INFRARED LIGHT FOR MINERAL DETERMINATION

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ABSTRACT

Many minerals that are opaque to visible light are transparent to infrared light. By adapting photoelectric cells, sensitive to infrared, to different optical instruments used in mineralogy, it is possible to obtain the refractive indices, birefringence, absorption indices, etc. The variations of the intensity of the infrared light transmitted by the mineral can be converted by the cell into variations in electric current. It is a relatively simple task to interpret these values of the current which are recorded on a sensitive galvanometer.

Until quite recently opaque minerals were identified by various methods such as macroscopic study, chemical analysis, microchemical tests, and a study of the optical characters in reflected light with the microscope (9, 11, 14, 17, 19, 24, 31, 32). About 1930, Orcel, in France, improved the optical methods in reflected light by the use of a photoelectric ocular for measuring the reflecting power of polished sections (3, 24, 25, 26, 27, 28, 29).

In 1935, I showed that many minerals which are opaque in visible light are transparent in thin sections in infrared light (near 9000 Å).

The first investigations were made by means of photography using the polarizing microscope and special plates (Agfa 850). The mineral studied was wolframite. The thickness of the sections was about one tenth of a millimeter. Wolframite is very transparent in infrared light. It was possible with different exposures to obtain extinction angles and other optical properties. Molybdenite was also studied; the interference figure and the optical sign were obtained. However, this rather easy method is time consuming (1, 21).

The investigations are considerably simplified by making use of photoelectric cells sensitive to infrared light (5, 7, 10, 13, 25). A photoelectric cell placed at an appropriate height above the eyepiece of the microscope will, with the use of a sensitive galvanometer, indicate the intensity of light transmitted by the thin section. This may be obtained with ordinary as well as with polarized light. This method may also be applied to studies with a prism refractometer, a total reflection refrac-

tometer, the universal stage, etc. The observations will be qualitative in the determination of extinction angles, pleochroism, refractive indices, birefringence, and optical sign in convergent light, etc. They will be quantitative in the measurement of absorption, reflecting power, etc.

After several experiments, an apparatus suitable for the above mentioned investigations was built in the laboratories of the Institute of Mineralogy, University of Liège, Belgium (1, 2).

DESCRIPTION

The infrared light may be obtained from different sources according to the type of research (Fig. 1). When a high degree of intensity is required, a filament bulb is very useful. I used a 1000 watt bulb with 110
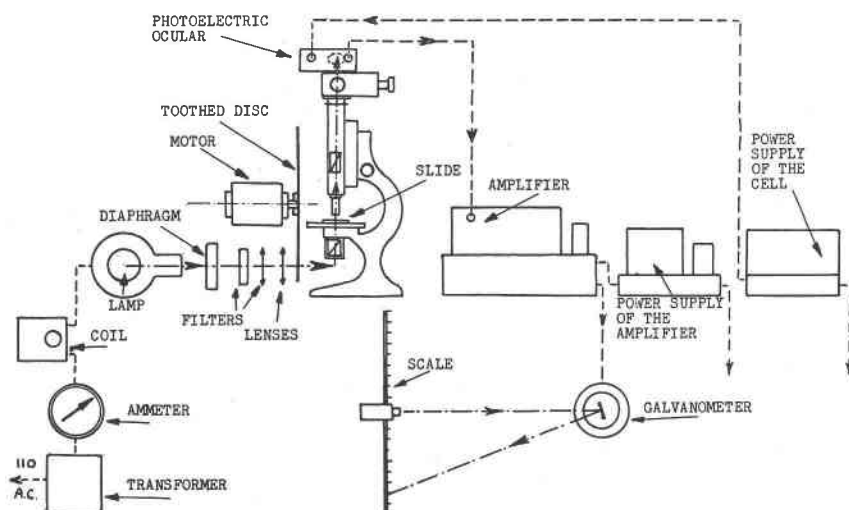

FIG. 1. Diagram of the apparatus.

volts A.C. Preferably the filament should be short and thick, giving a better calorific inertia. This type of filament diminishes the effect of the cyclic variation of current. Also a high degree of regularity may be obtained by the use of a voltage regulator with iron-hydrogen bulbs.

The light is concentrated by a set of lenses and a diaphragm, and is filtered. The filters are from the Jena Glass Works, Zeiss, or Reichert. The maximum intensity is attained near 8500 Å. When a low intensity suffices, a cesium arc lamp is recommended. With appropriate filters this lamp gives lines at 8521, 8761, 8943 Å. The principal line is at 8521 Å.

After passing through the lenses and filters and before entering the

microscope, the light is modulated to a constant frequency by a revolving toothed disc driven by a synchronized electric motor. The frequency of modulation is 166.66 . . . per second. Modulation is necessary if the current of the photocell is amplified.

The microscope used was a large field Leitz. The model with rotating nicols is more desirable because of its ease in centering. The light passes through the microscope and the thin section of the mineral, and enters the photoelectric ocular which replaces the visual eyepiece. The image of the mineral is projected on the anode of the photocell. A sliding prism permits visual examination by a lateral eyepiece (Fig. 2).
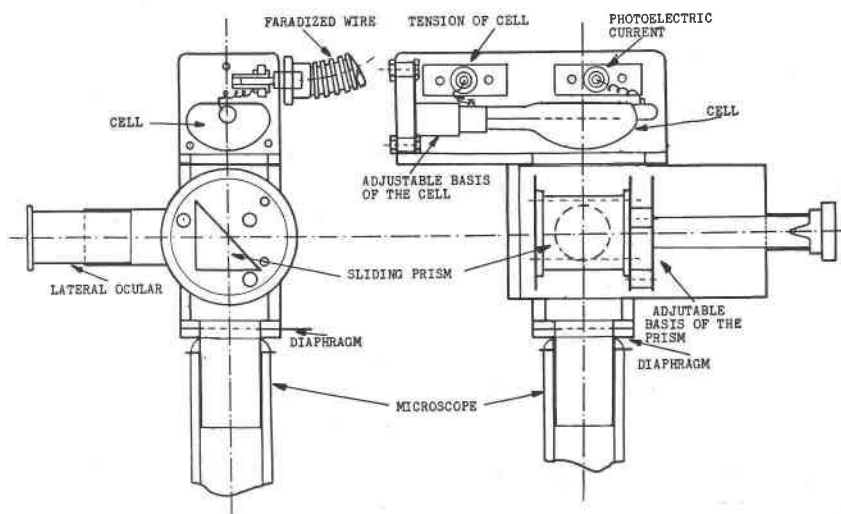

Fig. 2. Photoelectric ocular.

The photoelectric cell is carefully insulated and mounted in vibration-proof metallic box. It is also screened against electric perturbations. The photoelectric tubes (photoemissive model), are of two types: the gas tubes and the high vacuum tubes. The gas tubes are particularly suitable when a very high sensitivity is required, but they are not perfectly stable. The sensitivity of the 3535 Philips is about 160 microamperes per lumen with a cathode polarized at 100 volts; the spectral sensitivity is included between 5000 and 12000 Å with a maximum at about 7500 Å. The high vacuum cells are designed primarily for great stability and high precision. The tube M 122 Cesium special 1 Infram Pressler is sensitive between 5500 and 12000 Å. The power is 50 microamperes per lumen with 20 to 140 volts to the cathode. The variations of voltage on the cathode between these limits have no effects on the stability (5). Other models,

such as the 1P40 and 917 RCA, can be used. It would be particularly interesting to use an electron multiplier tube, because its power is about one ampere per lumen, but up to now only multipliers sensitive in visible light have been made.

The power supply of the cell can be a dry battery. I prefer to use a rectifier, the voltage of which is regulated by a neon tube. A divider gives all voltages between 0 and 360.

The current produced by the anode of the photoelectric cell is driven to the galvanometer, but generally it must be previously amplified. In that case the light must be modulated by the toothed revolving disc because the amplification of an undulatory current is easier than the amplification of a direct current.

The wire between cell and amplifier is well insulated and faradized; it is the same as that used in cameras for sound reproduction, but here experience shows that it is necessary to faradize the wire itself in a flexible metallic tube.

After many tests, a five push-pull triode stage amplifier was constructed (2). It is supplied by 110 volts A.C. The order of the tubes from the beginning to the end is: two 1H5, two 2A6, two 2A6, one 53, two 56 and one rectifier 5Z3. The first stage (two 1H5) is heated by a dry 1.3 volt battery for reducing the noise of the cathode. The others are 2.5 volt cathode tubes. As the amplifier was built during the war it was necessary to use ordinary tubes.

The resistance coupling is used between stages; however the third and the fourth stages are coupled by a low frequency coil tuned on the 166.66 periods of the modulation. So the amplification is increased and the parasitic frequencies are partly eliminated. The output transformer is also tuned to the modulation. The amplifier produces only a voltage amplification, therefore the output power is low.

The amplified current is rectified by a copper oxide Westinghouse unit and transmitted to the galvanometer. The galvanometer used is of the two sensitivities type, Hartman & Braun, with a maximum sensitivity of $0.3\ 10^{-9}$ ampere. The amplification factor is adjustable from zero to a maximum by potentiometers.

In addition, a loud speaker or a headphone is driven by a supplementary tube (2A3). It allows the sound of the modulation to be heard and, therefore, a first coarse adjustment can be made before the fine adjustment by means of the galvanometer.

OPERATIONS

1. *Microscope* (2). In parallel light, without analyzer and thin section, the amplifier is adjusted to give for example, the mark 1000 on the

scale of the galvanometer. For eliminating the absorption of the glass, a slide is previously put on the stage.

Different thin sections of a mineral, preferably cut in definite orientations, are successively placed on the stage. They will drive the spot of the galvonometer to different points on the scale. These values are proportionate to the values of light intensity.

The equation of absorption is (4,6)

$$I = KI_0 e^{-4\pi xz/\lambda}$$ with K = coefficient of reflected light
I_0 = intensity without thin section
I = intensity with thin section
x = coefficient of absorption
z = thickness of the section
λ = wave length of the light
$e = 2.7182818$

By solving this equation for different values of I and z, it is possible to obtain K and x, and draw the calculated curve of absorption of the mineral. For the smallest thickness, the curve must be corrected because a part of the light is reflected on the lower and the upper faces of the section.

For $z = 0$ on the corrected curve, the intensity I shows the reflecting power R of the mineral.

Using R, measured by reflected light, and x, an approximate value of the refractive index n can be determined by the equation

$$R = \frac{(n-1)^2 + n^2 x^2}{(n+1)^2 + n^2 x^2}.$$

If the mineral is pleochroic, the measurements will be made in the directions of maximum and minimum absorptions.

On rotation between polarizer and analyzer, an anisotropic mineral will show four extinctions and four maxima of transmitted light. They appear as the minima and maxima on the galvanometer. Extinction angles are referred to a direction of cleavage or elongation seen in visible light. The precision of these determinations is very high.

Using the Fedorov stage, the measurements are exactly the same as with visible light, perhaps a little more complicated, but the determinations are more exact. The maxima and minima of the light intensity are determinated with a fine precision by the photoelectric cell.

In the case of a section perpendicular to the optic axis of a uniaxial mineral, if the refractive index ω is determined, it is easy to obtain the value of the birefringence. If one horizontal axis of the stage is fixed at 45° to the planes of polarization of the nicols, the intensity of light will show successively different maxima and minima according to the retardations $\lambda/2$, λ, $3\lambda/2$, 2λ, . . . , if the stage is inclined to that axis. The

angles β_1, β_2, β_3, . . . , are read on the vertical circle of the stage. Four types of measurements of the angles β can be read: two in the first position of the axis for the opposite inclinations of the stage, and two after a 90° rotation of the axis. The average of four values of the β angles gives sufficient precision (2,22).

If the mica test plate is introduced into the slot of the microscope, the same operation will show an increase of the values of the β angles for a direction of the rotating axis, and a decrease of β for the perpendicular direction. By the orientation of the mica and the differences in the values of β, the optic sign is clearly indicated. Exactly the same reasoning is used in convergent visible light where two black spots are observed after the introduction of the mica plate.

With the values of β, ω, z (thickness), λ, and the optic sign, the equations are

$$\frac{k\lambda}{z\omega} = \sqrt{1 - \frac{\sin^2\beta}{\epsilon^2}} - \sqrt{1 - \frac{\sin^2\beta}{\omega^2}} \text{ for a positive sign,}$$

$$\frac{k\lambda}{z\omega} = \sqrt{1 - \frac{\sin^2\beta}{\omega^2}} - \sqrt{1 - \frac{\sin^2\beta}{\epsilon^2}} \text{ for a negative sign.}$$

These equations are easily solved and give the value of the birefringence $B = \omega - \epsilon$ or $B = \epsilon - \omega$ (22).

2. *Refractometer.* The indices of opaque minerals are generally too high for the use of the total reflection refractometer. The prism method with a horizontal goniometer is the most useful. The normal incidence method is preferable to the minimum deviation method, because often one face of the prism is cut parallel to one of the principal crystallographic planes of the mineral. The method is the same as in visible light (2, 4, 6, 12) (Fig. 3).

The prism is oriented and its angle measured in white light. When the incident face is perpendicular to the axis of the collimator, the ocular of the telescope is replaced by a photoelectric ocular. In front of the cell, an adjustable slit replaces the cross-hair used in the visual eyepiece. By rotating the ocular around the crystal, the image of the collimator slit will be transmitted across the ocular slit for one position of the circle. If the mineral is birefringent the two refracted beams are identified by means of a rotating nicol in the collimator. In view of the high values of the refractive indices the angle of the prism is generally between 5° and 20°.

The measurements are particularly precise (in many cases, more precise than in visible light) because, when the image of the slit is diffuse, the slit of the photocell determines exactly the position of maximum intensity.

The edge of the prism must be made and polished with care. It is necessary to grind and polish one face of the mineral carefully and to attach that face onto a piece of glass with balsam. Then, the other face is ground and polished through the mineral and the glass. The curvature
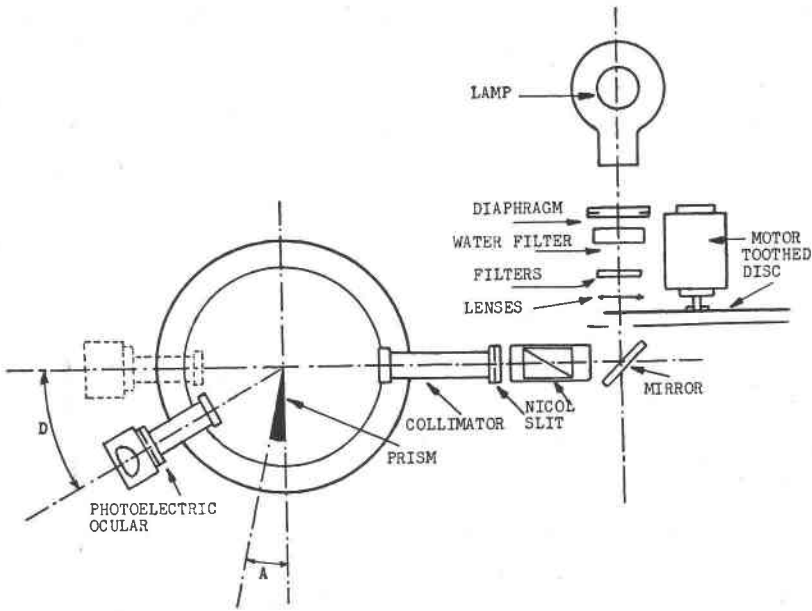

FIG. 3. Diagram of the photoelectric refractometer.

produced by polishing is then on the glass, and the edge of the prism is perfectly sharp and straight (Fig. 4). The prism is detached by solution of the balsam.
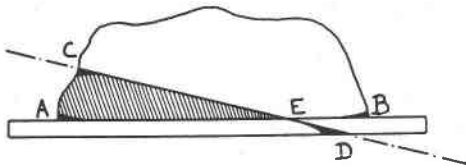

FIG. 4. Cutting of the prisms.

3. *Brewster angle* (6). The determination of the index by measurement of the Brewster angle by means of an horizontal goniometer is relatively precise.

4. *Reflected light.* The procedure of measuring reflecting power is the same as the Orcel method (3, 24, 25, 26, 27, 28, 29, 30).
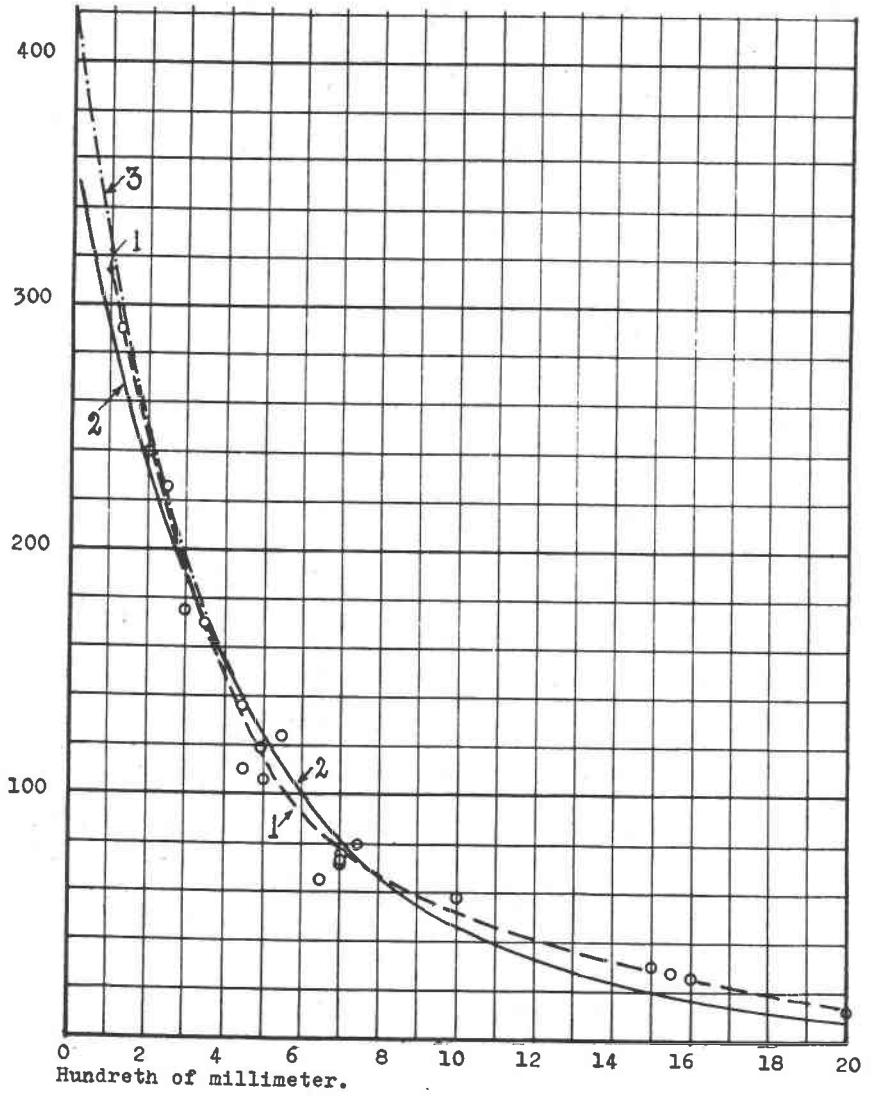
Fɪɢ. 5. Absorption of molybdenite. Curve 1, experimental curve. Curve 2, calculated curve. Curve 3, calculated and corrected curve.

RESULTS

Stibnite. Very transparent in infrared light. (8521 Å) (2,15,18).

$$\beta = 3.875 \qquad \text{parallel to } (001):(100)$$
$$\gamma = 4.137 \qquad \text{parallel to } (001):(010)$$

Reflecting power, measured: $R_\beta = 0.354$
$$R_\gamma = 0.374$$
calculated: $R'_\beta = 0.348$
$$R'_\gamma = 0.369$$
Absorption coefficient: $\qquad x_\beta = 0.000065$
$$x_\gamma = 0.000077$$

Molybdenite. Very transparent.

Uniaxial negative (determination made by the use of universal stage and photography) (2, 21, 22).

Optic axis perpendicular to (0001).

Refractive index, $\omega = 4.336 \pm 0.007$
$$\epsilon = 2.03$$

Birefringence determined on the universal stage: $B = 2.301$

Reflecting power: measured $\quad R_\omega = \quad 0.400$
calculated $\quad R'_\omega = \quad 0.391$
calculated $\quad R'_\epsilon = \pm 0.116$

Absorption: $x_\omega = 0.001489$ (Fig. 5)

Reflecting power calculated by the absorption: $R''_\omega = 0.398$

Hauerite (2). Isotropic. Very transparent.

Refractive index: $n = 2.634$

Tetrahedrite-tennantite (2). Isotropic. Variable transparency.

The refractive index, measured on 33 samples, is nearly constant from tetrahedrite to tennantite. The average is: $n = 3.014$.

The maximum is: $n = 3.128$; the minimum is: $n = 2.914$.

It seems that the index increases slightly with the Sb content.

The transparency decreases with the Fe content.

Bournonite (2). Very transparent. Biaxial, positive.

$$\alpha = 3.141 \text{ parallel to } (001):(010).$$
$$\beta = 3.166 \text{ parallel to } (001):(100).$$
$$\gamma = 3.280 \text{ parallel to } (100):(010).$$
$$2V = 52°. \qquad B = 0.139.$$

Stephanite (2). Very transparent. Biaxial, negative.

$$\alpha = 3.001 \text{ parallel to } (100):(010).$$
$$\beta = 3.053 \text{ parallel to } (001):(100).$$
$$\gamma = 3.077 \text{ parallel to } (001):(010).$$
$$2V = 67°. \qquad B = 0.076$$

Enargite (2). Transparent. Biaxial, positive.

Strong absorption parallel to (001):(100).

$$\alpha = 3.081 \text{ parallel to } (001):(010).$$
$$\beta = 3.089 \text{ parallel to } (001):(100).$$
$$\gamma = 3.120 \text{ parallel to } (100):(010).$$
$$2V = 54°. \qquad B = 0.039.$$

Hematite (2, 18). Transparent. Uniaxial, negative.

1. Samples from Elba Island, Italy.

$$\omega = 2.784.$$

2. Sample from Saxony, Germany. Fibrous hematite.

$$\epsilon = 2.690 \text{ parallel to the fibers.}$$
$$\omega = 2.769 \text{ perpendicular to the fibers.}$$

Strong absorption parallel to ω.

Strong dispersion.

This hematite is slightly hydrated and loses 0.35% H_2O at 250° C.

Goethite (2, 8, 18, 23, 30). Transparent in visible and infrared light.

Sample from Restormel Mines, Lanlivery, Cornwall, England.

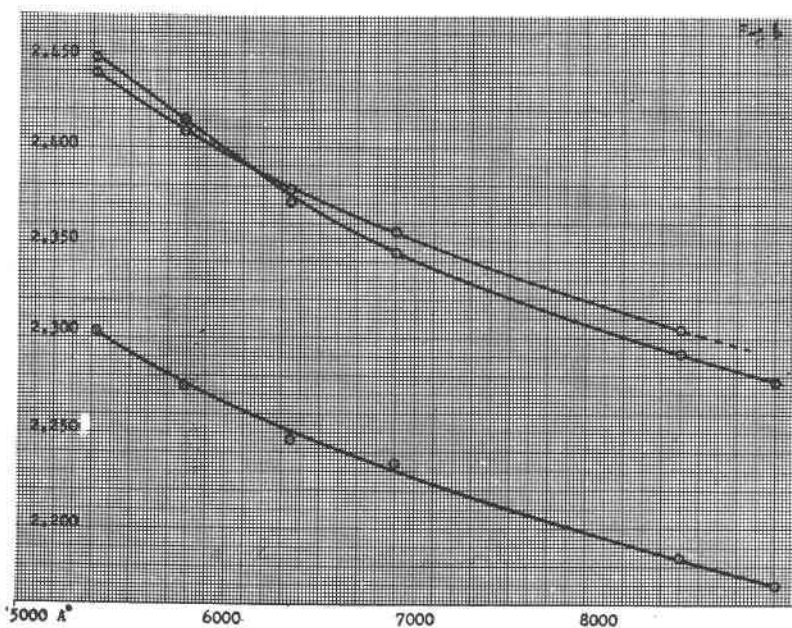| $\lambda = 9000$ Å	$\alpha = 2.170$	$\beta = 2.277$	$\gamma = $ ——	2V
8500	2.185	2.292	2.304	+36°
7000	2.234	2.344	2.356	+26°
6450	2.247	2.371	2.378	+17°
5890	2.275	2.409	2.415	−23°
5420	2.303	2.439	2.447	−25°

The goethite is uniaxial for $\lambda = \pm 6200$ Å (Fig. 6).

FIG. 6. Dispersion of goethite.

Chromite. Variable transparency. The absorption increases with the Fe to Cr ratio. The isomorphous mixture with magnetite produces the same effect.

The refractive index varies slightly with the Fe to Mg ratio.

Pure chromite,	$FeO \cdot Cr_2O_3$,	$n = 2.118$.
Ficotite,	(Fe, Mg)O $\cdot$ (Al, Cr)$_2$O$_3$,	$n = 2.078$.
Picrochromite,	$MgO \cdot Cr_2O_3$,	$n = 2.054$.

Different values were measured between these limits. The average is: $n = 2.07$.

Wo'framite (2, 14, 18, 32). Variable transparency. The absorption and the indices increase from huebnerite to ferberite.

Biaxial, positive. Axial plane perpendicular to (010).

$2V = \pm 75°$. Strong pleochroism.

Chemical analyses and measurements of refractive indices of 30 samples have permitted the drawing of a diagram showing the variations of the indices with composition. The dispersion of the points around the average curves is probably caused by scheelite $CaWO_4$ and an excess of FeO. The following values could be adopted: (Fig. 7).
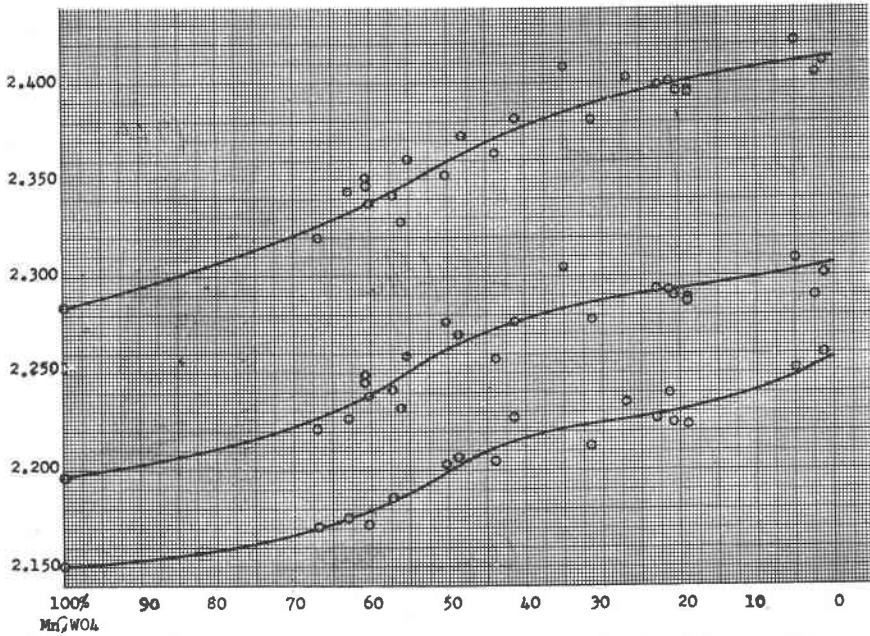

Fig. 7. Variation of the indices of wolframite according to the chemical composition.

			α	β	γ
Huebnerite	100% MnWO$_4$		$\alpha=2.150$	$\beta=2.195$	$\gamma=2.283$
Wolframite	60%	—	2.178	2.238	2.336
	50%	—	2.200	2.263	2.360
	30%	—	2.224	2.287	2.392
	20%	—	2.229	2.291	2.400
Ferberite	0%	—	2.255	2.305	2.414

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