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Leonardo Bosi, Daniela Gallo and Marco Zelada

Dipartimento di Fisica del Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy, and Sede di Lecco

Abstract. Accurate measurements of the quantum efficiency of the M-centre luminescence in NaF have been performed in the range of 20–300 K, by light excitation in the M_1 and M_F bands; as in the KCl case, the absence of energy transfer between F and M centres *after* the F-centre relaxation was ascertained. A discussion of the controversy in the literature concerning the existence of energy transfer is here presented: to reconcile the present results with the data and speculations of different authors it is proposed that the non-radiative energy transfer, if it exists, takes place *before* or *during* the F-centre relaxation. The absence of aging effects for the M-centre luminescence in NaF as well as the absence of perturbative effects of magnesium ions in NaF:Mg have been verified.

1. Introduction

It is known that an M centre produces the same luminescence when it is excited in the M_1 band or in the higher bands (M_F), located in the F-band absorption region [1–2].

Lambe and Compton [1] explained this effect by the transfer energy from excited F centres to M centres. However, since Okamoto [4] subsequently discovered M_F bands, Lambe's suggestion has been partially in doubt. Furthermore Bosi *et al* [3, 5, 6] showed that the M-centre radiative lifetime (nearly constant up to 250 K) is independent of the above excitation energies, and inferred that the higher M states relax in a single, completely degenerate state [7], corresponding to M_1 luminescence. In 1976 Briginets and Yurachkovskii [8] emphasized that, in principle, the possibility of an energy transfer after F-centre excitation is not excluded, and performed an experiment that shows a different M-luminescence behaviour, as a function of the temperature T, when a KCl sample is irradiated in M_1 or M_F bands: in particular M_F luminescence seemed [8] to follow the same law as the F-centre decay.

On the other hand, Bosi and Nimis [9] showed that the authors of [8] were not able to accurately separate the M luminescence from that of the F centre. In contrast, by using a single-photon technique, Bosi and Nimis accurately separated the M from the F luminescence (indeed there is a large difference between the F- and the M-centre lifetimes) and found that the relative efficiencies for the M-luminescence process by light excitation in M_1 and M_F bands follow the same law as a function of T (see figure 1 of [9]).

In this context (even if the following observation is not directly connected to the problem of the energy transfer) it was noted that the relative efficiency of the M luminescence decreases with increasing temperature, whereas the lifetime is constant. To explain this occurrence, Bosi supposed that the M centre can go non-radiatively from the unrelaxed

excited state either to the relaxed excited state or to the ground state with an activation energy: this idea was verified and adopted by other authors [10] in their studies concerning M centres in CaF_2 and SrF_2 doped with Li and Na.

In conclusion, there was no evidence of energy transfer between F and M centres [9]: indeed, such a process should imply a change in the M-luminescence efficiency connected to the F-centre de-excitation mechanism. For the same reason, an energy transfer involving the M-centre triplet state is disregarded: indeed, excitation to the triplet level induces [11] M_1 luminescence because of the fast relaxation to the singlet state. The suggestions of Bosi and Nimis [9] were also supported by theoretical considerations which are essentially based on the well known Dexter theory for the energy transfer processes presented in [12] and widely discussed in review papers [13, 14]. Dexter showed that the energy transfer efficiency is proportional to R^{-6} (R is the distance between the centres) and approximately proportional to the amount of overlap between the emission and the absorption spectrum of the transmitting and receiving centre respectively; thus Van Doorn [15] and subsequently Bosi and Nimis [9] showed that F and M centres would be very close together ($R < 10$ Å), i.e., a situation that is hardly likely.

Nevertheless, in 1990 De Kinder *et al* [16] claimed the existence of energy transfer between excited F centres and aggregate centres (namely M and N centres) in KCl, RbCl and KBr in connection with an inhomogeneous distribution of aggregate centres.

The latter authors, although quoting the results of Bosi *et al* [3] concerning the lifetime of the F centre in KCl, avoided taking into account the de-excitation mechanism proposed for the F centre by Bosi in the same paper [3] as well as in subsequent works concerning the same subject; what is more, they completely disregarded the proof of absence of energy transfer between F and M centres in KCl presented by Bosi and Nimis [9]. They examined [16] the possible decay mechanism of excited F centres, and made their claim on the basis of time-resolved ground-state recovery measurements and optical absorption data, but they were not able to obtain excitation and emission spectra. Furthermore, they stressed [16] that transient absorption measurements, performed in the past in heavily coloured KCl by Gadonas *et al* [17], which show increased transparency in the M and M_F bands 500 ps after pulsed excitation, fully support their claim. However, they [16] did not take into account (or investigate) the fact that such increased transparency can be related to the formation of the excited M centres in their singlet state (due to the influence of the light excitation) followed by the formation of the metastable M centres in their triplet state [11, 18]: this fact, obviously, is connected with the overlap of the F and M_F bands. Moreover, as anticipated, fast relaxation from the excited triplet state to the singlet state occurs [11]: consequently, only an increase of the characteristic M_1 luminescence is observed [11], but the spectral position, the band shape and the lifetime remain unchanged [11].

In conclusion we were compelled to test the possibility of an energy transfer between excited F and M centres by studying a new crystal (different from KCl, the subject of the above-discussed controversy). It must be recalled that one of the most important parameters connected with the possible occurrence of non-radiative transfer is the degree of overlapping between the emission band of the transmitting centre (F centre) and the absorption band of the receiving centre (M centre): this parameter is small for KCl, very small for NaF and negligible for RbCl and KBr. On the basis of this criterion we turned our attention to the second candidate (NaF) for such a process; furthermore, as shown in the next section, we were facilitated in such research since M-centre excitation and emission spectra are placed in a spectral region suitable for detection by our experimental apparatus.

2. Experimental details

The samples we investigated are the same employed in previous experiments concerning the M-centre emission properties (see [19] and [20] to which the reader is kindly referred). Nevertheless, for the sake of clarity, we recall the following facts.

In 1981 Bosi *et al* [21] showed that the additive colouration of NaF samples is favoured by the presence of substitutional Li^+ ions (~ 1 mol% LiF in the melt). Indeed, in the past, because of the difficulty of obtaining additive colouration, the samples used in the Colour Centre Physics Laboratories were always coloured with x- or γ-rays; the main disadvantage with this technique is the formation of a large and non-eliminable quantity of M^+ centres, whose luminescence is strong and partially overlaps the F-centre luminescence. Another disadvantage is the presence of several different aggregate and ionized centres in the samples that make the luminescence studies even more laborious. Thus, Bosi *et al* [22] obtained accurate measurements concerning the anomalous behaviour of the F-centre decay in NaF as well as concerning the F^--centre formation [23] using NaF:Li additively coloured samples.

In section 3 we will present our measurements, with a particular emphasis on the emission spectra as a function of the temperature, and, consequently, the determination of the luminescence quantum yield in the additively coloured NaF:Li samples. The results were found to be independent of the initial colour centre concentration. Please note, however, that emission and quantum yield employing NaF and NaF:Li x-ray coloured samples show the same features as the additively coloured ones even if these results are of worse quality because of the above-mentioned effects connected to the presence of various aggregate centres; moreover, the excitation spectra in x-ray coloured samples are scarcely detectable. Our measurements were carried out using a Perkin–Elmer LS-50 fluorimeter whose wavelength range of operation is 220–850 nm; the emission (as well as excitation) spectra were corrected for the variation of the lamp intensity and of the photomultiplier sensitivity as a function of the wavelength. The samples were mounted in a temperature controller K1C-SC Galileo cryocooler (vacuum apparatus supplied by Bis-Italia).

3. Results and discussion

Firstly, we present our results concerning the measurements performed immediately after the quenching and exposure at room temperature (RT) to F light of additively coloured NaF:Li samples. In figure 1 we show an example of the emission spectra we obtained when light excitation was carried out in the M_1 band, whereas in figure 2 we show some spectra obtained by light excitation in the M_F bands. It can be stressed that in the last case F-centre luminescence is present at $T < 150$ K. An accurate study concerning the F-centre luminescence quantum yield and lifetime has been presented previously by one of us [22]; as anticipated, the M luminescence in additively coloured NaF:Li samples was recently investigated by Bosi and Gallo [19, 20]. So we were able to separate the contribution of the F-centre luminescence from that of the M centre; a deconvolution program using two Gaussian functions was adopted.

In table 1 we present a survey of the results for the set of measurements. We feel it helpful to explain the meaning of the columns in table 1 and of the data analysis involved. At each T (column 1) the intensity of the M emission was integrated as a function of the wavelength, whether light excitation was carried out in the M_1 absorption band (column 2) or in the M_F absorption bands (column 6). Please note that light excitation was carried out at the maximum of the M_1 band; since a fixed value for the fluorimeter bandpass width was adopted, the intensity data (column 2) were corrected (column 4) taking into account
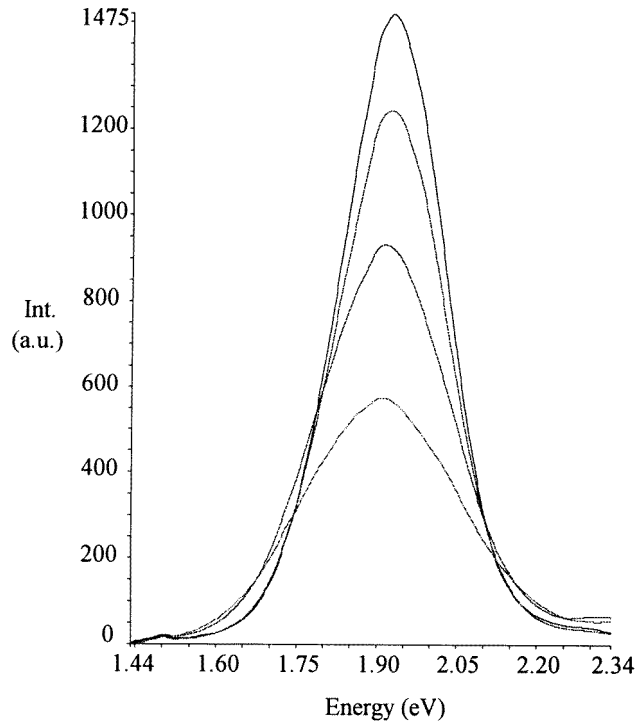
Figure 1. Emission spectra (excitation at the peak of M_1 band) obtained immediately after the quenching of an NaF:Li sample and exposure at RT to F light. Temperatures from the top, 20.15 K, 99.87 K, 200.5 K, 300.2 K. Fluorimeter bandpass width in excitation, 10 nm; in emission, 10 nm. An Oriel optical long-pass filter (cut on 400 nm) was inserted on the emission slit. The intensities are in arbitrary units (a.u.).

the change $H(T)/H(0)$ (see column 3) of the M_1 absorption band as a function of T (we disregarded the very small change of the oscillator strength value as a function of T). The data of column 6 were not corrected: actually, the peak position and halfwidth of the numerous M_F bands (corresponding to Π states) are not well known; moreover, because of the overlapping of the M_F bands, a broad band is observed whose change as a function of T is not relevant. The validity of this observation was confirmed by the interpolation of the above data (see columns 5 and 7) for the luminescence intensities obtained with the aid of an empirical expression for its temperature dependence:

$$I(T) = 1/[A \exp(-E_1/kT) + B \exp(-E_2/kT) + C]. \qquad (1)$$

This relationship was successfully introduced in the past by Hirai and Hashizume [2] in their studies concerning M luminescence in KCl and KBr. It is worthwhile stressing that the luminescence intensity $I(T)$ is proportional to the luminescence (absolute or relative) quantum yield $\eta(T)$: for this reason we indirectly obtained the behaviour of η as a function of T although we did not carry out absolute measurements.

As shown in table 1, both the $I_{corr}(M_1)$ and $I(M_F)$ values are well interpolatd by the function (1) and, what is more important, are practically well interpolated by the same function in the whole T range investigated (i.e. even below 150 K); indeed we found $E_1 = 6.58 \times 10^{-2}$ eV and $E_2 = 1.8 \times 10^{-4}$ eV for $I_{corr}(M_1)$, and $E_1 = 6.63 \times 10^{-2}$ eV
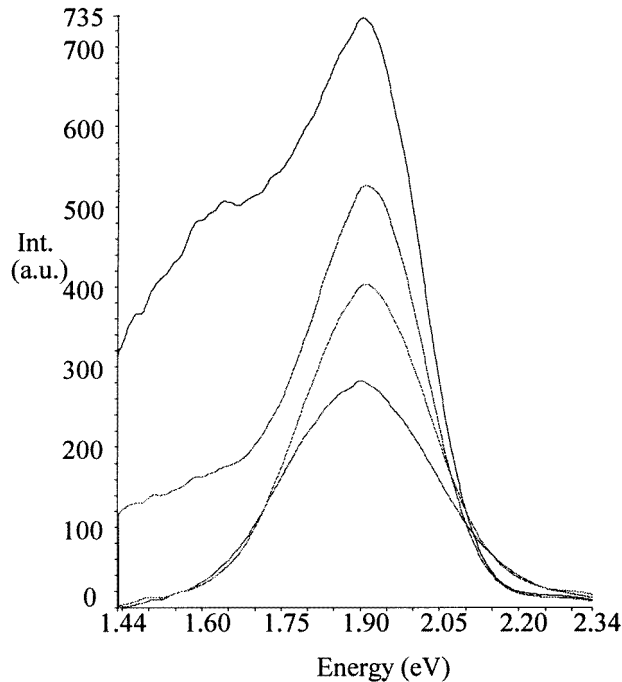
Figure 2. Emission spectra (excitation at 340 nm in the M_F bands), obtained immediately after the quenching of a NaF:Li sample and exposure at RT to F light. Temperatures from the top, 20.15 K, 101.3 K, 199.5 K, 298.8 K. Fluorimeter band pass width in excitation, 10 nm; in emission, 10 nm. An Oriel optical long-pass filter (cut on 400 nm) was inserted on the emission slit. The intensities are in arbitrary units (a.u.).

and $E_2 = 2.1 \times 10^{-4}$ eV for $I(M_F)$.

A similar behaviour (even if more qualitative) was observed when integrating the excitation spectra as a function of the wavelength: these spectra were recorded using the same experimental apparatus.

Furthermore, we want to stress that we obtained the same behaviour that had been found previously by Bosi and Nimis [24] for the quantum yield of the M luminescence in x-ray coloured NaF:Mg samples: in fact, they ascertained the absence of perturbative effects by magnesium ions on the decay properties of the M centre (in particular, no change of the lifetime value). In any case, for the sake of comparison, we present in figure 3 both $I_{corr}(M_1)$ and (M_F) data for the NaF:Li additively coloured sample (present work) together with the ones, $I_{Mg}(M_1)$, previously obtained [24] in the NaF:Mg sample by light excitation in the M_1 band (please note that the data are normalized to unity at the lowest T in order to obtain the relative quantum yield).

We would like to recall that one of the main advantages of the additive as against X- or γ-ray colouration is the time stability of the decay properties of the M centres. In fact, we repeated the above experiments by investigating the same sample after about a week. We obtained practically the same results for the luminescence quantum yield as in the previous experiment. On the basis of the data presented in table 2 we found $E_1 = 5.05 \times 10^{-2}$ eV and $E_2 = 3.9 \times 10^{-4}$ eV for $I_{corr}(M_1)$, and $E_1 = 5.24 \times 10^{-2}$ eV and $E_2 = 0.9 \times 10^{-4}$ eV for $I(M_F)$. Furthermore, there was no evidence of any change concerning peak energy,
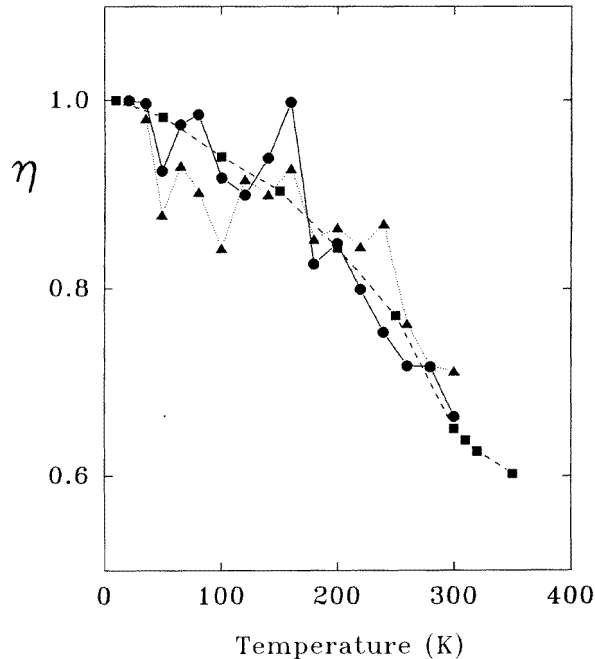
Figure 3. The relative quantum yield of the M-centre luminescence of additively coloured NaF:Li, excited in the M_1 absorption band (circles), additively coloured NaF:Li, excited in the M_F absorption bands (triangles) and x-ray coloured NaF:Mg, excited in the M_1 absorption band (squares). The lines do not have a physical meaning but must be considered as a guide for the eye only.

band shape or halfwidth data. In contrast, the intensity of the F luminescence was found to be strongly reduced. This fact can be easily explained by the well known Miehlich effect [25]: the F luminescence tends to decrease when the F-centre concentration, even if local, increases, i.e. when the mutual distance between F centres decreases. The Miehlich effect was explained by Bosi *et al* [3] on the basis of a tunnelling process between F centres before or during the relaxation after light excitation. As a further proof we recall that, as anticipated, the absolute quantum yield of the F luminescence decreases as a function of the absolute (initial) concentration as well as of the local F-centre concentration (an ageing effect which implies the shortening of the distance between F centres) but the F-centre luminescence lifetime is unchanged. This seems to be a general rule for the F centre in alkali halides: as regards the NaF case, we refer to the papers of Bosi *et al* [3 (see, for instance, figure 7), 21, 22, 24]. Nevertheless, we recall the existence of another effect: the change of the F-centre lifetime as a consequence of the interaction between F and α centres. This effect, extensively studied by Bosi and Nimis, is not connected with the present problem of ascertaining the existence of the energy transfer between F and M centres in alkali halides (for a critical review see [26]).

These results, together with those (obtained previously by Bosi *et al*) concerning the decay properties of F and M centres in pure and doped NaF samples, lead us to confirm also in NaF the absence of a non-radiative energy transfer between F and M centres *after* the relaxation of the excited F centre. In order to corroborate this conclusion, we would like to recall and discuss the properties of the energy transfer processes [12–14] in connection

Table 1. Results for an additively coloured NaF:Li sample immediately after the quenching and exposure to F light at RT. Column 1, temperatures T. Column 2, intensity, $I(M_1)$, of the M emission integrated as a function of the wavelength when light excitation in the M_1 absorption band was carried out. Column 3, ratio of the halfwidth, $H(T)$, of the M_1 absorption band at each T to the halfwidth, $H(0)$, at the lowest T. Column 4, data of column 3 corrected on the basis of $H(T)/H(0)$ ratios. Column 5, interpolation, $I_{int}(M_1)$, of the column 4 data by the function (1). Column 6, intensity, $I(M_F)$, of the M emission integrated as a function of the wavelength when light excitation in the M_F absorption band was carried out. Column 7, interpolation, $I_{int}(M_F)$, of the column 6 data by the function (1).

T (K)	$I(M_1)$ (a.u.)	$H(T)/H(0)$	$I_{corr}(M_1)$ (a.u.)	$I_{int}(M_1)$ (a.u.)	$I(M_F)$ (a.u.)	$I_{int}(M_F)$ (a.u.)
20.81	116 400	1.000	116 400	116 600	49 388	49 060
35.54	115 997	1.000	115 997	113 542	48 440	46 888
49.10	107 652	1.000	107 652	112 351	43 403	46 065
64.98	113 268	1.001	113 376	111 585	45 947	45 544
80.46	114 200	1.004	114 617	111 090	44 585	45 229
100.3	105 623	1.011	106 799	110 457	41 641	44 922
120.2	102 301	1.024	104 713	109 455	45 244	44 594
140.1	104 976	1.041	109 243	107 767	44 452	44 148
160.0	109 454	1.061	116 160	105 285	45 814	43 541
179.8	88 691	1.085	96 197	102 053	42 134	42 763
199.8	88 910	1.110	98 718	98 185	42 728	41 821
219.7	81 790	1.137	93 026	93 951	41 731	40 762
239.6	75 262	1.165	87 706	89 564	42 926	39 626
259.7	69 915	1.194	83 492	85 145	37 666	38 439
279.6	68 183	1.223	83 401	80 895	35 425	37 251
299.9	61 637	1.253	77 234	76 764	35 142	36 051

Table 2. Results for the same NaF:Li additively coloured sample investigated after about a week. The nomenclature is the same as in table 1.

T (K)	$I(M_1)$ (a.u.)	$H(T)/H(0)$	$I_{corr}(M_1)$ (a.u.)	$I_{int}(M_1)$ (a.u.)	$I(M_F)$ (a.u)	$I_{int}(M_F)$ (a.u.)
21.22	111 279	1.000	111 279	112 412	56 825	56 578
35.59	112 376	1.000	112 376	109 300	56 913	56 046
49.07	108 613	1.000	108 613	108 010	54 929	55 805
63.43	106 610	1.001	106 696	107 204	54 287	55 654
80.33	105 178	1.004	105 558	106 462	54 982	55 496
100.2	101 729	1.011	102 856	105 369	54 790	55 203
119.9	105 250	1.024	107 711	103 702	55 488	54 676
140.0	96 229	1.041	100 130	101 297	54 187	53 866
159.8	93 714	1.061	99 442	98 331	52 710	52 798
179.8	83 709	1.085	90 793	94 945	52 055	51 536
200.1	83 347	1.110	92 580	91 276	49 999	50 098
220.0	75 412	1.137	85 798	87 666	49 935	48 636
239.8	76 227	1.165	88 850	84 149	48 560	47 172
259.8	66 224	1.194	79 092	80 767	45 328	45 715
279.8	66 116	1.223	80 890	77 585	43 711	44 312
301.2	56 694	1.253	71 146	74 421	41 745	42 884

with our experiments.

Let us analyse the two different kinds of energy transfer which could be here considered:

radiative and non-radiative. The radiative transfer between two centres (transmitting and receiving) occurs when there is an appreciable overlap of the emission band of the transmitting centre (primary luminescence) and the absorption of the receiving centre (with a subsequent secondary luminescence): it is often referred to as 'trivial' since it implies a 'cascade' mechanism through the emission and reabsorption of photons. The radiative transfer does not imply change of the transmitting and receiving centre lifetime: a typical example is the energy transfer between M and M^+ centres in x-ray coloured NaF investigated and characterized by Bosi [27]. Since the F emission band and M absorption band scarcely overlap in NaF (as well as in KCl, RbCl and KBr), this kind of transfer is practically negligible.

The non-radiative transfer (described by Dexter [12]) could, in principle, be efficient even if the overlap between F emission and M absorption bands is small: furthermore, its probability depends on the concentration of the receiving centres (i.e. M centres). Starting from an experimental point of view, we rule out the possibility of non-radiative transfer *after* the F-centre relaxation, as follows. The F-centre lifetime does not depend on the F-centre concentration, nor on the presence of the M centres (whatever M concentration is employed): this rule was found to be valid for any alkali halide investigated (see the papers of Bosi *et al* here cited). Moreover the probability of a non-radiative transfer $1/\tau_{tr}$ might introduce a competitive channel on the decay mechanism of the F centre after relaxation: as well known, the reciprocal of the F-centre lifetime $1/\tau(T)$ is the sum [22] of a radiative term $1/\tau_R(T)$ and of a thermal de-excitation term $(1/\tau_0)\exp(-\Delta E/kT)$.

As a consequence, the presence of such a new competitive channel for the F-centre decay should produce a dramatic effect (if the non-radiative transfer exists) on the M-centre luminescence quantum yield in the $T < 150$ K region when the experiment employing M_F excitation light is performed. This occurrence was not observed either in NaF (present work) or in KCl [9].

In our opinion there is a possibility of reconciling our results with those of De Kinder *et al* [16], i.e. to suppose the existence of an F- to M-centre energy transfer *before* or *during* relaxation. This occurrence was expressly disregarded by De Kinder *et al* [16]: unfortunately, their statement was made not on the basis of experimental results but only on the basis of conclusions derived from a theory of different authors [28].

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