



## DISPERSION OF THE $F_2^+$ CENTER IN KCl CRYSTAL

D.A. Donatti and M.A. Aegerter

Departamento de Física e Ciência dos Materiais, Instituto de Física e Química de São Carlos,  
University of São Paulo, 13560 São Carlos - SP - Brasil

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The dispersion due to  $F_2^+$  center in KCl crystal is determined at liquid helium temperature through an ellipsometric technique using their polarization properties in the spectral region of the  $1s\sigma_g \rightarrow 2p\sigma_u$  transition. The maximum index change expressed as a function of the peak-to-peak dichroic absorption constant  $\alpha_d(\text{cm}^{-1})$  is given by  $(n_{//} - n_{\perp})_{\text{max}} = (3.4 \pm 0,2) \cdot 10^{-6} \alpha_d$  at  $E = 0,85 \text{ eV}$  and  $(n_{//} - n_{\perp})_{\text{max}} = -(2,35 \pm 0,2) \cdot 10^{-6} \alpha_d$  at  $0.94 \text{ eV}$ . The results are compared with a theory developed by Dexter.

The existence of optical dispersion curves, usually called anomalous dispersion is a phenomenon which is common to all materials near absorption bands. Color centers in ionic crystals are a priori good candidates for such a study since they present a wide variety of well known absorption bands in the UV, visible and near infrared spectral range. Unfortunately their contributions to the host lattice dispersion appear to be relatively small and are therefore difficult to measure through direct measurements. The dispersion due to anisotropic defects is however easier to determine since it is possible to utilize their polarization properties. This note outlines such a procedure applied to the experimental determination of the refractive index change in the near IR spectral region of the  $1s\sigma_g \rightarrow 2p\sigma_u$  absorption transition of  $F_2^+$  centers in KCl crystal. Anisotropic defects of the  $F_2^+$  and  $F_2$  type play nowadays an important technological role since they are used in color center lasers, photographic information storage etc, where phase variation and diffraction efficiency from oriented defects are of great importance.

A  $F_2^+$  center consists of two nearest-neighbor anionic vacancies which have trapped a single electron. It is analogous to a  $H_2^+$  molecular-ion imbedded in a dielectric matrix. The optical properties of this defect have been extensively studied in KCl crystal by Aegerter and Lüty<sup>1,2</sup>. This center lies in a  $\langle 110 \rangle$  lattice direction and has three symmetry axes along which their optical dipole moments lie. One is the  $\langle 110 \rangle$  vacancy axes which is the optical dipole direction of the near infrared  $1s\sigma_g \rightarrow 2p\sigma_u$  absorption band (z polarized). The other two are the  $\langle 110 \rangle$  and  $\langle 100 \rangle$  directions perpendicular to the vacancy axes (x and y polarized). The main transitions having these dipole directions lie in the visible range on the short wavelength side of the F center band and are labelled  $1s\sigma_g - 2p\pi_u$ .

$F_2^+$  centers can be created in different ways<sup>1,3,4</sup>. For simplicity we used a procedure discovered recently by Lüty et al<sup>3</sup> for which the creation mechanism is not fully understood yet but is extremely effective in KCl doped with SH<sup>-</sup>. The crystals cleaved to  $8 \times 4 \times 1.6 \text{ mm}$  are first X-rayed

at  $-40 \pm 1^\circ\text{C}$  during 4h (Mo anode working at 90KV, 20mA). The  $F_2^+$  centers are then created by shining white light from a halogen lamp at the same temperature. High concentration of "pure"  $F_2^+$  centers can be obtained in this way. They have a better thermal stability than those prepared with older technique<sup>1,4</sup> and if the irradiation light is not polarized, all the  $F_2^+$  centers are equally distributed along the six  $\langle 110 \rangle$  possible directions. The orientation of  $F_2^+$  centers along one particular  $\langle 110 \rangle$  direction occurs for  $T > 50\text{K}$  during the desexcitation process of the  $2p\pi_u$  excited states toward the first relaxed excited state  $2p\sigma_u^*$ . For example, shining 500 nm light (white light filtered by a SFK 9 filter) propagating along  $[100]$  and linearly polarized along  $[011]$  (excitation of the  $2p\pi_u$  transitions) excite all the defects except those having their vacancy axes along this  $[011]$  direction. They will eventually change their orientations until full  $[011]$  alignment is obtained. The dichroism is normally stable in the dark until 240 K, temperature at which the defects are destroyed.

The dispersion of the  $F_2^+$  centers was determined using a well known ellipsometric technique<sup>6</sup> which has also been used some years ago to measure the dispersion property of  $F_2$  centers in NaF<sup>7</sup>. If we assume that the defects have been partially aligned along the  $[0\bar{1}1]$  direction,  $[001]$  polarized light propagating along  $[100]$  in the  $1s\sigma_g \rightarrow 2p\sigma_u$  near infrared region is selectively absorbed by the z polarized component of the  $F_2^+$  centers; it will emerge with amplitude  $a_{[0\bar{1}1]} = a_{//}$  and  $a_{[011]} = a_{\perp}$  as measured through an analyzer oriented along  $[0\bar{1}1]$  and  $[011]$  respectively (fig. 1). Since the defects are partially aligned along  $[0\bar{1}1]$ , these amplitudes are different ( $a_{//} < a_{\perp}$ ) and have a phase difference given by

$$\delta = \frac{2\pi d}{\lambda} (n_{//} - n_{\perp}) \quad (1)$$

where  $n_{//}$  and  $n_{\perp}$  are respectively the refraction index for light polarized along  $[0\bar{1}1]$  and  $[011]$ ,  $\lambda$  is the wavelength of light in free space and  $d$  is the thickness of the crystal. The recombination of these components results in an elliptically polarized light. The semi-axes  $a_M$  and

$a_L$  and the orientation of the ellipse can be determined by measuring the transmitted intensity  $I_M$  and  $I_L$  by adequate rotation of an analyser. If  $\theta$  is the angle between  $a_{\perp}$  and  $a_L$  we have:

$$I_M = a_M^2 = (a_{\perp} \sin\theta)^2 + (a_{\parallel} \cos\theta)^2 + 2a_{\parallel} a_{\perp} \sin\theta \cos\theta \cos\delta \quad (2)$$

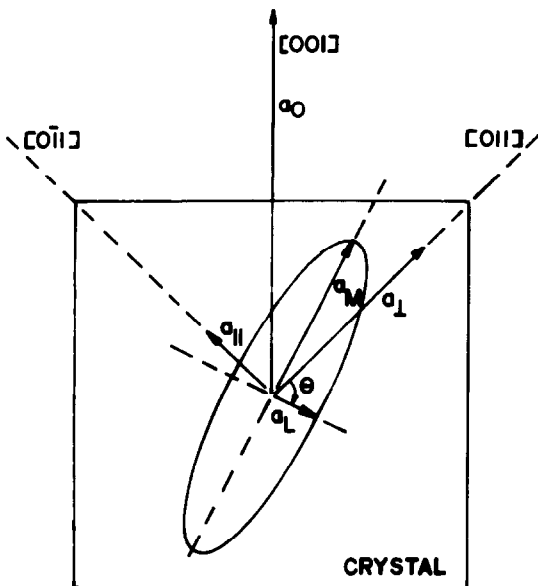
$$I_L = a_L^2 = (a_{\perp} \cos\theta)^2 + (a_{\parallel} \sin\theta)^2 - 2a_{\parallel} a_{\perp} \sin\theta \cos\theta \cos\delta \quad (3)$$

Solving for  $\delta$  in equation (2) and (3) and substituting in (1) we obtain:

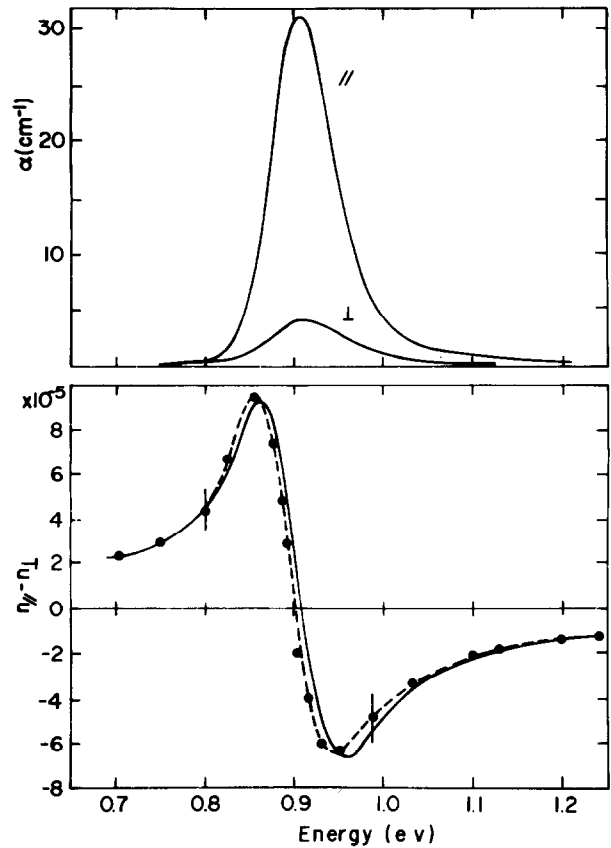
$$n_{\parallel} - n_{\perp} = \frac{\lambda}{2\pi d} \arccos \left\{ \frac{1 + \left[ \frac{a_{\parallel}}{a_{\perp}} \operatorname{tg}\theta \right]^2 - \left[ \operatorname{tg}^2\theta + \left( \frac{a_{\parallel}}{a_{\perp}} \right)^2 \right] \left( \frac{a_L^2}{a_M^2} \right)}{2 \frac{a_{\parallel}}{a_{\perp}} \left[ 1 + \frac{a_L^2}{a_M^2} \operatorname{tg}\theta \right]} \right\} \quad (4)$$

Measurements of the ellipses parameters  $a_{\parallel} = \sqrt{I_M}$ ,  $a_{\perp} = \sqrt{I_L}$  and  $\theta$  have been made from 1.0 to 1.8  $\mu\text{m}$  at 1.5 K for different degrees of  $F_2^+$  orientation using high quality 20mm  $\varnothing$  quartz polarizer and analyser (B. Halle Nachfl.) and a PbS cell. Figure 2 shows one typical result obtained with a 1.8mm thick crystal with partial  $F_2^+$  orientation. This ellipsometric technique allows to measure the absolute value of the change of the refractive index. The sign of the curve has been determined independently inserting between the crystal and the analyser a  $\lambda/4$  plate which, when correctly aligned, converts the elliptically polarized light into a plane polarized one, the sense of the rotation of the analyser giving the sign of  $(n_{\parallel} - n_{\perp})$ <sup>6</sup>. The dispersion increases with the degree of alignment and is typical of an anomalous curve due to isolated defects. As for the

case of  $F_2^+$  centers in NaF this indicates that  $F_2^+$  centers behave as a dilute set of uninteracting damped harmonic oscillators<sup>5</sup>.  $(n_{\parallel} - n_{\perp})$  vanishes near the peak of the  $F_2^+$  absorption band and has maximum values of opposite sign on either side of it. The maximum values are different because the absorption band is asymmetric<sup>2</sup>. The variation of the maximum index difference  $(n_{\parallel} - n_{\perp})_{\text{max}}$  varies linearly with the dichroic optical absorption constant  $\alpha_d(\text{cm}^{-1})$  over more than a decade of



1. Schematic arrangement for the analysis of the elliptically polarized light for  $F_2^+$  centers.



2. Absorption spectra of  $F_2^+$  centers ( $1s\sigma_g \rightarrow 2p\sigma_u$  transition) measured at 1.5 K in one particular stage of alignment (upper drawing). Light is propagating along  $[100]$  and is polarized along  $[011]$  ( $\parallel$ ) and  $[01\bar{1}]$  ( $\perp$ ). Lower drawing shows the corresponding dispersion spectrum: experimental ( $\bullet$ ) and theoretical (full curve). The ordinate of the theoretical curve has been multiplied by a factor 0.4. The small shift in energy ( $\sim 0,007$  eV) is due to a small difference in energy calibration of the dispersive instruments.

the concentration range of  $F_2^+$  centers

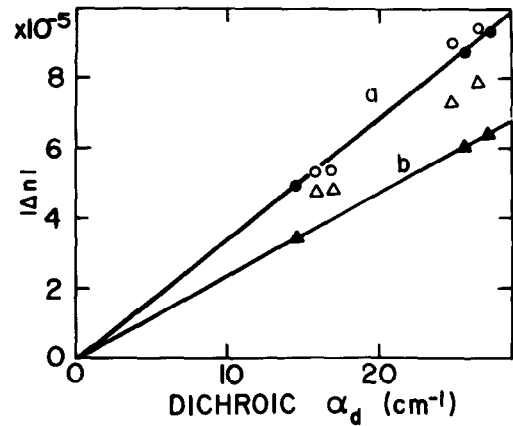
$$(n_{//} - n_{\perp})_{\max} = (3.4 \pm 0.2) \cdot 10^{-6} \cdot \alpha_d \text{ at } E = 0,85 \text{ eV}$$

$$(n_{//} - n_{\perp})_{\max} = -(2,35 \pm 0,2) \cdot 10^{-6} \cdot \alpha_d \text{ at } E = 0,94 \text{ eV}$$

The contribution of  $F_2^+$  centers to the overall refraction index is small but nevertheless leads to substantial phase variations. The change of index of refraction for defects in crystals has been theoretically investigated by Dexter<sup>8</sup>. Where the tight-binding model is valid, the crystal cubic and the defects well localized the change of the refraction index is approximately given by  $n = n_d + n_I$  where  $n_d$  represents the diminution of the refractive index as a results of the removal of part of the atoms of the lattice, usually a small effect and  $n_I$  is the effect of the defects.

$$\Delta n_I(E) = \frac{\pi c}{\pi} \int_0^{\infty} \frac{\alpha(E') dE'}{E'^2 - E^2} \quad (5)$$

Fig. 2 shows the comparison of such calculation based on relation (7) with one of the experimental determination. The agreement is good if we multiply the theoretical results by a factor of 0.4. For the calculation, Dexter assumed that the influence of the crystal on the oscillator was equivalent to the Lorentz local field such that the Lorentz-Lorenz law was applicable. This may not be true for anisotropic defects such as  $F_2^+$  centers and this may explain the multiplication factor used to fit the experimental results. The  $1s\sigma_g \rightarrow 2p\sigma_u$  transition of  $F_2^+$  centers presents a sharp zero phonon line at  $0,8123 \text{ eV}^2$ . Unfortunately in these KCl:SH<sup>-</sup> crystals, the zero phonon line is broad and appear with much lower intensity; it was impossible to obtain definite results concerning its contribution to the dispersion curve. The  $1s\sigma_g \rightarrow 2p\pi_u$  transitions in the visible range



3. Variation of the maximum index difference  $(n_{//} - n_{\perp})_{\max}$  as a function of the maximum dichroic optical absorption constant  $\alpha_d(\text{cm}^{-1})$ . The values  $(n_{//} - n_{\perp})$  are measured at 0,85 eV (curve a) and 0,94 eV (curve b) and  $\alpha_d(\text{cm}^{-1})$  at 0,92 eV. The experimental points (●, ▲) and (○, △) refer to two different crystals. The levels have been calculated with the Dexter theory using the multiplication factor 0.4.

also lead to the existence of anomalous dispersion curves. Measurements are underway and will be published later.

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