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Spectroscopic properties of $(F_2^+)_{\text{H}}$ centres in oxygen-, sulphur- and selenium-doped alkali halides

A El Akrimi†, P Ketolainen‡, J L Doualan, E Kawa§, J Margerie§ and B Rocher

Laboratoire de Spectroscopie Atomique, ERS 137 du CNRS, Institut des Sciences de la Matière et du Rayonnement, 6 boulevard Maréchal Juin, 14050 Caen Cédex, France

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Abstract. Laser-active (or potentially laser-active) $(F_2^+)_{\text{H}}$ centres have been investigated in NaCl:O²⁻, NaCl:S²⁻, NaCl:Se²⁻, KCl:O²⁻, KCl:S²⁻, KBr:O²⁻, KBr:S²⁻, KI:O²⁻, KI:S²⁻ and RbCl:O²⁻. In four of these crystals, $(F_2^+)_{\text{H}}$ centres were previously either entirely unknown or only allusively mentioned in the literature. Preparation procedures are described; absorption and emission spectra are studied, including zero-phonon lines when they exist. The stability of the centres in the dark at room temperature is also measured, since it is an important property for the eventual use of these centres as the active element of tunable lasers.

1. Introduction

F_2^+ centres in alkali halides are valuable laser materials (Mollenauer 1977, 1987), but they suffer from poor stability under intense pumping light; even at 77 K, the bivalencies reorient repeatedly and therefore perform a random walk through the lattice until they are finally captured by some other defect and become unavailable for laser emission. Since 1977, remedies for this problem have been actively searched for. Up to now, the best are the binding of the bivalency by a neighbouring substitutional O²⁻ anion (Pinto *et al* 1986) or by both an O²⁻ anion and a substitutional foreign alkaline cation (Wandt and Gellerman 1987). One thus obtains the so-called $(F_2^+)_{\text{H}}$ and $(F_2^+)_{\text{AH}}$ centres, respectively. $(F_2^+)_{\text{AH}}$ centres will be further discussed in a companion paper (El Akrimi *et al* 1994). The $(F_2^+)_{\text{H}}$ centre has been extensively studied in NaCl:OH⁻ or NaCl:O²⁻ where it is a very valuable laser-active element for the 1.45–1.75 μm wavelength range (Gellerman (1991) and references therein). $(F_2^+)_{\text{H}}$ centres in KCl:O²⁻ and KBr:O²⁻ have also been described in detail by Wandt *et al* (1987); the same centres in KI:O²⁻ and RbCl:O²⁻ were briefly studied by Girard and Doualan (1993). Moreover, it was soon noted that other divalent ions such as S²⁻ or Se²⁻ might have a stabilizing effect comparable with O²⁻. In the present paper, $(F_2^+)_{\text{H}}$ centres for which the stabilizing substitutional impurity is an oxygen, sulphur or selenium ion will be called for brevity $F_2^+:\text{O}^{2-}$, $F_2^+:\text{S}^{2-}$, or $F_2^+:\text{Se}^{2-}$, respectively. $F_2^+:\text{S}^{2-}$ centres in NaCl were amply described by Suzuki *et al* (1992) and by Casalboni *et al* (1992), while Gellerman (1991) mentions, without any detail, the observation of $F_2^+:\text{S}^{2-}$ centres in NaCl, KCl and KBr.

† Present address: Département de Physique, Université d'Annaba, BP 12, 23000 Annaba, Algeria.

‡ Permanent address: Physics Department, University of Joensuu, Postal Box 111, SF 80101 Joensuu, Finland.

§ Also at UFR de Sciences, Université de Caen, 14032 Caen Cédex, France.

The purpose of the present paper is to report observation of $F_2^+ : Se^{2-}$ centres in NaCl and of $F_2^+ : S^{2-}$ centres in KI, to describe the spectroscopic properties of $F_2^+ : S^{2-}$ centres in KCl and KBr, to add a few new details about $F_2^+ : O^{2-}$ centres in KI and RbCl and to compare all these data with the corresponding data for the well known $(F_2^+)_H$ centres, namely $F_2^+ : O^{2-}$ in NaCl, KCl, KBr and $F_2^+ : S^{2-}$ in NaCl.

Section 2 describes the preparation of samples. Section 3 deals with their absorption and emission spectra at 100 and 5 K, including zero-phonon lines when they are observed. Section 4 is concerned with the room-temperature stabilities in the dark of the different $(F_2^+)_H$ centres. Finally section 5 compares the experimental data and attempts are made to interpret them semi-empirically.

2. Preparation of samples

The crystals were grown in our laboratory by the Czochralski method out of a platinum crucible in a controlled atmosphere. The initial materials are alkali halide powders (Merck Suprapur), Na_2O_2 (Strem Chemicals, 93% purity), KO_2 (Johnson-Matthey, 96.5% purity) and Na_2S , K_2S and Na_2Se (Cerac, 99.9% purity). Table 1 summarizes the crystal growth parameters. When the doping is a superoxide (Na_2O_2 or KO_2), a partial pressure of oxygen is compulsory to prevent its thermal decomposition. It is well known (see, e.g., Wandt *et al* (1987)) that $F_2^+ : O^{2-}$ centres in NaCl may be formed equally well from OH^- or O_2^- doped crystals. Indeed, we found no significant difference between the parameters of $F_2^+ : O^{2-}$ centres obtained with either kind of doping.

After cleaving parallelepipeds of the desired dimensions (typically 10 mm \times 10 mm \times 2 mm) from the boules, the second step of the preparation is additive coloration of these platelets which is performed in a heat pipe device similar to that used by Mollenauer (1978). Coloration is somewhat more difficult for oxygen-doped alkali halides than for the corresponding pure crystals. Table 1 lists the coloration temperatures, vapour pressures and durations, together with the alkali metal used. Cooling of the sample after the coloration is not very rapid so that troublesome colloids develop. In order to remove them, we wrap the sample in a thin (0.05 mm) stainless steel foil, heat it for a few minutes at approximately 100°C below the melting point and quench it on a copper block at room temperature.

At this stage, the sample contains many F centres and $O^{2-} - \square$ (or $S^{2-} - \square$ or $Se^{2-} - \square$) defects, but very few $(F_2^+)_H$ centres. They must be obtained by aggregation of the two above-mentioned species (see, e.g., Gellermann (1991)); a suitable luminous irradiation near room temperature ionizes a F centre, the resulting anionic vacancy diffuses through the lattice until it meets an $O^{2-} - \square$ centre, an electron is captured by the system and a $(F_2^+)_H$ centre is thus obtained (see, for instance, curve 1 in figure 1 showing the absorption spectrum of NaCl:Se²⁻). This operation should be performed at a suitable temperature; if it is too low, anion vacancies do not diffuse at all, but, if it is too high, $(F_2^+)_H$ centres are thermally dissociated and one chiefly obtains other F-centre aggregates. Table 2 gives, for each crystal and doping, the irradiation wavelength and the temperature which we chose for this photoaggregation process, as well as the duration of the irradiation (with the light beam of an Osram HBO 100 high-pressure mercury lamp, filtered by a Schott Monochromat filter† and focused by an $f/4.5$ lens.)

This irradiation took place in a home-made liquid-nitrogen cryostat, with the sample fixed on a copper plate, linked to the cold finger by a copper cylinder 4 mm in diameter and

† For some crystals, unfiltered light was used, including the 365 nm mercury lines. In these cases, the F band was observed to grow further, in addition to the appearance of $(F_2^+)_H$ -centre absorption.

Table 1. Crystal growth and coloration. The impurity content is given in molar parts per million in the initial powder, since the concentration in the final crystal is unknown in most cases.

	Growth				Coloration			
	Impurity nature	Impurity concentration (ppm)	Atmosphere	Alkali metal	Temperature ($^{\circ}$ C)	Pressure (Torr)	Duration (h)	
NaCl:OH^-	NaOH	500	Ar	Na	600-700	40-70	2-3	
NaCl:O^{2-}	Na_2O_2	500	Ar+ O_2	Na	600-700	40-70	2-3	
NaCl:S^{2-}	Na_2S	170	Ar	Na	600-700	40-70	2-2.5	
NaCl:Se^{2-}	Na_2Se	170	Ar	Na	600-700	40-70	2-2.5	
KCl:O^{2-}	KO_2	466	Ar+ O_2	K	650	50-70	1.5-2	
KCl:S^{2-}	K_2S	86	Ar	K	650	50-70	2-3	
KBr:O^{2-}	KO_2	455	Ar+ O_2	K	600	10-30	0.5	
KBr:S^{2-}	K_2S	64	Ar	K	600	10-30	1-1.5	
KIO^{2-}	KO_2	500	Ar+ O_2	K	550-600	20-30	0.5-0.75	
KIS^{2-}	K_2S	86	Ar	K	600	30	0.75-1	
RbCl:O^{2-}	KO_2	436	Ar+ O_2	K	550	20-30	0.5-0.75	

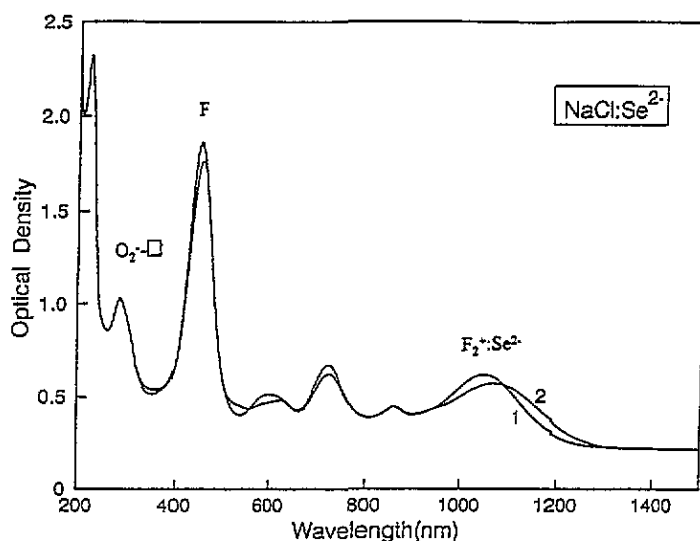


Figure 1. Absorption spectra of NaCl:Se^{2-} at 100 K: curve 1, after 10 min room-temperature irradiation with unfiltered light from a high-pressure mercury lamp; curve 2, after subsequent 20 min, 100 K, 436 nm irradiation.

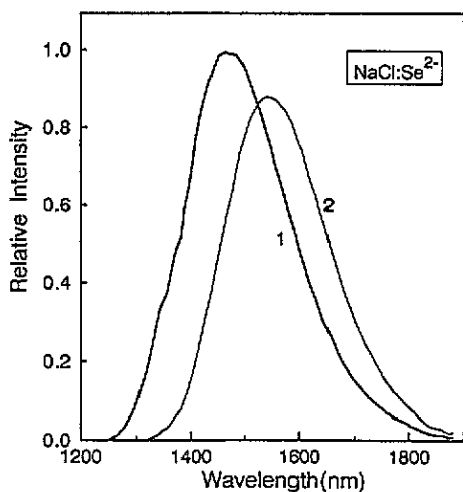


Figure 2. Emission spectra of $(\text{F}_2^+)_\text{H}$ centres in NaCl:Se^{2-} at 100 K: curve 1, type (a) centres; curve 2, type (b) centres.

35 mm long. A heating resistor, a thermal sensor and a servo-loop allowed us to regulate the sample temperature at any desired value between cryogenic temperatures and 295 K. However, since the copper plate was not in direct contact with the liquid-nitrogen bath, the lowest temperature obtained (without electric current in the heater) was 100 K. The same cryostat was also used for most experiments in sections 3 and 4 (with the exception of 5 K measurements, of course). This explains why most of our spectroscopic data are at 100 K. The shifts in the absorption and emission bands between 77 and 100 K are small enough to allow valuable comparison of our results at 100 K with those of other workers at 77 K.

In many crystals, $(\text{F}_2^+)_\text{H}$ centres are of two types with significantly different absorption and emission wavelengths (compare curves 1 and 2 of figures 1 and 2): type (a) which is obtained after photoaggregation near room temperature and which is metastable at liquid-

Table 2. Photoaggregation and, should the case arise, (F_2^+) (a) \rightarrow (b) photoconversion. In the third column, HBO means unfiltered light from a mercury high-pressure lamp.

	Photoaggregation			(a) \rightarrow (b) conversion at 100 K	
	Temperature (°C)	Wavelength (nm)	Duration (min)	Wavelength (nm)	Duration (min)
NaCl:OH ⁻ or O ²⁻	20	HBO	10–15	436	20
NaCl:S ²⁻	20	HBO	10–15	436	20
NaCl:Se ²⁻	20	HBO	10–15	436	20
KCl:O ²⁻	-10	546	10–15	$(F_2^+)_{\text{H}}$ converted into F_2^+ by 365 or 436 nm	
KCl:S ²⁻	-10	546	10–15	$(F_2^+)_{\text{H}}$ converted into F_2^+ by 365, 436 or 546 nm	
KBr:O ²⁻	-10	546	15	365, 436 or 546	2
KBr:S ²⁻	-8	546	15	No shift by 100 K irradiation ^a	
KI:O ²⁻	-5	365	15	546	5
KI:S ²⁻	-5	365	15	No effect of 100 K irradiation ^a	
RbCl:O ²⁻	-20	546	10	No effect of 100 K irradiation ^a	

^a The absence of (a) \rightarrow (b) conversion has been checked for each of the three following mercury lines: 365, 436 and 546 nm.

nitrogen temperature; type (b) which is stable at low temperatures, but unstable at 295 K.

One converts type (a) into type (b) by suitable 'F-light' irradiation[†] at approximately 77 K. Light irradiation at liquid-helium temperature does not perform the (a) \rightarrow (b) transformation, which shows that it is thermally activated, as noted by Gellermann (1991); in the case of NaCl:OH⁻, the phototransformation was found to be impossible below about 70 K. Table 2 contains the relevant parameters for the (a) \rightarrow (b) transformation. It should be emphasized, however, that the behaviour of $(F_2^+)_{\text{H}}$ centres under low-temperature 'F-light' irradiation is not universal. From this point of view, one may classify $(F_2^+)_{\text{H}}$ centres into three groups.

(i) The first contains the centres for which both type (a) and type (b) are observed as described above: $F_2^+:\text{O}^{2-}$ in NaCl, KBr and KI; $F_2^+:\text{S}^{2-}$ and $F_2^+:\text{Se}^{2-}$ in NaCl.

(ii) In the second group, $(F_2^+)_{\text{H}}$ centres are observed only under type (a). 77 or 100 K irradiation with 'F light' converts these centres into F_2^+ , which is rather odd: where has the O²⁻ or the S²⁻ ion gone? This is the case of $F_2^+:\text{O}^{2-}$ and $F_2^+:\text{S}^{2-}$ centres in KCl.

(iii) We observed that 100 K 'F-light' irradiation has no effect at all on the $F_2^+:\text{O}^{2-}$ centre of RbCl and on the $F_2^+:\text{S}^{2-}$ centre of KI. In the case of the $F_2^+:\text{S}^{2-}$ centre of KBr, it does not shift the absorption and emission bands appreciably, but it increases their intensities significantly. For these three $(F_2^+)_{\text{H}}$ centres, types (a) and (b), if they both exist, have very similar spectroscopic properties.

We were unable to find a simple rule to predict whether the behaviour of an $(F_2^+)_{\text{H}}$ centre under 100 K 'F-light' irradiation will belong to class (i), (ii) or (iii) above. Table 2 shows that it is neither purely a matter of the crystalline matrix, nor purely a matter of the nature of the divalent anion. KCl seems to stand apart, since behaviour (ii) has until now been observed only in KCl:O²⁻ and in KCl:S²⁻. It would be interesting to try KCl:Se²⁻. For the other matrices, one can meet either behaviour (i) or (iii), with the latter perhaps slightly favoured by S²⁻ doping (but this behaviour is not observed in NaCl:S²⁻, while it is in RbCl:O²⁻).

[†] In fact, this transformation uses the transition from the ground to the second excited state of $(F_2^+)_{\text{H}}$ centres, which turns out to be in the vicinity of the F band.

3. Absorption and emission spectra of $(F_2^+)_{\text{H}}$ centres

3.1. Broad bands

The hydrogen molecular ion model (Aegerter and Lüty 1971) may be extended from F_2^+ to $(F_2^+)_{\text{H}}$ centres. In this model, the longest-wavelength absorption band is called $1s\sigma_g \rightarrow 2p\sigma_u$ and, of course, the corresponding emission band is $2p\sigma_u \rightarrow 1s\sigma_g$. We plot in table 3 the values that we measured for the peak wavelengths of these two bands at 100 and 5 K. 100 K values are compared with the 77 K positions published by other workers, when available; discrepancies are moderate, and they give an idea of measurement uncertainties. We observed that our own results are not perfectly reproducible from sample to sample. This may arise from at least two causes.

(1) For absorption spectra, there is some uncertainty concerning the background correction, which can be especially important when $(F_2^+)_{\text{H}}$ bands are broad and weak.

(2) $(F_2^+)_{\text{H}}$ (a) may not be a single centre but a mixture of two or several different species, the relative concentrations of which could differ from experiment to experiment, leading to the observed 'random' variations in spectra. We have indeed noticed a few indications of the existence of such mixtures. For instance, figure 3 shows the 100 K fluorescence spectra of $F_2^+ : O^{2-}$ centres of KBr under 1.4, 1.5 and 1.6 μm excitation. The curves clearly show a relative shift, which demonstrates that the (apparently Gaussian) 1540 nm absorption band is a blend of at least two components; maybe types (a) and (b) already coexist after -10°C photoaggregation, or type (a) is a mixture of two different subtypes (figure 4 of Wandt *et al* (1987) shows four different possibilities for the geometry of $(F_2^+)_{\text{H}}$ centres).

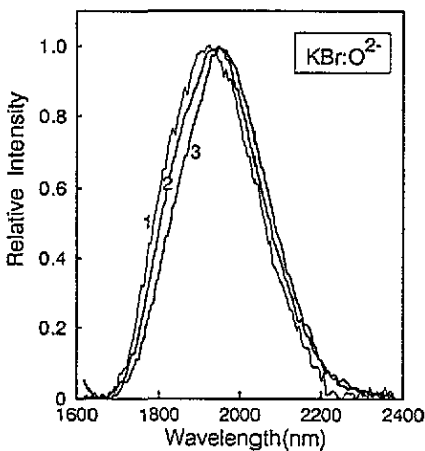


Figure 3. Emission spectrum of $(F_2^+)_{\text{H}}$ (a) centres in $\text{KBr}:\text{O}^{2-}$ at 100 K: curve 1, excitation at 1.4 μm ; curve 2, excitation at 1.5 μm ; curve 3, excitation at 1.6 μm . The three curves have been normalized to the same maximum amplitude.

As may be seen from table 3, emission bands do not shift appreciably between 100 and 5 K; they undergo only a moderate sharpening: 8–16%. On the other hand, there is in most cases a sizeable displacement (10–35 nm) of absorption bands toward longer wavelengths when the temperature decreases. The exceptions are $\text{NaCl}:\text{S}^{2-}$ (b) and $\text{NaCl}:\text{Se}^{2-}$ (b) (no significant shift), the $(F_2^+)_{\text{H}}$ centre in $\text{KI}:\text{S}^{2-}$ (27 nm shift toward shorter wavelengths) and $\text{KI}:\text{O}^{2-}$ (b) centre which is atypical in many other respects and which will be discussed in particular in section 3.1.4. The prevalent long-wavelength shift of $(F_2^+)_{\text{H}}$ absorption bands on cooling is noteworthy for two reasons.

Table 3. Peak wavelengths of the broad bands $1s\sigma_g \rightarrow 2p\sigma_u$ and $2p\sigma_u \rightarrow 1s\sigma_g$.

Crystal	Centre	Peak wavelength (nm)							
		Type (a)				Type (b)			
		Absorption		Emission		Absorption		Emission	
LNT	5 K	LNT	5 K	LNT	5 K	LNT	5 K		
NaCl	F_2^+	1020 ^a		1480 ^a					
	$F_2^+ : O^{2-}$	1050 ^b	1065 ^b	1483 ^b	1483 ^b	1082 ^b	1088 ^b	1539 ^b	1539 ^b
		1050 ^a		1490 ^a		1090 ^a		1590 ^a	
	$F_2^+ : S^{2-}$	1053 ^b	1062 ^b	1475 ^b	1475 ^b	1088 ^b	1088 ^b	1555 ^b	1555 ^b
	1051 ^c		1490 ^c		1084 ^c		1540 ^c		
	$F_2^+ : Se^{2-}$	1052 ^b	1062 ^b	1478 ^b	1478 ^b	1078 ^b	1078 ^b	1552 ^b	1552 ^b
KCl	F_2^+	1385 ^b	1385 ^b	1692 ^b	1692 ^b				
		1380 ^d		1680 ^d					
	$F_2^+ : O^{2-}$	1460 ^b	1470 ^b	1778 ^b	1778 ^b	Same wavelengths as F_2^+			
		1450 ^d		1780 ^d					
	$F_2^+ : S^{2-}$	1640 ^b	1660 ^b	2012 ^b	2012 ^b	Same wavelengths as F_2^+			
KBr	F_2^+	1490 ^d		1800 ^d					
	$F_2^+ : O^{2-}$	1540 ^b	1562 ^b	1916 ^b		1580 ^b	1612 ^b	1980 ^b	
		1530 ^d		1890 ^d		1580 ^d		2040 ^d	
		1530 ^a		1890 ^a		1580 ^a		1980 ^a	
	$F_2^+ : S^{2-}$	1673 ^b	1705 ^b	2095 ^b	2095 ^b	Type (b) identical with type (a)			
KI	F_2^+	1610 ^e		2150 ^e					
	$F_2^+ : O^{2-}$	1575 ^b	1610 ^b	2058 ^b		1725 ^b	1580 ^b	2430 ^b	
		1580 ^f		2040 ^f		1700 ^f		2400 ^f	
	$F_2^+ : S^{2-}$	1717 ^b	1690 ^b	2340 ^b		Type (b) identical with type (a)			
RbCl	$F_2^+ : O^{2-}$	1608 ^b	1640 ^b	1960 ^b		Type (b) identical with type (a)			
		1615 ^f		1950 ^f					

^a Wandt *et al* (1987).^b This work.^c Suzuki *et al* (1992).^d Gellermann (1991).^e Schneider (1981).^f Girard and Doualan (1993).

LNT is 100 K for this work and 77 K for the data of most other workers.

(i) It is of opposite sense to most colour centres, the absorption bands of which move to shorter wavelengths at low temperatures, in keeping with contraction of the crystalline lattice and the Mollwo-Ivey formula.

(ii) For type (a) which can be observed in a wide range of temperatures, the long-wavelength shift of the $(F_2^+)_{\text{H}}$ absorption band is of the same order of magnitude between liquid-nitrogen temperature and liquid-helium temperature as between room temperature and liquid-nitrogen temperature, contrary to the common behaviour (saturation of thermal displacements at the lowest temperatures).

This uncommon thermal wavelength dependence should perhaps be related to the above-formulated hypothesis of several kinds of defects with slightly different optical properties. However, the excitation energy for converting these centres into one another should be very low to allow establishment of thermal equilibrium between them at temperatures much lower than 100 K.

After these general remarks concerning broad-band spectra, let us make now a few specific comments on each crystal.

3.1.1. $(F_2^+)_H$ centres in NaCl. Absorption and emission wavelengths are nearly the same for NaCl:O²⁻, NaCl:S²⁻ and NaCl:Se²⁻ (table 3). This has already been noted by Suzuki *et al* (1992) for oxygen and sulphur dopings. In the novel case of NaCl:Se²⁻, one may fear that the selenium ion, owing to its large radius, should not have entered into the NaCl lattice and that the observed centres should really be F₂⁺:O²⁻ or F₂⁺:S²⁻, resulting from an impurity accidentally inserted during the crystal growth. This pessimistic hypothesis is discarded for the following reasons.

(i) For the same coloration conditions and duration, NaCl:OH⁻ or NaCl:O²⁻ crystals become dark blue, with a large amount of colloids, while NaCl:Se²⁻ crystals become light green, with considerably fewer colloids. On the other hand, in order to obtain laser action without fading, both crystals require, in addition to the 1.06 μm pump, auxiliary 'F-light' irradiation (as already described by Pinto *et al* (1986)) but, at 20 K, switching off this auxiliary light completely kills the emission in the case of selenium stabilization and only decreases it for oxygen doping.

(ii) It is highly improbable that sulphur ions may have been introduced into our 'NaCl:Se²⁻' crystals, in view of the purity of our initial materials and the care with which the crystal growth was performed.

Therefore, we conclude that we have really observed F₂⁺:Se²⁻ centres and that they have absorption and emission bands at wavelengths very close to those of the F₂⁺:O²⁻ and F₂⁺:S²⁻ centres. This result will be discussed in section 5.

3.1.2. $(F_2^+)_H$ centres in KCl. Contrary to the case in NaCl, F₂⁺:S²⁻ centres have in KCl a quite different absorption wavelength from F₂⁺:O²⁻. By 100 K irradiation with 'F light', both F₂⁺:O²⁻ and F₂⁺:S²⁻ centres are destroyed and transformed into intrinsic F₂⁺ centres†, a behaviour which was much studied in the case of F₂⁺:O²⁻ by previous workers (Wandt *et al* 1987, Lifante *et al* 1990).

3.1.3. $(F_2^+)_H$ centres in KBr. As in KCl, the absorption and emission bands of F₂⁺:S²⁻ (a) centres are significantly displaced towards longer wavelengths with respect to those of F₂⁺:O²⁻ (a). 100 K irradiation with 546, 436 or 365 nm does not shift the absorption and emission bands of F₂⁺:S²⁻. It only increases their peak intensity by approximately 40%. This behaviour would occur if the two types (a) and (b) did exist in KBr:S²⁻, with a somewhat stronger oscillator strength for type (b), and if absorption and emission transitions of both types were situated at the same spectral position, within the experimental uncertainties due to the breadth of bands.

3.1.4. $(F_2^+)_H$ centres in KI. As observed by Girard and Doualan (1993) KI:O²⁻ (b) centre has an unusual absorption behaviour; at 100 K, it yields a very broad band, the peak of which we find impossible to locate accurately (see curve 2 in figure 4). By subtracting an estimated background, we obtain a tentative approximate value of 1725 nm. On cooling to 5 K, this band narrows somewhat and its maximum is now observed at 1580 nm. This value is very surprising for two reasons: it is smaller than the peak absorption wavelength

† To perform this conversion, 365 or 436 nm lines of mercury are efficient for both F₂⁺:O²⁻ and F₂⁺:S²⁻, while 546 nm is efficient only for F₂⁺:S²⁻.

of $(F_2^+)_{\text{H}}$ (b) centres at 100 K and it is also smaller than the wavelength of the F_2^+ band in pure KI (1610 nm according to Schneider (1981)). The first observation is contradictory to the most usual behaviour of $(F_2^+)_{\text{H}}$ absorption bands (which shift to longer wavelengths with decreasing temperature). However, the problem may arise from an inaccurate estimate of the position of the broad $(F_2^+)_{\text{H}}$ band in $\text{KI}:\text{O}^{2-}$ at 100 K. The second observation is at variance with the general observation that $(F_2^+)_{\text{H}}$ bands are located at wavelengths longer than the corresponding F_2^+ bands (see, e.g., Gellermann (1991)). Thus, we may wonder whether the bands that we observe at 1725 nm (100 K) and 1580 nm (5 K) are really due to $(F_2^+)_{\text{H}}$ (b) centres.

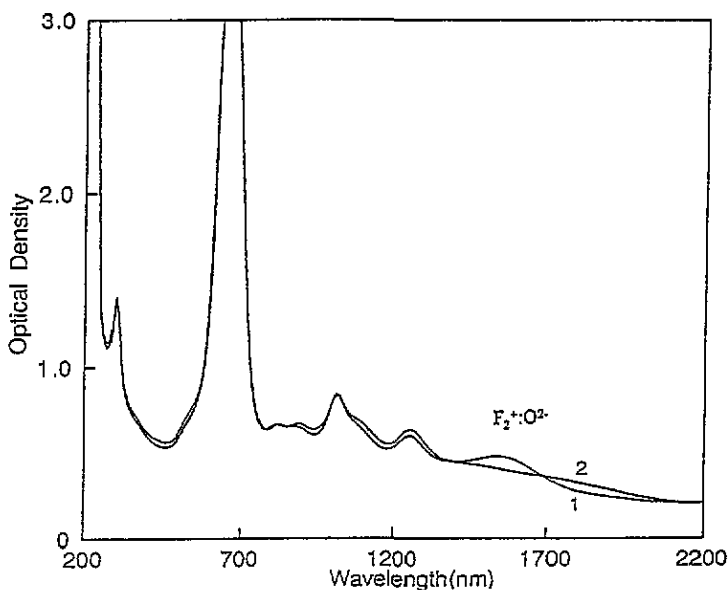


Figure 4. Absorption spectrum of $(F_2^+)_{\text{H}}$ centres in $\text{KI}:\text{O}^{2-}$ at 100 K: curve 1, type (a) obtained after 15 min, 365 nm irradiation at -5°C ; curve 2, type (b) ? obtained after 5 min additional 546 nm irradiation at 100 K.

The absorption band of type (a) (curve 1 in figure 4) is reasonably sharp. It is observed at 1575 nm and 1610 nm for 100 K and 5 K, respectively. The temperature dependence of its position is therefore in agreement with the customary behaviour of $(F_2^+)_{\text{H}}$ centres. However, as for $(F_2^+)_{\text{H}}$ (b) centres, the ordinary displacement to longer wavelengths when going from F_2^+ to $(F_2^+)_{\text{H}}$ is not observed.

On the other hand, emission spectra of type (a) and (b) centres are quite 'normal'. It turns out that the fluorescence of type (a) distinctly displays a secondary maximum at around 2400 nm, in addition to the chief peak at 2040 nm (figure 5). This merely means that, after -5°C irradiation with 365 nm light, the sample already contains a sizable concentration of type (b), in addition to the prevailing type (a) centres. After 546 nm irradiation at 100 K, the fluorescence consists of only one band at 2430 nm, which indicates that the (a) \rightarrow (b) conversion is almost total.

We also studied the intensity of fluorescence of $F_2^+:\text{O}^{2-}$ (b) centres at 100 K, under excitation by the light of a $1.56 \mu\text{m}$ colour centre laser, as a function of the angle θ between the $[0, 0, 1]$ direction of the sample and the polarization of the exciting light. The

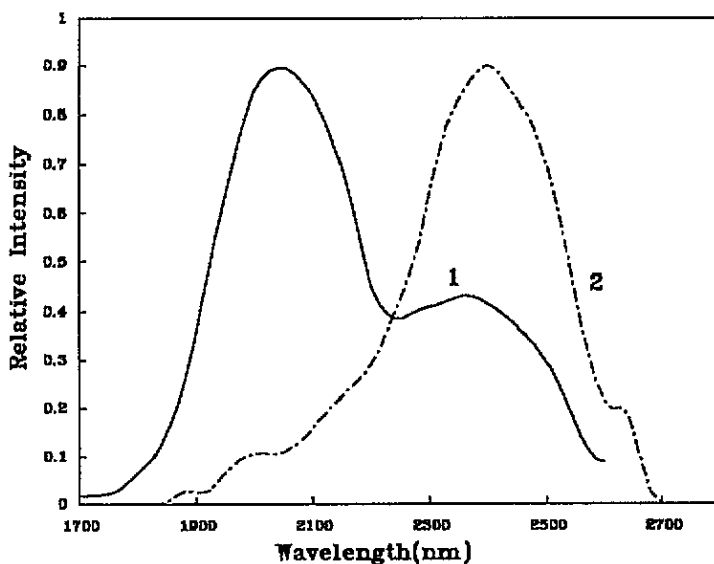


Figure 5. Emission spectrum of $(F_2^+)_H$ centres in $KI:O^{2-}$ at 100 K: curve 1, after 15 min, 365 nm irradiation at $-5^\circ C$; curve 2, after 5 min additional 546 nm irradiation at 100 K.

results were analysed with the help of Feofilov's (1954) paper and they were found to be in perfect agreement with the hypothesis that the transition between the ground and first excited states of investigated centres is polarized along crystalline $[1, 1, 0]$ axes, both in absorption and in emission. This observation supports the $(F_2^+)_H$ identification for the centre with fluorescence around 2430 nm.

In $KI:S^{2-}$, $(F_2^+)_H$ centres have a behaviour more similar to that of $KBr:S^{2-}$ than to that of $KI:O^{2-}$; type (a) is clearly observed, both in absorption and in emission, but 100 K irradiation with the lines 546, 436 or 365 nm has no effect at all on the spectra, not even modifying the intensity of the absorption band, in contradistinction to the case of $KBr:S^{2-}$. The absorption band of $(F_2^+)_H$ (a) centres of $KI:S^{2-}$ shifts to shorter wavelengths on cooling from 100 to 5 K, but, even at the latter temperature, it remains red-shifted with respect to the intrinsic F_2^+ band in KI.

3.1.5. $(F_2^+)_H$ centres in RbCl. The behaviour of $(F_2^+)_H$ centres is exactly the same in $RbCl:O^{2-}$ as in $KI:S^{2-}$; only one type of these centres is observed and irradiation at 100 K, whatever its wavelength, has no detectable effect on the spectrum.

3.2. Sharp lines

We have searched in the absorption spectrum at 5 K for zero-phonon lines which could be associated with $(F_2^+)_H$ centres in all the crystals that we have studied, but we observed none in most cases, although a number of sharp lines were seen at shorter wavelengths, in the spectral domain of N bands. The only three crystals for which we found zero-phonon lines in the $(F_2^+)_H$ spectral domain are $KCl:O^{2-}$, $KCl:S^{2-}$ and $KBr:S^{2-}$ (table 4). Zero-phonon lines of $F_2^+:O^{2-}$ centres in KCl were extensively studied by Wandt *et al* (1987) and Lifante *et al* (1990). We fully agree with their results, including the effects on these lines of 'F-light' irradiation, which are different at 5 K and at liquid-nitrogen temperature.

On the other hand, we are not aware of any previous data concerning zero-phonon lines of $F_2^+:S^{2-}$ centres in KCl and KBr. Our observations are qualitatively similar for

Table 4. Zero-phonon lines of $(F_2^+)_{\text{H}}$ centres at 5 K.

	Observed position (nm)				Expected position (nm)
	Absorption		Emission		
KCl:O ²⁻	1613.5 ^a	1620.0 ^a	1613.7 ^a	1620.7 ^a	1609
	1613.0 ^b	1620.5 ^b			
	1613.6 ^c	1620.5 ^c			
KCl:S ²⁻	1837 ^a	1868 ^a	1838 ^a	1866 ^a	1819
KBr:S ²⁻	1908 ^a	1943 ^a	1908 ^a	1936 ^a	1880

^a This work.^b Wandt *et al* (1987).^c Lifante *et al* (1990).

$F_2^+:\text{O}^{2-}$ and for $F_2^+:\text{S}^{2-}$ centres in KCl; in the latter case, two lines are observed at 1837 and 1868 nm, i.e. with an energy splitting 3.6 times that for $F_2^+:\text{O}^{2-}$. The positions of these two lines should be compared with the wavelength estimated from broad-band absorption and emission maxima, assuming a linear electron-phonon coupling: $\lambda_{\text{zp}}^{-1} = \frac{1}{2}(\lambda_{\text{abs}}^{-1} + \lambda_{\text{em}}^{-1})$. One thus obtains 1819 nm, in good agreement with the observed values.

By irradiation at approximately 77 K with 436 nm light (and subsequent cooling to 5 K), the lines at 1837 and 1868 nm of KCl:S²⁻ vanish, while the 1525.9 nm zero-phonon line of intrinsic F_2^+ centres appears. This is quite similar to the behaviour of $F_2^+:\text{O}^{2-}$ centres and confirms that $(F_2^+)_{\text{H}}$ centres have been converted into F_2^+ (section 3.1.2). On the other hand, by 5 K irradiation with 436 nm light, the relative intensities of 1837 and 1868 nm lines remain unaltered, in contradistinction to $F_2^+:\text{O}^{2-}$ centres, for which the same processing bleaches the 1613.5 nm line and increases the intensity of the 1620 nm line significantly (see Wandt *et al* (1987), Lifante *et al* (1990) and also figure 6 of the present paper).

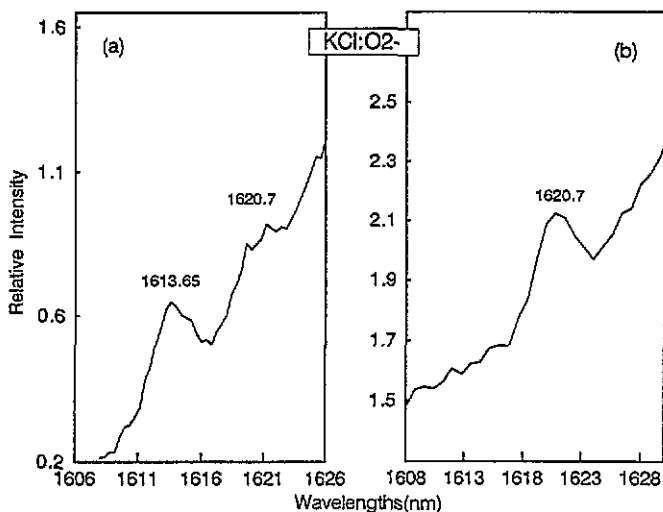


Figure 6. Emission spectrum at 5 K showing the zero-phonon lines of $F_2^+:\text{O}^{2-}$ centres in KCl: (a) after photoaggregation of the centres at -10°C ; (b) after further 436 nm irradiation for 20 min at 5 K, showing the disappearance of the line at 1613.7 nm and an increase in the line at 1620.7 nm.

In the case of KBr:S^{2-} , one also observes two sharp transitions at 1908 and 1943 nm, in the spectral region where the zero-phonon line(s) of $(\text{F}_2^+)_\text{H}$ centres is (are) expected to be located (table 4). Within 5%, the energy difference between these two lines is the same as between the two lines observed in KCl:S^{2-} . We do not at present know whether this equality is merely a coincidence, or whether it has a deeper physical meaning. 5 K irradiation with 546, 436 or 365 nm light has no effect on the intensity of the 1908 and 1943 nm lines of KBr:S^{2-} , as in KCl:S^{2-} and contrary to KCl:O^{2-} .

The six spectral lines listed in table 4 were also observed in emission, which proves that all of them are indeed, as assumed above, zero-phonon transitions and not vibrational satellites. For these experiments, the sample, at 5 K, was excited with a white lamp through a suitable interference filter. The emitted light was analysed with a Jobin-Yvon grating spectrometer, with 0.75 mm slit widths, corresponding to $\Delta\lambda = 3.9$ nm. This was the result of a compromise between sensitivity and spectral resolution. The signal-to-noise ratio was much poorer than in absorption experiments. As an example, figure 6 shows spectra of KCl:O^{2-} obtained after a 2 h accumulation of data in the memory of a microcomputer. The poor signal-to-noise ratio causes inaccuracies in the position measurements, which accounts for the differences from the absorption data (table 4).

One may wonder why two zero-phonon lines are observed in each case (KCl:O^{2-} , KCl:S^{2-} and KBr:S^{2-}). In KCl:O^{2-} , the conversion under 5 K 'F-light' irradiation (see figure 6) strongly suggests the existence of two very similar centres, with only 25 cm^{-1} between the positions of their first excited levels. Thus, the broad absorption and emission bands of both species are indistinguishable, while their sharp zero-phonon lines are clearly separated. In KCl:S^{2-} , the disappearance of both lines at 1837 and 1868 nm by 'F-light' irradiation at 100 K and their replacement by the zero-phonon line of intrinsic F_2^+ centres is evidence that both these lines are connected with $(\text{F}_2^+)_\text{H}$ centres. As they were shown above to be both genuine zero-phonon transitions, they should arise again from two slightly different types of $\text{F}_2^+:\text{S}^{2-}$ centre, but with no interconversion by 'F-light' irradiation at 5 K. Finally, in KBr:S^{2-} , the existence of two zero-phonon lines at 1908 and 1943 nm is the only experimental hint concerning the possible existence of two different types of $\text{F}_2^+:\text{S}^{2-}$ centre; however, it is quite possible that only one of these lines is the zero-phonon line of $\text{F}_2^+:\text{S}^{2-}$ centres, the other arising from some different origin.

We were disappointed to observe no zero-phonon transition for any of the $(\text{F}_2^+)_\text{H}$ centres which exist under two noticeably distinct types (a) and (b) (NaCl:O^{2-} , S^{2-} or Se^{2-} , KBr:O^{2-} and KI:O^{2-}). Such sharp lines would have been very useful to understand better the (a) \leftrightarrow (b) transformation and to decide whether type (a) is pure or is itself a mixture of subtypes, as suspected in section 3.1. Let us recall that such a mixture is quite plausible since four different microscopic structures for $(\text{F}_2^+)_\text{H}$ centres have been suggested by Wandt *et al* (1987).

4. Stability of $(\text{F}_2^+)_\text{H}$ centres in the dark at room temperature

For the practical use of $(\text{F}_2^+)_\text{H}$ centres as laser materials, it is almost necessary that they should be stable for at least a few tens of minutes at room temperature, in order to allow their handling: transfer from the apparatus for photoaggregation (at temperatures in the range from -5 to -20°C) to the cold finger of the laser, emptying and outgassing of the vacuum enclosure, and beginning of cooling of the cryostat. Moreover, if the active sample is stable at room temperature for much longer periods (several weeks), its storage will be much easier. We have therefore performed tests according to the following scheme: during

most of the time, the sample is kept in the dark at room temperature, but at regular intervals we cool it to 100 K in order to measure its absorption spectrum. Figure 7 shows the result of this series of measurements in the case of NaCl:S^{2-} . It can be seen that the absorption amplitude y (in arbitrary units) varies exponentially with time:

$$y = 40.0 + 47.1 \exp(-0.077t)$$

with t in days.

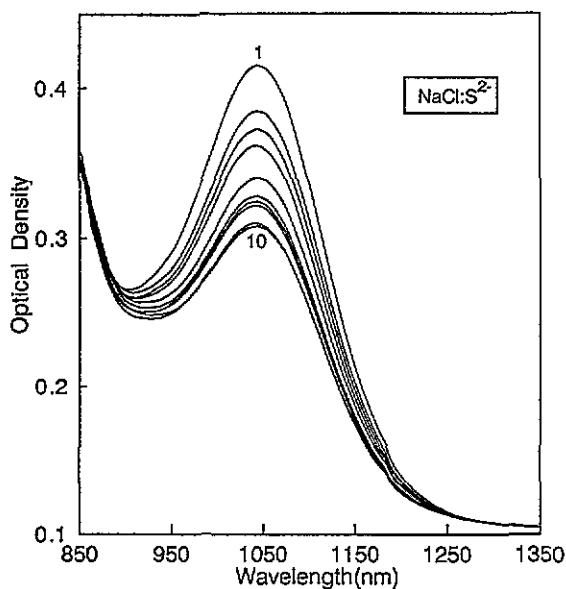


Figure 7. Bleaching of absorption of $(F_2^+)_{\text{H}}$ centres of NaCl:S^{2-} in the dark at room temperature: curve 1, 3d; curve 2, 5d; curve 3, 9d; curve 4, 12d; curve 5, 16d; curve 6, 19d; curve 7, 22d; curve 8, 26d; curve 9, 31d; curve 10, 32d.

This means that the decay time constant is fairly large ($\tau = 13$ d) and, what is more interesting, that this decay does not affect all the $(F_2^+)_{\text{H}}$ centres. The proportion of centres which still exist after an 'infinite' time† at room temperature in the dark is

$$R = 40.0 / (40.0 + 47.1) = 0.46.$$

We verified that the centres which thus outlive after 32 d are really $(F_2^+)_{\text{H}}$ centres, with the same properties as those of a fresh sample (and not some new kind of centre with a similar absorption spectrum). For this purpose, we measured their absorption and fluorescence spectra at 100 K and found them to be identical to the spectra of type (a). Then we irradiated the sample at 100 K with 436 nm and obtained afterwards absorption and emission spectra which were typical of type (b). The only noticeable difference from a fresh sample was that the (a) \rightarrow (b) conversion was accompanied by a significant increase in the number of $(F_2^+)_{\text{H}}$ centres. Thus, it seems that the thermal bleach in the dark at room temperature is partly reversible under irradiation at 100 K by 436 nm light.

We performed experiments similar to that giving the results in figure 7 on NaCl:O^{2-} , NaCl:Se^{2-} , KCl:O^{2-} and KBr:O^{2-} . The results are given in table 5 which lists the time constants τ and the fractions R of 'infinite-lifetime' centres. On the other hand, the

† During the limited duration of an experiment (1 month in the present case), it is impossible to distinguish a very slow exponential component (time constant of several months) from a genuine non-zero horizontal asymptote.

Table 5. Stability of $(F_2^+)_{\text{H}}$ centres in the dark at room temperature. R is the proportion of centres with 'infinite lifetime'.

	τ (d)	R
NaCl:O ²⁻	7.4	0.41
NaCl:S ²⁻	13.0	0.46
NaCl:Se ²⁻	10.7	0.54
KCl:O ²⁻	2.4	0.06
KBr:O ²⁻	1.0	0.00

experiment is impossible for KCl:S²⁻ and KBr:S²⁻ in which $(F_2^+)_{\text{H}}$ -centre lifetimes are comparable with (or smaller than) 15 min, i.e. the time necessary to bring back the sample to room temperature and to cool it again to 100 K. Finally, no detailed experiments were attempted in the cases of KI:O²⁻, KI:S²⁻ and RbCl:O²⁻, but the comparison of two spectra before and after storage for a few hours in the dark at room temperature showed that their ratio R is zero and their lifetime τ at most 1 h, and perhaps as short as those of KCl:S²⁻ and KBr:S²⁻. In the cases of KI:O²⁻ and KI:S²⁻, the thermal bleach at room temperature is full reversible by the process which initially creates the centres: irradiation by 365 nm light at -10 °C. On the other hand, this reversibility does not exist for RbCl:O²⁻; following thermal bleach at room temperature, $(F_2^+)_{\text{H}}$ centres in this crystal can be regenerated only after anneal of the samples near the melting point and rapid quench at room temperature.

From the results above and from table 5, it appears that $(F_2^+)_{\text{H}}$ centres are much more stable at room temperature in NaCl than in KCl, KBr, KI or RbCl. As for the choice of the stabilizing divalent anion, S²⁻ is more successful than oxygen in the NaCl lattice†. On the other hand, S²⁻ is a much worse stabilizer than O²⁻ in KCl and in KBr. The reason for this very different efficiency of sulphur in various crystals is currently unknown.

5. Discussion

Sennaroglu and Pollock (1991) proposed a simple model for calculating the spectral properties of $F_2^+ : O^{2-}$ centres in NaCl:OH⁻. The F_2^+ colour centre was represented by a hydrogen molecular ion embedded in a dielectric continuum and the effect of the adjacent oxygen ion was treated as an electrostatic perturbation. These workers were thus able to explain with a good accuracy the observed shifts between $(F_2^+)_{\text{H}}$ and F_2^+ absorption and emission transitions, including absorptions in the relaxed excited state. Doualan *et al* (1992) extended the model of Sennaroglu and Pollock both to other matrices and to other $(F_2^+)_{\text{H}}$ -like centres. One of their predictions was that, in a fixed host crystal, the absorption and emission bands should be located at the same energy, with a good accuracy, for $F_2^+ : O^{2-}$, $F_2^+ : S^{2-}$ and $F_2^+ : Se^{2-}$ centres. At the time when the paper by Doualan *et al* was published, the only experimental data available for comparison were those of $F_2^+ : S^{2-}$ in NaCl, which are in good agreement with the expectation; table 3 shows that absorption and emission bands are located at nearly the same position for $F_2^+ : O^{2-}$ and $F_2^+ : S^{2-}$ of NaCl, both for type (a) and for type (b). It turns out that the prediction of Doualan *et al* (1992) also works quite well for the $F_2^+ : Se^{2-}$ centre of NaCl. However table 3 shows that the agreement for NaCl is probably due to the whims of fate; indeed, in KCl, KBr and KI, the absorption wavelengths for $F_2^+ : S^{2-}$ centres are significantly larger than for $F_2^+ : O^{2-}$ in the same matrix.

† Suzuki *et al* (1992) observed similarly that the thermal stability of $F_2^+ : S^{2-}$ centres was twice that of $F_2^+ : O^{2-}$ in the 268–290 K range. However, they did not mention a 'permanent' population of very-long-lived $(F_2^+)_{\text{H}}$ centres.

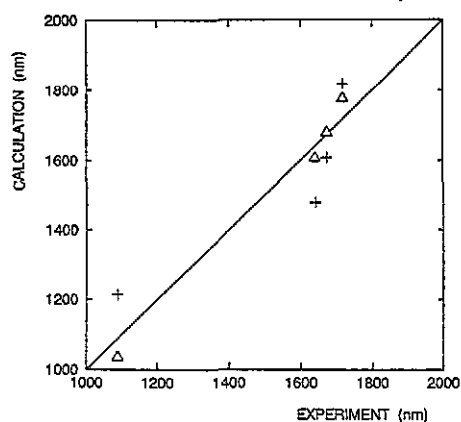


Figure 8. Comparison of experimental and calculated absorption wavelengths of $F_2^+ : S^{2-}$ type (b) centres in different matrices: +, calculations using equation (1); Δ , calculations using equation (2).

Table 6. Semi-empirical calculations of absorption and emission wavelengths (in nanometres) of $(F_2^+)_{\text{H}}$ centres. In equations (1) and (2), d is expressed in ångströms. The values of d and ϵ are from appendix A of Fowler (1968). $n = 6$ crystals are included in the calculations for $F_2^+ : O^{2-}$ centres and $n = 4$ for $F_2^+ : S^{2-}$ centres.

	Mollwo-Ivey equation (1)			Girard-Doualan equation (2)		
	A	x	σ (nm)	$10^3 \times \alpha$	$10^3 \times \beta$	σ (nm)
$F_2^+ : O^{2-}$						
(a) Absorption	178.3	1.795	108	-7.928	14.854	61
Emission	324.1	1.485	43	-4.606	9.400	69
(b) Absorption	140.2	2.021	57	-6.678	12.971	36
Emission	189.6	1.975	97	-3.218	7.168	70
$F_2^+ : S^{2-}$						
(a) Absorption	166.4	1.898	182	-10.507	18.071	46
Emission	207.7	1.935	93	-5.700	10.610	31
(b) Absorption	189.0	1.794	168	-9.938	17.268	61
Emission	262.5	1.743	65	-4.993	9.617	53

Therefore, the model of Sennaroglu and Pollock (1991), as revised by Doualan *et al* (1992) should be given up because it is not reliably predictive.

On the other hand, Girard and Doualan (1993) showed that two semi-empirical formulae are able to predict fairly accurately the location of absorption and emission bands of $F_2^+ : O^{2-}$ (b) centres. According to the well known Mollwo-Ivey law,

$$\lambda = Ad^x \quad (1)$$

where A and x are adjustable parameters and d is the nearest-neighbour cation-anion distance in the lattice. However, somewhat better results may be obtained by

$$\lambda = \frac{\epsilon^2}{\alpha d / \epsilon + \beta} \quad (2)$$

where α and β are adjustable parameters and ϵ is the high-frequency relative dielectric constant of the host crystal. Equation (2) was derived by Girard and Doualan from the hydrogen molecular ion model of F_2^+ centres (see, e.g., Aegerter and Lüty (1971)).

We verified that all the data in table 3 may be represented either by equation (1) or by equation (2), adjusting A and x , or α and β , separately for the eight cases (O^{2-}

or S^{2-} doping, type (a) or (b), absorption or fluorescence). In all instances but one, experimental results are better represented by equation (2) than by equation (1), which lends credit to the analysis of Girard and Doualan (1993). As an illustration, figure 8 compares experimental wavelengths for the absorption of $F_2^+ : S^{2-}$ (b) centres with the values calculated using equation (1) (crosses) and equation (2) (open triangles). Table 6 lists the values of parameters A , x , α and β , together with the RMS deviation σ defined as

$$\sigma = \left(\sum_{i=1}^n \frac{(\lambda_{\text{calc}} - \lambda_{\text{exp}})^2}{n - p} \right)^{1/2} \quad (3)$$

where n is the number of experimental data and $p = 2$, the number of adjustable parameters. In the case of $F_2^+ : O^{2-}$, the experimental data of Girard and Doualan for RbBr have been included in the calculation. When the (a) \leftrightarrow (b) transformation is not observed, as for instance with $KCl : O^{2-}$, the experimental absorption and emission wavelengths are included in both calculations for $(F_2^+)_H$ (a) and for $(F_2^+)_H$ (b). This amounts to postulating that both types exist with indistinguishable absorption and emission spectra. One could also assume that only one type, either (a) or (b), exists for these crystals and, in this case, the experimental data should be included only for the fit concerning this particular type. However, we did not obtain a significant improvement by deleting the data of $KCl : O^{2-}$ from the type (a) calculation or from the type (b) calculation. In fact, the accuracy of the empirical formula (2) is of an order of magnitude comparable with the distance between the transitions of the (b) and (a) centres in the same matrix (and equation (1) is even less precise). Therefore, equation (2) with the parameters α and β listed in table 6 will probably be useful in the future to calculate the position of absorption and emission bands of $(F_2^+)_H$ centres in alkali halides not yet studied, but it is not accurate enough to allow predictions concerning the (a)–(b) splittings.

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