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COLOUR CENTRES LIFETIME MEASUREMENTS USING SYNCHROTRON RADIATION AND PHASE FLUOROMETRY

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The measurements of emission lifetime and time-resolved spectroscopy have been of great importance in understanding the properties of electronic excited states of defects in insulating crystals[1].

In this communication we present the first application of the phase and modulation method[2,3] to the physics of colour centres.

If we excite a fluorescent sample with a sinusoidally intensity modulated light beam at frequency ν also the intensity of the emitted radiation will be modulated at the same frequency but shows a phase shift φ with respect to the exciting beam and a modulation μ (the ratio between the a.c. and d.c. part of the signal) smaller than that of the excitation.

The phase shift φ and the ratio $M=\mu_{em}/\mu_{exc}$ contain all the informations about the emission response function, $I(t)$, of the system.

The most general expressions for φ and M are given by:

$$\tan\varphi = S(\omega)/G(\omega) \ , \qquad M = (S^2(\omega) + G^2(\omega))^{1/2} \tag{1}$$

where $S(\omega)$ and $G(\omega)$ are the sine and cosine Fourier transforms of the emission response function[4],

$$S(\omega) = \int_0^\infty I(t) \sin(\omega t)\, dt \Big/ \int_0^\infty I(t)\, dt \ ,$$

$$G(\omega) = \int_0^\infty I(t) \cos(\omega t)\, dt \Big/ \int_0^\infty I(t)\, dt.$$

In the case of an emission response function of the form $I(t) =$

$= \Sigma_i \alpha_i e^{-t/\tau_i}$ the expressions (1) can be written as

$$\tan\varphi = \Sigma_i \left[f_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2} \right] \Big/ \Sigma_i \left[f_i \frac{1}{1+\omega^2\tau_i^2} \right] ,$$

$$M = \left[\left(\Sigma_i f_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2} \right)^2 + \left(\Sigma_i f_i \frac{1}{1+\omega^2\tau_i^2} \right)^2 \right]^{1/2} , \qquad (2)$$

and $f = \alpha_i \tau_i$.

From the knowledge of φ and M at different frequencies we can obtain the unknown lifetimes τ_i by means of fitting procedures based on non-linear least-squares analysis[5] that use expressions (2) with τ_i and f_i as free parameters.

Since we need to know φ and M at different frequencies, it is important to have an exciting light source that easily produces intensity modulation of the beam at several frequencies. A high repetition rate pulsed light source, such as synchrotron radiation, has a large number of modulation frequencies simultaneously present. The light beam time structure shows equally spaced (period t_o), very narrow gaussian pulses of half width σ. The Fourier transform of this particular time structure consists of a discrete set of frequencies multiple of the fundamental revolution frequency ($\nu_o = 1/t_o$) of the electrons inside the storage ring. The intensity of these harmonics decreses with a gaussian envelope of half width $1/\sigma$[6].

Since the source is intrinsically modulated at all the harmonics of the fundamental frequency, the luminescence signal contains at the same time in all the harmonics the information on the emission response function. The relevant experimental quantities, φ and M, at each harmonic are obtained by using a special electronic "cross-correlation" technique[7].

With this technique we have measured the lifetime of several colour centres in NaF, namely the F, F_2, F_3^+ centres, reported in Table I at 85K.

TABLE I

Centre	lifetime (ns)	
	this measurement	Refs.(8,9)
F	51 ± 2	55
F_2	10.2 ± 0.2	12.3 ± 1
F_3^+	8.55 ± 0.05	----

The data for F and F_2 centres are in good agreement with those reported in literature[8,9]. The lifetime of the F emission has been never measured before.

In general the reported lifetime of the F_3 centre is longer than that of the F_2 centre[10]. The shorter value that we have measured for the F_3^+ centre indicates that in the ionized centre the electrons are less coupled to the lattice and the relaxed excited state is rather compact so that the transition probability to the ground state is closer to the value observed in molecules. The small electron-lattice coupling in the aggregate centres, particularly in NaF, is confirmed by the observation of a narrow zero-phonon line associated with F_3^+[11].

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