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F center associated with a pair of OH^- defects in cesium halides

Matthias Krantz and Fritz Luty
Department of Physics, University of Utah, Salt Lake City, Utah 84112

Volkmar Dierolf and Hans Paus
II. Physikalisches Institut, Universität Stuttgart, D-7000 Stuttgart, Germany

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A defect type consisting of an F center attached to a pair of OH^- molecular ions ["$F_{H2}(OH^-)$ center"] has been found in highly OH^--doped CsCl and CsBr. Its formation kinetics is based on optically induced F-center migration with primary association with single OH^- ions ["$F_H(OH^-)$ centers"] followed under prolonged irradiation by their bleaching and F-center association with OH^--ion pairs. When performed with polarized light, this process produces linear dichroism by selective polarized bleaching, indicating $\langle 100 \rangle$ symmetry of the $F_{H2}(OH^-)$ complex. The two attached OH^- defect ions split the F band into ~1-eV-separated absorptions polarized parallel and perpendicular to the $\langle 100 \rangle$ axis of the complex, a splitting unique in size among all F aggregate centers. Spectral and temperature dependence of magnetic-circular-dichroism measurements and the derived negative spin-orbit parameter confirm the uniaxial symmetry and one-electron perturbed F-center character of this defect.

I. INTRODUCTION

F centers associated with single molecular defect anions ("F_H centers") have been a subject of intense recent investigations.[1–4] Their interesting properties are based on the strong interaction between the optically excited F electron and the molecular defect which leads to effective electronic-vibrational (*e-v*) energy-transfer processes.[5–7] In the case of CN^- molecules, these defect pairs have been used successfully to produce laser-active devices.[8,9] It was found that the mutual influence of the center constituents on each other is most pronounced when they are located on $\langle 100 \rangle$ next-nearest-neighbor positions, as is the case in crystals of CsCl structure with simple-cubic translational symmetry. These F_H centers have the same C_{4v} point-group symmetry as the F-center–cationic-impurity pair (F_A center) in crystals with NaCl structure. The perturbation by the defect ions in both kinds of centers reduces the site symmetry for the F electron and splits its absorption band into separated electronic transitions polarized parallel and perpendicular to the pair axis. This splitting is usually smaller than 0.2 eV for all F_A centers with cationic impurities, becomes larger for F_H centers with CN^- molecular ions (~0.25 eV in CsCl), and reaches an exceptionally large splitting for the F-center–OH^- pair (~0.75 eV in all cesium halides). In spite of a very strong interaction between the F electron and the molecular ion, the $F_H(OH^-)$ center still preserves the character of an F center in a strongly perturbed environment of tetragonal symmetry.[4,10]

The described analogy of F_A and F_H centers (in hosts of NaCl and CsCl structure, respectively) in terms of their symmetry and absorption properties raises an interesting question: Can F centers in cesium halides become associated not only with a *single* but also with a *pair* of anionic defects, just as F centers in KCl can be associated with a pair of Na^+ impurities forming an "F_B center?"[11] This could be of particular interest for molecular-ion pairs, which show already as single defects pronounced perturbation effects on the electronic states and transitions of the F center.

We found indeed a complex of this type in highly OH^--doped CsCl and CsBr. This "$F_{H2}(OH^-)$ center" is studied in this paper in terms of its formation kinetics, optical, and magneto-optical properties in an attempt to derive its symmetry and microscopic configuration.

II. F_{H2}-CENTER FORMATION

Figure 1 summarizes all the essential spectral results for the CsCl host. Additively colored OH^--doped Cs halide crystals, thermally annealed at 450 °C and quenched to room temperature (RT), contain statistically distributed F centers and OH^- defects with F-center absorption spectra indistinguishable from those in pure crystals [Fig. 1(a)]. Optical irradiation into the F band at $T = 160$ K for an appropriate time associates all the F centers with single OH^- molecules forming $F_H(OH^-)$ centers, which show a characteristic wide splitting of the single F absorption into two bands [Fig. 1(b)]. This new absorption is due to a twofold (spin-orbit-split) transition [$F_H(2)$] and a single transition [$F_H(1)$], polarized perpendicular and parallel to the center axis, respectively.[4,10] This primary complex dissociates at $T = 180$ K under optical excitation of the high-energy band, causing a back conversion to F centers but also partially a gradual buildup of a secondary, more stable complex [$F_{H2}(OH^-)$ center]. Evidently, photoionized F centers which dissociate from single-OH^- defects at 180 K and can move in the crystal by thermal migration have a small chance to

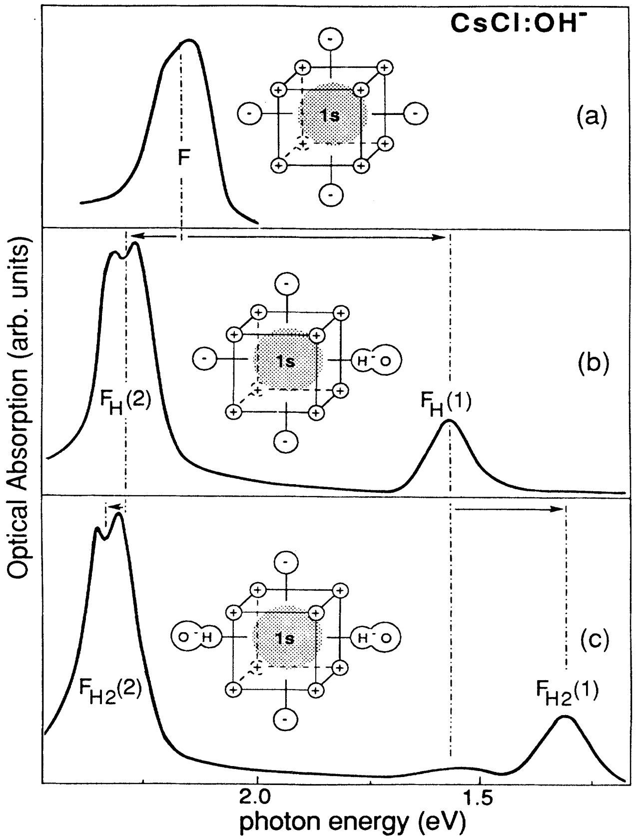

FIG. 1. Absorption spectra at $T=13$ K of the same additively colored CsCl crystal (doped with 1 mol % CsOH$^-$) in three subsequent stages: (a) after quenching, pure F centers; (b) after short ($\sim$5 min) bleaching, $F_H(\mathrm{OH}^-)$ centers; (c) after long ($\sim$18 h) bleaching, $F_{H2}(\mathrm{OH}^-)$ centers. The spectra in (b) and (c) are expanded by a factor of 2 compared with (a). The insets indicate besides the F-center model in (a) the favored configurations for F_H and F_{H2} centers in (b) and (c), respectively.

associate with additional traps (OH$^-$-defect pairs?) with a larger binding energy.

Multiple repetition of this optically-induced $F_H(\mathrm{OH}^-)$ aggregation and dissociation process by alternate bleaching into the F and $F_H(2)$ band at $T=180$ K finally leads to a predominance ($\sim$100% in CsCl and 80% in CsBr) of this secondary center compared with the primary F_H centers. Due to the strong spectral overlap of the $F_H(2)$ and F band, it is also possible to produce this center by prolonged bleaching (e.g., $\sim$18 h) into the F-band region at $T=180$ K, thereby performing simultaneously the processes described above. This formation process is very similar to the one found in KCl:Na where a short irradiation leads to the primary $F_A(\mathrm{Na}^+)$ center, while further bleaching produces the secondary-F-center-Na$^+$-pair complex, called a $F_B(\mathrm{Na})$ center.[11]

Figure 1(c) shows the absorption of $F_{H2}(\mathrm{OH}^-)$ centers in CsCl. It remains similar in spectral structure and indication of a splitting in its high-energy absorption, compared with the $F_H(\mathrm{OH}^-)$ center. The main change is an increase of the already large band separation of the F_H center (0.75 eV) into the unusually large separation ($\sim$1.0 eV) for the F_{H2} center, mostly produced by a further shift of the $F_{H2}(1)$ band to low energy (see Table I). The results obtained for CsBr crystals are essentially the same, spectrally shifted toward lower energies by about 0.2 eV relative to CsCl.

TABLE I. Absorption energy in eV of F, F_H(OH) and $F_{H2}(\mathrm{OH}^-)$ centers.

Host	F	$F_H(2)$	$F_H(1)$	$F_{H2}(2)$	$F_{H2}(1)$
CsCl	2.14	2.31	1.58	2.33	1.31
CsBr	1.96	2.10	1.35	2.13	1.14

III. MICROSCOPIC CONFIGURATION AND SYMMETRY OF THE CENTER

As the secondary aggregate center can only be formed in colored and OH$^-$ doped crystals, obviously it could in principle be either an F-center pair associated with a single OH$^-$ molecule or a single F center associated with an OH$^-$-defect pair. These two possibilities can clearly be distinguished. In lightly-OH$^-$-doped and strongly colored crystals, the described $F_{H2}(1)$ absorption at 1.31 eV in CsCl cannot be formed; instead, a weak and narrow ($\sim$0.1-eV) absorption at 1.16 eV appears additionally to the primary $F_H(\mathrm{OH}^-)$ aggregate under prolonged irradiation. Its formation kinetics and thermal and/or optical stability features are very similar to the ones of the "normal F_2 center," which appears also and is located with its low-energy absorption at 1.27 eV. Therefore it can be directly related to an F-center pair associated with a single OH$^-$ defect, i.e., an $(F_2)_H(\mathrm{OH}^-)$ center. In contrast to this, optical aggregation in a heavily-OH$^-$-doped and low-colored crystal never forms this 1.16-eV absorption; instead, the absorption change described in Fig. 1(c) appears. This strongly suggests that the building blocks of our center are one F center and two OH$^-$ molecules. Figure 2 illustrates [in an anionic (100) plane of the cesium halide crystal] several possible microscopic configurations. We try three experimental approaches to distinguish them and select the most likely one.

A. Formation kinetics

In a crystal of CsCl structure, the initially present close OH$^-$-defect pairs will exist in principle on ⟨100⟩, ⟨110⟩, or ⟨200⟩ neighboring lattice sites—either statistically or selectively distributed in their probability due to binding energies for a particular preferred configuration. The photoionized F center, migrating in the crystal as an empty anion vacancy by thermally activated diffusion hopping, can reach an existing OH$^-$ pair. When arriving at a ⟨100⟩ or ⟨110⟩ neighboring place to an OH$^-$ defect which is part of a pair, it can by one further jump process exchange its site with the OH$^-$ ion, thus altering the

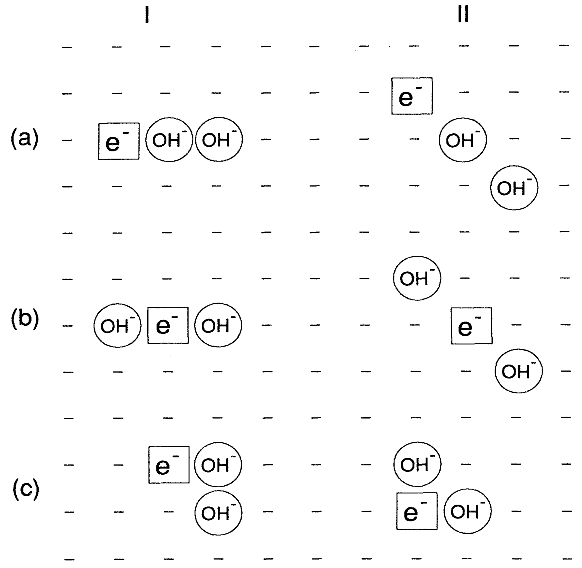

FIG. 2. Six possible configurations of an F center associated with a pair of OH^- defects, with the pair axis either in a ⟨100⟩ direction (I) or a ⟨110⟩ direction (II), illustrated schematically in an anionic (100) plane of a cesium halide (under neglect of OH^- dipole orientation).

original pair symmetry and establishing the F-OH^--pair configuration of lowest total energy. For instance, when a vacancy approaches a ⟨100⟩ or ⟨110⟩ OH^--pair configuration [I(a) or II(a) in Fig. 2] along the pair axis, it can in both cases exchange configuration (a) into (b) with a single jump process. Similarly, the two configurations (*I*c) and (*II*c) with F centers perpendicular to the OH^--pair axis can exchange into each other with one vacancy jump. In fact, each of the six configurations illustrated in Fig. 2 can convert into any of the other ones with a small number (1 to 3) of jumps. In summary: the resulting F_{H2}-center configuration is not dependent on (or predictable from) the symmetry of the originally present OH^- pairs, but will establish the configuration of lowest total energy by OH^--vacancy-site exchanges.

These considerations can be extended even a step further: As the primary $F_H(OH^-)$ defect, when photoionized, becomes a vacancy–single-OH^--defect complex, site-exchange processes of this pair can even help to transport the otherwise immobile single-OH^- defect by step diffusion through the lattice. Therefore the existence of close OH^- pairs is not even a precondition for F_{H2}-center formation, because they can in principle be formed by single-OH^--defect migration based on its site exchange with an anion vacancy.

B. Linear dichroism produced by polarized selective bleaching

As the formation kinetic (A) did not allow us to distinguish between the various possible configurations in Fig. 2, we used polarized light to produce linear dichroism. Unlike for F_A centers in KCl,[12] no direct reorientation of the center itself by polarized excitation could be achieved neither for the primary $F_H(OH^-)$ nor for the secondary $F_{H2}(OH^-)$ center. Therefore, another technique has been applied, using two approaches: (a) polarized bleaching into the $F_{H2}(2)$ band at $T = 180$ K after F_{H2} formation, and subsequent aggregation with F light, and (b) using polarized light already in the F_{H2}-center-formation process. Both techniques are essentially based on selective destruction and new formation of the center occurring separately in (a) or simultaneously in (b). Therefore, no dichroic effect could be achieved at temperatures below the onset of vacancy mobility and defect destruction ($T \approx 150$ K). Above that temperature, both methods yield the same results: (1) light polarized parallel to a ⟨100⟩ crystal axis produces a ⟨100⟩ dichroism of opposite sign for the two absorption bands of both F_H and F_{H2} centers (Fig. 3), and (2) light polarized parallel to ⟨110⟩ does not lead to any dichroism. When comparing these dichroic results with the six center models illustrated in Fig. 2, the following can be stated about the energies of the eigenstates based on symmetry arguments and reasonable assumptions.

(a) Configurations II(a) and II(b), with a ⟨110⟩ axial arrangement of the OH^- pair and the F center, are very similar in symmetry to the F_2 or $F_2{}^+$ center in hosts of NaCl crystal structure. Their high-energy (F-center-like) transitions occur polarized perpendicular to the ⟨110⟩ defect axis (and although not degenerate can lie close and overlap strongly), while their low-energy transition will be polarized parallel to the ⟨110⟩ axis. The observed inability to produce any dichroism under ⟨110⟩ polarized selective bleaching in the high-energy band clearly excludes these configurations.

(b) For configuration II(c)—which in its C_{2v} point-group symmetry is an analog to the $F_B(2)$ center in KCl:Na—only a single high-energy (B_2) transition along a ⟨100⟩ direction perpendicular to its (100) mirror plane is expected, while the two (B_1 and A_1) transitions within this plane and polarized parallel and perpendicular to the ⟨110⟩ OH^--pair axis will lie at lower energy (and could be nearly degenerate, like in the $F_B(2)$ center. Selective bleaching in the nondegenerate ⟨100⟩ high-energy band should indeed not produce any dichroism when performed with ⟨110⟩-polarized light as observed. However, the measured oscillator strength ratio between the high- and low-energy bands (which equals 3.2 for CsCl) does not agree with the value of 0.9 predicted for this II(c) configuration, and most convincing the MCD results discussed later are in contradiction with this model.

(c) Configuration I(c) is similar to II(c), although it has a lower symmetry within its (100) mirror plane. The single transition perpendicular to this plane in a ⟨100⟩ direction should be least affected by the OH^- ions and therefore lies at the highest energy similar to the II(c) configurations. As argued above under (b), this model has to be excluded from further consideration.

(d) The two remaining configurations I(a) and I(b) with a ⟨100⟩ axial arrangement of both OH^- ions and the F center will have two degenerate high-energy transitions and one single low-energy transition, perpendicular and parallel, respectively, to the center axis. Their oscillator

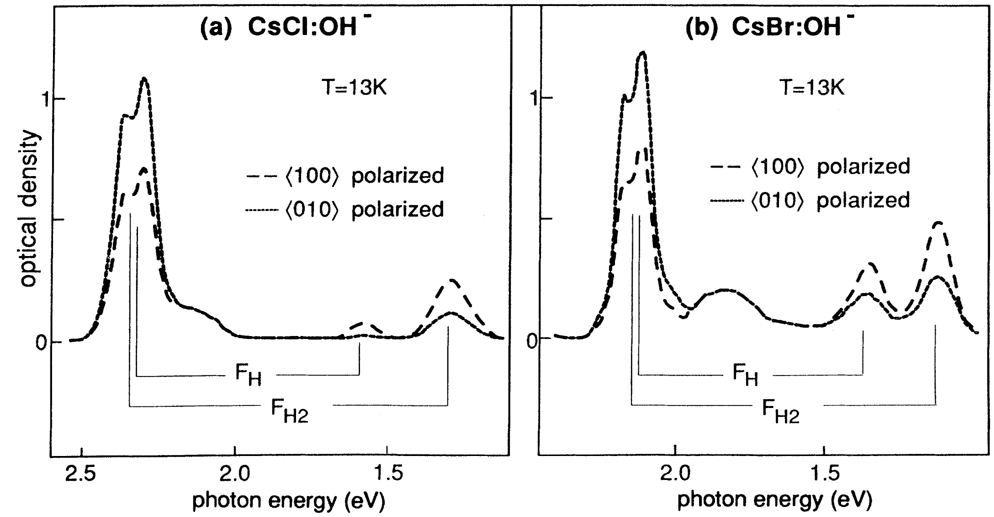

FIG. 3. ⟨100⟩ linear dichroism in the absorption spectrum of $F_{H2}(\mathrm{OH}^-)$ centers in CsCl (a) and CsBr (b), obtained by selective ⟨100⟩-polarized bleaching and aggregation processes described in text.

strength ratio predicted to be 3.6 for both these models closely fits the measured 3.2 value. Moreover, both these models fit very well the observed ⟨100⟩ dichroic behavior and its absence under ⟨110⟩-polarized selective bleaching.

C. Magnetic circular dichroism of $F_{H2}(\mathrm{OH}^-)$ centers

Final confirmation of the structural model of this defect—and particularly its one-electron paramagnetic character—was achieved by magnetic-circular-dichroism (MCD) measurements performed in both CsCl and CsBr hosts. For this purpose the same experimental setup and partially the same samples as in the previous paper[10] have been used, so that qualitative comparisons with the results for F_H centers can be made very easily and reliably.

The F_{H2} MCD is very similar in strength and spectral shape to that of the F_H center and shows the following (see Fig. 4).

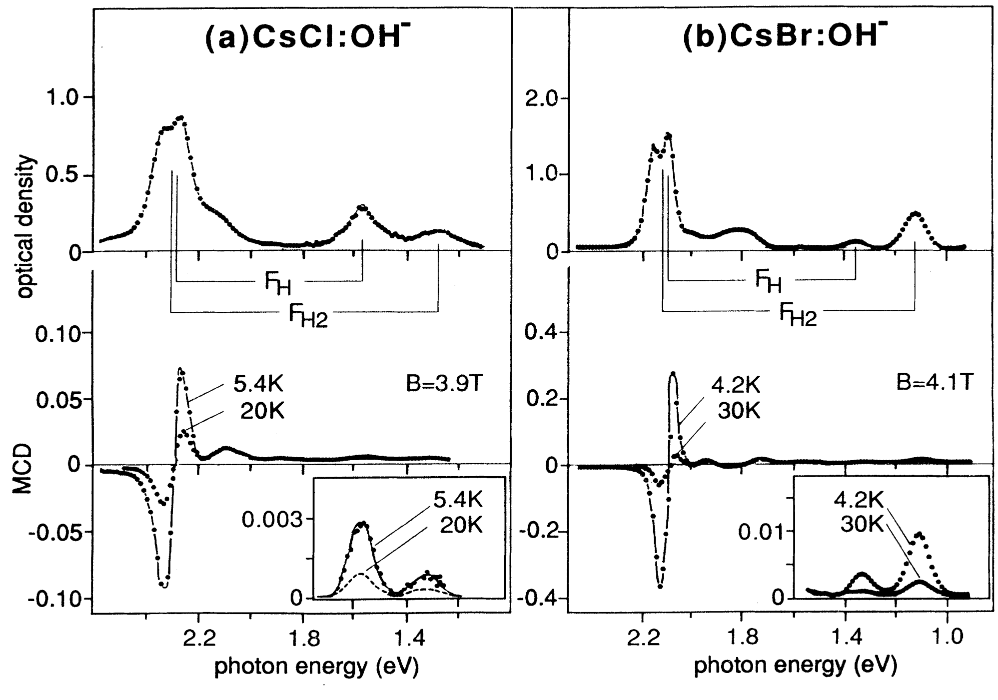

FIG. 4. Absorption and MCD spectra of $F_{H2}(\mathrm{OH}^-)$ centers in CsCl (a) and CsBr (b) at $T=4.2$ K. The insets show the MCD (enlarged about ten times) observed in the spectral region of the low-energy transition of F_H and F_{H2} centers.

(a) A derivativelike first-moment change in the $F_{H2}(2)$ absorption.

(b) A very small positive MCD in the $F_{H2}(1)$ band due to a zero-moment (area) exchange.

(c) The prediction[14] that the summation over the whole MCD spectrum yields zero is only fulfilled if both bands are included.

These results indicate that both absorption bands belong to the same center with a single low-energy transition and two high-energy states. The substructure of the high-energy band, already observable in the optical-absorption spectra [Figs. 1(c) and 4], is due to two transitions split predominantly by a strong spin-orbit (s.o.) effect with a negative s.o. parameter Δ_2. This unambiguously excludes the configurations I(c) and II(c) of Fig. 2 for which the high-energy transition is a single one. For the models II(a) and II(b) the $F_{H2}(2)$ band is due to $\langle 001 \rangle$- and $\langle 110 \rangle$-polarized transitions perpendicular to the $\langle 110 \rangle$ pair axis. The corresponding nondegenerate states should be separated considerably under the different influence of the OH^- molecule and not, as our MCD results show, by the s.o. interaction. Together with the conclusions obtained from linear dichroism, however, the MCD results leave only the configurations I(a) and I(b) as possible candidates. We will consider only these two models of tetragonal symmetry for the further evaluation and discussion of the MCD, which are based on methods and theories outlined in the previous paper[10] and are not repeated here.

Due to the incomplete $F_H \rightarrow F_{H2}$ conversion, their close-lying high-energy spectral band overlap partially and make a quantitative MCD analysis of the spin-orbit parameter Δ_2 in that spectral regime difficult. Qualitatively, we see that the F_{H2} aggregation only shifts the absorption band to higher energy without changing its shape, while the MCD signal clearly indicates that Δ_2 and the coupling to lattice modes is very similar to the F_H center.

The well-separated $F_{H2}(1)$ band, however, allows reliable measurements of the MCD temperature behavior, even in the CsCl crystal with the low F_{H2}-center concentration (Fig. 5). The linear $\tanh(\mu_B B/kT)$ dependency clearly indicates the one-electron character of the complex. Furthermore. a quantitative analysis was possible for the CsBr sample. Using the moment method of Henry, Schnatterly, and Slichter[13] and spectroscopic data of the F_H center,[10] our MCD results yield a spin-orbit parameter $\Delta_{12} = -39$ meV, a significantly lower absolute value compared with those of the F and $F_H(OH^-)$ center ($\Delta_F, \Delta_{12} = -48$ meV).[10] The size and sign of the s.o. parameters of the F center can be understood on the basis of orthogonalization of its wave functions to occupied states of the neighboring ions.[14] For this case the s.o. parameter is negative and mainly due to "transferred s.o. interaction" from the host ions which depend on their s.o. energy and the spatial overlap of their states with the F-center wave functions. Pure replacement of next-nearest-neighbor (NNN) halogen host-ions by OH^- molecules with a smaller s.o. energy give, in principle, rise to a Δ anisotropy[15] with a reduction of $|\Delta_{12}|$ compared with $|\Delta_F|$. Due to the dominating s.o. role of the unchanged Cs^+ ions for the Δ values (≈ 40 meV), however, the replacement effect is too small to account for the observed $|\Delta_{12}|$ reduction.[10] Apparently the presence of two OH^- impurities induces a decrease of spatial overlap between Cs^+ and F-center states, either by distortion of the nearest-neighbor (NN) Cs^+-ion positions (most likely of E_g symmetry) or change in the extent of the F-center wave function.

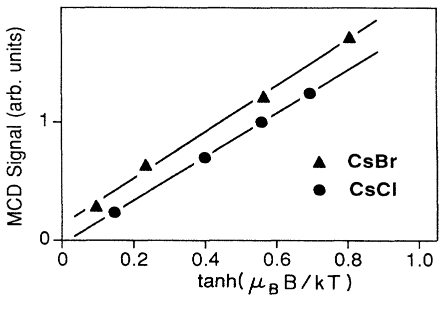

FIG. 5. Temperature dependence of the MCD in the $F_{H2}(1)$ band of CsCl+0.2 mol % CsOH (●) and CsBr+1 mol % CsOH (▲).

The observed Δ reduction favors configuration I(b) over I(a), because an ion exchange on a next-nearest-neighbor $\langle 100 \rangle$ site is expected to have a stronger influence on the s.o. properties than an exchange on a $\langle 200 \rangle$ site. The preferred I(b) configuration is directly analogous to the most stable tetragonal D_{4h} configuration (I) of the F_B complex in KCl:Na, an F center located centrally between two nearest-neighbor Na^+ cations.[11]

IV. ADDITIONAL PROPERTIES AND FINAL DISCUSSION OF THE $F_{H2}(OH^-)$ CENTER

The thermal stability of the $F_{H2}(OH)$ center is very similar to that of the F_H center: annealing in the dark at $T = 250$ K results in dissociation and the formation of F centers. Different from the F_H center, however, the complex is rather unstable under optical irradiation. In CsCl bleaching into either absorption band results in the formation of F'-like bands even at lowest temperatures ($T = 13$ K). The same thing happens in CsBr but at higher temperatures ($T > 80$ K) and only by bleaching into the high-energy $F_{H2}(2)$ band. Irradiation at $T = 13$ K into the broad F'-like band restores in both crystals the original F_{H2} centers.

In the initial stage of the F_{H2}-center formation with statistically distributed F centers and OH^- molecules, the normal F-center luminescence is totally quenched due to the high OH^- concentration ($> 0.2\%$) we used in our samples.[2] Aggregation to a single OH^- molecule—as a first step—yields, however, electronic F_H luminescence[4] which vanishes under further aggregation of the F centers to OH^--molecular-ion pairs. The instability under laser excitation mentioned above makes it difficult to investigate the luminescence behavior of the complex, but careful measurements indicate that there is no $F_{H2}(OH^-)$

emission in the whole spectral range from 1.2 eV (electronic emission) to 0.4 eV (vibrational OH^- emission). This total emission quenching indicates that there are rather efficient nonradiative processes involved in the deexcitation and ionization of the F_{H2}-center electron.

In our discussions dealing with all center models in Fig. 2, we have so far not yet made any statement about the orientation of the OH^- electric dipole for the various configurations, which could be very important for selecting the one of lowest energy. Recent calculations by Gash[16] using the pseudopotential method have shown the great influence of the OH^- molecular and displacement dipole moments on the eigenstates and the splitting of the two absorption bands of $F_H(OH^-)$ centers. The best agreement for the absorption energies could be achieved with the OH^- dipole moments pointing towards the F electron as shown in Fig. 1(b). We speculate that the second OH^- molecule in our F_{H2} center is oriented in the same way, i.e., oppositely relative to the first OH^-, as we have tentatively illustrated it in Fig. 1(c). For this (D_{4h}) mirror symmetry of the complex, the two positive (proton) ends of the neighboring OH^- ions could contribute both to the binding energy of the F electron in its $1s$ ground state and, even much more, to a very strong lowering of the energy of the unrelaxed $2p_z$ state polarized along the defect axis z. Mirror-symmetric displacement dipoles due to shifts of the OH^- ions along the z axis can still enhance this energy lowering of the defect eigenstates, explaining at least partially the observed large splitting of the $2p_z$ versus $2p_{xy}$ unrelaxed states in absorption. Additionally, the presence of a strong E_g lattice distortion expected for this complex of D_{4v} symmetry could contribute to the splitting of the excited p states (and to its Δ anisotropy, as dicussed in Sec. III C).

The relaxation process after optical absorption produces for "normal" F centers besides lattice relaxation a considerable expansion of the $2p$ excited state from a "compact" to a "diffuse" one and a mixture with the $2s$ state, bringing the energy of the relaxed excited state very close to the conduction band. In our $F_{H2}(OH^-)$ complex, additional displacements of the OH^--ion positions and changes in the dipole orientation can occur under relaxation. Very high electric fields, produced by OH^- dipole positions and orientations, could produce field ionization of the electron from the relaxed excited state, as it is observed under applied external fields for normal F centers. This could explain the efficient photoionization down to lowest temperature observed under optical excitation in both bands for CsCl, and the absence of a characteristic F_{H2}-center luminescence.

An alternative interpretation is the assumption that electron-vibration (e-v) energy transfer from the optically excited F electron to OH^- vibrational modes (and subsequent v-v energy transfer and migration among the free OH^- defects) plays an important role in the nonradiative F-electron relaxation process. This process has been considered for the observed highly efficient quenching of F luminescence by OH^- defects in KCl (Ref. 2) and has, at least partially, been confirmed by anti-Stokes resonance Raman studies and theoretical treatments of $F_H(OH^-)$ and $F_H(OD^-)$ centers in KCl.[6] Efforts to extend these (e-v) energy-transfer studies to the $F_{H2}(OH^-)$ and $F_{H2}(OD^-)$ centers in cesium halides are at present underway.

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