# PHOTOCHEMICAL PRODUCTION OF F CENTERS IN KBr CRYSTALS DOPED WITH Se<sup>2-</sup>

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Received 6 May 1987

The photochemical production of F centers in KBr:Se<sup>2-</sup> crystals has been investigated using crystals doped by a method different to that used by others. The formation of F centers is a complicated process and depends on the intensity of irradiating light, temperature and wavelength. Low-power irradiation favors F center formation by ionization of free Se<sup>2-</sup> in freshly quenched crystals. Low-temperature UV laser irradiation forms both normal F centers and one other center with an absorption band very close to the normal F center. The nature of this second center is not known.

## 1. Introduction

The production of F centers by ultraviolet irradiation of alkali halide crystals containing bivalent chalcogenide ions has been reported by a number of workers [1-10]. As the presence of these ions requires charge compensating vacancies it has been assumed that the formation of F centers involves initial absorption by  $X^{2-}$  vacancy pairs and transfer of the excited electron to the vacancy followed by thermal motion of the F center (away from the  $X^{-}$ ). Hennl [9] reported the formation of F centers bound to S<sup>-</sup> and Se<sup>-</sup> by irradiation at liquid-helium temperatures of KBr and KI containing S<sup>2-</sup> and Se<sup>2-</sup>. We have recently studied the optical spectroscopy of KBr:Se<sup>2-</sup> crystals, doped by a different method to that used by Hennl [11], and we have arrived at a different assignment of the absorption spectrum [12,13]. We have also studied the photochemical production of F centers in these crystals and we have reached different conclusions about the mechanism of their formation. More work is necessary to understand fully the phenomenon of F center production in these crystals, and we hope that our communication will stimulate further work in this area.

#### 2. Experimental

The methods used for crystal growth and sample quenching were the same as described earlier [14,15].  $K_2Se$ , added to the molten KBr, was made by reacting potassium and selenium in liquid ammonia.

Absorption spectra were measured with a Cary 17 spectrophotometer under microprocessor control. For low-temperature measurements, samples were placed in a gas flow tube inserted in the neck of a liquid-helium storage dewar and controlled boil-off of the liquid was used to cool the samples. Irradiation of the samples at room temperature was carried out by means of a 150 W xenon lamp. A Molectron UV 1000 nitrogen laser (29670 cm<sup>-1</sup>) was used for the low-temperature irradiation, with the sample inside a flow tube placed in the sample compartment of the spectrophotometer. Either broad band or (interference) narrow band UV filters were used during all irradiation experiments. The basic mag-

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<sup>0 009-2614/87/\$ 03.50 ©</sup> Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division)

netic circular dichroism (MCD) equipment has been described elsewhere [16]. The samples were placed in an Oxford Instruments SM4 superconducting solenoid and a MINC microprocessor system was used to control all aspects of data collection. Data handling and analysis were carried out with special routines using a VAX 11/750 computer.

It is essential when quenching KBr:Se<sup>2-</sup> crystals that the samples are heated to not less than 50°C below the melting point and after quenching the samples should be kept well below room temperature. Otherwise clusters of Se<sup>2-</sup> and vacancies will be found.

### 3. Results and discussion

The dependence of F center production, in a freshly quenched sample, on the energy of the exciting radiation was determined using interference filters. Light of wave number greater than 28570 cm<sup>-1</sup> (3.54 eV) is needed to produce F centers in KBr:Se<sup>2-</sup>. F centers are not produced when the crystal is irradiated in the two lowest energy absorption bands at 24600 cm<sup>-1</sup> (3.05 eV) and 26770 cm<sup>-1</sup> (3.32 eV). These two bands are usually assigned to the  $p^6 \rightarrow p^5s$ transition in Se<sup>2-</sup>.

The need to irradiate with light which is higher in energy than that of the band or bands assigned to the  $p^n \rightarrow p^{n-1}$ s transition in the chalcogenide ion to photochemically produce F centers has also been noted in NaCl:S<sup>2-</sup> [6], KCl:S<sup>2-</sup>, KBr:S<sup>2-</sup> [17], LiF:O<sup>2-</sup> [18] and KI:S<sup>2-</sup> [10], as well as in earlier measurements on KBr:Se<sup>2-</sup> [11].

Fig. 1 shows the absorption spectral changes observed after periods of room temperature irradiation of a KBr:Se<sup>2-</sup> sample along with the corresponding MCD spectra measured using another sample cleaved from an adjacent region of the same, freshly quenched, crystal. In each case the samples were cycled between room temperature, for irradiation, and low temperature, for measurement. The rate of production of F centers is rapid and saturation is reached quickly, so that further irradiation produces no further change.

The room-temperature irradiation leads to a decrease in the intensity of the two absorption bands at 24600 and 26770 cm<sup>-1</sup>, which we assign to the



Fig. 1. (A) Absorption spectra of KBr:Se<sup>2-</sup> (thickness 0.12 cm) measured at 10 K after room temperature irradiation using a filtered xenon lamp (Corning 7-60 filter) for various times (in min). (B) MCD C terms (difference between 1.4 and 4.1 K MCD spectra) measured using a similar sample to that in (A). The irradiation times are shown in min.

isolated Se<sup>2-</sup> ion. There are two C terms <sup>#1</sup> in the MCD measurements, one positive at  $25100 \text{ cm}^{-1}$  and one negative at  $21800 \text{ cm}^{-1}$ . One of these broad absorptions (at  $25100 \text{ cm}^{-1}$ ) lies underneath the two bands assigned to Se<sup>2-</sup> ions. The two MCD C terms grow at a similar rate to the absorption of the F center and as they are paramagnetic we assign them to the expected Se<sup>-</sup> center. The MCD signal of the F center saturates quickly. We ascribe this to an increase in bandwidth, which leads to larger cancellations as the F center absorption increases.

Room-temperature irradiation of samples containing photochemically produced F centers with 16290 cm<sup>-1</sup> light, which is within the absorption band of the F center, leads to a rapid reduction of the intensity of the absorption of the F center. However, the intensity of the bands at 24600 and 26770 cm<sup>-1</sup>, which are due to Se<sup>2-</sup>, is not fully recovered. Presumably aggregation of F centers competes with the trapping by Se<sup>-</sup> ions of electrons released from the F centers.

<sup>&</sup>lt;sup>#1</sup> See e.g. Shatz and McCaffery [19] for a discussion of the various terms in magnetic circular dichroism.



Fig. 2. (A) Absorption spectrum of freshly quenched KBr:Se<sup>2-</sup> crystal (full curve), spectrum after 2 min irradiation with nitrogen laser at 250 K (----) and spectrum after keeping the sample at 300 K for 30 min (---). All spectra measured at 10 K. (B) Absorption spectrum of the crystal in (A) after room temperature irradiation at 16130 cm<sup>-1</sup> (full curve), spectrum after 1 min irradiation with nitrogen laser at 300 K for 30 min (---). All spectra measured at 10 K.

F centers generated by X-ray irradiation of a crystal grown from the purified KBr used to prepare our KBr:Se<sup>2-</sup> crystals have the same position and bandwidth as the F centers produced photochemically in our KBr:Se<sup>2-</sup> samples. The position and width of F centers are the same in other KBr crystals [20].

A nitrogen laser was used for the UV irradiation in two experiments. In one, a sample was irradiated for a short time at 250 K using a partially focused beam. This produced a broader F center absorption (fig. 2A) and a decrease in the  $Se^{2-}$  absorption. The center or centers responsible for the extra width in the F center band was not very stable. When the sample temperature was increased to 300 K, kept there for 30 min and then reduced to 10 K to record the absorption spectrum, the absorption on both the low- and high-energy sides had decreased but the peak had changed little. The remaining absorption band was of the same width as the normal F center band (fig. 1) with some extra absorption remaining on the high-energy side. The Se<sup>2-</sup> absorption band had recovered essentially to its initial intensity. The remaining F center band was stronger than the saturation value achieved by its excitation with a xenon lamp at room temperature (fig. 1A).

The sample was then irradiated at 300 K with  $16130 \text{ cm}^{-1}$  light to remove about half of the F centers (fig. 2B) and again irradiated with the laser for 1 min this time at 300 K. Very much less of the extra absorption on both sides of the normal F band was found and, again, it was removed by keeping the sample at 300 K. There were, however, only minor changes in the Se<sup>2-</sup> absorption. These experiments show that laser excitation may produce F centers in these crystals without removal of Se<sup>2-</sup>.

The second set of experiments was designed to explore the nature of the center (which we will refer to as the second center) responsible for the extra absorption band or bands near the normal F band. A sample, held in a flow tube in the sample compartment of the spectrophotometer, was irradiated at 240 K using polarized laser light, incident from a horizontal direction normal to the optical path of the sample compartment, along a fourfold axis of the crystal. The polarization of the irradiating light was vertical and the absorption spectra were measured, at 10 K, for horizontal and vertical polarization directions, along the other two fourfold axes of the crystal. The absorption spectra were identical in each polarization. The sample was then irradiated (at 240 K) with vertically polarized light of a wave number,  $15380 \text{ cm}^{-1}$ , which is absorbed more strongly by the second center than by the normal F center. After cooling to 10 K, the absorption spectra were recorded with polarized light. The spectra were again identical for each polarization. It can be seen (fig. 3) that irradiation with 15380 cm<sup>-1</sup> light at 240 K removes only a portion of the second center (further irradiation left the spectra unchanged). The difference spectra show that irradiation leads to a marginal increase of the free F center absorption and a small increase of a broad absorption band at about  $25000 \text{ cm}^{-1}$ , which might be attributed to the Se<sup>-</sup> observed in the MCD (fig. 1).

The lack of linear dichroism in any of these spectra is important. Our assignment of the bands at 24600 and 26800 cm<sup>-1</sup> in the spectrum of the freshly quenched crystal to isolated  $Se^{2-}$  appears to be consistent with this result. The assignment of these bands to  $Se^{2-}$  vacancy pairs, as others have done [10], and their subsequent dissociation to form  $Se^{-}$  ions and



Fig. 3. (A) Absorption spectrum of freshly quenched KBr:Se<sup>2-</sup> (curve (1)), spectrum after irradiation with nitrogen laser (polarized) at 240 K (curve (2)) and spectrum after irradiation at 15380 cm<sup>-1</sup> at 240 K until no further change (curve (3)). All spectra measured at 10 K. (B) Difference between curves (1) and (2) in (A) (curve (4)) and difference between curves (2) and (3) in (A) (curve (5)).

F centers, either nearest neighbour or next nearest neighbour pairs, would lead to dichroism in the observed spectra.

The experimental results of Hennl [9], mentioned in section 1, could not be repeated. Irradiation at 10 K using the nitrogen laser produced only a very small number of F centers using the same optical arrangement as for the other experiments. Prolonged irradiation by the third harmonic of a Nd/YAG laser (9398 cm<sup>-1</sup>) did lead to coloring of the sample at 10 K, presumably due to multiphoton processes because of the high power density inherent in this laser. It should be noted that the samples used by Hennl were prepared by a different method and may have other centers present besides those involving Se<sup>2-</sup>.

## 4. Conclusion

The formation of F centers in KBr:Se<sup>2-</sup> crystals by ultraviolet irradiation only occurs as a result of absorption of light of wave number greater than about 28570 cm<sup>-1</sup>, at least for non-laser sources. Such excitation leads to the formation, at room temperature, of free F centers, a decrease of absorption due to  $Se^{2-}$ , and the appearance of some  $Se^{2-}$  centers, detected by their paramagnetic properties. The optical production of F centers is thermally activated and cooling the sample during irradiation markedly reduces their formation.

Our experiments do not support a model which proposes that the formation of F centers involves the absorption of light by  $Se^{2-}$  vacancy pairs and subsequent thermal dissociation into  $Se^{-}$  and free F centers [10]. Rather the F centers form from free anion vacancies which trap electrons released by the ionization of free  $Se^{2-}$  ions.

Irradiation with lasers at low temperatures leads to the formation of normal F centers in addition to another center with absorption near to the normal F band. With laser excitation all the F centers do not appear to result from  $Se^{2-}$  ionization. More research is needed before much can be said about the structure of the second center; a  $Se^{-}-F$  pair is one possibility.

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