5}$$

The C 's cannot be expected to be the same for the two curves, since they depend on the concentrations.

It is seen that the model relates the X and S band, as ε_3 is just the distance between these. The band 8 cm^{-1} over the X band is not observed in the spectra.

The population of the excited state has been considered proportional to the intensity of the emission, which is only correct as long as the ratio between the number of transitions to the 0 level and those to the phonon side band is constant. This ratio is $\exp(-c)$ where

$$c = \sum_i \Delta_i \coth(\hbar\omega_i/2kT)$$

The sum is over the normal modes, and Δ_i is the displacement in space between the potential minima of the levels involved. For the transition to the ground state this ratio has been observed to change by a factor of 1.8 only from 4 to 30 K for the X -level. As the X and S systems are very similar in both emission and absorption, their potential surfaces must be very similar, giving very small values for Δ_i compared to those for transitions to the ground state. From this it is concluded that the ratio at least for the upper and lower levels are temperature independent, and the λ 's therefore reasonably constant.

No attempts shall be made here to assign the X -band to a particular impurity, as this question is being investigated.⁴

The experimental results on the lifetime of the $\text{Cu}^{2+} - \text{Mn}^{2+}$ pairs predict an impurity level at 17853 cm^{-1} and an intermediate level at 17347 cm^{-1} . The intermediate level was not detected, but the levels found at 17827 and 17808 cm^{-1} are both well within the experimental limits also with regard to lifetime. The data are not good enough to determine which line would be the best candidate, and a model involving four impurities would contain so many parameters that any set of data would fit. The data do, however, show that there is no coupling to the $S - X$ system.

CONCLUSION

The new band detected in the emission from KZnF_3 containing Cu^{2+} and Mn^{2+} impurities has the selectively detected excitation spectrum and the emission spectrum very similar to those of the Mn^{2+} single ions. The temperature dependence of the intensity, however, shows a hump around 10 K and a very steep rise at lower temperatures. The

decay time of the $\text{Cu}^{2+} - \text{Mn}^{2+}$ pairs in KZnF_3 shows a temperature dependence that cannot be matched to the simple expression $1/T = a + b \exp(-\varepsilon/kT)$. It has, however, been shown that a simple model that allows excitation transfer to take place between species can reproduce the data. Formula for the temperature dependence of the intensity and decay time have been evaluated according to the model, and consistency with the experimental results has been proven. Contrary to what is usually believed, it is therefore concluded that transfer of excitation energy between species in KZnF_3 can be realized.

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