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Optical and Thermal Bistability of Two $F_H(OH^-)$ Center Configurations in KBr and KI.

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Abstract. – F center/ OH^- defect pairs ($\ll F_H(OH^-)$ centers \gg) in KBr and KI exhibit a novel and unpredicted twofold optical absorption behavior, which at low temperatures can be optically converted and reconverted in a stable and reversible way. Obviously this effect is caused by the bistability of two different orientational configurations of the OH^- impurity ion relative to the F center. The temperature dependence of the two absorption bands and their magnetic circular dichroism have been determined.

1. Introduction.

F_H centers in alkali halides, formed by association of F centers with diatomic molecular ions like OH^- and CN^- , are under intense recent study due to their interesting and novel physical properties [1-4]. Particularly the F center/ OH^- pairs ($\ll F_H(OH^-)$ centers \gg) reveal a pronounced duality of physical behavior in host crystals of CsCl or NaCl structure:

a) In CsCl, CsBr and CsI hosts, the association produces a stable F center/ OH^- pair on $\langle 100 \rangle$ next nearest-neighbor lattice sites, characterized by a strong (~ 0.7 eV) splitting of the electronic absorption and new (short life-time) electronic and vibrational emission properties [5].

b) In contrast to this, F center/ OH^- association in crystals of NaCl structure only broadens and shifts the normal F center absorption without splitting and change of its oscillator strength. Under optical excitation in this band, however, all physical properties of the relaxed excited F state (like $\sim \mu s$ electronic emission and/or photoionization) are totally suppressed [2], and an extremely rapid radiationless return of the electron into its ground

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state occurs [6]. This optical cycle obviously produces energy transfer into the OH⁻ molecular stretching mode, as observed (at least in KCl) by anti-Stokes resonance Raman measurements [7].

Among the four host crystals of NaCl structure *b*) studied so far (KCl, RbCl, RbBr and KBr), the $F_H(\text{OH}^-)$ absorptions are «red-shifted» compared to the F band at high temperatures and remain red-shifted down to lowest temperatures in the three first above-mentioned hosts. In the exceptional case of KBr only, an unusually strong temperature-dependence of the $F_H(\text{OH}^-)$ absorption peak has been observed [8], changing its position from a red-shift to a blue-shift compared to the F band when cooling from 100 to 12 K. We extend in the present work this preliminary observation to lower temperature (2 K), to magneto-optical (MCD) measurements, and to a new host (KI). This extension leads to the discovery of an interesting—and so far unique—optical and thermal bistability of an F center/molecular defect pair in both KBr and KI host crystals.

2. Experimental results.

The additively colored KBr:OH⁻ and KI:OH⁻ crystals (produced in the Utah Crystal Growth Laboratory) were measured for low-temperature absorption and magnetic-circular-dichroism (MCD) spectra in a He cryostat containing a superconducting magnet immersed in the liquid He bath. The measurements were performed on the quenched crystal before and after optical irradiation at $\sim -30^\circ\text{C}$, *i.e.* both the pure F center and fully converted $F_H(\text{OH}^-)$ center system.

Figure 1 shows the results for a KBr:OH⁻ crystal obtained after optical conversion and immediate cooling in the dark to 1.9 K. The $F_H(\text{OH}^-)$ center is characterized by an absorption band (peak at 588 nm, halfwidth HW = 0.17 eV) and a related MCD spectrum, as shown under «I» in fig. 1*a* and *b*). Weak optical irradiation with monochromatic light at 580 nm converts these spectra into a red-shifted (peak at 614 nm) and broadened (HW = 0.26 eV) absorption spectrum and related MCD spectrum, marked with «II» in fig. 1*a*) and *b*). As indicated in fig. 1, optical irradiation at 650 nm reconverts these spectra II back into the spectra I. This bidirectional conversion can be repeated as often as desired without any irreversible loss of absorption or MCD. Obviously we observe optical bistability of two different configurations I and II of the F center/OH⁻ defect pair. The analysis of the MCD spectra shows that both center configurations I and II yield—within experimental accuracy—the same negative spin-orbit splitting ((28 ± 0.5) meV), a value about 25% larger than the spin orbit splitting ((22 ± 1.8) meV) of F centers in pure KBr. This result unquestionably confirms that the two optical bistable absorptions I and II are due to one-electron F -center-type defects in two different configurational arrangements relative to the OH⁻ defect. The partial overlap of these two absorptions may still prevent total optical conversion and makes it difficult to achieve exact measurements of the «pure» $F_H[\text{I}]$ and $F_H[\text{II}]$ center spectra.

In KI:OH⁻ similar results about a bistability of two $F_H(\text{OH}^-)$ center configurations were obtained. As illustrated in fig. 2, the spectral separation of the two absorptions is much smaller than is KBr. This strong spectral overlap makes anything close to a total I → II or II → I conversion impossible, and allows only production of and measurements with an unknown majority of one component compared to the other. Both absorption and MCD results, however, show that two optically convertible one-electron F -center-type defect configurations (with similar negative spin-orbit splittings) are present and stable at low temperatures.

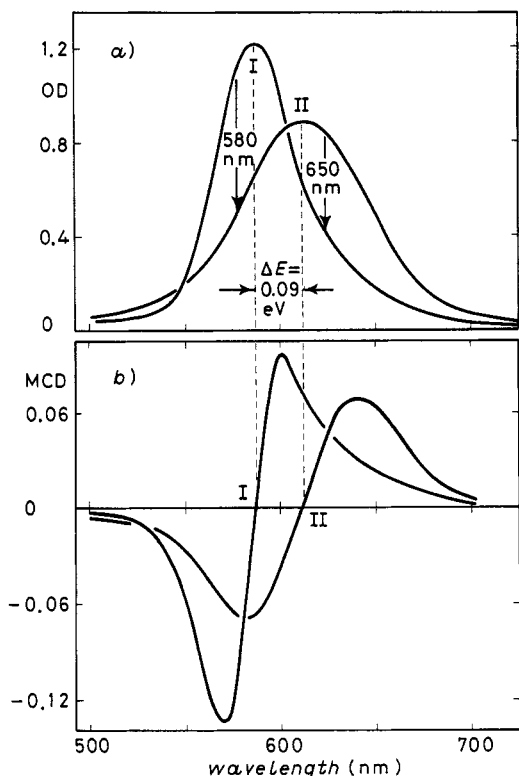


Fig. 1.

Fig. 1. - Optical absorption (a) and MCD spectra (b) of the two configurations I and II of $F_H(OH^-)$ centers in KBr + 1.5% KOH at $T = 1.9$ K.

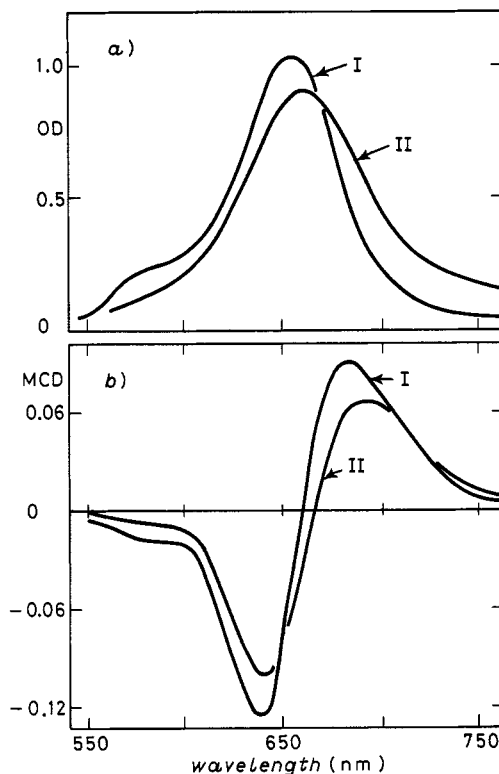


Fig. 2.

Fig. 2. - Optical absorption (a) and MCD spectra (b) of the two configurations I and II of $F_H(OH^-)$ centers in KI + 1% KOH at $T = 1.9$ K.

The important question, how the bistability is developed and destroyed under temperature variation, has been carefully investigated only for the better spectrally separated KBr $F_H(OH^-)$ case (using above 12 K a separate variable-temperature cryostat and different spectrometer). Figure 3 shows the measured $F_H(OH^-)$ absorption peak position E_{max} —compared to the F band peak—in a «thermal cycling» process starting at high temperatures. Above 150 K (range «D») the F_H peak is located on the red side of the F band and follows closely its «normal» temperature variation (partially produced by thermal lattice expansion). Cooling below 150 K (range «C») produces an abnormally strong blue-shift of the F_H band, intersecting the F band position and placing it on the high-energy side of F at its final 2.105 eV low-temperature value. Only in the $T \leq 5$ K range «A» bistability works and optical conversion into the strongly red-shifted band II can be achieved. If heating beyond $T \approx 5$ K is done with the F_H center in the blue-shifted state I, the peak position follows exactly the cooling curve. However, if started from the optically converted red $F_H[II]$ state, thermal back-conversion from II to I occurs in the narrow range B ((5 ÷ 10) K), so that under further heating above 10 K the same $E_{max}(T)$ behavior is obtained as under cooling. Any stable optical conversion change from this $E_{max}(T)$ behavior can no longer be achieved in the $T > 10$ K ranges C and D.

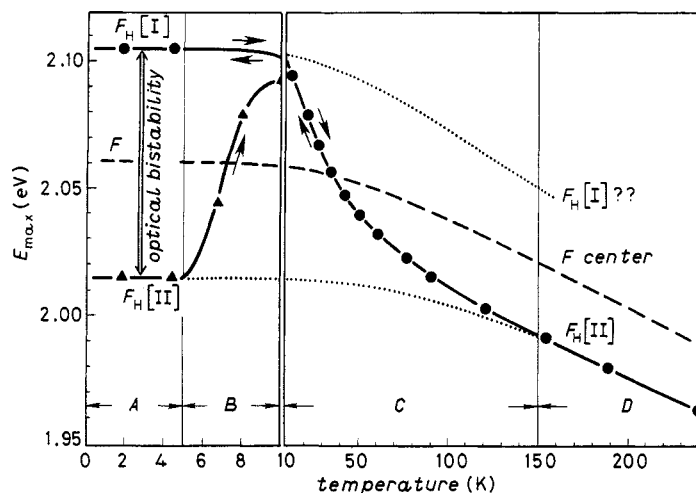


Fig. 3. – Temperature dependence of the $F_H(\text{OH}^-)$ absorption peak E_{\max} in comparison to that of the F center in KBr. The bistability and conversion behavior between configurations I and II in the temperature ranges A, B, C and D are discussed in the text.

3. Discussion.

We restrict our discussion to the case of KBr for which both spectral separation and temperature dependence of the $\text{I} \rightleftharpoons \text{II}$ configurational changes are observed. For isolated OH^- defects in KBr it is well known that their dipole axes are oriented along the $\langle 100 \rangle$ directions [9]. In spite of a rather high-energy barrier between the six equivalent $\langle 100 \rangle$ states (estimated to be about $\Delta E \approx 0.1 \text{ eV}$), OH^- reorientation occurs even at lowest temperatures with a very high rate ($\tau^{-1} \approx 10^8 \text{ s}^{-1}$ at 1.3 K) by quantum-mechanical tunnelling [10]. Under applied electric field or uniaxial stress, which splits the equivalent energy states by Δ up to $\sim 1 \text{ meV}$, one-phonon assisted tunnelling produces at low temperatures the above-mentioned reorientation rate with a linear T -dependence.

The introduction of an F center as a neighbor introduces—by elastic and electric distortions—a perturbation on the sixfold potential of the OH^- molecule which can be much larger than applied field or stress. Recent ENDOR experiments have shown that in the $F_H(\text{OH}^-)$ center in KCl the F center and OH^- molecule occupy $\langle 200 \rangle$ neighboring positions [11]. The overall $\langle 100 \rangle$ tetragonal symmetry of this defect-pair will preserve for the OH^- molecule its preferred $\langle 100 \rangle$ orientations, but will split its sixfold degeneracy into three levels: two single states of the OH^- molecule parallel to the pair axis (with its dipole moment pointing either towards or away from the F center), and a fourfold degenerate state of the OH^- orientation in the four $\langle 100 \rangle$ directions perpendicular to the pair axis. Current ENDOR studies [12] suggest that configurations I and II correspond to one of these parallel and perpendicular orientations, respectively, as indicated in the lower part of fig. 4. This assignment is qualitatively confirmed by our observation that the two low-temperature absorptions I and II lie blue- or red-shifted nearly symmetrically (by $\pm 0.045 \text{ eV}$) from the F band, suggesting in a simple Ivey law picture a contraction or expansion of the effective vacancy volume by about $\pm 3\%$, due to different orientations of the neighboring OH^- molecule. The K^+ ion located between F center and OH^- ion can move towards or away from the F center depending on the \parallel or \perp orientation of the OH^- ellipsoidal elastic dipole tensor.

Figure 4 illustrates schematically a proposed OH^- reorientation potential with two

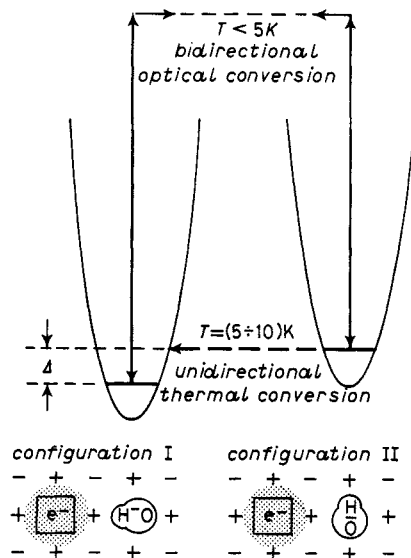


Fig. 4. - Tentative models for $F_H(OH^-)$ defect configurations I and II. A simplified energy potential diagram for reorientation of the OH^- between its two directions indicates schematically the optical ($T = (0 \div 5) K$) and thermal ($T = (5 \div 10) K$) conversion $I \rightleftharpoons II$.

unequal energies $E(I) < E(II)$ for the two configurations. As at low temperatures $T < 5 K$ both configurations are stable in the dark as long as observed, their possible reorientation rate $\tau < 10^{-4} s^{-1}$ is at least 12 orders of magnitude smaller than the $\tau^{-1} \approx 10^8 s^{-1}$ rate of free OH^- ions. Consequently the barrier height ΔE separating the two potential wells must be considerably higher than $\Delta E \approx 0.1 eV$ of the free OH^- making tunneling rates through the barrier immeasurably small for $T < 5 K$. In this temperature range (A) only optical excitation can produce bidirectional optical conversion between the two configurations I and II. Above 5 K the rate of tunneling in combination with phonon emission of the energy difference $\Delta = E_I - E_{II}$ becomes high enough to produce in range B a unidirectional $II \rightarrow I$ conversion into the deeper well. It is not yet clear if the conversion measured under heating of the crystal through the narrow (5 ÷ 10) K range reflects thermal equilibrium values I and II or a gradual conversion based on heating speed and a slow temperature-dependent unidirectional transition rate. Careful experiments on this question are at present under way.

It is not easy to interpret the thermal back-conversion $I \rightarrow II$ occurring very gradually over the wide temperature range (10 ÷ 150) K. The measured E_{max} values in this range are identical under heating and cooling, fully persistent at fixed temperatures, and impossible to be changed by optical irradiation. Evidently we are dealing with thermal equilibrium values which are a temperature-dependent mixture of configurations I and II. Two interpretations are feasible:

A) In a totally rigid potential with fixed Δ value over the whole temperature range (C), a gradual $I \rightarrow II$ conversion can only occur on the basis of kT becoming larger than Δ . Effective tunneling will lead under rising temperature to increasing population of configuration II, which due to its fourfold degeneracy becomes predominant over the population of the nondegenerate level I for $kT > \Delta$. Opposite to the schematic illustration in fig. 3, the final equilibrium at $T > 150 K$ (range D) will *not* be pure $F_H(II)$ centers, but a

mixture, e.g., $n_{II}:n_I \approx 4$ (as long as we disregard the OH^- configuration parallel to the pair axis with electric-dipole orientation opposite to the one considered in fig. 4). Based on this assumed model, an approximate value of $\Delta \approx 5$ meV results from the measured data in fig. 3.

B) A second interpretation is based on the reasonable assumption that the low-temperature reorientation potential (fig. 4) becomes gradually changed under temperature increase above 10 K. General lattice expansion and/or changes in the position of the axially shifted K^+ ion between the F center and OH^- defect could be the origin. It seems attractive to assume that the 10 K situation $E(I) < E(II)$ with thermal equilibrium $n(I) > n(II)$ changes gradually under temperature increase into the opposite one, such that $n(II) > n(I)$ is obtained at ~ 150 K and for even higher temperature (range D) essentially only the configuration II is occupied. This is supported by the fact that for $T > 150$ K the «normal F -center-type» $E_{\max}(T)$ behavior is observed; extrapolation of this normal T -dependence (lower pointed curve in fig. 3) through range C leads at low temperature into the optically produced stable $F_{\text{H}}[\text{II}]$ configuration. Similarly a thermal persistence of the pure $F_{\text{H}}[\text{II}]$ system when heating from low temperature into range C could lead to the upper dotted line extrapolation in fig. 3.

Evidently more detailed ENDOR and optical experiments are needed in order to fully clarify the exact I and II model and their static and dynamic interrelation, particularly in the temperature ranges B and C .

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