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Determination of the oscillator strength of F centres in KBr–In by photostimulated luminescence

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Abstract. Using the photostimulated luminescence of {F–In²⁺} defect pairs in KBr–In a very sensitive method for the determination of the oscillator strength of F centres has been proposed. Its main advantage is that there is no need to know any absorption characteristics nor the concentration of F centres. Some criteria for the applicability of this method are analysed.

1. Introduction

In the physics of colour centres, the oscillator strength f defining the absorption transition probability is a very informative characteristic for any local centre. The practical importance of the oscillator strength determination arises because, if it is known, one can obtain the concentration N of the centres under study in a particular sample by means of the well known Smakula formula [1]

$$Nf = \frac{mc}{2\pi^2 e^2 h} \sqrt{\epsilon_0} \left(\frac{E_0}{E_{\text{eff}}} \right)^2 \int \kappa(\hbar\omega) d(\hbar\omega) \quad (1)$$

where ϵ_0 is the dynamical dielectric constant, E_0 the average field in the medium, E_{eff} the effective field acting on the colour centre and $\kappa(\hbar\omega)$ the absorption coefficient. The value of the integral in equation (1) depends on the band shape. Whatever the actual shape of the spectrum is, we may write

$$\int \kappa(\hbar\omega) d(\hbar\omega) = S \kappa_M H$$

where κ_M (cm⁻¹) is the peak value of the absorption band, H (eV) its half-width and S the shape factor. It is well known that S is $\frac{1}{2}\pi = 1.57$ for the Lorentzian shape and $\frac{1}{2}(\pi/\ln 2)^{1/2} = 1.07$ for the Gaussian shape [1, 2].

From the experimental point of view, the determination of f consists of the determination of the number N of the colour centres by methods independent of the absorption measurements [1, 3, 4]. There are several methods for direct determination of N : measuring the magnetic susceptibility [5] or electron spin resonance [6], a variety of chemical methods [2, 3, 4] and some other techniques [1, 4].

Since F centres have been studied much more than other colour centres, we focus our attention on them in this paper.

In this paper a new optical procedure for the measurement of the oscillator strength of F centres in alkali halides doped with ns^2 ions A^+ ($\equiv \text{In}^+, \text{Tl}^+, \text{Ga}^+$, etc) is proposed and applied to the UV-irradiated KBr-In crystals. Its main advantage is that there is no need to know any absorption characteristics (such as κ_M and H) nor the concentration of F centres. The proposed method is based on the phenomenon of the photostimulated luminescence (PSL) in preliminary irradiated alkali halides doped with ns^2 ions [7–11] and some other ions (e.g. Eu) [12]. At present it is well known that the PSL in these crystals is due to {F- A^{2+} } defect pairs, e.g. {F- In^{2+} } [7–9], {F- Tl^{2+} } [9, 10], {F- $\text{Pb}^{3+}\text{V}_\text{c}$ } [11] and {F- Eu^{3+} } [12].

Work on the {F- A^{2+} } pairs in alkali halides has been in progress for some years and a considerable amount of data reflecting their properties has been amassed [7–19].

{F- A^{2+} } pairs can be created either by optical creation of excitons in the fundamental exciton absorption band [7, 8, 11, 13, 16–18] or by x-ray [9, 10, 11, 15, 19] and electron irradiation [11].

In order to destroy {F- A^{2+} } pairs the crystal is illuminated by light into the F band (hereafter called F light). Owing to the absorption which is characterized by the optical cross section σ , the F-centre electrons are excited and captured by the A^{2+} centre. This capture is accompanied by the PSL. It seems that the mechanism of this electron transfer between the F centre and A^{2+} centre nearby is stimulated tunnelling from an excited F centre [10, 12, 14]. This is also the case for the PSL in europium-activated mixed halide crystals, such as BaFX:Eu (X \equiv Cl, Br) [15, 16].

The basic principles of the method proposed here are described below. Then the detailed experimental procedure and results are presented. Finally, conclusions and some comments are given.

2. The method proposed

Following tradition [1, 3] we use equation (1) with the Lorentz local field [1, 3, 6] and a Lorentzian shape of the absorption band. In this case, equation (1) may be rewritten in the following way:

$$f = 1.29 \times 10^{17} (1/N_F) [n/(n^2 + 2)^2] \kappa_M H. \quad (2)$$

In order to determine f by means of equation (1) it is necessary to know three experimental characteristics: N_F , κ_M and H . Now let us remember that κ_M and N_F are related by the equation

$$\kappa_M = \sigma_M N_F \quad (3)$$

where σ_M is the effective absorption cross section in the absorption band peak. Then from equations (2) and (3) we easily obtain

$$f = 1.29 \times 10^{17} [n/(n^2 + 2)^2] \sigma_M H. \quad (4)$$

A great advantage of equation (4) comes from the fact that f is a function of only *two* experimentally determined characteristics of local centres—in contrast with the Smakula formula (2) where, in order to determine f , *three* characteristics (N_F , H and κ_M) are required. Thus, equation (4) may be used to determine f if one can determine the effective absorption cross section by means of an independent procedure. Below, such a procedure based on the PSL phenomenon is given.

From our previous experiments [7, 8, 11, 18] on exciton-produced close F and A^{2+} centres the decay time τ of optical recovery of the PSL using constant F light depends on

the F-light intensity as follows: $\tau \sim 1/I_F$. Moreover, the monitored luminescence signal is a superposition of several (one, two or three) experimental decay components [14, 16]. The decay time τ_i of each component depends on the F-light intensity as follows:

$$\tau_i = 1/\sigma_i I_F \quad (5)$$

where σ_i are the effective absorption cross sections of the components. The conclusion suggests that the absorption process of the F proton should be the slowest in the PSL recovery process [14, 17, 18].

Now our purpose is to investigate this dependence (5) for KBr-In crystals irradiated in the fundamental exciton absorption band, paying special attention to the quantitative estimation of σ for F centres entering the {F-In²⁺} pairs.

3. Experimental procedure

The crystal KBr-In was grown by the Stockbarger method in our laboratory. The concentration of In⁺ was estimated to be $9 \times 10^{16} \text{ cm}^{-3}$. The crystal was placed in a special box and UV irradiation was performed with an LDD-400 lamp. The UV light from the LDD-400 lamp passed through an SPM-1 monochromator before entering the crystal. The UV light power was monitored with a PTH-30 thermoelement. To excite the PSL the irradiated crystal was illuminated with a He-Ne laser or halogen lamp in combination with an interference filter. The PSL (430–530 nm) was detected with a photomultiplier and its decay time was recorded with an ENDIM-662.01 recorder.

For our purpose it was necessary first of all to obtain a highly homogeneous coloration of the crystal. This required the use of a spatially uniform UV light intensity as well as a sufficiently thin ($d = 0.028 \text{ cm}$) crystal sample. In order to provide a more uniform distribution of F centres along the exciton penetration depth the crystal was irradiated equally on both sides. For this procedure a special turning mechanism was made. Estimations show that the unevenness of the F-centre distribution along the depth is approximately 20%. This unevenness can be allowed because the value of the concentration is of an illustrative character and is not used for definition of σ by means of (5).

In order to determine the optical absorption cross section by means of (1) it is necessary to have a constant stimulated F-light intensity I_F in the irradiated crystal. An appropriate method has been described in [14, 18].

4. Results

After the UV irradiation ($\lambda = 200 \text{ nm}$; intensity $I_\lambda = 4.2 \times 10^{10} \text{ photons cm}^{-2} \text{ s}^{-1}$) of the KBr-In crystal with a dose in the range 1.0×10^{12} – $6.0 \times 10^{13} \text{ photons cm}^{-2}$, the PSL decay reveals only an exponential component. It is shown in figure 1 for a UV dose D of $8.4 \times 10^{12} \text{ photons cm}^{-2}$ and $I_F = 9.2 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$. The corresponding decay time τ of this component and σ calculated by means of equation (5) are shown in table 1 for a series of absorbed doses D . As follows from table 1 the value σ defined by us is in good agreement with that obtained in terms of the standard absorption methods [2, 19]. This coincidence of the σ -values indicates that the exponential component of the PSL observed for doses in the range 1.0×10^{10} – $6.0 \times 10^{13} \text{ photons cm}^{-2}$ is directly connected with the F centres.

Now we need to know the value of H to put in equation (4). The value of H may be

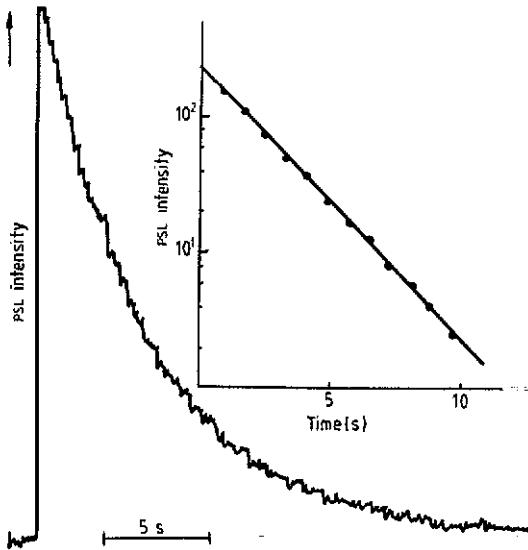


Figure 1. The PSL decay curve of the UV-irradiated KBr-In ($\lambda = 200$ nm; $I = 8.4 \times 10^{12}$ photons cm^{-2}) under F-light illumination ($I_F = 9.2 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1}$). In the inset this decay curve is plotted on a semilogarithmic scale; $\lambda_F = 632.8$ nm.

Table 1. Decay time τ of the PSL recovery and calculated effective absorption cross section σ of F centres in KBr-In for a series of doses D .

N	D (photons cm^{-2})	τ (s)	σ (10^{-16}cm^2)	Reference
1	1.0×10^{12}	5.4	2.0	Present work
2	5.0×10^{12}	5.4	2.0	Present work
3	8.4×10^{12}	5.4	2.0	Present work
4	5.0×10^{13}	5.4	2.0	Present work
			2.0	[2]
			2.0	[17]

found from the stimulation spectrum. It was measured for the KBr-In crystal after the UV irradiation ($D = 8.4 \times 10^{12}$ photons cm^{-2}) utilizing the PSL experiment at selected stimulation wavelengths. The calculated optical cross section as a function of the stimulating light energy for the F component is presented in figure 2. The stimulation spectrum peaks at 1.97 eV with a half-width $H = 0.32$ eV. It is similar to the absorption spectra published earlier [18] except that in our case it is slightly narrower. We ascribe this to our more precise determination of the band half-width, since it is obvious that in absorption measurements the aggregate centre bands are covered by the F band and they distort its shape [17, 21, 22].

Now, when the σ_M^- and H -values have been obtained from the PSL stimulation experiments, we may calculate f by means of equation (4). Substituting $\sigma_M^- = 2.0 \times 10^{16} \text{cm}^2$, $H = 0.32$ eV and $n = 1.559$ [3, 4] into equation (4) we get $f = 0.66$. This result is shown in table 2 together with all previous published data on f for KBr-In crystals.

Approximate values of the F-centre densities are also shown; for our case the value $N_F \approx 10^{12} \text{cm}^{-3}$ was estimated in the same way as in [18].

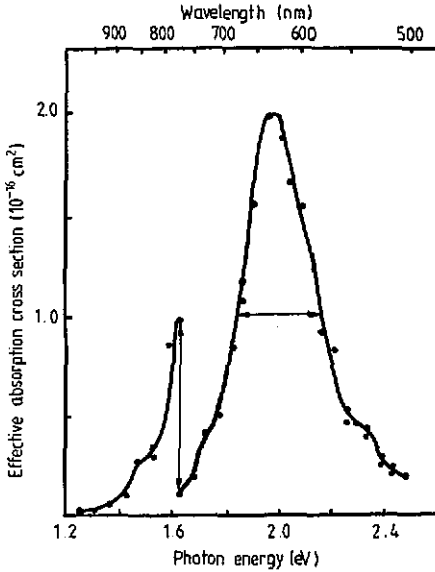


Figure 2. Optical excitation cross section of F-centre electrons for KBr-In plotted as a function of the stimulating light energy.

Table 2. Oscillator strength f of F centres in KBr crystals, determined by different methods. The values of F-centre densities characterizing the sensitivity of each method are listed.

Method	F-centre density (cm^{-3})	f	Reference
Magnetic susceptibility	10^{17}	0.71	[5]
Chemical	10^{17}	0.85	[2]
Chemical	10^{17}	0.72	[3, 4]
PSL	10^{12}	0.66	Present work

5. Concluding comments

A new method for determining the oscillator strength of the F centres which are located in the form of close {F-In²⁺} defect pairs in KBr-In is proposed.

The distance between the F and In²⁺ centres varies from $4a$ to $8a$, where a is the lattice constant of KBr [14].

The method proposed is very sensitive owing to its capability for detecting a very low defect concentration (down to 10^{12} cm^{-3}). For example, in our experiments when $D = 1.0 \times 10^{12} \text{ photons cm}^{-2}$ the concentration of stable F centres generated is not more than 10^{12} cm^{-3} [7, 14, 18].

Unfortunately, the method proposed is not universal since it could be applied to activated crystals only and it fails if applied to those containing non-luminescence impurities. The method can work only in the case when electron colour centres are paired with appropriate hole centres.

In this paper we consider the case of exciton defect creation when {F-In²⁺} pairs are

produced. The method suggested cannot be applied to other defect creation mechanisms without careful checking, e.g. electron-hole defect creation or F-centre creation in alkali halides activated with ns^2 ions by thermo-optical ionization in activator C-band irradiation. When a KBr-In crystal is irradiated in the activator C band ($\lambda = 245$ nm), the Schottky vacancies capture electrons, thus creating F centres. In this case {F-In $^{2+}$ } pairs are non-existent and the corresponding decay time τ of optical recovery of the PSL using constant F light ($I_F = 9.2 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1}$) equals $\tau_c = 450$ s. This value probably reflects a succession of repeated processes, namely F-centre excitation, F-centre ionization, electron capture by an anion vacancy, repeated F-centre excitation and so on until electron capture occurs in the anion vacancy which is situated close to the A^{2+} centre [14, 18]. A number of such repeated processes could be estimated as $n = \tau_c/\tau = 450/5.3 \approx 85$ [18].

The method can also be applied in the case when electron colour centres are paired with self-trapped holes V_k , e.g. $\{A^0-V_k\}$ where A^0 ($\equiv Ag^0, Na^0, Tl^0$, etc) is the electron centre.

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References

- [1] Smith D Y and Dexter D L 1972 *Prog. Opt.* **10** 165
- [2] Doyle W T 1958 *Phys. Rev.* **111** 1072
- [3] Bosi L, Fantola-Lazzarini A L, Lazzarini E, Margiliano Ramaglia V and Tagliacozzo A 1975 *Phys. Status Solidi b* **69** 519
- [4] Bosi L, Fantola-Lazzarini A L and Lazzarini E 1974 *Phys. Status Solidi b* **66** 285
- [5] Rauch C Y and Heer Y C V 1957 *Phys. Rev.* **105** 914
- [6] Selsbee R H 1956 *Phys. Rev.* **103** 1675
- [7] Kalniņš R, Pļaviņa I and Tāle A 1984 *Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tekh. Nauk* **4** 59
- [8] Pļaviņa I 1986 *Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tekh. Nauk* **4** 26
- [9] Nagli L E 1985 *Sov. Phys. Solid State* **27** 2819
- [10] Nagli L E 1985 *Phys. Status Solidi b* **127** 319
- [11] Vlasov G, Kalniņš R, Nagli L E, Obedkov V, Pļaviņa I and Tāle A 1980 *Avtometriya* **1** 66
- [12] Murrieta H S, Medrano C P, Rubio Y O, Mladenova M and Georgiev M 1987 *Cryst. Lat. Defects Amorph. Mater.* **17** 1297
- [13] Nagli L E and Dyachenko S V 1986 *Soviet Phys. Solid State* **28** 3570
- [14] Kalniņš A, Pļaviņa I, Popov A I and Tāle A 1989 *Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tekh. Nauk* **4** 3
- [15] Seggern H, Voigt T, Knüpfer W and Lange G 1988 *J. Appl. Phys.* **64** 1405
- [16] Seggern H, Voigt T and Schwartzmichel K 1988 *Siemens Research Development Report No. 17*, p 124
- [17] Kalniņš A, Pļaviņa I, Popov A I and Tāle A 1988 *Izv. Akad. Nauk Latv. SSR, Ser. Fiz. Tekh. Nauk* **4** 9
- [18] Kalniņš A, Pļaviņa I, Popov A I and Tāle A 1990 *Phys. Status Solidi b* **160** 1
- [19] Seggern H, Meijerink A, Voigt T and Winnacker A 1989 *J. Appl. Phys.* **66** 4418
- [20] Parker Y H 1961 *Phys. Rev.* **124** 703
- [21] Fowler W B 1968 *Physics of Colour Centres* (New York: Academic) p 628
- [22] Compton W D and Rabin H 1964 *Solid State Physics* vol 16 (New York: Academic) p 121