Optical Activity, Circular Dichroism, and Absorption of Crystalline Nickel Sulphate

L. R. INGERSOLL, *University of Wisconsin, Madison, Wisconsin,*

P. RUDNICK, F. G. SLACK AND N. UNDERWOOD, *Vanderbilt University, Nashville, Tennessee*

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Previous measurements of the optical rotatory power of crystalline $\alpha - NiSO_4 \cdot 6H_2O$ in the visible spectrum have now been extended to cover the wave-length range from 0.25μ to 2.2μ. Circular dichroism and absorption measurements have also been made over the infra-red range. Striking anomalies in the rotatory dispersion curve appear at 0.69μ and particularly at 1.16μ, corresponding to absorption and circular dichroism maxima at these wave-lengths. The theoretical relation between rotatory power and dichroism is verified quite exactly and in detail, particularly with regard to the 1.16μ band.

INTRODUCTION

THE optical activity of the crystalline alpha-hexahydrate of nickel sulphate has been measured for the visible[1] and near ultraviolet[2] spectral regions. The abnormal variation of the rotatory power with wave-length indicated that a major anomaly was to be expected in the infra-red.[2] This has been confirmed by the measurements here reported, which extend the rotatory power curve in both the infra-red[3] and ultraviolet to cover all the wave-length range from 0.25μ to 2.2μ. The vast majority of substances show a variation of rotatory power roughly as the inverse square of the wave-length. The relatively few materials which depart widely from this behavior, i.e., whose rotatory power is appreciably influenced by critical frequencies in the optical range, are of special interest. Nickel sulphate proves outstanding in this respect.

The property of circular dichroism, which is intimately associated with anomalous rotatory power, has also been measured for this material in the near infra-red.[4] This property consists of a difference in absorption for right-hand and left-hand circularly polarized radiation, and is most readily detected by the ellipticity which it produces in an incident plane polarized beam. Measurements of total absorption for the same infra-red region are also reported.

The infra-red measurements were made at the University of Wisconsin and those in the ultra-violet at Vanderbilt University. The two techniques are naturally different and will be described separately in the next two sections. In both cases the crystal specimens employed were laminae cleaved from Baker's or Merck's C.P. crystals, with thicknesses from 0.3 mm to 3.4 mm. These were examined by radiation transmitted normally and hence parallel to the optic axis, since the cleavage is along the 001 plane which is normal to the optic axis in the tetragonal crystal.[5]

METHOD AND APPARATUS—INFRA-RED

The apparatus for measuring optical rotation and the ellipticity of circular dichroism was a modification of that already described,[6-8] and need be discussed only briefly. Light from a special strip-filament tungsten lamp L (Fig. 1), after reflection from a concave mirror and passage through a Rochon double-image prism D_1 (only one beam used), was converged to a focus on the crystal C and then passed through a Wollaston double-image prism D_2. A concave mirror then formed two images with vertical and horizontal planes of polarization on the two slits (vertically in line) of a spectroradiometer having a differential vacuum bismuth-tellurium thermopile T with receiver strips 0.6×10 mm. The spectrometer had a 9-cm high 45° glass prism, which was transparent as far in the infra-red ($\lambda 2.4\mu$) as it has proved feasible to do

[1] N. Underwood, F. G. Slack and E. B. Nelson, Phys. Rev. **54**, 355 (1938).

[2] F. G. Slack and P. Rudnick, Phil. Mag. **28**, 241 (1939).

[3] Preliminary report by L. R. Ingersoll, P. Rudnick and F. G. Slack, Phys. Rev. **55**, 672A (1939).

[4] Preliminary report by L. R. Ingersoll and P. Rudnick, Phys. Rev. **57**, 70A (1940).

[5] C. A. Beevers and H. Lipson, Zeits. f. Krist. **83**, 123 (1932).

[6] L. R. Ingersoll, Phys. Rev. **9**, 257 (1917).

[7] L. R. Ingersoll and W. R. Winch, Phys. Rev. **44**, 399 (1933).

[8] L. R. Ingersoll, J. Opt. Soc. Am. **27**, 411 (1937).
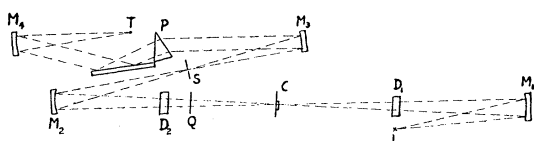
FIG. 1. Arrangement of apparatus for infra-red measurements.

polarization work of this sort. It was used in a Wadsworth mounting with mirrors of 40 cm focal length. For some of the work a higher dispersion was secured by replacing M_4 by a 60-cm mirror. All concave mirrors were aluminized. The spectrometer mirrors were of special Bausch and Lomb manufacture and their high quality was proved by Foucault knife-edge tests. The galvanometer was a Kipp and Sons type Zc.

The transmission of a crystal specimen could be measured at any wave-length by closing one slit completely with a shutter and observing galvanometer deflections with and without the crystal in the beam (the polarizing prisms having been removed), care being taken to keep the deflections within the limit of linearity, as determined by calibrated sector disks.

Figure 2 shows the method of measuring rotation. With the polarizer plane at azimuth $45°$, as in (a), the two energy components falling on the differential thermopile are equal and the galvanometer shows no deflection. Insertion of the crystal will unbalance this condition, as in (b), because of rotation due to the crystal, but (c) turning the polarizer through an equal angle in the opposite sense will restore the balance. Actually it was found convenient to modify this ideal method to that illustrated in (d) and (e). When the polarizer was rotated $90°$, x' changed to x'' (equal to y'), etc., with a corresponding change in the sign of the galvanometer deflection. By rotating the polarizer through the angle 2α, as in (e), the original galvanometer reading was restored.

The method of measuring ellipticities followed closely that already described.[8] Some 30 sheets of almost perfect optical mica, 5 cm square, were secured after much testing, which were quarter-wave plates for a series of wave-lengths from 0.6μ to 2.3μ. Since each plate could be used without appreciable error for a small spectral range on each side of the wave-length for which it was a true quarter-wave plate, it

was possible with these plates to cover all wave-lengths of this region. The procedure was to mount a quarter-wave plate suitable for the desired wave-length at Q in a large conical bearing which permitted its rotation through exactly $90°$. Such rotation turned the plane of the resultant plane polarized light through 2ϵ (ϵ, ellipticity), where tan ϵ is the ratio of the axes of the ellipse.* This rotation was measured by comparing the resultant galvanometer deflection with that produced by a small ($3°$) known rotation of the polarizer D_1.

In measuring ellipticity due to circular dichroism it was not found possible to avoid additional ellipticity due to double refraction effects, such as would result from imperfect orientation of the crystal, or perhaps imperfections or strain in it. Ellipticity of such origin, however, must be reversed in sign if the polarizer is rotated through $90°$, while ellipticity due to circular dichroism will remain unaltered. Measurements of ellipticity were therefore made for two orientations of the polarizer differing by $90°$ and their mean taken as the ellipticity due to dichroism alone. This procedure was tested by introducing deliberately a large double-refraction effect by rotating the crystal as much as $6°$ about a transverse axis. There was no change in the measured dichroism under these circumstances.

To secure sufficient energy for these spectroradiometric measurements it was necessary, as already mentioned, to use a conical beam, but to avoid birefringent effects it was necessary to keep the angle of the cone small, i.e., to deviate as little as possible from parallelism to the optic
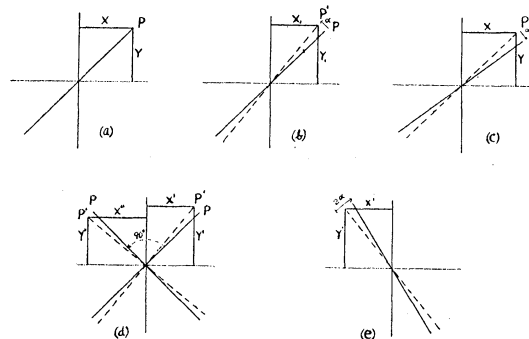

FIG. 2. Diagrams illustrating the method of measuring rotations. P is plane of polarization of the beam as it leaves the polarizer D_1; P' is plane after leaving crystal C.

* Reference 8, p. 412.

axis. The crystal lamina was mounted over a 5-mm aperture in a holder which allowed the crystal surface (001 plane) to be adjusted normal to the axis of the beam. A 15-mm or 25-mm diaphragm, located at Q, 50 cm from C (Fig. 1) limited the angle of the cone so that no part of the beam deviated more than 1.1° or 1.7°, respectively, from the optic axis. Measurements with the two diaphragms gave practically identical values for the cases of both rotation and ellipticity measurements, so it was concluded that no appreciable error resulted from lack of strict parallelism with the optic axis. In the case of the dichroism measurements, such errors would be eliminated anyway by the treatment of the data mentioned above.

METHOD AND APPARATUS—ULTRAVIOLET

The arrangement of the apparatus used for measurement of rotations in the ultraviolet is shown schematically in Fig. 3. Radiation from the quartz mercury arc A passed through the Bausch and Lomb double prism monochromator B. The emergent monochromatic radiation then traversed successively the Glan-Thompson polarizer C, removable 45° glass plate D (used in orienting the crystal), the nickel sulphate crystal E, the Wollaston double-image prism F, and finally fell on the photographic film in the holder G, registering two narrow images of the monochromator exit slit. The dimensions of the apparatus were such that no ray deviated from the optical axis of the system by more than 1°.

It is obvious that the two photographic images produced by the Wollaston could be brought to equal density, by adjusting the plane of polarization of the incident radiation to an azimuth approximately 45° from the extinction points. This condition would be altered on insertion of the crystal, but the balance could be restored by rotating the polarizer to compensate for the rotation introduced by the specimen. This is illustrated in Fig. 2 (a), (b), (c). All photographs were measured with a microphotometer and the angles corresponding to equal densities of the two images were found by graphical interpolation. The amplifier used in the microphotometer employed the circuit described by Gabus and Pool[9] with a slight modification. A variable

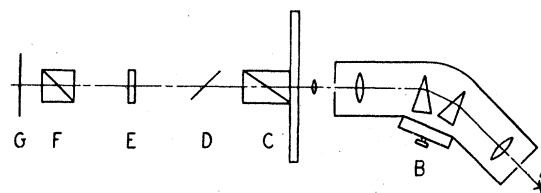[9] G. H. Gabus and M. L. Pool, Rev. Sci. Inst. **8**, 196 (1937).

FIG. 3. Arrangement of apparatus for ultraviolet measurements.

bias was used on the control grid (actually the normal suppressor grid, as the grids are used in novel fashion), greatly facilitating the use of the amplifier and making it easier to adjust. The photo-cell (RCA type 922) was mounted over the eyepiece of the microscope, the usual illumination system being replaced by an assembly made for illuminating moving picture sound tracks.

To illustrate the method, the measurements obtained for the mercury line at 2804A are presented. Knowing approximately the zero points and rotations from previous trial photographs, four exposures, differing by −3°, −1°, +1°, and +3° from the expected correct position, were made both for the zero position and the rotated position in each quadrant—32 exposures in all for this wave-length. The relative density of the two images in each photograph was measured by placing the less dense image in the microscope field, and then adjusting the light until the galvanometer read 100. The more dense image was then immediately moved into the measuring position by means of the mechanical stage. Under these circumstances the galvanometer read directly the relative transmission of the denser image. Each set of the four relative transmission measurements is plotted graphically as shown in Fig. 4. Angular positions of the polarizer are abscissae and relative transmissions ordinates. The straight line through the four points intersects the line of equal transmissions, i.e., 100 percent, at the match point or angular position for equal density of the two images. Fig. 4 shows two such lines, one from data obtained with a 1.31-mm crystal in the optical path and the other with the crystal removed. The angular difference between the two match points is the rotation produced by the crystal. The value in this case is 39.8° −25° or 14.8°, which gives a rotatory power of
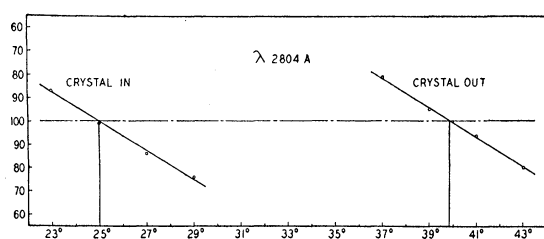
FIG. 4. Graph illustrating the method of determining rotations photographically. The abscissae are polarizer positions and the ordinates indicate relative transmissions in percent. Points are plotted above or below the mid-line depending on which of the two images is the denser.

11.3°/mm. This procedure was carried out for each of the wave-lengths used. The data shown in Fig. 4 are typical and indicate that the technique yields good results.

When the polarizer was set exactly 45° from the two planes of transmission of the analyzing Wollaston, the two images were not quite of equal density. This is at least in part caused by a difference in their size, and may also be a result of different absorption or reflection losses in the prism. Consequently, the match-points are not quite midway between the extinction points, and not quite 90° from one another. The effect is, however, common to the zero-point photographs and the rotation photographs, and causes no serious difficulty.

EXPERIMENTAL RESULTS

The measurements of rotation in the ultra-violet were made on two crystals, with respective thicknesses of 1.31 mm and 3.42 mm, the former giving right-handed rotations and the latter left-handed. The thicker specimen was used for most of the measurements except those near the absorption band around 3850A. Both crystals were used at 2804A, where the two values of the rotatory power agreed within 0.07°/mm. Measurements were made for a series of ultra-violet lines of the mercury arc extending from 2537A to 3650A. The results, expressed as rotatory power in degrees per millimeter, are given in the first section of Table I, and plotted as points in Fig. 5. A smooth curve has been drawn through the experimental points in this figure. Some of these data, and one additional measurement at 4047A, were also plotted in Fig. 6(a). No measurements between 3650A and

4047A have been possible because of an intense absorption band in this region. The break in the curve of Fig. 6(a) indicates the presence of this band and an associated rotational anomaly.

Four crystal specimens were used for the measurements in the infra-red, of thicknesses 0.33 mm, 0.64 mm, 0.83 mm, and 1.325 mm, obtained by micrometer caliper measurement. The 0.83 crystal gave positive rotations (clockwise to the observer) at the longest and shortest wave-lengths (i.e., where the rotation is "normal"

TABLE I. Rotatory power, circular dichroism, and absorption coefficient of crystalline α—$NiSO_4 \cdot 6H_2O$ from 0.25μ to 2.2μ. The ultraviolet data are direct experimental values. The infra-red data are taken from the smooth curves in Fig. 6. The columns of differences were obtained by subtracting computed from experimental values.

WAVE-LENGTH IN MICRONS	ROTATORY POWER IN DEGREES PER MM	DIFFERENCE EQ. (10)	CIRCULAR DICHROISM, DEGREES OF ELLIPTICITY PER MM	DIFFERENCE EQ. (9)	ABSORPTION COEFFICIENT PER MM
Ultraviolet					
0.2537	18.4	−0.07			
0.2654	14.8	+0.03			
0.2804	11.4	−0.03			
0.2967	8.62	−0.2			
0.3130	6.92	−0.1			
0.3341	5.34	+0.1			
*0.3400	*4.9	+0.1			
*0.3500	*4.3	+0.2			
0.3650	3.11	−0.04			
0.4047	2.8	−0.05			
Visible					
*0.43	*1.85	+0.1			*1.0
*0.45	*1.20	+0.04			*0.4
*0.50	*0.05	−0.07			*0.1
0.55	−0.9	−0.1			0.4
0.60	−1.85	−0.2	0.45	−0.02	1.8
Infra-red					
0.63	−2.20 (max.)	−0.3	—	—	—
0.65	−2.15	−0.2	1.30	−0.04	3.4
0.675	—	—	—	—	3.5 (max.)
0.69	—	—	1.45 (max.)	+0.1	—
0.70	−1.75	−0.3	—	—	3.4
0.74	−1.65 (min.)	−0.3	—	—	—
0.75	—	—	1.05	−0.02	2.3
0.80	−2.25	−0.4	0.45	+0.07	1.1
0.85	−3.25	−0.5	0.35	−0.02	0.7
0.90	−4.60	−0.6	0.65	−0.1	0.9
0.95	−5.90	−0.4	1.65	−0.2	1.4
1.00	−6.95	−0.3	3.7	−0.02	2.1
1.02	−7.05 (max.)	−0.2	—		—
1.05	−6.70	−0.2	6.7	+0.2	2.7
1.10	−4.50	−0.2	9.7	+0.2	3.1
1.155	0.00	−0.1	11.5 (max.)	−0.2	3.3
1.175	—	—	—	—	3.4 (max.)
1.20	+3.50	+0.2	10.2	+0.2	3.3
1.25	5.55	−0.2	7.5	+0.4	3.0
1.30	—	—	4.9	+0.1	2.5
1.305	6.40 (max.)	−0.2	—	—	—
1.35	5.90	−0.2	2.9	−0.1	2.0
1.40	5.10	−0.04	1.70	−0.3	1.9
1.45	4.25	+0.04	1.00	−0.3	2.3
1.50	3.45	+0.02	0.55	−0.2	2.5 (max.)
1.55	—	—	0.25	−0.1	—
1.60	2.35	−0.1	0.10	−0.03	2.2
1.70	1.80	−0.1	—	—	2.0
1.80	1.40	−0.1	—	—	1.5
1.90	1.15	−0.1	—	—	3.2
1.98	—	—	—	—	8.8 (max.)
2.00	0.95	−0.1			—
2.10	0.80	−0.1			4.7
2.20	0.65	−0.2			2.9

* These data were taken from previous publications, by Slack and Rudnick, reference 2, or by Underwood, Slack and Nelson, reference 1.
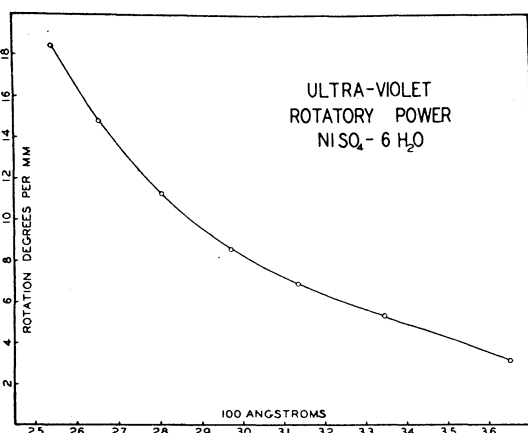
FIG. 5. Rotatory power of $\alpha-\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ in the ultraviolet.

in sign); the other three crystals were opposite in sign. Since no detectable difference in magnitude appeared in the rotatory powers derived from the two types of crystal, no attention was given to absolute sign in combining the data.

While temperature is a secondary factor in this work and was not under special control room temperature did not vary greatly from 24°C during these measurements and may be taken to have that value.

In selecting data for the final determination of rotatory power, no individual readings were rejected, but certain groups of measurements were omitted from the final plotting, largely as a matter of convenience. These were data taken with a filter or with the small diaphragm previously mentioned, which were not significantly different from the other results and at the same time were naturally a little less self-consistent because of the reduced intensity of radiation. The measurements which were retained were all obtained with the larger (25 mm) diaphragm. As mentioned before, a 40-cm focus mirror was employed at M_4 (Fig. 1) in the greater part of the work. This gave an effective slit width ranging from 0.02μ at wave-length 0.6μ to 0.09μ at 1.8μ. Some measurements with higher resolving power were obtained by use of the 60-cm mirror at M_4. The range of wave-lengths extended from 0.6μ to 2.2μ.

The observations (230 in number) remaining after the above-mentioned exclusion were expressed as rotatory power in degrees per milli-
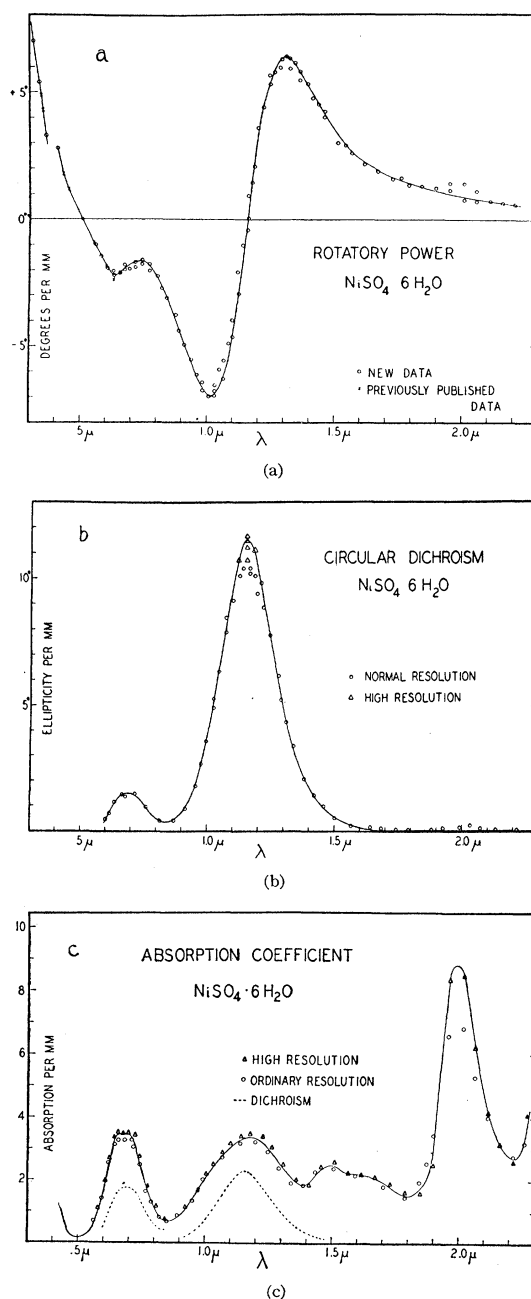

(a)

(b)

(c)

FIG. 6. Optical properties of $\alpha-\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ in the visible and infra-red. (a) Rotatory power. (b) Circular dichroism. (c) Absorption coefficient. Data shown in (a) and (c) for the visible region are taken from previous publications (references 1 and 2).

meter and plotted; the smooth curve shown in Fig. 6(a) was then drawn through them. It was not feasible to show all of the experimental points or the full extent of their self-consistency

in this small figure. Hence only a small number of the experimental points are actually shown, but these include the points departing most from the smooth curve, thus indicating the extreme limits of variation among the measurements. The deviations from the curve near the peaks (approximate wave-lengths 0.7μ, 1.0μ, and 1.3μ) arise mainly from the differences in resolving power; higher resolving power gave slightly sharper peaks which were of course preferred in drawing the smooth curve. The scatter near 2.0μ reflects the difference between data from thick and thin crystals, the latter giving lower values. Values of the rotatory power read from the smooth curve appear in Table I. The wave-lengths of the peaks of the curve are indicated in the table as exactly as they could be determined.

Circular dichroism was measured over the same (infra-red) wave-length range in the two crystals of thickness 0.33 mm and 0.83 mm, which were of opposite sign. The larger diaphragm (25 mm) was used throughout; the lower resolving power was used except for a few measurements in the neighborhood of the principal maxima. The sign of the dichroism agreed, as expected, with that of the rotation at longer wave-lengths, and was ignored in combining the data. All measurements (101 in number), without any rejections, were reduced to ellipticity in degrees per millimeter of thickness of a very thin crystal,[10] then were plotted and through them was drawn the smooth curve of Fig. 6(b). Here again the small figure cannot show all the points or their full self-consistency, but the extreme divergences are shown. In particular, the scattered high dispersion measurements at the peak (1.155μ) were derived from a thick crystal which transmitted little radiation at that wave-length, while the peak of the smooth curve

was fixed by three measurements on the thinner crystal which agreed with one another within 1 percent. The values of dichroism entered in Table I were read from the smooth curve.

The precision of the infra-red measurements appears to be limited by the finite resolving power used, and possibly by other sources of small systematic errors, since the small systematic differences for crystals of different thickness, or for different resolving powers, exceeded the random errors during any one run, except where the intensity of radiation was least. We believe the values in Table I for the infra-red region, both of rotatory power and ellipticity, have a probable error of $0.1°/mm$ or at most $0.2°/mm$. The uncertainty is perhaps a little greater at the sharpest peaks of both curves, which may still be a little rounded by finite resolution, and also at the very steep places on both curves, where only a very slight revision of the assigned wave-lengths would be required to produce a change of $0.2°/mm$ in rotation or ellipticity at a given wave-length. The scale of infra-red wave-lengths was checked at several well-separated points and is believed dependable to about 0.01μ. The probable error of the ultraviolet measurements is considered also to be within $0.2°/mm$.

Transmission was measured as a function of wave-length over the same infra-red range covered by the rotation and dichroism measurements, for three of the crystals (0.33 mm, 0.64 mm, 0.83 mm thickness). Absorption coefficients per millimeter were computed, assuming 4 percent reflection loss at each surface, and plotted in Fig. 6(c). The values from the crystals of different thickness agree well except in the very intense absorption band at 2.0μ, where a small amount of scattered light greatly lowers the apparent absorption of the thicker crystals and probably affects even the data from the thinnest crystal. Some systematic difference between the results with high and low resolving power appears in the wave-length region from 1.1μ to 1.8μ. A smooth curve has been drawn in Fig. 6(c) which compromises these differences and follows the points from the thinnest crystal near 2.0μ.

DISCUSSION OF RESULTS

The carriers of all the absorption bands shown in Fig. 6(c) are known with at least reasonable

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[10] In treating the ellipticity data two approximations were made for which corrections were later applied where necessary. The first was that galvanometer deflections were assumed proportional to angles of rotation equal to the ellipticity ϵ, and to $(\epsilon - 3°)$, where the $3°$ is a rotation introduced for calibration purposes. More strictly, the deflections are proportional to $\sin 2\epsilon$ and $\sin 2(\epsilon - 3°)$. The second approximation was that the ellipticity was proportional to the thickness of the specimen, whereas it actually approaches $45°$ as a limiting value for great thicknesses. First-order correction for these two approximations was made by multiplying by the respective factors $(1 - 4/3\epsilon^2)$ and $(1 + \frac{2}{3}\epsilon^2)$, which combine conveniently to $(1 - \frac{2}{3}\epsilon^2)$, where ϵ is the ellipticity actually measured, expressed in radians.

certainty. The bands with centers at 0.385μ and 0.69μ together produce the green color characteristic of divalent nickel salts in aqueous solution or in hydrated crystals, and are to be attributed to the hydrated nickel ion.[11] The band at 1.16μ is believed to belong to the same system, corresponding to the band at 1.2μ observed by Houstoun[11] for the aqueous solutions of six nickel salts. These three bands contribute to the rotatory power and are therefore presumably electronic in character.

The two bands which center near 1.5μ and 2.0μ have been identified as due to water of crystallization, by their close correspondence in position and absolute intensity with known bands of liquid water.[12] They are vibrational in character and, as expected, make no appreciable contribution to the rotatory power. The experimental data, both for dichroism and rotatory power, show a little suggestion of anomaly within the very intense band at 2.0μ, but we interpret this as an effect of scattered radiation, since it was least noticeable for the thinnest crystal, whose transmission was 10 percent at this wave-length.

Since electronic bands do not usually occur in the infra-red region, anomalous rotatory dispersion in the infra-red is correspondingly unusual. The anomaly at 1.16μ, is, furthermore, because of its favorable position, remarkably well isolated from the "normal" rotatory dispersion controlled by the far ultraviolet absorption. At the center of this band, the contributions to rotatory power by all other bands in the spectrum can hardly exceed $0.7°/mm$, or 10 percent of the greatest rotations in this region. We know of few other instances where one anomaly is so completely isolated. This band therefore affords a highly favorable opportunity for quantitative study of the associated rotatory dispersion and dichroism.

Circular dichroism consists of a difference in absorption coefficients for the two senses of circularly polarized light, and rotatory power arises from a corresponding difference in refractive indices. It is to be expected that differ-

ence in absorption and difference in refraction will be related in much the same way as are total absorption and refraction, and this is qualitatively true. A narrow absorption line showing circular dichroism will make a contribution to the rotatory power at any wave-length not too remote from it. The variation of this contribution with wave-length resembles an anomalous dispersion curve, the contribution outside of the line itself being of the form $A/(\lambda^2-\lambda_0^2)$ or $B\nu^2/(\nu_0^2-\nu^2)$. The magnitude and sign of A and B are completely fixed by the dichroism of the line. If $d\alpha$ is the contribution to rotatory power at frequency ν made by an absorption line at frequency ν_1, ϵ the ellipticity produced by the dichroism per unit length for short paths, and $d\nu_1$ the effective width of the line (more exactly, $\epsilon d\nu_1$ is the area under the curve of ϵ against ν_1 within the line), then[13]

$$d\alpha = \frac{2}{\pi} \frac{\nu^2}{\nu_1^2-\nu^2} \frac{\epsilon d\nu_1}{\nu_1}. \tag{1}$$

Kuhn and Braun[14] have integrated this equation for the case of a broad absorption band within which the total absorption coefficient is a Gaussian probability function on a frequency scale. Such a broad band is regarded as a composite of many narrow lines, and the ratio of dichroism to total absorption for these lines is taken proportional to their frequency. The following relations then hold:

$$\tfrac{1}{2}(a_l+a_r) = a = a_0 \exp\left[-\{(\nu_0-\nu)/\theta_\nu\}^2\right], \tag{2}$$

$$\tfrac{1}{4}(a_l-a_r) = \epsilon = \epsilon_0\frac{\nu}{\nu_0} \exp\left[-\left(\frac{\nu_0-\nu}{\theta_\nu}\right)^2\right], \tag{3}$$

$$\alpha = \frac{2}{\pi^{\frac{1}{2}}}\epsilon_0\frac{\nu}{\nu_0}\left[J\left(\frac{\nu_0-\nu}{\theta_\nu}\right)-\frac{\theta_\nu}{2(\nu_0+\nu)}\right]$$

$$\equiv \alpha_\nu(\epsilon_0, \nu_0, \theta_\nu), \tag{4}$$

$$\cong \frac{2}{\pi^{\frac{1}{2}}}\epsilon_0\theta_\nu\lambda_0^3\frac{1}{\lambda^2-\lambda_0^2}. \tag{4'}$$

Here a is the total absorption coefficient for unpolarized light, a_l and a_r the coefficients for the two senses of circularly polarized light, ϵ

[11] R. A. Houstoun, Proc. Roy. Soc. Edinburgh **31**, 538 (1911); also R. A. Houstoun and J. S. Anderson, *ibid.*, **31**, 547 (1911).
[12] Int. Crit. Tab. **5**, 269 (1929).

[13] See T. M. Lowry, *Optical Rotatory Power* (Longmans, Green), Chap. XXXIV.
[14] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 281 (1930).

ellipticity as above, and α the partial rotatory power contributed by the whole band. ν_0 is the frequency of the maximum of total absorption, and a_0 and ϵ_0 the respective values of a and ϵ at that frequency, while θ_ν is a constant determining the width of the absorption band. λ_0 is the wave-length corresponding to the frequency ν_0. $J(x)$ is a function given by

$$J(x) = e^{-x^2} \int_0^x e^{y^2} dy \tag{5}$$

$$\cong x - (2/3)x^3 + \cdots \quad \text{for } x \text{ small} \tag{5'}$$

$$\cong 1/(2x) + 1/(4x^2) + \cdots \quad \text{for } x \text{ large.} \tag{5''}$$

This function controls the rotatory power within the band, being zero at $x=0$, assuming its greatest positive and negative values when x is, respectively, about $+0.9$ and -0.9, and falling back to zero at $x = \pm \infty$. Kuhn[15] has published numerical values of J, and the approximate values given by (5') and (5'') are also useful for $x < \frac{1}{2}$ or >3. The expression (4') for rotatory power is valid at sufficient distances from the absorption band, and is derived from (4) by the use of the first term of the asymptotic expansion (5''). In (4'), θ_ν must be expressed as a wave number.

Lowry and Hudson[16] found that the corresponding relations for a band in which the total absorption curve was Gaussian on a wave-length scale involve the same function $J(x)$. In this case

$$a = a_0 \exp\left[-\{(\lambda - \lambda_0)/\theta_\lambda\}^2\right], \tag{6}$$

$$\epsilon = \epsilon_0 \frac{\lambda_0}{\lambda} \exp\left[-\left(\frac{\lambda - \lambda_0}{\theta_\lambda}\right)^2\right], \tag{7}$$

$$\alpha = \frac{2}{\pi^{\frac{1}{2}}} \epsilon_0 \frac{\lambda_0}{\lambda}\left[J\left(\frac{\lambda - \lambda_0}{\theta_\lambda}\right) + \frac{\theta_\lambda}{2(\lambda + \lambda_0)}\right]$$

$$\equiv \alpha_\lambda(\epsilon_0, \lambda_0, \theta_\lambda) \tag{8}$$

$$\cong \frac{2}{\pi^{\frac{1}{2}}} \epsilon_0 \theta_\lambda \lambda_0 \frac{1}{\lambda^2 - \lambda_0^2}. \tag{8'}$$

When Eq. (4), (4'), (8), or (8') is used over a sufficiently wide spectral range, the right member of the equation should contain an additional factor $(n^2+2)/(n_0^2+2)$, where n and n_0 are indices of refraction at respective frequencies ν and ν_0 (or wave-lengths λ and λ_0).

Circular dichroism should determine the associated partial rotatory power completely and uniquely through Eq. (1), which contains no adjustable constants. Our data have been used to test this relation in the following way: First expressions of the type of (3) and (7) were combined to give the best realizable numerical representation of the dichroism. The corresponding values of partial rotatory power were then computed from (4) and (8) and subtracted from the experimental values. The resulting differences, presumably the contribution of the far ultraviolet absorption, proved to be reasonably well, though not perfectly, representable by two terms of the Drude type (Eq. (4') or (8')). Eqs. (9) and (10) are the outcome of this procedure.

$$\epsilon = \frac{1.165}{\lambda}\left\{6.95 \exp\left[-\left(\frac{\lambda - 1.165}{0.151}\right)^2\right] + 4.27 \exp\left[-\left(\frac{0.858 - \nu}{0.120}\right)^2\right]\right\}$$

$$+ \frac{0.695}{\lambda} 1.545 \exp\left[-\left(\frac{1.44 - \nu}{0.192}\right)^2\right], \tag{9}$$

$$\alpha = \frac{n^2+2}{n_0^2+2}\left[\alpha_\lambda(6.95, 1.165, 0.151) + \alpha_\nu(4.27, 0.858, 0.120) + \alpha_\nu(1.545, 1.44, 0.192)\right.$$

$$\left. + \frac{0.009}{\lambda^2 - 0.150} + \frac{0.575}{\lambda^2 - 0.035}\right]. \tag{10}$$

In these equations, ellipticities and rotations are expressed in degrees per millimeter, wave-lengths in microns, and frequencies are replaced by wave numbers in reciprocal microns. Numerical values of the fraction containing the indices of refraction in Eq. (10) were obtained from a previously published dispersion formula.[2] They

[15] W. Kuhn, Freudenberg's *Stereochemie*, p. 381. See also reference 13.
[16] T. M. Lowry and H. Hudson, Phil. Trans. Roy. Soc. **232**, 117 (1933).

ranged from 1.06 at 0.25μ to 1.01 at 0.5μ, the values being practically 1.00 for all longer wave-lengths. The differences between the values of rotatory power and dichroism given by Eqs. (10) and (9) and the experimental data appear in the third and fifth columns of Table I. It may be noted that the dichroism near 0.69μ is represented by Eq. (3), while that near 1.16μ is intermediate in character between (3) and (7) and is represented by a linear combination of bands of the two types with their centers coincident. Eq. (9) yields a peak at 0.69μ which is a little too sharp and one at 1.155μ which is not quite sharp enough, but on the whole it represents the observed dichroism without serious error. The corresponding values of rotatory power, from Eq. (10), reproduce the observations practically within the experimental uncertainties everywhere except in the spectral region from 0.6μ to 1.0μ. The discrepancy in this range, however, varies quite smoothly and gradually with wave-length. The maximum disagreement of $0.6°/\text{mm}$ at 0.9μ, and the irregularity at 1.2μ both fall at steep places on the curve, where they might be removed by comparatively small shifts along the wave-length axis. *No trace of the maxima and minima of the total rotation curve appears in the residual differences;* this result is regarded as a sensitive and successful test of the theoretical relation (1) between circular dichroism and partial rotatory power.

The ratio $(a_l - a_r)/a$ is called by Lowry[17] a dissymmetry factor. Its value at the center of the 1.16μ band is 0.24, which is unusually high; in the 0.69μ band the ratio is only 0.03. This factor is expected to be proportional to frequency within any one band; this implies that the maximum of dichroism will occur at a slightly higher frequency than the maximum of total absorption. This appears to be the case in the 1.16μ band, but both dichroism peaks are narrower than those of total absorption, and the

proportionality with frequency is not quantitatively borne out.

In a review of the theory of optical activity Condon[18] has defined a quantity R, called rotational strength, which is a property of a single molecule associated with one transition in its absorption spectrum and measures the magnitude and sign of the dichroism and rotatory power contributed by that transition. A closely analogous quantity S, called the line strength, measures the contribution of the same transition to total absorption and refractivity. For the 1.16μ band, $R = 1.7 \times 10^{-40}$, and $S = 3.2 \times 10^{-39}$ if determined from the dichroism curve and the dissymmetry factor 0.24 (or 4.3×10^{-39} may be estimated from the total absorption). From quantum-mechanical theory one may take these two quantities to have respective orders of magnitude pm and p^2, where p and m are the magnitudes of the matrix elements associated with the transition in question in the respective matrices of electric and magnetic dipole moment, even though the explicit expressions given by Condon are for random orientation. It follows that in this case p is of the order of 0.02, in terms of the atomic unit equal to the dipole moment of the hydrogen atom in its normal state, and m is of the order of 0.3 Bohr magneton. This band therefore falls in the class mentioned by Condon for which the rotatory power exists by virtue of a strong magnetic moment and a relatively weak electric moment associated with the transition.

[17] T. M. Lowry, *Optical Rotatory Power*, p. 394.

[18] E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).