The Faraday Effect of Colored Rocksalts

By

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1. Introduction

As is well known, the pure rocksalt crystals have the diamagnetic
property in the magneto-rotatory power (1), but we found that colored
rocksalt crystals, which contain F-centers, show a particular property
in the rotation of the plane of polarization by the Faraday effect (2).
This phenomenon results from the electrons captured in the lattice
vacancies of Cl^- ions in rocksalt crystals. We believe that the results
of our measurements on the magneto-rotatory power of F-centers for
the light of Na D-lines, as well as its dispersion curve in the neigh-
bourhood of F-band, give us some important informations about the
intrinsic nature of F-centers, which has been discussed from every
point of view.

2. Experiments

Colored rocksalt crystals were produced by applying the electric
field of about 400 volts per cm between a plate anode and a point
cathode to pure crystals heated at temperatures of 570—600° C in an
electric furnace. The colored crystals thus obtained contain the density
10^{15}—10^{17} per cm^3 of F-centers. This density N_0 was optically deter-
mined from the absorption coefficient k_{max} at absorption maximum and
the half-band breadth h of F-band, according to Smakula's formula (3):

$$fN_0 = 1.31 \times n_0/(n_0{}^2 + 2)^2 \times k_{max} h \times 10^{17} \quad \text{for NaCl},$$

where $n_0/(n_0{}^2 + 2)^2 \sim 0.079$, and f is oscillator strength and is equal
to 0.7. The magneto-rotatory angle of polarized light for Na D-lines
was measured on these colored crystals by means of " crossed Nicols
method." Thus, it was found that this angle is smaller than that of
pure transparent ones and that the difference of both angles is pro-
portional to the density of F-centers contained in the colored crystals;

in other words, the Verdet constant of F-centers is negative and its absolute value is proportional to their density. For the specific rotation, [V], of F-centers of Na D-lines we obtained the value of 1×10^3 min/Gauss·cm per gr/cm³ (4), by giving the model of a neutral Na atom to F-center.

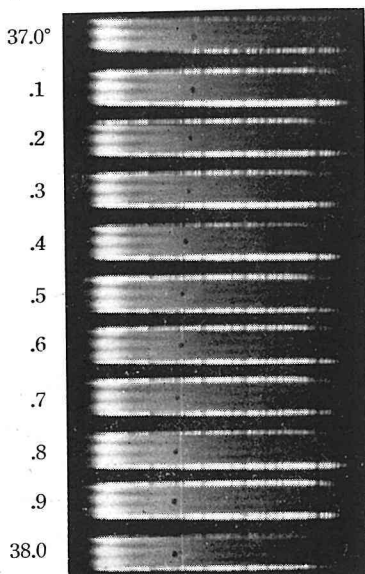In succession to the above described experiment we measured the dispersion curve of magneto-rotatory power by taking spectrograms of the interference fringes as shown in Fig. 1 produced through Wild's polarimeter (5), which consists of polarizer, analyser and Savart plate, the latter being put just before the analyser (6). The place, where the fringes on spectrograms disappear, moves as the polarizer is rotated. It is indicated by a black point on each spectrogram of Fig. 1. The whole arrangement is shown in Fig. 2.
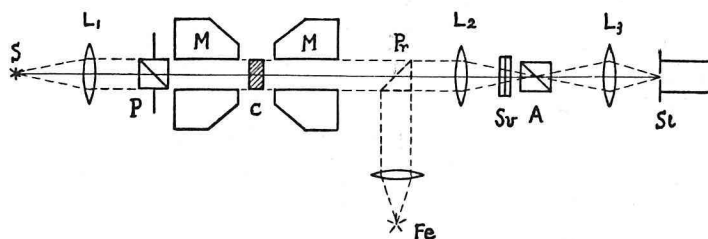
Rotation angle
of polarizer

Fig. 1. Spectrograms of the interference fringes produced through Wild's polarimeter.

Fig. 2. The arrangement for measuring the rotatory polarization.
S: light source (100 V—500 W), L_1, L_2, L_3 and L_4: lenses, M: electromagnet (Weiss type), C: sample crystal, Pr: a small prism, P: polarizer, A: analyser, Sv: Savart plate, Sl: slit of spectrograph, Fe: Fe arc.

In this figure a small prism Pr is movable and pushed into the optical path to take spectra of Fe arc as comparison. An electromagnet M may be cooled by water and yields 7780 Gauss for the current of 10 Amp. This intensity of the magnetic field was determined by the

measurement on the magneto-rotatory angle of water for Na D-lines.* A Hilger Uviol Glass spectrograph was used in the near ultra-violet region.

Our measurement was carried out in the range from Na D-lines to about 390 mμ and the result is as follows: the magneto-rotatory angle (Verdet constant) of F-centers has negative signs on the longer wave-length side, while it happens the inversion of rotation at one point on the shorter wave-length side of the absorption maximum of the F-band and after that the rotation shows positive signs. In Table I the values of Verdet constants of F-centers are shown for various wave-lengths. In Fig. 3 the magneto-rotatory dispersion curve is shown (7).

TABLE I. The values of the Verdet constant of
F-centers for various wave-lengths ($N_0 \sim 10^{16}$)

Wave-length in $\overset{\circ}{A}$	Verdet constant in min/Gauss $\cdot$ cm
5893 (Na D)	-0.4×10^{-3}
5372	-0.8
5326	-1.5
5230	-1.5
5168	-2.6
5139	-2.2
5050	-2.7
4958	-2.8
4920	-2.9
4872	-3.0
4737	-2.3
4603	-2.2
4531	-2.2
4380	-1.9
4326	-1.7
4305	-0.5
4255	-0.2
4144	-0.1
4046	$+0.8$
4007	$+0.7$
3969	$+0.8$
3928	$+1.1$

* The Verdet constant of water for Na D-lines is
$$V_D = 0.01311 \, (1 - 0.0000305 \, t - 0.00000305 \, t^2) \text{ for } 3° < t < 98° \text{C}.$$
Cf. J. W. Roger and W. Watson, Phil. Trans., A, **186** (1895), 621; ZS. f. Phys. Chem., **19** (1896), 323.
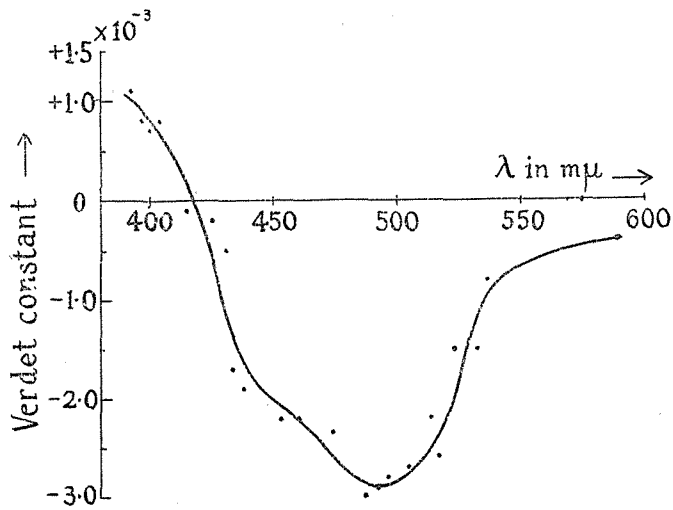
Fig. 3.   The magneto-rotatory dispersion curve of F-centers.

3.   Conclusion

As for the nature of F-centers in alkali-halide crystals several explanations have been brought out, but it is now generally accepted that they are due to electrons captured in the vacant sites of Cl^- ions in the crystal lattice (8).   On the basis of such a qualitative interpretation, Tibbs (9) treated F-centers as an one electron problem; assuming the potential field of F-centers to be constant near the center and to be $1/(k_0 r)$ at large distance from it (where k_0 is the optical dielectric constant), he calculated the values of the energy levels of the ground state (1s), the first excited state (2p) and the bottom of conduction band respectively.   To such a quasi-atomic model of F-centers, for which the periodicity of lattice and the interaction of lattice vibration with F-centers are neglected, the general theory of the Faraday effect for an atom proposed by Rosenfeld (10) may be applied.   But, Z. Yamashita and M. Watanabe (11) showed that this simple application cannot explain our particular phenomenon such as the negative magneto-rotatory power of the colored crystals for Na D-lines.   So they corrected their calculations in respect to the interaction of lattice vibration by the same way as Smakula's treatment (3) about the shape of F-band, which rests on the classical dispersion theory, and they took into account the fact semi-experimentally that non-central fields are dominant in the high excited states, being composed of complex states of nearest neighbours Na^+ and Cl^- ions.   Their calculations showed

the possibility of the negative rotation of F-centers for Na D-lines and moreover they determined the shape of the magneto-rotatory dispersion curve, which is qualitatively consistent with our experimental one as shown in Fig. 3. (The Verdet constant of F-centers has negative signs in the range from Na D-lines to one point on the shorter wavelength side of the F-band maximum and beyond this point it becomes positive.)

Apart from finest details of the dispersion curve, not yet resolved in our experiment, the theory of Yamashita and Watanabe is still semi-empirical, so long as the wave functions of the high excited states of F-centers cannot be definitely known. From these reasons we cannot compare and examine in full the theoretical and experimental results, but it is interesting to see that there is, as mentioned above, a qualitative coincidence between them. Of course, our experiment should be refined to get a more accurate dispersion curve and it would be necessary to measure the temperature dependence of the Faraday effect, as pointed out from the theoretical considerations; while, on the theoretical side, other various processes of calculation might be possible. We hope that more exact results concerning this problem will be reported.

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