VARIATIONS IN CHEMICAL AND PHYSICAL PROPERTIES OF FLUORITE*

ROBERT D. ALLEN, *332 Villanova Drive, Claremont, California*

ABSTRACT

In a laboratory study of 39 fluorite specimens the following properties were considered: color, index of refraction, unit cell dimension, chemical composition, x-radiation effects, ultra microscopic appearance and luminescence. Spectrographic analyses revealed the following minor elements: Be, Na, Mg, Al, Si, Mn, Fe, Cu, Sr, Y, Zr, Ag, Ba, La, Eu, Yb, and Pb. A high percentage of strontium is almost always present: 0.05–0.5%. Other elements which occur in practically all fluorites are Mg, Al, Mn, and Y. Minor elements are sometimes found as major constituents in minerals associated with fluorite. The total range of variation in refractive index (Na, 20° C.) was 0.00111. Fluorites with principal light absorption at long wave lengths are characterized by abnormally low refractive indices unless minor constituents obscure the effect; fluorites with principal absorption at short wave lengths are characterized by abnormally high refractive indices. Abnormally low refractive indices are explained by a fluorine deficiency which is electrostatically compensated by colloidal calcium; abnormally high indices are attributed to excess calcium in structural holes. The value a_0 for synthetic fluorite of optical grade is 5.46295 Å ± 0.00010 at 28° C. No significant variations in unit cell dimension were found. Calculations based upon the lattice constant support the hypothesis that the short wave length absorption maximum of fluorite is produced by "color centers." Fluorite colors are correlated with size of light scattering centers as follows: green-small, blue-medium and violet-large. Light is scattered by aggregates of neutral calcium atoms. The color most commonly produced by x-rays is blue; yellow or brown fluorites usually become colored intense blue-black. Atomic calcium, which causes "F centers" in yellow-brown fluorite, is believed to coagulate into colloidal particles which in turn produce the blue color.

TABLE OF CONTENTS

I. Historical Review

Refractive Index

Accurate measurements on optical quality fluorite have been reported by Gifford (1902; 1910) and Merwin (1911). Gifford's measurements were obtained through the method of minimum deviation while Merwin's represent data compiled from refractometer determinations. Both men concur in the following: $n_{Na} = 1.43385$ at 20° C. The premise that refractive index variations accompany color variations in fluorite is supported by several publications. Hlawatsch (1897) reported $n_{Na} = 1.43342$ to 1.43328 in dark violet blue fluorites. Morgante (1939) found $n_{Na} = 1.4335$ to 1.4330 in green fluorites; the index dropped progressively with increasing depth of color. Dudenhausen (1904) reported abnormally low indices for three blue, one violet and three yellow fluorites. Two violet fluorites from Weardale gave slightly high values. Hlawatsch (1897) found abnormally high indices in Weardale material.

Luminescence

Haberlandt (1934; 1938) has shown that rare earths frequently cause fluorescence in fluorite. Fluorescence is characteristic of the trivalent positive ions of the rare earth metals europium, terbium, samarium and gadolinium (Pringsheim, p. 76, 1943). In contrast to this rare earth-induced "line fluorescence," band fluorescence spectra are produced by the bivalent rare earth ions as follows: europium, blue; ytterbium, yellowish green; samarium, red; thulium, red (Přzibram, 1937). Gunnell (1933) and Haberlandt (1940) have independently reported that included hydrocarbons cause a yellowish fluorescence. Iwase (1933; 1934), Haberlandt (1935) and Wick (1937) have established the fact that fluorite thermoluminescence spectra commonly contain abundant rare earth lines.

Color

Wyrouboff (1866) was an early advocate of the organic coloring theory. Blount and Sequeira (1919) and Garnett (1920) demonstrated the presence of hydrocarbons in fluorite. Recently Morrison (1935) has attributed the yellow to brown color of Clay Center, Ohio, fluorite to a bituminous impurity. The inspection (Přzibram, 1936) of a large number of fluorite absorption spectra between 660 and 350 mμ shows two principal absorption maxima: (1) 380 to 405 mμ; (2) 575 to 650 mμ. The organic theory of color has declined in importance since the discovery that the absorption maxima of fluorite can be artificially induced by various physical techniques.

Přzibram (1938) ascribed the short wave length absorption maximum

to bivalent europium and samarium. However, Yoshimira (1933), Eysank (1936) and Mukherjee (1948) have concluded that the natural color of fluorite is not related to the varieties of rare earths contained in it.

Doelter (1925) expressed the belief that fluorite is colored by colloidal calcium. Göbel (1931) gave support to the colloidal theory through observations with the ultramicroscope. The smallest Ca particles give green, while an increase in size causes blue, violet and colorless. Yoshimura (1933) has proposed a colloidal mechanism to explain variations in the absorption spectrum of fluorite. Mollwo attributes the long wave length absorption maximum to colloidal calcium (Přzibram, 1936).

Pohl has developed a new approach (Hughes, 1936) to the problem of color in alkali halides. Color is interpreted as being caused by "F centers" (color centers). These are associated with surplus metal atoms in the crystal. The surplus atoms are thought to occur as positive metal ions and electrons dissociated from each other. The behavior of "F centers" suggests that they are electrons bound to internal surfaces in the crystal, the positive ions serving to offset the negative space charge which would result from electrons alone. The wave length of the corresponding absorption maximum, is determined by the unit cell dimension, not by the nature of the excess metal. Natural crystals may contain "F centers," but the latter can also be artificially induced in the following ways: (1) by irradiation with ultraviolet light or x-rays; (2) by exposure of the crystal at high temperature to a metal vapor; (3) by introducing electrons into a warmed crystal from a pointed cathode.

Mollwo colored fluorite by introducing electrons from a pointed cathode. At 1500° C. the concentration of color centers reached 10^{22} per cc. Crystals with such concentrations were less dense than normal, a result which is consistent with the view that incoming electrons displace fluorine ions. Other workers have artificially produced absorption maxima in fluorite. Kellermann (1937) produced yellow coloration in fluorite by radium irradiation at low temperatures. Leitmeier (1925) explains the cobalt blue color of radium-treated fluorite as the result of separation of electrons from fluorine ions. Cathode rays (Doelter and Leitmeier, 1931) and deuteron bombardment (Cork, 1942) may also be used to produce the long wave length absorption maximum.

Wöhler and Kasarnowski (Doelter and Leitmeier, 1931) colored a colorless fluorite deep blue with calcium vapor. This proved to be a stable color. The calcium excess was found by analysis to be 2.4%. In contrast, Mollwo (1934) showed that quenching an additively colored crystal produces the short wave length absorption maximum. Existing natural or artificial absorption maxima in fluorite may be transformed

by physical influences. Thus, pressure causes a blue or green fluorite to become violet (Přzibram, 1929). In general, the long wave length absorption maximum is shifted toward shorter wave lengths by pressure, heat and radiations of various wave lengths.

The artificial production of color in fluorite by radium suggests that natural colors may have developed in response to hard radiation. Hoffman (1937) believes beta- and gamma-radiation partially break fluorite down into elemental fluorine and calcium. This belief is supported by the presence of fluorine gas in fluorite associated with radioactive minerals. Schilling (1926) cites the presence of radioactive haloes in fluorite from Wölsendorf. Both he and Göbel attribute the formation of colloidal calcium to a partial destruction of the fluorite structure; radiation splits off electrons from fluorine ions and fluorine gas is released, the electrons being captured by calcium ions. Přzibram (1947) has stated that in naturally colored fluorites the uranium content is great enough to account for color formation. Evidence also exists which points to a primary crystal structural interpretation of color. Barnes and Holroyd (Mellor, vol. III, p. 692, 1923) claim to have synthesized crystals of fluorspar exhibiting all natural colors. They conclude that color is an optical phenomenon dependent on the crystallization and physical state of the substance. Haberlandt and Schiener (1935) have described in detail relations between color and crystallographic orientation in fluorite.

Minor Elements

The literature of trace elements is summarized in Table 1. After every element capital letters indicate the means of analysis while arabic numerals indicate the appropriate references at the end of this paper.

II. Experimental Observations

General Tabulation of Descriptive and Experimental Information

Table 2 summarizes descriptive and experimental information pertaining to the 39 fluorite specimens examined in this investigation. In the first column are given reference numbers by which the specimens have been identified throughout the investigation. The second and third columns contain respectively the localities and colors (as seen in hand specimens). Except in the case of synthetic fluorite these are natural colors. In the fourth column the forms on specimens which exhibit crystal faces are listed. In column five type of occurrence is designated by Roman numerals in the manner prescribed below: I, Deposits associated with igneous rocks to which they are presumed genetically related; II, Deposits associated with typically hydrothermal minerals,

ROBERT D. ALLEN

TABLE 1. Minor Elements Reported in Fluorite

Letters refer to methods of analysis:
A—absorption spectrum analysis.
B—chemical analysis.
C—cathodo-luminescence spectrum analysis.
D—emission spectrum analysis.
E—radio-fluorescence spectrum analysis.
F—thermoluminescence spectrum analysis.
G—triboluminescence spectrum analysis.
H—ultraviolet fluorescence spectrum analysis.
I—x-ray fluorescence spectrum analysis.
Numbers refer to references at the end of the paper.

Element	Methods of Analysis								References
Aluminum	B	D							1, 2, 3, 7, 56, 58
Argon	B								2
Barium	B	D							3, 7
Beryllium	B	D							1, 3
Carbon	B	D							2, 7, 43, 61
Cerium	B	D							3, 4
Chlorine	B								66
Chromium	D								3
Copper	B	D							1, 3
Dysprosium	B	C	D	F	G	H	I		4, 19, 21, 34, 44, 59, 60, 63, 64, 65, 69
Erbium	B	C	D	H	I				4, 19, 21, 34, 44, 60, 69
Europium	C	E	F	H	I				23, 34, 38, 44, 50, 60, 63, 65, 69
Gadolinium	B	C	D	F					4, 32, 44, 59, 60, 63, 69
Helium	B								7
Hydrogen	B	D							2, 7, 43, 61
Iron	B	D							1, 2, 3, 7, 41, 45, 56, 58
Lanthanum	B	D							3, 4
Lead	B	D							3, 45, 58, 66
Lithium	B	D							1
Magnesium	B	D							2, 3, 7, 41, 45, 56, 58
Manganese	B	D	F	G					3, 7, 18, 19, 41, 45, 56, 58, 65
Neodymium	A	B	C	D					3, 4, 19, 30, 44, 69
Nitrogen	B								2, 7
Oxygen	B	D							2, 7, 8, 43, 61
Phosphorus	B								2, 7
Potassium	B	D							1, 3
Praseodymium	A	C	D	I					4, 30, 34, 69
Samarium	A	B	C	D	E	F	H	I	4, 19, 21, 34, 38, 44, 49, 52, 54, 59, 60, 63, 64, 65, 69
Scandium	D								3
Silicon	B	D							3, 7, 8, 41, 45, 58
Silver	B	D							3, 66
Sodium	B	D							1, 3, 7, 56
Strontium	B	D							1, 3, 42, 58
Sulphur	B								1, 2
Terbium	C	D	F	G	H	I			19, 21, 32, 34, 44, 49, 59, 60, 63, 64, 65, 69
Thorium	B								7, 58
Tin	D								45
Uranium	B	H							7, 22
Vanadium	D								3
Ytterbium	B	D	E	F	H				4, 19, 21, 28, 29, 38, 50
Yttrium	B	D	F	H					3, 4, 19, 21, 28, 29, 38, 58

but not known to be near igneous rocks; III, Deposits in sedimentary rock with evidence for magmatic origin lacking. In column six refractive indices for sodium light (20° C.) are given. The unit cell dimension was measured on about one half of the suite and is recorded in column seven. Information pertaining to trace elements appears in column eight. Only elements in quantity greater than 0.005% are listed. X-ray-induced color data are presented in column nine. In every case the induced color is followed by a Roman numeral which designates the degree of coloration as follows: I, very strong; II, strong; III, moderate; IV, weak; V, none observed.

Refractive Index and Dispersion

In order to attempt the detection of slight but significant variations in the refractive index of fluorite a method of refractometry of the highest accuracy had to be selected. The method of minimum deviation was the logical choice. The maximum usable prism angle for fluorite is 87°40′ and maximum accuracy in refractive index determinations is achieved when the prism angle approaches this value. Indices of refraction were corrected to 20° C. according to the formula $n(20) = n(T) + (0.00001)$ $(T\text{-}20)$, where T equals the temperature at which measurement was made.

The magnitude of determinate error in this group of measurements is small. The average of five separate determinations on a perfect prism of optical fluorite (cut from specimen No. 38) was 1.43385 (20° C.). This is in exact agreement with the findings of Gifford (1902) and Merwin (1911). Indeterminate error is subject to treatment under the theory of probable error. Five separate prisms were prepared from specimen No. 38 with varying quality of signal reflections. These prisms were measured and the resulting indices of refraction were employed to calculate probable errors for the various wave lengths of light utilized. These were as follows: 6550 Å, ±0.00002; 5893 Å*, ±0.00001; 5780 Å, ±0.00002; 5461 Å, ±0.00002; 4359 Å, ±0.00003. According to convention the limit of error is taken to be three times the probable error.

In Table 3 the results of this investigation are presented. Specimens No. 2, 33, and 34 have been omitted from the tabulation; several unsuccessful attempts were made to cut transparent prisms from them. In some· cases readings could not be obtained using one or more wave lengths of light due to inefficiency of light transmission.

---

* Average wave length of the sodium doublet.

TABLE 2. DESCRIPTIVE AND EXPERIMENTAL INFORMATION

Ref. No.	Locality	Color	Form	Type Occurrence	n_{Na} (20° C.)	a_0 (Å units)	Minor Elements (>0.005%)	X-ray Induced Color and Intensity	
1	Göschener Alp, Switzerland	pale rose	{111}	III	1.43385	—	Al, Sr, Y, Yb	violet	II
2	Mt. Antero, Colorado	deep violet (outer portion)*	{111}	I	—	—	Sr	—	V
3	Mt. Antero, Colorado	colorless (inner portion)*	{111}	I	1.43373	—	Be, Sr	blue	III
4	Striegau, Silesia	very pale violet	{111}	I	1.43359	5.46324	Al, Sr	—	IV
5	Cave-in-Rock, Illinois	pale blue (outer portion)	{010}	II	1.43433	5.46304	Mn, Sr	blue	III
6	Cave-in-rock, Illinois	pale violet (central portion)	{010}	II	1.43361	5.46342	Sr	blue	III
7	Cave-in-rock Illinois	amber (inner portion)	{010}	II	1.43393	—	Sr	blue	II
8	Brienz, Tyrol	pale green	{010}	III	1.43363	5.46281	Sr, Y	bluish green	III
9	Grand View Mine, Black Range, Grant Co., New Mexico	colorless	{111} and {110}	I	1.43387	—	Sr	blue	IV
10	Macomb, New York	pale green	{010} and subordinate {111}	II	1.43365	5.46286	Sr, Y	blue	II
11	Near Rossie, New York	colorless (outer portion)	{010}	II	1.43376	—	Sr, Y, Zr	blue	II
12	Near Rossie, New York	pale green (inner portion)	{010} and subordinate {111}	II	1.43349	5.46326	Sr, Y, La	green	III
13	East Pool Mine, Cornwall	very pale blue	{010}	I	1.43366	—	Sr, Y	blue	III
14	St. Agnes Mine, Cornwall	very pale blue	{010}	I	1.43360	5.46336	Sr, Y	blue, green and violet	III
15	Stolberg, Germany	colorless	(Conchoidal fracture)	II	1.43379	—	Sr, Y	blue	II
16	Hessenbach Mine, Baden	pale bluish green	{010}	I	1.43415	5.46321	Na, Fe, Sr, Y	blue	II
17	Livingston Co., Kentucky	yellow	{010}	I	1.43405	—	Sr	blue-black	I
18	Livingston Co., Kentucky	pale blue	—	I	1.43407	—	Sr	blue	IV
19	Livingston Co., Kentucky	violet (color zoned)	{010}	I	1.43358	5.46321	Sr	—	V
20	Weardale, England	green	{010}	II	1.43440	5.46329	Sr, Y, La, Eu, Yb	bluish green	III
21	Weardale, England	pale brown	{010}	II	1.43460	5.46321	Sr, Y, Eu	gray	III
22	Weardale, England	colorless	{010}	II	1.43420	5.46274	Sr, Y, Eu	gray-blue	II
23	Madoc, Ontario	very faint lavender (outer portion)	—	I	1.43390	—	Sr, Y, Ba	green	III
24	Madoc, Ontario	green (inner portion)	—	I	1.43417	5.46343	Sr, Y, Ba, La	green and blue	II
25	Marienberg, Saxony	pale brown	{010}	I	1.43402	—	Al, Sr, Y	blue-black	I
26	Cornwall	pale olive	{010}	I	1.43393	—	Sr, Y, Pb	blue-black	I

† Made from Illinois fluorite.
‡ Made from Mexican fluorite.
* Numbers 2 and 3 are the same mineral specimen; this usage is followed throughout the table.

TABLE 2—(*Continued*)

Ref. No.	Locality	Color	Form	Type Occurrence	n_{Na} (20° C.)	a_0 (Å units)	Minor Elements (>0.005%)	X-ray Induced Color and Intensity	
27	Wölsendorf, Bavaria	golden brown	{010}	I	1.43426	5.46313	Al, Sr, Y	blue-black	I
28	Přibram, Bohemia	pale brown	{010}	I	1.43402	—	Al, Si, Sr, Y	blue-black	I
29	Rabenstein, Tyrol	colorless	—	II	1.43392	—	Na, Al, Sr, Y, Pb	blue	II
30	Cornwall	blue (color zoned)	—	I	1.43359	5.46343	Al, Sr, Y	blue	II
31	Clay Center, Ohio	brown	{010}	II	1.43460	5.46277	Sr, Y, Ba	brown	III
32	Westmoreland, New Hampshire	green	{111}	I	1.43420	5.46315	Al, Sr, Y, Yb	deep green	III
33	Greenleaf #1 Mine, Luna Co., New Mexico	faint green (inner portion)	—	I	—	—	Al, Si, Sr, Y	blue	II
34	Greenleaf #1 Mine, Luna Co., New Mexico	pale pinkish violet (outer portion)	—	I	—	—	Al, Si, Sr, Y, Ba, Yb	blue	II
35	(Synthetic)†	colorless	—	—	1.43388	—	Sr	violet	II
36	(Synthetic)†	orange	—	—	1.43388	—	Sr	mauve	IV
37	(Synthetic)†	very faint green	—	—	1.43375	—	Sr	blue	III
38	(Synthetic)†	colorless (optical)	—	—	1.43385	5.46295	Al, Sr	blue	IV
39	(Synthetic)‡	pale lavender	—	—	1.43409	—	Sr	violet	II

The total range of variation in the index of refraction for sodium light (20°) is 0.00111 ± 0.00002, where the error limit indicated is equal to twice the probable error of a single measurement. The lowest value reported is 1.43349 (green fluorite from Rossie); the highest value reported is 1.43460 (brown fluorite from (1) Weardale and (2) Clay Center).

An attempt was made to correlate refractive index with occurrence. No obvious relation exists between sodium index and mode of occurrence. Even in different colored specimens from the same locality, index measurements usually have very little in common. Three blue fluorites from Cornwall gave the following values: 1.43359, 1.43360 and 1.43362. A yellow fluorite and a blue fluorite from Livingston Co., Kentucky, gave 1.43405 and 1.43407, respectively. Weardale measurements are unique: colorless—1.43420; green—1.43440; brown—1.43460.

Refractivity bears a striking relation to color in fluorite.

All natural violet specimens have indices below normal. Yellow and brown specimens have indices above normal. In general, blue and green fluorites have indices which are either considerably above or considerably below normal. The rose specimen has an index of 1.43385, the optical value; the lavender specimen's index exceeds this value by 0.00005. Colorless specimens rarely show great abnormality.

A green synthetic fluorite shows a relatively low index; a violet one gives a relatively high measurement.

ROBERT D. ALLEN

TABLE 3. INDICES OF REFRACTION

Spec. No.	$n(6550 \text{ Å})$	$n(5893 \text{ Å})$	$n(5780 \text{ Å})$	$n(5461 \text{ Å})$	$n(4359 \text{ Å})$	$n(4359)$ $-n(6550 \text{ Å})$
1	1.43266	1.43385	1.43424	1.43499	1.43965	0.00699
3	—	1.43373	—	—	—	—
4	1.43229	1.43359	1.43381	1.43473	1.43958	0.00729
5	1.43317	1.43433	1.43466	1.43552	1.44025	0.00708
6	1.43220	1.43361	1.43386	1.43472	1.43928	0.00708
7	1.43248	1.43393	1.43420	1.43501	1.43966	0.00718
8	1.43235	1.43363	1.43396	1.43484	—	—
9	1.43262	1.43387	1.43421	1.43505	1.43969	0.00707
10	1.43241	1.43365	1.43392	1.43474	1.43941	0.00700
11	1.43248	1.43376	1.43404	1.43491	1.43971	0.00723
12	1.43203	1.43349	1.43376	1.43459	1.43905	0.00702
13	1.43231	1.43366	—	1.43484	—	—
14	1.43235	1.43360	1.43393	1.43480	1.43942	0.00707
15	1.43243	1.43379	1.43412	1.43495	1.43950	0.00707
16	1.43273	1.43415	1.43440	1.43526	1.43995	0.00722
17	1.43274	1.43405	1.43432	1.43516	1.43995	0.00722
18	1.43272	1.43407	1.43441	1.43531	1.43991	0.00719
19	1.43230	1.43358	1.43387	1.43475	1.43937	0.00707
20	1.43310	1.43440	1.43473	1.43553	1.44023	0.00713
21	1.43332	1.43460	1.43490	1.43575	1.44055	0.00723
22	1.43304	1.43420	1.43460	1.43551	1.44015	0.00711
23	1.43263	1.43390	1.43414	1.43508	1.43968	0.00705
24	1.43281	1.43417	1.43441	1.43531	1.44004	0.00723
25	1.43275	1.43402	1.43426	1.43534	—	—
26	1.43260	1.43393	1.43424	1.43508	1.43971	0.00711
27	1.43298	1.43426	1.43454	1.43543	1.44019	0.00721
28	1.43277	1.43402	1.43435	1.43517	1.43989	0.00712
29	1.43290	1.43392	1.43439	1.43521	1.43988	0.00698
30	1.43238	1.43359	1.43393	1.43491	1.43937	0.00699
31	1.43331	1.43460	1.43481	1.43591	1.44050	0.00719
32	1.43276	1.43420	1.43448	1.43539	1.43998	0.00722
35	1.43257	1.43388	1.43416	1.43508	1.43956	0.00699
36	1.43277	1.43388	1.43415	1.43498	1.43979	0.00702
37	1.43239	1.43375	1.43404	1.43482	—	—
38	1.43252	1.43385	1.43423	1.43507	1.43970	0.00718
39	1.43281	1.43409	1.43435	1.43523	1.43982	0.00701

The writer is of the opinion that significant variations in dispersion have not been found. The probable error in every dispersion measurement is equal to the sum of the probable errors of the two boundary indices. These are ± 0.00002 for $n(6550 \text{ Å})$ and ± 0.00003 for $n(4359 \text{ Å})$. The sum is thus ± 0.00005. The range of dispersion variation reported is ± 0.00015. This is equal to three times the probable error, i.e., the quantity which is generally considered to be the limit of error.

Unit Cell Dimension

High precision measurements of the fluorite unit cell edge are practically nonexistent. Most experimental values in the literature lack accuracy beyond the second decimal place. The best experimental value appears to be the one given in the *Strukturbericht* (*Zeits. Krist.*, pp. 185–186, 1913–1928): $a_0 = 5.451$ kX units). The calculated a_0, assuming a specific gravity of 3.181, is 5.452 (kX units). This calculated value is in good agreement with the experimental results obtained by the writer. The "back reflection" technique coupled with analytical extrapolation to $\theta = 90°$ has been employed (Cohen, 1935; 1936).

Determinations of a_0 have been carried out on only about one-half of the fluorite specimens. Synthetic fluorite (No. 38)* has been adopted as the standard of reference. Seventeen other specimens have been selected for measurement on the basis of their indices of refraction (Na). Eight of these had the lowest refractive indices; nine had the highest refractive indices. It was believed that in this manner any measurable variation of unit cell dimension with refractive index would be detected. The assumption is made that variation in the unit cell dimension would be reflected by the refractive index; thus, measurement was needed on only those specimens which had the most abnormal indices to ascertain whether or not cell dimension variations could be detected.

A symmetrical focusing back-reflection camera was used with copper x-radiation. The camera diameter was found by micrometer measurement to be 99.85 mm. at 28° C. The temperature at which fluorite specimens were x-rayed was 28° C. $\pm 1°$ C.

Before commencing film calculation it was necessary to index a fluorite film to determine *hkl* values corresponding to the three predominant reflections. These indices were found to be 444, 533 and 620, respectively.

As a check on the absolute accuracy of the technique, a photograph of Leadville pyrite was taken. A value of 5.4067 kX units (25° C.) was found by measurement of two reflections and extrapolation to $\sin^2 \theta = 1$. This value checks very well with one reported by Wasserstein (1949). To test the relative accuracy of the back-reflection technique five photographs were taken of synthetic optical fluorite. The range of possible error indicated was ± 0.00038 Å. The calculated probable error was ± 0.0001 Å.

Experimental results have previously been tabulated in Table 2.

Measurements on (1) optical fluorite, and (2) seventeen other fluorites yielded the following ranges of variation:

Optical fluorite	± 0.00038 Å
Other fluorites	± 0.00035 Å

* Supplied by Harshaw Chemical Co., Cleveland, Ohio.

It appears that the limits of possible random error obtained from five photographs of optical fluorite are qualitatively comparable with the limits of variation as obtained from photographs of the seventeen test specimens. Furthermore, the latter seventeen values lie within the absolute range of variation (due to random error) as determined from specimen No. 38.

A second point of importance is this: no obvious correlation can be made between variations in index of refraction and the variable measurements of cell edge. Since the latter determinations apparently lie within the limits of possible error it must be concluded that no significant differences among the specimens have been uncovered.

The value of a_0 for optical fluorite (average of five measurements) is 5.46295 Å $\pm$ 0.00010 Å at 28° C.

Semi-Quantitative Spectrographic Analyses

Analysis of fluorite specimens for minor elements was accomplished by emission spectrography using the cathode glow method. Use is made of the very high sensitivity of excitation that exists in the small region of the electric arc near the negative electrode when this is used to hold the sample. The arc is so adjusted that radiation from just above the cathode passes through the optical system of the spectrograph. Samples were mixed with an equal weight of purest graphite. A direct current carbon arc and grating spectrograph were employed. Semi-quantitative determinations were accomplished by comparison of unknown spectra with standard spectra taken with seven groups of standard samples. The findings are summarized in Table 4.

Elements which occur in practically all fluorites are magnesium, aluminum, manganese, strontium, and yttrium. An amazingly high percentage of strontium is almost always present: 0.05–0.5%. Fairly common in trace amounts are beryllium, silver, barium, ytterbium, and lead.

Mt. Antero beryllium-containing fluorite is associated with beryl, phenakite, and bertrandite. Quartz accompanies silicon-bearing fluorite from (1) Přzibram, and (2) Greenleaf Mine. The iron-rich fluorite from Hessenbach Mine is found encrusted by limonite. Celestite accompanies strontium-rich Clay Center fluorite. A barium-bearing fluorite from Madoc is found associated with barite. Thus, minor elements are sometimes found as major constituents in minerals associated with fluorite.

It has not been possible to assign any particular color to a given impurity or group of impurities. The only observation that can be made is this: all three fluorite specimens containing lanthanum are green. In general, the violet fluorites are the purest; they are notably free from rare earths.

TABLE 4. SPECTROGRAPHIC ANALYSES

Symbol meanings: A   0.5–5.0%
B   0.05–0.5%
C   0.005–0.05%
D   0.0005–0.005%
E   less than 0.0005%
F   not found

Specimen No. 40: a control run of purest graphite

	Be	Na	Mg	Al	Si	Mn	Fe	Cu	Sr	Y	Zr	Ag	Ba	La	Eu	Yb	Pb
1	F	F	E	C	F	E	F	F	B	C+	F	E	D	F	F	C	F
2	D	F	E	D	F	E	F	F	B	E	F	E	F	F	F	F	F
3	C	F	E	E	D	E	F	F	B	D	F	F	F	F	F	F	F
4	D	F	E	C	F	E	F	F	C	E	F	F	F	F	F	F	F
5	F	F	E	D	F	B–	F	F	B	E	F	F	F	F	F	F	F
6	E	F	E	D	F	E	F	F	C	E	F	F	F	F	F	F	F
7	E	F	E	D	F	F	F	F	D	B	D	F	E	F	F	F	F
8	F	F	E	D	F	D	F	F	B	C	F	F	D	F	F	F	E
9	F	F	D	D	F	D	F	F	B	E	F	F	F	F	F	F	E
10	F	F	E	D	F	D	F	F	B	C+	F	F	F	F	F	F	F
11	F	F	E	D	F	E	F	F	B	C+	C	F	F	F	F	F	E
12	F	F	E	D	F	E	F	F	B	C	D	F	F	C	F	F	E
13	F	F	E	D	F	E	F	F	B	C	F	F	F	F	F	F	F
14	E	F	E	D	F	E	F	F	B	C	F	F	F	F	F	F	F
15	F	F	E	D	F	F	F	F	B	C+	F	F	F	F	F	F	E
16	F	C	D	D	D	E	B	B	B	C+	F	F	D	F	F	F	E
17	F	F	E	D	F	F	F	F	B	E	F	F	F	F	F	F	F
18	F	F	E	D	F	E	F	F	B	E	F	F	F	F	F	F	E
19	F	F	E	D	F	F	F	F	B	E	F	F	F	F	F	F	F
20	E	F	E	D	D	E	F	F	B	C+	F	E	F	C	C	C	F
21	D	F	E	D	F	E	F	F	B	C+	F	F	F	F	C	E	F
22	D	F	E	D	F	D	F	F	B	C+	F	E	F	F	C	E	F
23	F	F	E	E	F	F	F	F	B	C+	F	F	B	F	B	E	F
24	F	F	E	E	F	F	F	F	B	C+	F	E	B	C	F	E	F
25	F	F	E	C+	F	D	F	F	B	C	F	D	F	F	F	E	F
26	F	F	E	E	E	D	F	F	B	C+	F	D–	F	F	F	D	C–
27	F	F	E	C	F	E	F	F	B	C+	F	E	F	F	F	E	E
28	F	F	E	C	B	E	F	E	B	C+	F	F	F	F	F	E	E
29	F	C	E	C+	F	E	F	F	B	C–	F	F	F	F	F	F	C–
30	F	F	E	C	F	E	F	F	B	C+	F	F	F	F	F	E	E
31	F	F	D	D	F	F	F	F	A–	C–	F	F	B	F	F	F	F
32	F	F	E	C	F	F	F	F	B	C+	F	F	F	F	F	C	D
33	F	F	E	C+	C	F	F	F	B	C+	F	D	F	F	F	D	F
34	F	F	E	C	C	F	F	F	B	B–	F	F	B	F	F	C	F
35	F	F	E	D	F	F	F	F	B	D	F	F	F	F	F	F	F
36	F	F	E	D	F	F	F	F	B	D	F	F	F	F	F	F	F
37	F	F	E	D	F	F	F	F	B	D	F	F	F	F	F	F	F
38	F	F	E	C	E	F	F	F	B	D	F	F	F	F	F	F	E
39	E	F	E	D	F	F	F	F	A–	D+	F	F	F	F	F	F	F
40	E–	E	E–	E–	E–	E–	D	E–	C–	F	E	E–	E–	F	F	F	F

Irradiation Experiments

It is well known that radiation can produce colors in fluorite. To study this variable property, samples from the entire suite of specimens were irradiated 24 hours with unfiltered copper x-radiation. Data have been summarized in Table 2. Five yellow-brown specimens showed extraordi-

narily intense blue-black coloration. In specimen No. 17 the induced color penetrated to a depth exceeding one centimeter. The induced color in 24 of 39 specimens was blue. Some specimens showed what was probably a mixture of induced blue and the initial body color of the specimen: orange specimen No. 36 became mauve. This may also be the case in green fluorites which show a deeper green after irradiation. In other cases the induced color is definitely not blue, i.e., in specimens No. 35 and 39. Of especial interest are specimens in which more than one color is induced (Nos. 14 and 24). The association of this phenomenon with cleavage in specimen No. 14 suggests that a relation exists between color and structural disturbance.

To test the effect of x-radiation on refractive index, seven fluorite prisms were irradiated: Nos. 1, 14, 17, 21, 26, 36, and 38. An exposure time of only a few hours was needed on specimens 17 and 26. The technique employed was to irradiate prisms at one end of the prism edge only. A given prism was oriented on the goniometer head and brought to the position of minimum deviation for sodium light. Then the prism was moved vertically on the goniometer head so that refracted light passed first through an unirradiated portion and then through an irradiated portion of the fluorite. In no case did the signal show any displacement from its original position. It must be concluded that no change in refractive index as a result of x-radiation has been proved.

Dark-Field Observations

Dark-field observations were carried out on the fluorite prisms used in making refractive index determinations. A petrographic microscope with high power objective and diaphragmed light source were employed.

Scattering centers were mainly in green, blue, violet, and pink fluorites. Green fluorites showed individual tiny circular spots of light. These were most densely distributed in the deepest green specimens, i.e., Nos. 12, 20, and 32. In the deeper blue fluorites most of the scattering centers had a somewhat different appearance. Circular spots of light were frequently seen in roughly equidimensional aggregates. Violet and pink fluorites showed still larger aggregates. In violet specimens Nos. 2, 6, and 19 some of the scattering centers showed definite linear arrangement parallel to crystal faces. Less numerous scattering centers were also seen in some brown-yellow and colorless specimens; in these colors scattering was of the fine type seen in the green specimens. The scattering phenomenon was also seen in fluorite artificially colored by irradiation. No. 37 (artificial blue) showed coarse aggregates. For purposes of comparison a specimen of blue halite was examined. Scattering centers were very similar to those seen in violet fluorite, both with respect to size and density of distribution.

These observations could be interpreted as support for the colloidal calcium theory of color stated by Göbel.

Luminescence

Luminescence experiments in this investigation have been carried out in a qualitative fashion which is in sharp contrast to the rigorous luminescence spectral analyses made by Haberlandt and other workers. For this reason they have been of very restricted value in developing a general picture of structural variations in fluorite. Space does not permit a description of the experiments carried out or tabulation of data accumulated. In view of the limited applicability of emission spectrographic analysis to the detection of several rare earths, however, a very general use of luminescence phenomena to this end has been made. Luminescence phenomena in calcium fluoride, with the exception of excitation by manganese or hydrocarbons, are caused by trivalent rare earth ions (line spectra) and four bivalent rare earth ions (band spectra), i.e., europium, ytterbium, samarium, and thulium. In relating luminescence (and therefore rare earth content in most cases) and color the following observations seem pertinent: (1) Ultraviolet fluorescence and phosphorescence are usually absent in violet and pink varieties; (2) the prevalence of strong thermoluminescence in green fluorites suggests the universal presence of rare earth activators; (3) blue fluorites are second to the green in thermoluminescent power while violet, brown and colorless specimens show the effect only occasionally; (4) yellowish-white fluorescence, seen in yellow-brown specimens from Cave-in-Rock and Clay Center, is probably due to included organic material. The thermoluminescence data strongly suggest that green fluorites always contain abundant rare earths. Other fluorites which exhibit strong thermoluminescence presumably also contain rare earths. Luminescence experiments and spectrographic analyses both attest to the relative purity of violet fluorites.

Miscellaneous observations made in connection with thermoluminescence experiments are given below. As a result of heating, most fluorites lose their color. Violet specimens become pink. Some green and brown specimens fail to decolorize completely. Decrepitation and bleaching occur between 150° and 200° C. for most specimens. None of the synthetic specimens shows any thermoluminescence or decrepitation.

III. CORRELATION AND INTEGRATION OF DATA

The Relation of Refractive Index to Chemical Composition

The optical properties of ionic crystals are to a first approximation those of the aggregate of ions. Ionic refractivities are additive. The re-

fractivity of the individual ions is a measure of the deformability or polarization of the electronic structure by the electric vector of incident light, and is therefore largest for ions with a large and loosely bound electron configuration. Three general rules relating refractive index to the character of an ion can be applied in qualitative fashion: (1) refractive index is increased by an increase in ionic radius; (2) refractive index is raised by an increase in atomic weight; (3) increase in the positive charge of an ion depresses the refractive index.

The way in which a minor element occurs in fluorite must be known before any prediction can be made as to its effect on the refractive index. It is probable that the following reported impurities substitute for calcium in the ionic structure: Na, Mn″, Fe″, Sr, Y, Zr, Ba, La, Eu, Yb, and Pb. Silver and copper may substitute for calcium in atomic form

TABLE 5: CORRELATION OF ELEVATED REFRACTIVE INDICES WITH IMPURITIES OF HIGHER REFRACTIVE POWER THAN CALCIUM

Specimen No.	n_{Na} (20° C.)	Minor Elements
5	1.43433	Mn
16	1.43415	Fe
20	1.43440	Eu, La, Yb
21	1.43460	Eu
22	1.43420	Eu
24	1.43417	Ba, La
31	1.43460	Ba, Sr
32	1.43420	Yb
39	1.43409	Sr

provided that a compensatory mechanism exists. (Neutral atoms could be compensated for by the presence of trivalent cations or by partial omission of anions, i.e., fluorine.) The small ions of Be, Mg, Al, and Si probably cannot substitute for the calcium ion. Perhaps they occur in structural holes or in microscopically included foreign matter.

A limited number of fluorites, which exhibit abnormally high indices of refraction, contain minor elements which would be expected to increase the over-all refractivity of the fluorite structure (Table 5). Specimens No. 20, 21, and 22 contain europium and show abnormally high indices. Barium probably accounts for the high refractive indices of specimens No. 24 and 31. Other minor elements believed to increase total refractivity include manganese, iron, lanthanum, ytterbium, and strontium.

Specimens Nos. 26 and 29 have slightly high refractive indices; these may be caused by the presence of a trace of lead in each specimen. Ele-

ments which have no apparent effect upon the refractive index (in the concentration in which they are present) include the following: Be, Na, Mg, Al, Si, Cu, Y, Zr, and Ag.

More interesting than the refractive indices which are explained by the presence of impurities are those for which no apparent explanation exists. Most outstanding, nine specimens of green, blue and violet colors exhibit abnormally low indices of refraction. Four yellow-brown fluorites (Nos. 17, 25, 27, and 28) have abnormally high indices for no apparent reason. A blue fluorite (No. 18) has an unexplained high refractive index. Unaccounted for is the presence of rare earths (other than yttrium) in fluorites with normal or low indices, i.e., specimens Nos. 1 and 12. The heavy rare earths would be expected to increase the index. A comparison of results on green and brown Weardale fluorites reveals an anomaly. The green specimen with abundant rare earths has a lower refractive index than the brown specimen which contains only europium. Another anomalous situation is presented by specimens Nos. 23 and 24. Both contain about 0.1% Ba but show widely different indices. An interpretation of the facts brought out above will be reserved until color is discussed later.

Dependence of Color Centers Upon the Lattice Constant

The exceedingly constant value of a_0 has significance with regard to the theory of "F centers." It has been shown by Pohl (Hughes, 1936) that the location of the characteristic F band for a given alkali halide is a function of the interplaner spacing as follows:

$$(V_{max})(d^2) = k,$$

where "V_{max}" is the frequency at maximum absorption, "d" is the lattice spacing and "k" is a constant.

If this type of relation holds for alkaline earth halides, it can readily be seen that various colors of fluorite are not to be explained on the basis of an F band whose location is subject to variation. The very constancy of a_0 for calcium fluoride rules out this possibility.

Mollwo (1934) has attributed the short wave length absorption maximum of fluorite to the presence of "F centers." It is a simple matter to prove the validity of his assumption by mathematical means. The above equation is used to determine the constant, "k," for (1) NaCl and (2) CaF_2. In Table 6 the pertinent figures relating to these equations are given.

A Theory of Color

The writer proposes a theory of the color of fluorite which has much in common with proposals made by Mollwo (1934) and Göbel (1931).

TABLE 6. DATA PERTAINING TO F CENTERS IN CALCIUM
FLUORIDE AND SODIUM CHLORIDE

Compound	Wave Length	Frequency	$(a_0)^2$	k
CaF_2	4000 Å	$.75 \times 10^{15}$	29.8	2.23×10^{16}
NaCl	4400 Å	$.68 \times 10^{15}$	32.0	2.18×10^{16}

The values for "k" are within 2.5% of each other.

The short wave length absorption maximum (380 to 405 mμ) is ascribed to "F centers" such as occur in alkali halides. The long wave length absorption maximum (575 to 650 mμ) is ascribed to colloidal calcium. The smallest colloidal particles cause absorption in the red region (green fluorite). An increase in size of colloids causes the absorption maximum to be displaced first into the orange range, then finally into the yellow causing blue and violet colors, respectively.

Evidence from this Investigation

Dark field observations, lattice constant determinations, spectrographic analyses, refractive index determinations, and x-radiation experiments have proved to be especially helpful in developing a theory of color.

Dark field observations made in the course of this investigation are in good agreement with those made earlier by Göbel. Light scattering centers were smallest in green fluorite, of intermediate size in blue fluorite and largest in violet fluorite. The long wave length absorption maximum is thus attributed to colloidal calcium by the writer. This view is strengthened (see below) by refractive index data and x-radiation results.

The short wave length absorption maximum (in most cases) is attributed to the presence of "F centers." Support for this stand is obtained by use of the formula $(V_{max})(d^2) = k$, which Pohl has developed in studying "F centers" in alkali halides. The frequency corresponding to 4000 Å (the short wave length maximum) and the square of a_0 are substituted in the equation. The value obtained for k is within 2.5% of k for sodium chloride.

Spectrographic analyses fail to reveal any correlation between the color of fluorite and the content of rare earths or transition elements, noted coloring agents. The only observation which can be made is this: all three fluorites containing lanthanum are green. In general, the violet fluorites are the purest; they are remarkably free of rare earth elements. Thermoluminescence experiments indicate the prevalence of rare earths in green fluorites.

A further line of evidence supports the conclusions drawn by the writer. It has been pointed out that colored fluorites are characterized by refractive indices which are either considerably higher or remarkably lower than the value for optical fluorite. All fluorites in which the short wave length absorption maximum is prominent, i.e., yellow or brown specimens, have indices which are higher than normal. Fluorites in which the long wave length maximum is prominent have refractive indices which are either higher (eight specimens) or lower (ten specimens) than normal. It has been shown that in some cases elevated indices can be traced to highly refractive impurities. Of the eight long wave length maximum specimens seven contain such minor elements. But of the eight yellow-brown specimens only two contain such impurities. We are now in a position to make a generalization: Fluorites with principal absorption at long wave lengths are usually characterized by abnormally low refractive indices unless minor constituents obscure the effect; fluorites with principal absorption at short wave lengths are characterized by abnormally high refractive indices. Anomalous indices of refraction would be accounted for by departure from the stoichiometric ratio of the calcium fluoride formula. Thus, fluorine deficiency compensated for by colloidal calcium would explain abnormally low refractive indices; and a calcium excess, present as elemental calcium in structural holes, would account for elevated indices. In short, the charge requirement in each case is satisfied by partial neutralization of calcium. Omission of fluorine satisfies the space requirements for formation of colloidal calcium in the one case. In the other case it must be pointed out that it is rather difficult to imagine the large calcium *atom* fitting into a structural hole. The calcium atom has nearly twice the radius of the divalent calcium ion. But the separation of the calcium atom and its valence electrons, i.e., formation of an "F center," makes the picture easy to visualize. A hole in the fluorite structure could easily contain a divalent calcium ion.

The striking effect of x-radiation on five yellow and brown fluorites is readily explained by the writer's theory. Atomic calcium, which causes "F centers" in yellow-brown fluorite, is believed to coagulate into colloidal aggregates which produce the blue color of irradiated fluorite. Presumably fluorine must migrate in the crystal to permit this coagulation. Mollwo's experiment of electron introduction into fluorite has proved that fluorine migration is a feasible process.

However, not all brown and yellow fluorites can be considered to contain "F centers." Specimens from Clay Center and Cave-in-Rock do not show striking color change when irradiated. Their yellowish white ultraviolet fluorescence suggests that color may be the result of enclosed

hydrocarbons. Brown Weardale fluorite also fails to exhibit the irradiation effect. Perhaps as suggested by Přzibram (1938) the color is due to bivalent europium which is known to be present.

Blue material from Livingston Co., Kentucky, is unusual in that it has an unusually high refractive index without the presence of an impurity to explain the index. Associated with the blue fluorite is yellow fluorite whose index of refraction is identical within the limits of experimental error. It is suggested that colloidal calcium in the blue specimen resulted from coagulation of "F centers" formerly present.

The fact that artificial irradiation does not change the index of refraction is regarded as support for the present hypothesis. If x-radiation merely causes a coarsening of pigment particle size it would not be expected to effect a change in index. No change in density would be experienced by the irradiated substance.

The Mechanism of Color Origin

Two opposite points of view have been taken on the question of the mechanism of color origin. According to the prevalent school of thought color in fluorite is caused by radioactivity. We have seen that Schilling (1926) and Göbel (1931) attribute the formation of colloidal calcium to a partial destruction of the fluorite structure by radioactive influences. It is also possible that color is of primary origin. Evidence has been cited above which points to such an explanation. Přzibram (1934) concludes that the size of colloidal sodium particles in halite varies directly with the rate of growth. Macroscopic structural features in fluorite suggest that color is a primary property of the mineral. Color-zoning is commonly observed, especially in violet fluorite. Perhaps, as Přzibram suggests for halite, a relation exists between rate of crystal growth and size of colloidal particles.

The writer believes it is possible that color in fluorite is not infrequently produced by a defect structure. Omission of fluorine ions could result in the presence of colloidal calcium. Alternately, if excess calcium ions were caught in structural holes they would have to become neutral. In this manner F centers could come about—a natural form of additive coloring. This explanation is in agreement with refractive index findings reported in an earlier section.

The presence of large amounts of rare earths in green fluorites is capable of an explanation without invoking any particular rare earth ion to perform the work of pigment. Přzibram (1938) has demonstrated that europium exists in the bivalent state at 300–400° C. whereas at lower temperatures it assumes the trivalent form. A fluorite crystallizing at a high temperature could take up bivalent rare earth ions in its struc-

ture. Upon cooling the rare earths might oxidize to the trivalent state reducing adjacent calcium ions. Reduced calcium might then coagulate into small particles which characterize green fluorite.

REFERENCES

1. ALIMARIN, I. P., AND AREST-YAKUBOWICH, R. E., *Bull. Soc. Naturalists, Moscou*, ser. 2, **42**, 575–583 (1934).
2. BLOUNT, B., AND SEQUEIRA, J. H., *Jour. Chem. Soc. London, Trans.*, **115**, 705–709 (1919).
3. BRAY, J. M., *Am. Mineral.*, **27**, 769–775 (1942).
4. CHANG, TING-CHAO, *J. Shanghai Sci. Inst.*, no. 2, 115–155 (1943).
5. CORK, J. M., *Phys. Rev.*, **62**, 80–81 (1942).
6. DOELTER, C., *Tschermaks Min., Petr. Mitt.*, **38**, 456–463 (1925).
7. DOELTER AND LEITMEIER, Handbuch der Mineralchemie, **4**, pt. 3, 193–269 (1931.)
8. DOMANGE, L., *Compt. Rend. Acad. Sci.*, Paris, **194**, 1667–1669 (1932).
9. DUDENHAUSEN, H., *Neues Jahrb. für Min.*, **i**, 8–29 (1904).
10. EYSANK, E., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **145**, 387–406 (1936).
11. GARNETT, C. S., *J. Chem. Soc. London, Trans.*, **117**, 620–622 (1920).
12. GIFFORD, W. J., *Proc. Royal Soc. London*, **70**, 329–340 (1902).
13. GIFFORD, W. J., *Proc. Royal Soc. London*, Ser. A, **84** (1910).
14. GÖBEL, L., *Zeits. Krist.*, **76**, 457 (1931).
15. GUNNELL, E. M., *Am. Mineral.*, **18**, 68–73 (1933).
16. HABERLANDT, H., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **143**, 591–596 (1934).
17. HABERLANDT, H., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **144**, 663–666 (1935).
18. HABERLANDT, H., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **146**, 1–10 (1937).
19. HABERLANDT, H., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **147**, 137–150 (1938).
20. HABERLANDT, H., *Chemie der Erde*, **13**, 212–230 (1940).
21. HABERLANDT, H., KARLIK, B., AND PŘIZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **144**, 77–83 (1935).
22. HABERLANDT, H., KARLIK, B., AND PŘIZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **144**, 135–140 (1935).
23. HABERLANDT, H., KARLIK, B., AND PŘIZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **144**, 141–149 (1935).
24. HABERLANDT, H., AND SCHIENER, A., *Zeits. Krist.*, **90**, 193–214 (1935).
25. HLAWATSCH, C., *Zeits. Krist.*, **27**, 605–607 (1897).
26. HOFFMANN, J., *Chemie der Erde*, **11**, 368–374 (1937).
27. HUGHES, A. L., *Review of Modern Physics*, **8**, 294–315 (1936).
28. HUMPHREYS, W. J., *Astrophys. Jour.*, **20**, 266–272 (1904).
29. HUMPHREYS, W. J., *Astrophys. Jour.*, **22**, 157 (1905).
30. IWASE, E., *Inst. Phys. and Chem. Research, Tokyo*, Scient. Papers, **22**, 233–241 (1933).
31. IWASE, E., *Inst. Phys. and Chem. Research, Tokyo*, Scient. Papers, **23**, 22–23 (1933)
32. IWASE, E., *Inst. Phys. and Chem. Research, Tokyo*, Scient. Papers, **23**, 153–161 (1934).
33. IWASE, E., *Inst. Phys. and Chem. Research, Tokyo*, Scient. Papers, **23**, 212–223 (1934).
34. IWASE, E., *Bull. Inst. Phys. and Chem. Research, Tokyo*, **21**, 61–65 (1942).

35. KELLERMANN, E. W., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **146,** 115–144 (1937).
36. LEITMEIER, H., *Tschermaks Min., Petr. Mitt.*, **38,** 591–598 (1925).
37. MELLOR, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, **II,** 538; **III,** 688–696 (1923).
38. MERKADER, S., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **149,** 349–365 (1940).
39. MERWIN, H. E., *Am. Jour. Sci.*, **32,** 429–432 (1911).
40. MOLLWO, E., *Nachr. Ges. Wiss. Göttingen*, Fachgruppe 2, **1,** 79–89, (1934).
41. MORGANTE, S., *Periodico Min. Roma*, **10,** 379–396 (1939).
42. MORRISON, R. B., *Am. Mineral.*, **20,** 780–790 (1935).
43. MORSE, H. W., *Proc. Am. Acad. Arts, Sci.*, **41,** 587–613 (1905).
44. MUKHERJEE, B., *Indian J. Physics,* **22,** 221–228 (1948).
45. NORTHUP, M. A., AND LEE, I. O., *Jour. Opt. Soc. Am.*, **30,** 206–223 (1904).
46. PRINGSHEIM, P., AND VOGEL, M., Luminescence of Liquids and Solids, Interscience Publishers (1943).
47. PŘZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **138,** 263–269 (1929).
48. PŘZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **143,** 489–496 (1934).
49. PŘZIBRAM, K., *Zeits. Physik*, **102,** 331–352 (1936).
50. PŘZIBRAM, K., *Zeits. Physik*, **107,** 709–712 (1937).
51. PŘZIBRAM, K., *Nature*, **139,** 329 (1937).
52. PŘZIBRAM, K., *Neues Jahrl. Mineral., Geol.*, Ref. **I,** 356–357 (1937).
53. PŘZIBRAM, K., *Nature*, **141,** 970 (1938).
54. PŘZIBRAM, K., *Sitz.-ber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. IIa, **147,** 261–270 (1938).
55. PŘZIBRAM, K., *Acta Phys. Austriaca*, **I,** 131–136 (1947).
56. ROLL, K. H., *Yale Sci. Mag.*, **19,** no. 2, 10–11, 26, 32 (1944).
57. SCHILLING, A., *Neues Jahrb. Min., Abt. A.*, **53,** 241–265 (1926).
58. STARIK, I. E., KRAVCHENKO, L. L., AND MELIKOVA, O. S., *Comptes Rendus de l'Acad. des Sciences de l'URSS*, **32,** no. 4, 254–255 (1941).
59. URBAIN, G., *Comptes Rendus de l'Acad. des Sciences, Paris*, **143,** 825–827 (1906).
60. URBAIN, G., *Annales de Chimie et Physique*, **18,** 222–386 (1909).
61. VAN DER LINGEN, S., *Zeits. Physik*, **53,** 581–586 (1929).
62. WICK, F. G., *Phys. Rev.*, **24,** 272–282 (1924).
63. WICK, F. G., *Jour. Opt. Soc. Am.*, **21,** 223–231 (1931).
64. WICK, F. G., *Jour. Opt. Soc. Am.*, **27,** 275–285 (1937).
65. WÜLFING, E. A., *Neues Jahrb. für Mineralogie*, **ii,** 166–169 (1907).
66. WYROUBOFF, G., *Bull. de la Soc. Chim. de Paris*, 16 (1866).
67. YOSHIMURA, J., *Inst. of Phys. and Chem. Research, Tokyo*, Scient. Papers, **20,** 170–177 (1933).
68. YOSHIMURA, J., *Inst. of Phys. and Chem. Research, Tokyo*, Scient. Papers, **23,** 224–247 (1934).