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On Concentration Self-Quenching of Chromium Phosphorescence in $K_3[Cr_xCo_{1-x}(CN)_6]$ Mixed Crystals*

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The self-quenching of chromium phosphorescence in $K_3[Cr_xCo_{1-x}(CN)_6]$ mixed crystals has been studied in the range of very high chromium concentration and a minimum in emission quantum yield has been found at about 80% Cr. Comparison of the Cr emission intensities from $K_3[Cr(CN)_6]$ doped with 1% of various impurities suggests that the "impurity quenching" observed in the range 90 to 100% Cr may be a result of the site asymmetry introduced by the impurity. It is suggested that at least two mechanisms of self-quenching are operative in this concentration range and the nature of these is discussed in relationship to present theories of radiationless transitions.

Die Eigenlöschung der Cr(III)-Phosphoreszenz wurde in $K_3[Cr_xCo_{1-x}(CN)_6]$-Mischkristallen im Bereich hoher Cr-Konzentrationen untersucht. Die Quantenausbeuten der Emission zeigten ein Minimum bei etwa 80% Cr. Ein Vergleich der Lumineszenzintensitäten von $K_3[Cr(CN)_6]$ mit 1% verschiedener Zusätze läßt vermuten, daß die im Bereich von 90–100% Cr beobachtete Löschung von einer durch die Verunreinigung verursachten Gitterstörung herrührt. — Es wird angenommen, daß in dem untersuchten Konzentrationsbereich mindestens zwei Mechanismen der Eigenlöschung wirksam sind, die anhand der gegenwärtigen Theorien der strahlungslosen Übergänge diskutiert werden.

«L'auto étouffement» du chrome phosphorescent à partir de $K_3[Cr_xCo_{1-x}(CN)_6]$, cristaux mélanges avait été étudié dans la région de très haute concentration de chrome et un minimum d'emission quantique, il en résultait environ 80% Cr. Comparé à l'intensité d'émission de chrome à partir de $K_3[Cr(CN)_6]$ contaminé par 1% de diverses impuretés indique que «l'étouffement d'impureté» qui était observé dans la région de 90 à 100% Cr, peut être le résultat de l'emplacement assimétrique introduit par l'impureté. — Il a été suggéré qu'au moins deux mécanismes «d'auto étouffement» sont à l'oeuvre dans cette région de concentration et leur nature décrite en relation avec les présentes théories de transitions sans radiation.

1. Introduction

Almost invariably, when the concentration of a luminescent species doped into a host lattice is increased above a certain value, the luminescence quantum yield begins to decrease. This concentration self-quenching has been observed in a variety of systems, in some cases being associated with a change in the character of the emission with increasing concentration [1].

The systems studied fall into three categories. In the first are those where the excitation energy appears to be quite localized and the self-quenching occurs only over very small distances in the lattice [2]. In the second category are the systems where once more the energy is localized but now the quenching inter-

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* Dedicated to the memory of Professor Hans-Ludwig Schläfer.

actions are of much longer range [2]. It is possible to consider the behaviour of both types of system from the standpoint of localized exciton theory (Frenkel excitons) [3] but for consideration of quenching processes this offers no particular advantage other than a convenient terminology.

In the third category are those systems where energy transfer is so rapid that localization of the excitation energy can or does not occur (Wannier excitons) [3]. In this case quenching is thought to occur by migration of the exciton to quenching sites in the crystal [4, 5]. In all three cases the quenching sites may be aggregates of the luminescent species, impurities, or lattice defects.

The mechanisms responsible for the energy transfer are the same in all cases; long range resonance transfer as a result of multipolar interactions, possibly phonon-assisted, or exchange interactions of short range. Dexter [6] has given the important factors as the overlap of donor emission with acceptor absorption, the transfer distance and in the case of exchange, the overlap of the relevant orbitals. Orbach has extended this to cover the phonon-assisted case [7].

In the previous work on the system $K_3[Cr_xCo_{1-x}(CN)_6]$ the existence of a very short range self-quenching process for $[Cr(CN)_6]^{3-}$ phosphorescence was recognized [8]. The $K_3[Co(CN)_6]$ host lattice appeared not to quench the emission. Satisfactory theoretical description of the emission quantum yield concentration dependence was obtained using a model in which single Cr ions emitted with constant quantum yield whereas pair or higher aggregates were completely quenched. In this way the number of active neighbour sites on which the presence of a second Cr would cause quenching of an excited Cr ion was found to be six, rising to 12 with increasing Cr concentration.

In that work the luminescence quantum yield of pure $K_3[Cr(CN)_6]$ was considerably higher than in the 60 to 90% Cr materials, suggesting that in the high Cr concentration region the presence of Co for some reason caused quenching. The possibility was proposed that this might be a site asymmetry effect, independent of the nature of the impurity and arising from the absence of some of the paramagnetic Cr ions. The present work presents an examination of this based upon some new experimental data.

2. Experimental

The compounds used in this work were prepared by the precipitation technique previously described, starting with the same potassium hexa-cyanochromate (III). Such materials were previously shown to have the orthorhombic crystal structure [8].

The techniques and apparatus used for the measurement of emission and reflectance spectra, and of the relative integrated emission intensities, are all as previously described in detail [8].

3. Results and Discussion

The reflectance spectra of $K_3[Cr(CN)_6]$, $K_3[Co(CN)_6]$ and the 50% doped compound have been previously published [8]. Since the maximum of the $^4T_{2g} \leftarrow {}^4A_{2g}$ $[Cr(CN)_6]^{3-}$ absorption band lies at 373 nm, and at wavelengths

Table 1. *Dependence of relative integrated emission intensity and relative quantum yield on chromium concentration*

Mole fraction Cr	%R	I_{corr}	ϕ_{rel}
1.0	28.9	63	1.0
0.99	26.7	17	0.28
0.95	33.1	9.6	0.15
0.90	39.6	0.52	0.009
0.80	34.2	0.54	0.011
0.70	42.0	0.68	0.016
0.60	42.3	0.97	0.26
0.50	45.0	5.4	1.4

%R Percent reflectance of tablet at 404 nm.
I_{corr} Relative integrated emission intensity corrected for reflectance [8]
ϕ_{rel} Quantum yield of chromium phosphorescence relative to pure $K_3[Cr(CN)]_6$; corrected where necessary for $[Co(CN)_6]^{3-}$ absorption.

Table 2. *Relative integrated* Cr(III) *emission intensities of* $K_3[Cr(CN)_6]$ *containing 1% of various impurities*

Mole fraction Cr	Mole fraction impurity	%R	I_{corr}	ϕ_{rel}
1.0	—	28.9	63	1.0
0.99	0.01 $[Co(CN)_6]^{3-}$	26.7	17	0.28
0.99	0.01 $[Fe(CN)_6]^{4-}$	23.5	9.0	0.14
0.99	0.01 $[Fe(CN)_6]^{3-}$	22.1	6.0	0.095
0.99	0.01 $[Ni(CN)_4]^{2-}$	26.0	7.7	0.12

For explanation of %R, I_{corr} and ϕ_{rel} see caption to Table 1.

longer than this the effects of $[Co(CN)_6]^{3-}$ absorption are minimized, 404 nm (Hg line) was chosen as the most convenient wavelength of irradiation.

The results in Table 1 show clearly that with increasing Cr concentration the luminescence yield goes through a minimum at about 80% Cr. At this point the quantum yield of emission is extremely low, being little greater than the background scatter of the apparatus. This extends and confirms our previous observation that in the range of concentration 90 to 100% Cr, Co apparently acts as a quencher.

The reflectance spectra of $K_3[Cr(CN)_6]$ doped with 1% of $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ or $[Ni(CN)_4]^{2-}$ showed no significant differences in reflectivity at 404 nm. Thus, effects due to inner filtering by the impurity should not influence the luminescence behaviour of $[Cr(CN)_6]^{3-}$ in the compounds for this wavelength of irradiation. The results of the luminescence work on these compounds are shown in Table 2. Unfortunately the emission is weak so it was not possible to prove experimentally that no change in the emission spectrum resulted from the doping, but this is in any case improbable. The extent to which quenching occurs on addition of 1% of an impurity is seen to be only approximately independent of the nature of the impurity. This is not in complete agreement with expectations based on the site asymmetry suggestion and any complete explanation of the data would have to account also for these differences. Here, however, only the gross features of the data can be considered.

Our previous studies of the Cr concentration dependence of the Cr phosphorescence quantum yield showed that it remained high and constant up to about 10 to 15% Cr. Above this the quantum yield and, above 25% Cr also the lifetime, decreased rapidly. From these observations it was deduced that the essential quenching mechanism in the crystals was short range Cr/Cr quenching. A statistical treatment of the data showed that self-quenching by Cr on any of six neighbour sites, rising to twelve at higher concentrations of Cr, gave good agreement with the data up to 60% Cr. Thus it was clear that significant energy migration occured only to a distance of less than one unit cell length (7 Å).

The data presented now for the high Cr concentration region require transfer of excitation energy over still larger distances.

In a crystal lattice of this type where the distribution of the Cr and Co on the available lattice sites is random, one may calculate the mole fraction of Cr ions with n neighbour Cr's arranged on any of Z active sites, as [2],

$$(x_{\mathrm{Cr}})_{\mathrm{Cr}_n} = \frac{Z!}{n!(Z-n)!} x_{\mathrm{Cr}}^n (1 - x_{\mathrm{Cr}})^{Z-n} .$$

If one assumes that all Cr ions with six neighbour Cr ions emit with some quantum yield ϕ, while those with five Cr neighbours are inactive, then calculations of the concentration dependence of ϕ are not in agreement with observation. If instead, one assumes as before that Cr_5 sites act as quenchers, but now calculates the number of adjacent lattice sites, Z, that are deactivated by each such site, then one obtains the observed reduction in Cr intensity for the 99% compounds if Z is the order of 100 to 300.

This result may be interpreted as showing that at these high concentrations of Cr the excitation energy is less localized during the excited state lifetime and migrates to quenching sites. This value of Z is equivalent to migration over a distance of two to three unit cell lengths (20 Å) which in view of previous estimates for analogous systems is perfectly reasonable. This supports our previous suggestion that, due to the probability of such migrations increasing with Cr concentration, the number of effective quenching sites Z would be expected to be a function of the Cr concentration.

The Nature of the Quenching Processes

This study of the luminescence yield concentration dependence shows that there are operating in these crystals at least two mechanisms of quenching of differing importance. Over the whole range of Cr concentration a very short range mechanism accounts for the main quenching process. That this remains important in the concentrated systems is shown by the fact that pure $K_3[Cr(CN)_6]$ emits only with one two-thousandth of the quantum yield of the dilute compounds. At very high concentrations of Cr a second minor mechanism appears. It is not entirely independent of the nature of the impurity but it does seem as a first approximation to be more due to the absence of the displaced paramagnetic Cr than to the kind of impurity, and may therefore be considered a site asymmetry effect.

It is clear the observed quantum yield fall-off with concentration might be due either to decrease in the intersystem crossing rates or to increased radiationless deactivation. The lifetime measurements, however, show that the latter is of major importance and may be taken to be the effect operating to reduce emission yields. Furthermore decreases in intersystem crossing rates large enough to account for the observed effects would be most unlikely.

Much theoretical work on radiationless transitions has now appeared [4, 9–12]. Often concern is mainly with the theory of such processes in isolated molecules. Thus it is not directly relevant to the present discussion where the processes of interest are basically intermolecular, or environmental.

For present purposes the factors that may be important in determining the rate of a radiationless conversion and any acceleration of it are, (i) the energy gap between the initial and final states, (ii) the Franck-Condon overlap factors, (iii) interactions with the surrounding lattice vibrations and (iv) any spin restrictions on the process. It seems apparent that the only factor that can be changing significantly with Cr/Co ratio is the spin factor. In connection with this, the point of view has recently been expressed that the conventional descriptions of excited states are misleading, and that stationary states of mixed character are formed upon absorption so that internal conversions and intersystem crossings need never be considered [9]. However enough evidence shows that the two types of excited state exist, that the suggestion in this form is untenable.

Because of the very short range nature of the major quenching process and its consequent rapid concentration dependence [8] it seems that the most likely mechanism for the quenching is through exchange interactions between adjacent ions. That these might act to increase the rate of radiationless deactivation to the ground state seems likely since they could lead to mixing of the spin states of the separate ions. A transition to the ground state would then be possible without violation of spin selection rules.

Thus for the excited state of a pair ion, combination of the excited state ^2E_g with ground state $^4A_{2g}$ leads to two new states with total spin 2 and 1 respectively. Similarly the combination of two quartet ground states will lead to four states with total spin, 3, 2, 1, and 0. Then radiationless transitions between the spin two and spin one states of excited and ground state pair ions do not violate the $\Delta S = 0$ spin selection rule. Since present theoretical treatments of the radiationless process do not specifically include means of estimating the magnitude of the spin-forbiddenness factor (but see Ref. [9]) no quantitative test of this suggestion is presently possible. It seems, however, that such a theory is required in view of the demonstrated importance of this factor in determining radiationless transition rates.

A mechanism such as the above can not explain the quantum yield rise in the high Cr concentration range. It appears as if the site asymmetry produced by an impurity in the lattice of almost pure $K_3[Cr(CN)_6]$ can also, to a minor extent, lower the spin restriction on the radiationless transition to the ground state.

Assuming that a suitable interaction mechanism exists, substitution of a paramagnetic Cr by the diamagnetic Co can be seen to impose an asymmetry on the neighbour Cr ions, lying approximately along the C_3 axis. This lowers the symmetry of the adjacent Cr sites to D_{3d}. In the double group for O_h, ${}^4A_{2g}$ has the representation U'_g, going over in D_{3d} to the representations E'_g and E''_g. In O_h and in D_{3d}, ${}^2E_g$ has the same representation, E'_g. Thus lowering the symmetry to D_{3d} in this way may increase the mixing of the spin and orbital functions of the excited and ground states that is already inherent in O_h [13]. It is suggested that this may account for the acceleration of radiationless deactivation observed.

Despite the calculations carried out for the case of enhancement of radiative spin forbidden transitions by paramagnetic species [14], it seems inevitable that the mechanism of the above effect is magnetic. The crystal of $K_3[Cr(CN)_6]$ is not magnetically oriented at room temperature but nevertheless an excited Cr ion in a Cr_5 site would experience a rapidly varying inhomogeneous magnetic field due to its asymmetric environment. This could provide a perturbing mechanism for mixing of the doublet and quartet states in the way discussed above. As support for this suggestion one may point to similar observations on the quenching of Eu^{3+} by paramagnetic ions in which the efficiency of a particular ion appeared related to its total orbital angular momentum [15]. Unfortunately the extension of this suggestion in a quantitative way is not obvious.

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References

1. Imbusch, G. F.: Physic. Rev. **153**, 326 (1967).
2. van Uitert, L. G., Johnson, L. F.: J. chem. Physics **44**, 3514 (1966).
3. Dexter, D. L., Knox, R. S.: Excitons. New York: Interscience Publishers 1965.
4. Lower, S. K., El-Sayed, M. A.: Chem. Rev. **66**, 199 (1966).
5. Hochstrasser, R. M.: Rev. mod. Physics **34**, 531 (1962).
6. Dexter, D. L.: J. chem. Physics **21**, 836 (1953).
7. Orbach, R.: In: Optical properties of ions in crystals, H. M. Crosswhite and H. W. Moos. New York: Interscience Publishers 1967.
8. Kirk, A. D., Ludi, A., Schläfer, H. L.: Ber. Bunsenges. physik. Chem. **73**, 669 (1969).
9. Henry, B. R., Kasha, M.: Ann. Rev. physic. Chem. **19**, 161 (1968).
10. Robinson, G. W., Frosch, R. P.: J. chem. Physics **37**, 1962 (1962); **38**, 1187 (1963).
11. Bixon, M., Jortner, J.: J. chem. Physics **48**, 715 (1968).
12. Jortner, J., Berry, R. S.: J. chem. Physics **48**, 2757 (1968).
13. Hempel, J. C., Matsen, F. A.: J. physic. Chem. **73**, 2502 (1969).
14. McGlynn, S. P., Azumi, T., Kinoshita, M.: Molecular spectroscopy of the triplet state. Englewood Cliffs, New Jersey: Prentice Hall, Inc. 1969.
15. van Uitert, L. G., Iida, S.: J. chem. Physics **37**, 986 (1962).

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