where

$$M_{\parallel}^2 = |\langle 1s|z|2s'\rangle|^2$$

and

$$M_{\perp}^2 = |\langle 1s|x|2s'\rangle|^2 = |\langle 1s|y|2s'\rangle|^2.$$

Thus, the change in radiative lifetime at low temperatures is related to the polarization as

$$\Delta\tau/\tau = -\tfrac{2}{3}[1/(1+\alpha^2)]P. \qquad (4)$$

Models which invoke tunneling or p-state orientation do not predict the change in lifetime.

At higher temperatures, emission from the higher lying $2p'$ states becomes important. In the simplest model,

$$P(T) \approx P(0)\frac{1-e^{-\delta E/kT}}{1+3Re^{-\delta E/kT}}, \qquad (5)$$

where $R = (1+\tfrac{2}{3}\alpha^2)/\alpha^2$ is the ratio of $2s'$ and $2p'$ lifetimes.

Using Eq. (4) to determine the mixing parameter, and $P(T)$ to determine δE, we find for KCl, $\alpha \simeq 0.7$, $\delta E \simeq 0.017$ eV and for KF, $\alpha \simeq 0.7$, $\delta E \simeq 0.016$ eV. These parameters are consistent with the temperature dependence of the lifetime reported earlier.[4]

The energy separation δE is consistent with recent theoretical estimates[10,11] for the $2s$-$2p$ separation in the relaxed states when mixing is ignored.

The large value of the mixing parameter implies that the states of the undistorted center would be nearly degenerate. This complicates the problem considerably, and suggests that a treatment following the approach of Öpik and Pryce[9] may be necessary.

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MAGNETIC CIRCULAR POLARIZATION OF F-CENTER EMISSION*

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Magnetic-field-induced circular polarization of F-center emission has been observed in KF. The effect is small and temperature independent in the range 1.3 to 4.2°K, and is interpreted as orbital Zeeman mixing with $g_{\mathrm{orb}} \sim 0.04$.

A new model for the states of the excited F center in alkali halides was presented in the preceding Letter.[1] Numerous attempts to observe electron spin resonance or magneto-optic effects in the "relaxed" excited states have been unsuccessful. In this Letter, we report the successful observation of such an effect, a small magnetic-field-induced circular polarization of the F-center emission in potassium fluoride. The small size and temperature independence of this effect support the new model.

KF was chosen for this study because its F-center absorption and emission bands lie at wavelengths which are technically favorable for high sensitivity. From earlier emission studies[1,2] we know that the relaxed excited states of the F center in KF are very similar to those in KCl and other "standard" alkali halides.

Samples of Harshaw KF were cleaved to dimensions of a few mm and colored by x irradiation at 78°K until the F-center concentration was about $10^{16}/\mathrm{cm}^3$. The sample then was placed in the bore of a small superconducting solenoid in an immersion optical cryostat. This produced fields up to 25 kG along the optical axis at sample temperatures of 1.3 to 4.2°K. F emission was excited by the 436-nm line from a 150-W Hg lamp through a monochromator and No. 4-96 Corning filter, and was detected on the opposite side of the sample through another monochromator and No. 2-60 filter with a cooled S-1 photomultiplier. The difference between the intensities of left- and right-hand circularly polarized emission was measured using an electro-optic light modulator and phase-sensitive detection at ~717 Hz.

A typical difference curve is shown in Fig. 1, together with the dc emission signal which was recorded simultaneously. The effect at 19 kG in this example is a fractional change $[\Delta = (I_+ - I_-)/I]$ of -1.0×10^{-3} favoring right-circular polarization $(x-iy)$ when $\vec{k}$ and $\vec{H}$ are in the $+z$ direction. This zeroth-moment change depends linearly on H and is independent of temperature, as shown in Fig. 2. No first-moment change was detected.

The theory and analysis of dichroism in F-center absorption have been described in detail by Henry and Slichter.[3] The situation for emission will be different, both because the relaxed excited states are different from those seen in absorption, and because the degeneracy is now in the initial states. We start with the same magnetic interaction, $\mathcal{H}_{\text{int}} = \mathcal{H}_{\text{s.o.}} + \mathcal{H}_z = \lambda\vec{L}\cdot\vec{S} + \beta\vec{H}\cdot\vec{L}$, and infer from the experiment which terms are important.

The temperature independence of the result indicates that Boltzmann population effects are not important, and that the magnetic interaction is temperature independent. The first implies that the emitting level is not split by the field and is separated from higher lying levels by $\delta E \gg kT$. The second implies that the spin-orbit contribution is negligible. Either the spin-orbit coupling constant λ is greatly reduced in the relaxed state, or there is no net spin polarization ($\langle S_z\rangle = 0$), or both. Several workers[4,5] have found that spin polarization can be destroyed by optical pumping, and we suspect that this is the most likely explanation here.

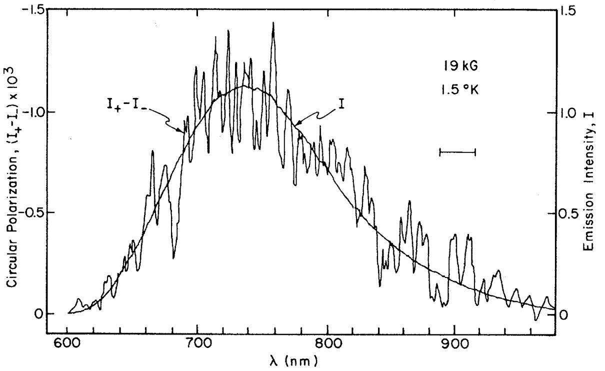

FIG. 1. The magnetic circular polarization signal and the dc emission signal recorded simultaneously for F-center emission in KF.

The orbital Zeeman interaction is temperature independent. The relatively small size of the circular-polarization signal implies that the orbital moment is strongly reduced.

The model for the relaxed excited states discussed in the preceeding Letter has the qualitative features needed. At low temperatures, the emission occurs only from the lowest state which, for distortion in the x direction, is of the form $(|2s\rangle + \alpha|2p_x\rangle)/(1+\alpha^2)^{1/2}$. The magnetic interaction mixes $|2p_x\rangle$ with the state $|2p_y\rangle$, an energy δE above it, so that the lowest state becomes

$$|\psi\rangle \sim |2s\rangle + \alpha|2p_x\rangle + \epsilon\alpha|2p_y\rangle, \tag{1}$$

where

$$\epsilon = \frac{-\langle 2p_y|L_z|2p_x\rangle(\beta H_z + \lambda S_z)}{\delta E}. \tag{2}$$

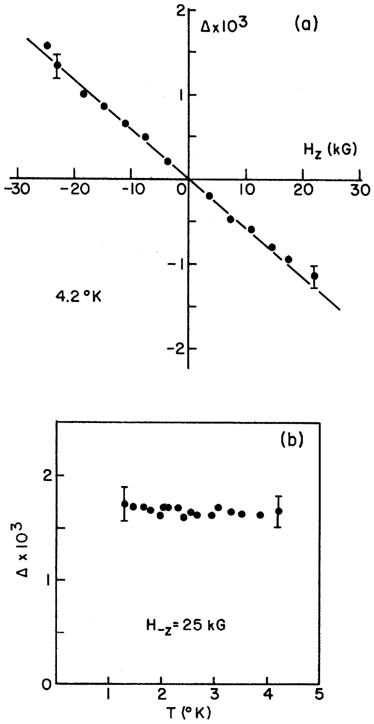

FIG. 2. Magnetic circular polarization $[\Delta = (I_+ - I_-)/I]$ of F-center emission in KF as a function of (a) applied field and (b) temperature. The solid line in (a) corresponds to Eq. 4.

The effect of this mixing is to increase the transition probability for the polarization $x-iy$ and decrease it for $x+iy$. To first order, the change for this one center is $(I_+-I_-)/I \simeq 4\epsilon$. There is no change in the energy of the emission to first order in ϵ.

In the case where $\langle S_z \rangle = 0$, the spin-orbit contribution cancels for an average over all centers, while the orbital Zeeman contribution does not. The resultant circular polarization can be written

$$\Delta = -\frac{4g_{\text{orb}}\beta H_z}{\delta E}, \qquad (3)$$

where $g_{\text{orb}} = |\langle 2p_y | L_z | 2p_x \rangle|$. This result has the same form as the observed effect

$$\Delta_{\text{exp}} = -(6\pm1)\times10^{-8} H_z, \qquad (4)$$

where H is given in gauss. Since δE was estimated to be ~0.016 eV from the Stark effects in emission, this would imply that $g_{\text{orb}} \simeq 0.04$. Such a strong reduction of the orbital g value is not unusual for color centers. It might result from countercirculating current on the neighboring ions,[6] or from even-parity Jahn-Teller distortion,[7] or both.

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Note added in proof.—After this Letter was submitted, a paper by Mollenauer et al.[8] appeared reporting the indirect observation of ESR in the relaxed excited state of the F center. Although the behavior we observe is quite different from theirs, and we measure orbital rather than spin g values, the two experiments are consistent. They were able to detect microwave-induced spin flips at resonance in the excited state because the normal spin memory of the F center in a single excitation cycle is very high (~99%). However, it is possible to quench the spin polarization by intense optical pumping if the spin-lattice relaxation time T_1 is sufficiently long compared with the recycling time. We have verified that the spin polarization is destroyed under the conditions of our experiment in KF. This was demonstrated by monitoring the magnetic circular dichroism of the F absorption band as a function of pumping-light intensity. A detailed account of this work will be published elsewhere.

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OPTICAL PROPERTIES OF SINGLE-CRYSTAL FILMS OF $CdCr_2S_4$

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We report on the preparation and optical properties of single-crystal films of $CdCr_2S_4$. The present data show no large blue shift associated with magnetic ordering near the Curie temperature contrary to that previously observed in bulk $CdCr_2S_4$ data. A large red shift correlated to the magnetic ordering is observed for a peak in the highly absorbing region. The weakness and narrowness of this absorption is inconsistent with that expected for band-to-band transitions resulting in unbound electrons and holes. We suggest an exciton model to explain this absorption.

The absorption edges of magnetic semiconducting chromium chalcogenide spinels are known to shift dramatically near the Curie point.[1-4] The usual shift is to lower energies (red shift) with increasing magnetic order (decreasing temperature); however, a large opposite blue shift was observed for $CdCr_2S_4$.[1] Several models have been proposed to explain these large magnetic shifts[5-10]; however, the need to simultaneously account for both senses of shifts has placed a