FARADAY ROTATION OF THE Z_1 CENTER IN KCl*

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In alkali halides doped with divalent cations (like Ca^{++}, Sr^{++}, and Ba^{++}), F centers can be converted photochemically into a series of secondary centers, the Z centers. To understand the formation kinetics and nature of these centers much work has concentrated on the primary reaction product of this conversion, the Z_1 center. From numerous experiments and speculations[1-10] the four different structure models shown in Fig. 1 have been derived. Early optical experiments[1,2] seemed to be consistent with model A or B assuming for the $F \to Z_1$ conversion process only an electron transfer from the F to the new center. Later Härtel and Lüty[6] identified the ionic character of this process (similar to that of the F_A- and M-center formation) and arrived at a model of type C or D. Electron-spin resonance[3,4] shows an unresolved F-like signal which has often been interpreted with model B since this is the only model with the same symmetry as the F center. ENDOR measurements[10] could not unequivocally decide between the four models but made type C or D plausible. Evidently the given models can be divided into two groups according to the location of the center electron: (1) impurity-ion centered or (2) vacancy centered. Faraday-rotation experiments give a clear decision between these two possibilities.

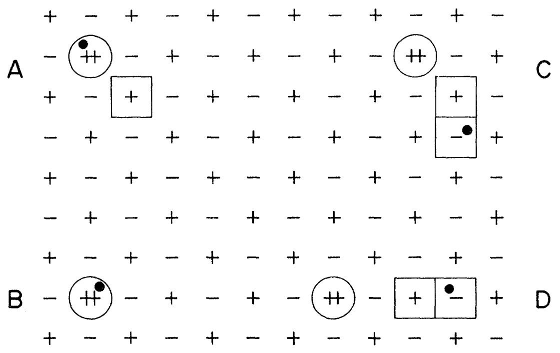

FIG. 1. The four different structure models proposed for the Z_1 centers, according to Refs. 1, 2, 6, and 10.

Our experimental arrangement was similar to that described by Mort, Lüty, and Brown[11] and used a 50-kG superconductive magnet. In $CaCl_2$- and $SrCl_2$-doped and additively colored KCl the Z_1 centers were formed by irradiating the crystal with F light at −40°C.[6] As an example Fig. 2 shows the absorption and rotation spectrum after optimum $F \to Z_1$ conversion in KCl:Ca (for KCl:Sr both patterns look very similar). Besides a small residual F band the Z_1-center absorption consists of the main Z_1 band at 2.1 eV and a broad accompanying band at 2.4 eV. The measured spectrum of the Faraday rotation [full line Fig. 2(b)] can be divided into a pattern for the Z_1 and the small

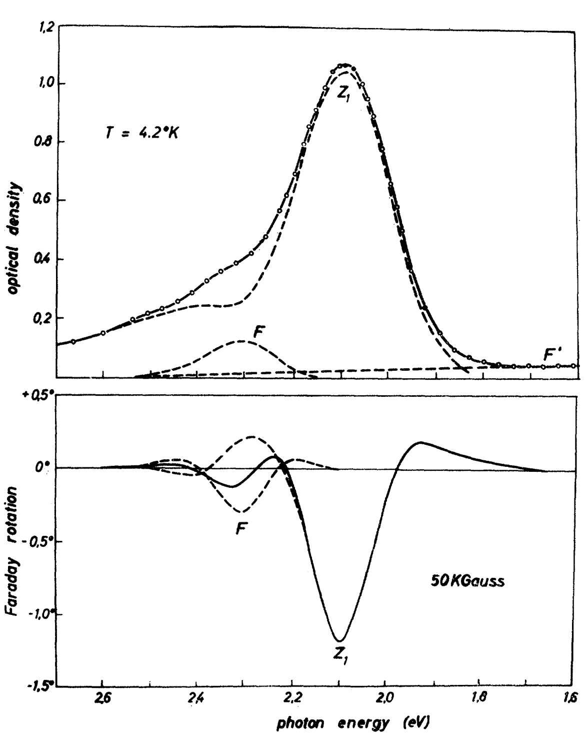

FIG. 2. Absorption and Faraday rotation spectrum of Z_1 centers in KCl:Ca (full lines, measured spectrum; dotted lines, decomposition into F- and Z_1-center parts).

residual F band. Doing this a small (negative) rotation remains for the 2.4-eV band. A variation of the Z_1 rotation with temperature (Fig. 3) reveals the existence of a paramagnetic and diamagnetic part of the Faraday rotation similar to the F-center rotation.

The analysis of the rotation was made using the "rigid shift approximation"[11] since moment analysis[12] would require very accurate separation of the different absorption and rotation patterns. Following in principle the deduction of Ref. 11 or Henry, Schnatterly, and Slichter[13] (but using the correct Kramers-Kronig relation[14] for circularly polarized light in the conversion of the index of refraction to the absorption constant) one arrives at the same final formula as Ref. 11. Approximation of the absorption band by a Gauss function of maximum α_m and half-width W (F center 159 meV, Z_1 center 252 meV at liquid-helium temperature) leads to the following expression for the minimum rotation:

$$\theta_{\min} = -\left(\frac{\ln 2}{\pi}\right)^{-1/2} \frac{2\alpha_m l}{W} g_{\text{orb}} \beta H - \tfrac{1}{3}\Delta \tanh \frac{g_1 \beta H}{2kT}$$

or

$$\theta_{\text{red}} = g_{\text{orb}} - \frac{1}{3}\frac{\Delta}{\beta H} \tanh \frac{g_1 \beta H}{2kT}$$

(l is the thickness of the probe; g_{orb} is the g factor and Δ the spin-orbit splitting energy of the excited state; g_1 is the g factor of the ground state, with good approximation =2 for F and Z_1 center[3,4]).

The application of this analysis to the data of Fig. 3 yields Δ and g_{orb} values for F and Z_1 centers. The good agreement of our F-center results ($\Delta = -10.5$ meV and $g_{\text{orb}} = 1.2$) to the values from Refs. 11 and 12 assures the consistency of the methods used for measurement and computation. For the Z_1 center we find a spin-orbit splitting

$$\Delta Z_1(\text{Ca}) = -7.6 \pm 0.5 \text{ meV}$$

and

$$\Delta Z_1(\text{Sr}) = -8.0 \pm 0.5 \text{ meV},$$

while in both cases $g_{\text{orb}} = 1.4 \pm 0.2$ is obtained.

The sign and magnitude of the Z_1 spin-orbit splitting clearly reflect the location of the Z_1-center electron. For an electron centered at the impurity ion the spin-orbit interaction would be mainly due to circulation currents in the central field of the ion nucleus. So Δ should be positive (as observed, e.g., for the $A_g{}^0$ center[15]) and show a strong variation between Ca^{++} and Sr^{++} (free-ion spin-orbit energies +28 and +100 meV, respectively). A negative value of Δ, however, is expected for a vacancy-centered electron wave function overlapping some of the ions around the vacancy.[16] Orthogonalization to the filled orbitals of these ions (which is necessary to satisfy the Pauli exclusion principle) induces circulations of current about the neighboring nuclei that are opposite to the central

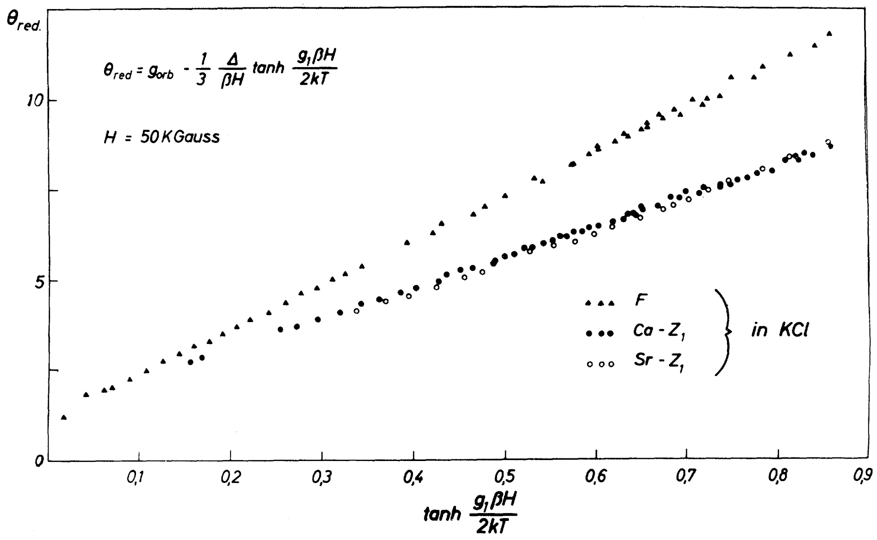

FIG. 3. Temperature dependence of the reduced Faraday rotation for F centers and Z_1 centers in KCl:Sr and KCl:Ca (θ_{red} is corrected for the temperature dependence of the absorption bands above 20°K).

circulation. As their contributions are much stronger than the contribution from the circulation in the weak central field of the vacancy, a negative spin-orbit splitting results. Thus the observed negative sign and magnitude of Δ indicate that the Z_1-center electron is vacancy centered and overlaps the surrounding lattice similar to the F-center electron. Moreover the insensitivity of Δ against $Ca^{++} \rightarrow Sr^{++}$ substitution suggests a non-nearest-neighbor site of the impurity ion at the vacancy. Similar conclusions have been drawn from the corresponding insensitivity of optical-absorption[6] and ENDOR[10] measurements. Thus the Faraday-rotation results lend strongest support to a vacancy-centered model of type C or D for the Z_1 center.

The absorption band at 2.4 eV accompanying the Z_1 band [Fig. 2(a)] resembles in relative location and spectral shape very much the K band of the F center. Following the interpretation by Smith and Spinolo,[17] its origin would be unresolved transitions into higher p states, which apparently for the Z_1 center have much higher relative oscillator strength than for the F center. Accurate experiments on the Faraday rotation of this band are under way.

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TRANSMISSION SPECTRA OF ZnO SINGLE CRYSTALS

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The fundamental absorption edge and the exciton structure of zinc oxide (ZnO) was first studied systematically by Thomas,[1] and the observation of exitons as polaritons has also been reported by Hopfield and Thomas.[2] The latter work was probably stimulated by results on the fundamental spectra of ZnO reported by Park et al.[3] Different interpretations for much of the experimentally observed structure have been given by these workers; a particular consequence of this is a discrepancy in the values quoted for both the spin-orbit interaction energy and the exciton binding energies. The difficulty derives from the interpretation of the reflection spectra which are highly complex near the absorption edge.

Transmission experiments using polarized light have been made on single crystals of ZnO at liquid-helium, liquid-nitrogen, and room temperatures. By using crystals as thin as 0.1 μm, transmission measurements have been made to photon energies greater than the band gap, and the method is similar to that used for wurtzite zinc selenide.[4] Thin platelets of ZnO were grown by the vapor transport method, using argon as the carrier gas. These crystals have the wurtzite structure with the c axis lying along the growth plane. Transmission electron-microscopy and -diffraction studies showed that most of these platelets were good single crystals free from defects such as stacking faults, though isolated crystals