

HACKMANITE AND ITS TENEBRESCENT PROPERTIES

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ABSTRACT

A brief review of reversible optical bleaching is given in terms of the band theory of solids. A model is then proposed for evanescent pink sodalite (hackmanite) which is consistent with these ideas. Optical, x-ray and chemical measurements are in qualitative agreement with this model. It is shown that the presence of sulfur (1, 2), or manganese (3) is not a necessary condition for the evanescence. This is in agreement with the observations of Walker and Parsons (4) on hackmanite from Bancroft, Ontario, and Miser and Glass (5) on hackmanite from Magnet Cove, Arkansas. Synthetic materials have been prepared which exhibit darkening under 2537 Å u.v. and subsequently bleach under visible light or heat.

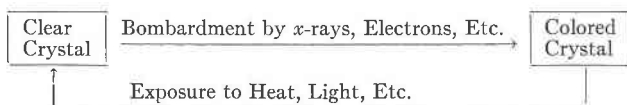
HISTORICAL BACKGROUND

Our studies of hackmanite and tenebrescence originated with W. E. Bradley, Director of Research, Philco Corporation. He felt that substances which exhibited purely optical reversible bleaching (if they existed) were capable of extensive electronic applications. Dr. W. G. Gibson was asked by Mr. Bradley if he knew of any natural mineral which darkened under ultra-violet light and bleached under visible radiation. Dr. Gibson consulted the Delaware County Institute of Science (Media, Pa.) and Mr. Fox of that organization suggested the mineral, hackmanite, which was reported by O. Ivan Lee (3) to exhibit this effect.

Members of the Institute and of the Academy of Natural Sciences (Phila.) furnished a few small specimens. W. E. Bradley visited Bancroft, Ontario, and obtained more specimens with the assistance of Mr. Louis Moyd, an economic geologist of that region. It was with the latter specimens that most of our measurements were obtained.

I. INTRODUCTION

The properties of crystals which have been discolored and then bleached by various radiations constitute one of the central problems in solid-state physics. The term "tenebrescence," Latin-tenebrae (shadows), has been applied to this reversible process which may be graphically depicted as follows:



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A qualitative model of the phenomenon has been constructed from the results of the quantum theory of solids and the researches of Pohl and his co-workers with the F-centers (color centers) of the alkali halides (6-9). Most fundamental investigations of tenebrescence have dealt exclusively with the alkali halides, since, in addition to their relative simplicity, they were readily available in large single crystals of high optical purity (10).

The reversible discoloration of alkali halides was originally observed by E. Goldstein (11) late in the last century. The characteristic colors produced in KCl (magenta), NaCl (yellow), KI (blue), and KBr (blue-green) under electron bombardment faded upon exposure to ambient light. Later investigators observed that the discoloration could also be produced by α -rays, very short wave length ultra-violet, or by addition of a stoichiometric excess of the alkali metal.

In addition to the alkali halides, a large group of other materials exhibit tenebrescence. These include: the silver halides (12), the alkaline earth fluorides (13), magnesium oxide (14), titanium dioxide (15), and a great many minerals (16).

In the following discussion, our interest will be focused on the properties of a particular mineral, hackmanite, which is also known as evanescent pink sodalite. This interest in hackmanite is due to its unique property of darkening under *long* wavelength ultra-violet.

Hackmanite antedates the alkali halides in terms of the bleaching aspects of tenebrescence. In 1834, Robert Allan in his *Manual of Mineralogy* stated, "Its color is green unless freshly fractured, when it presents a brilliant pink tinge, but this on exposure to light goes off in a few hours." Mineralogists regarded this record as poorly founded and Allan's discovery was ignored. In 1901, the first of a series of investigations (1), (17), (4) confirmed his observations. The tenebrescence cycle was completed by Lee's discovery (3), that exposure to ultra-violet light up to about 4800 Å produced the characteristic magenta coloration which could be bleached by a bright light. Lee's investigations have yielded most of the physical information on hackmanite (as reported in the literature) and his results therefore merit some further discussion.

Hackmanite when subjected to excitation from an iron-spark discharge (2 cm. 10 sec.) showed a brilliant salmon pink fluorescence and a weak blue-white phosphorescence. The induced color faded in the dark very slowly but exposure to a 60W lamp for 30 sec. gave almost complete reversal. The respective wavelengths are:

Darkening: 2250-4800 Å

Bleaching: 4800-7500 Å

The peak efficiency of bleaching occurs at wavelengths shorter than yellow. Following reversal, there is some partial recovery of coloration if the specimen is kept in the dark for more than five weeks.

Lee's analysis of the tenebrescence phenomenon in hackmanite appears to have been dominated by the researches of Doelter (18) who thought, that color changes in minerals through ultra-violet, (u.v.) x -ray, and Ra -radiation were due to oxidation and reduction changes of metallic oxides. The work of the Göttingen group on the tenebrescence of the alkali halides had not yet found its way into English technical literature.

Although Lee's article posed some tantalizing questions, no further work was done in the directions he suggested as far as we could determine. Other reports of the evanescent pink sodalite keep cropping up in the literature and some of these are listed in (19-21).

II. THE COLOR CENTER MODEL FOR HACKMANITE AND SODALITE

The optical properties of hackmanite can be described in terms of the band theory of solids. Consider Fig. 1. Figure 1*a* is the representation of an insulator with the highest filled band and the empty conduction band shown. This may be considered as the band picture of pure sodalite. Figure 1*b* indicates that narrow bands of additional permissible energy levels may arise. Those marked *F* can be considered due to normal lattice imperfections such as cracks, strains, and missing ions. These constitute electron traps and upon capture of an electron are converted into F-centers. This corresponds to the situation in the alkali halides and the terminology of color centers in alkali halides will be applied to hackmanite optical phenomena. It should be considered that Fig. 1*a* represents an ideal case and that in most crystals, levels corresponding to *F*(1*b*) will be found even if no chemical impurities are added. The levels at *U* are responsible for the sensitivity of hackmanite to ultra-violet and may be considered as arising from the introduction of a substitutional or interstitial

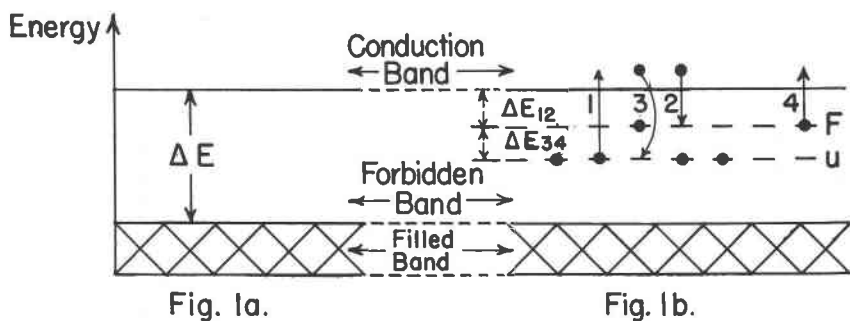


FIG. 1

impurity into the sodalite lattice. This model makes possible the complete description of the evanescence phenomena in terms of electronic transitions.

Consider the completely bleached crystal. If it is exposed to ultraviolet (2000–3600 Å; upper limit given as 4800 Å by Lee) electrons are raised from the normally populated levels at U into the conduction band (process (1) $-\hbar\nu = \Delta E_{12} + \Delta E_{34}$). These conduction band electrons then have the option of either being trapped at an empty F-level (2) thus forming an F-center or recombining with holes in the U levels (3), i.e., there is a strong competition between traps at F and holes at U for the conduction band electrons.

The transition (2) is assumed responsible for the bright salmon-orange fluorescence of hackmanite observed during the U. V. irradiation.

The crystal is now in the colored state since the trapped electrons at F constitute F-centers. If a quantum of radiation corresponding to $\hbar\nu = \Delta E_{12}$ is incident on the crystal it may be absorbed by an F-center. The electron in the F-center is excited into the conduction band where the same (2)–(3) competing processes take place. After a sufficient time, the crystal can be considered as bleached. Thermal bleaching occurs in an analogous manner although in this case, the activation energy is lowered by the lattice vibrations. If we assume that the capture cross-section (σ) of the U-levels is of the same order of magnitude as the capture cross-section (σ) of F-levels, then we may conclude that substances showing a high degree of darkenability have a low bleaching efficiency and conversely.

In order to complete our picture we must use this model to explain the discoloration of clear hackmanite left in the dark. Assume that at absolute zero ($T = 0^\circ\text{K}$) the U-levels are completely populated whereas the F-levels are all empty. At any other temperature there exists a finite probability of transition from the U-levels to the F-levels, and vice versa, and at this temperature there is a unique equilibrium distribution of the electrons among these levels. The temperature dependence of this equilibrium distribution may be determined from statistical considerations as:

$$n = Ae^{-\Delta E/2kT}$$

wherein n represents the number of F-centers, ΔE , a thermal activation energy which is at least less than $\Delta E_{\text{max}} = \Delta E_{34}$, A is a constant depending on the original number of empty F-levels per cm^3 and the original number of filled U-levels per cm^3 . For hackmanite, it is found that ΔE is rather small ($\Delta E_{\text{max}} \cong 1 \text{ ev}$) so that at room temperature, we

should expect an appreciable number of F-centers to be formed in crystals shielded from light as is observed.

III. OPTICAL MEASUREMENTS

In order to determine the trap and activator spectrum of hackmanite which differentiates it from sodalite, an investigation of the absorption coefficient (K) was undertaken. The work was hampered by the inability to procure clear homogeneous crystals of hackmanite. Scattering effects of minute impurities in the specimens investigated were neglected. The absorption coefficient was measured using two different methods.

(a) Method 1

Measurements of K were obtained in the range of 4200 Å–6200 Å in steps of 25 Å using the apparatus setup of Fig. 2. A balancing circuit using a compensating photocell for stray radiation is not shown. The calibration and use of the spectrometer are described in the Bausch and Lomb Spectrometer Catalogue 33-82-09. The results given in Fig. 3 show the existence of an absorption band whose amplitude depends on time of exposure to the ultra-violet. The position of the maximum is invariant with the exposure time and corresponds to an F-level depth of 2.34 electron-volts (e.v.).

(b) Method 2

We were able to extend the range of our measurements by use of the Beckmann Model DU Spectrophotometer. I was permitted to use this instrument through the courtesy of Dr. P. H. Miller, Jr., and the Physics Department of the University of Pennsylvania. D. A. Melnick assisted in these measurements.

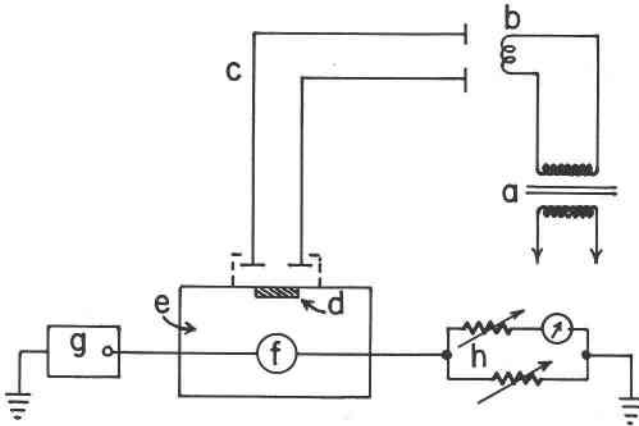
Readings were taken every 50 Å units in the new range of 2200 Å–18,000 Å. Much tedious calculation was avoided in using this instrument since density values can be directly obtained through the calibration of the equipment. The results are shown in Figs. 4 and 5. The shape of the absorption curve (ΔK) in Fig. 5 is of particular interest since it exhibits a unique characteristic of the F-bands in the alkali halides: a linear rise in the short wavelength region which is believed to be due to the excitation of the localized F-center electron into hydrogen like energy levels. The continuous absorption here is of the same order of magnitude as the band absorption.

The rise of the absorption coefficient in the ultra-violet is marked by a series of peaks. This effect may be due to a set of discrete activating levels instead of the narrow continuous band previously thought to be respon-

sible for the darkening of hackmanite under U.V. As expected, K decreases somewhat in the U.V. region after exposure.

We can thus state the following general conclusions from our work with absorption coefficients:

1. The peak of the F-band (if we may so designate it) in hackmanite occurs at $5300 \pm 50 \text{ \AA}$ which corresponds to a value of about 2.34 electron volts. We consider this as the difference in the $1S$ and $2P$ states of an F-center electron, but to a good approximation it represents the depth



- a- Sola, constant voltage transformer
- b- 100 watt mazda bulb with reflector
- c- Bausch and Lomb large Spectrometer
- d- Ground and polished specimen of Hackmanite
- e- Light tight box
- f- Photomultiplier (RCA-931A)
- g- Regulated power supply for Photomultiplier
- h- Galvanometer System

Apparatus for measurement of Absorption Coefficient

FIG. 2

of the electron traps below the conduction band. The peak of the F-band is not dependent on the amount of prior excitation.

2. There is an auxiliary band which might be an F^1 band at 6000 \AA . This could be verified by a close inspection of its temperature properties.

3. The quantum yield for hackmanite is very low when compared with substances such as KCl which have been darkened under electron bombardment. For the specimens investigated, the maximum number of color centers obtainable is $n_0 = 10^{17}/\text{cm}^3$. This number (n_0) may be calculated from the absorption coefficient (ΔK) by use of an expression due to Smakula (22).

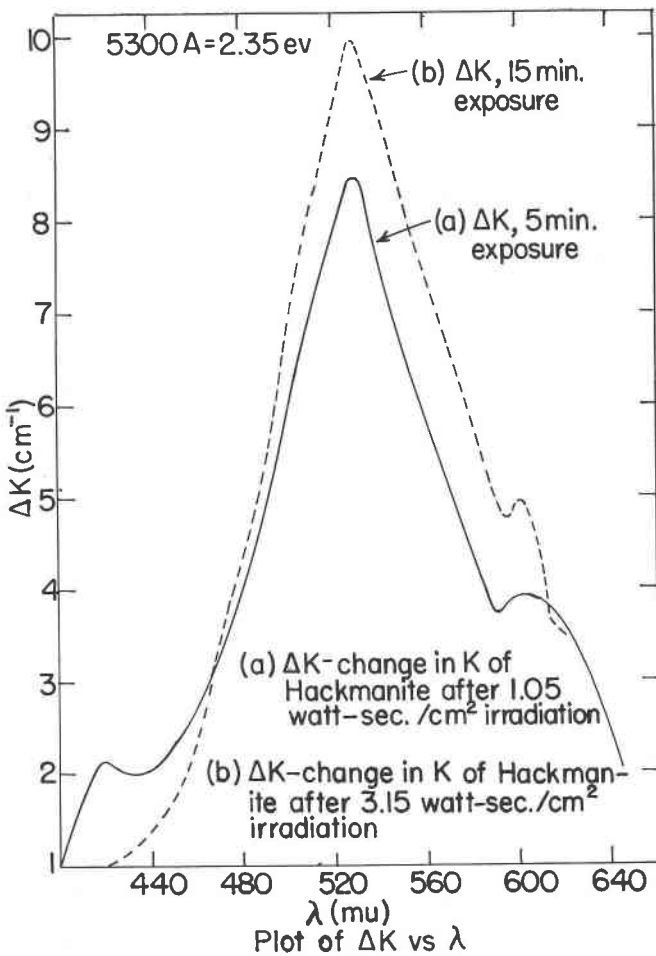


FIG. 3

4. The absorption band produced in hackmanite, protected from external radiation, is of the same general form as the F-band with its peak at $5300 \pm 50 \text{ \AA}$. There are some irregularities in it which do not occur in

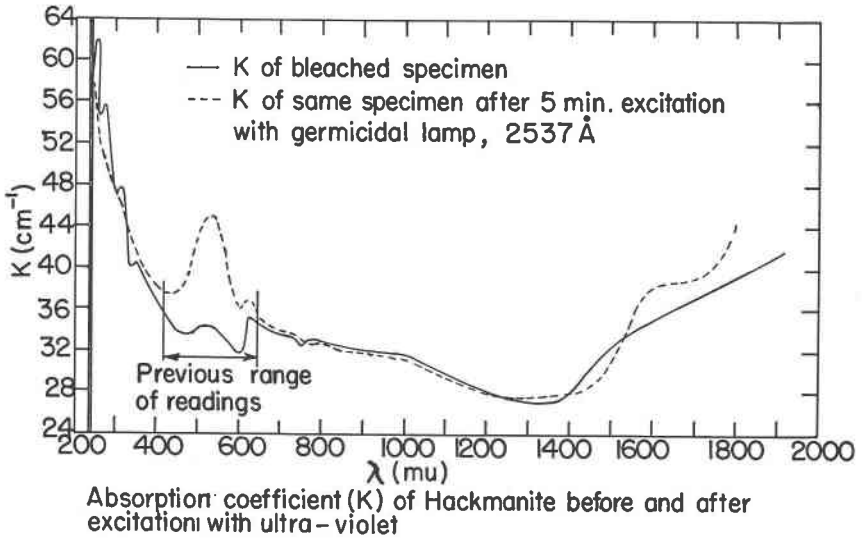


FIG. 4

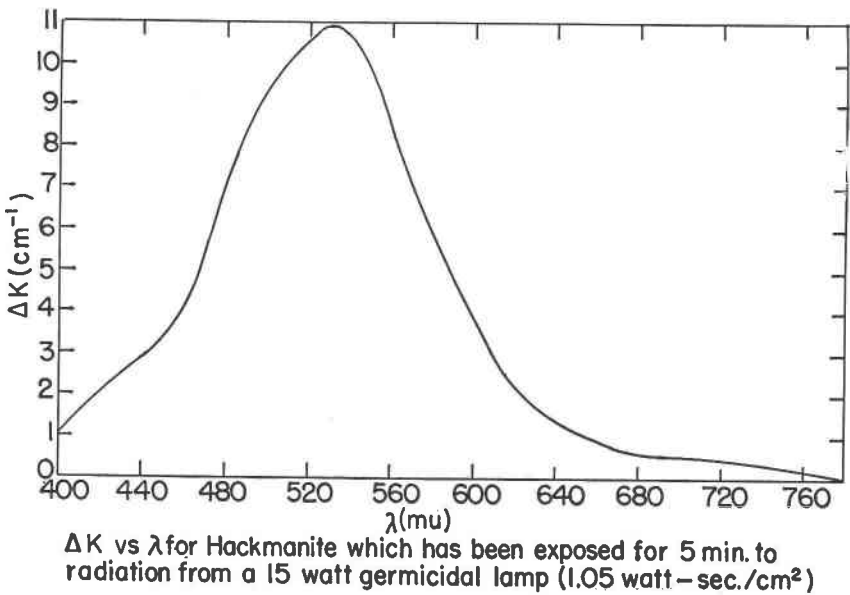


FIG. 5

TABLE 1

<i>Sodalite</i> (Blue)				<i>Hackmanite</i>				
Author	Thomson	Vredenburg	Miser & Glass	Borgström	Walker & Parsons	Lee	Miser & Glass	Medved
Source	Greenland	Rajputana, India	Magnet Cove, Ark.	Kola Pen., U.S.S.R.	Bancroft, Ont.		Magnet Cove, Ark.	Bancroft, Ont.
Comp %								
SiO ₂	38.52	38.055	38.36	36.99	37.08	—	36.70	—
Al ₂ O ₃	27.48	31.300	32.09	31.77	32.58	—	32.01	—
Na ₂ O	23.50	24.77	24.73	25.84	22.26	—	24.79	—
Cl	3.0	7.18	6.79	6.44	6.82	—	7.00	—
Fe ₂ O ₃	—	trace	0.07	0.17	—	—	0.07	} .00x
FeO	—	—	none	—	—	—	none	
TiO ₂	—	—	none	—	—	—	none	none
MnO	—	—	0.06	—	trace	.0015	none	.000x
MgO	—	—	none	none	0.03	—	none	none
K ₂ O	—	—	0.12	0.16	0.53	—	0.17	1.0–5.0
CaO	—	0.001	0.5	—	—	—	0.29	1.0–5.0
CO ₂	—	—	—	—	0.32	—	—	—
Li	—	—	—	—	—	.01	—	—
Ga	—	—	—	—	—	.01	—	.00x
Pb	—	—	—	—	—	.005	—	none
Be	—	—	—	—	—	trace	—	none
Ba	—	—	—	—	—	trace	—	none
Sr	—	—	—	—	—	trace	—	.00x
Nd	—	—	—	—	—	} 1 line @4303	—	—
S	—	—	none	0.39	none		—	trace
SO ₃	2.10	trace	trace	—	—	—	trace	none
P	—	—	—	—	—	trace	—	—
H ₂ O	1.70	0.82	0.86	—	0.67	—	0.36	0.24–0.35

the band produced under U.V. and these were not always reproducible. The temperature variation of the intensity produced over a given length of time should give us conclusive evidence as to the validity of our hypothesis concerning this phase of darkening.

IV. CHEMICAL CONSIDERATIONS

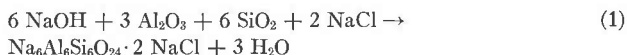
Table 1 is a summary of the available information on the chemical composition of hackmanite and sodalite. From a comparison of the various analyses we made the following tentative conclusion:

- (a) The amount of SiO₂ in hackmanite is less than that in sodalite by $\cong 1\%$.
- (b) The data on manganese is conflicting.
- (c) The data on sulfur is conflicting.
- (d) There is less water in hackmanite than in sodalite.

Since manganese and sulfur are important elements in phosphor synthesis, we were particularly interested in the dependence of the tenebrescent properties of hackmanite on the relative amounts of these elements.

Dana (2) claims that hackmanite is sodalite containing 6.23% of Na₂S, i.e., it is a mixture of sodalite and lapis-lazuli (lazulite). He does not give the source of his information but since he lists the Kola Peninsula (USSR) as the site of occurrence, we concluded that his information came from the paper by Borgström (1). However, no S⁼ or SO₃⁼ was found in the hackmanite specimens we investigated. These were from Bancroft, Ontario. (We have prepared a synthetic material whose properties resemble those of hackmanite and which is essentially pure sodalite which has been heated in a reducing atmosphere with no sulfur present—see below.)

The synthesis of sodalite was carried out using the work of the BPI group as its basis (23). Where the BPI group used Na₂CO₃ we used NaOH i.e.

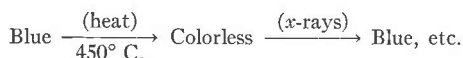


A stoichiometric mixture of Al₂O₃, SiO₂, NaOH and NaCl according to eq. 1 was thoroughly mixed in a porcelain mortar and subsequently ball-milled. The resulting powder was tightly packed into a covered platinum crucible, immersed in a sand bath and placed into the cold oven. The temperature was then slowly raised to 1060° C. where it remained for a 24–72 hour period. Crystal growth at this temperature occurs pyrolytically, i.e., we are below the melting point of sodalite (which is about 1100°) and the formation of sodalite occurs through the medium of solid state reactions. If the temperature was permitted to exceed 1060° C. by any appreciable amount, sodalite was not formed. Instead, an opaque glass was obtained giving a diffuse diffraction pattern and a tan coloration under *x*-rays. The formation of this glass may be considered as analogous to the transformation of a nepheline melt into carnegieite if appropriate mineralizers are not present (24). Crystallization from the melt was therefore not accomplished. Attempts to grow larger crystals by means of mineralizers (LiF, NaWO₄, etc.) were not successful. Powder patterns identified the product as pure sodalite. This sodalite darkened under *x*-rays to give the characteristic magenta coloration. Measurements showed that the induced absorption band peaked at 5300 Å. This con-

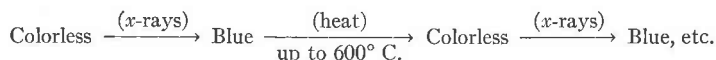
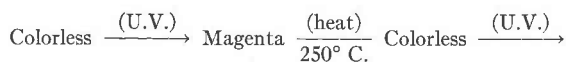
stituted a strong verification of the color center hypothesis, since the traps responsible for the F-band in hackmanite are proven to be unique to the sodalite lattice. They cannot owe their origin to the presence of extraneous impurities since this coloration was induced in pure sodalite. The x -rays provided sufficiently energetic photons (ΔE) so that the excited electrons could bridge the forbidden gap between the conduction band and the filled band (see Fig. 1*a*).

In connection with the absorption bands produced by x -rays in the sodalite-hackmanite system some interesting facts came to light concerning the natural minerals. The following sequence of events was observed.

For Natural Sodalite



For Natural Hackmanite



The color changes of blue sodalite to colorless and of hackmanite irreversibly bleached by heat were accompanied by weight losses. Hackmanite and sodalite samples were weighed before and after heat treatment. The results are shown in Table 2.

TABLE 2

<i>Hackmanite</i>			<i>Sodalite</i>		
Temp. ° C.	% Wt. Loss	Loss of U. V. Sen.	Temp.	% Wt. Loss	Loss of Color
1000	1.26	yes	600° C.	1.37	yes
800	0.72	yes	500° C.	1.42	yes
500	0.35	yes	550° C.	1.28	yes
200	0.056	no			

During these experiments it was found that the surface of hackmanite changes in appearance from a crystalline translucent material to chalk white. Part, but not all of the loss, was shown to be water. It is of interest to note that:

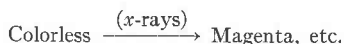
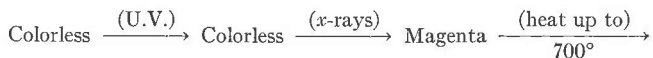
1. The heat treatment serves to shift the position of the F-band to longer wavelengths

in addition to driving off the activating impurities in hackmanite which give rise to the U-levels.

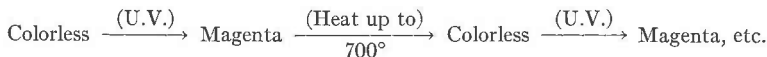
2. Sodalite which is heated above 450° C. and not exposed to radiation such as x -rays is colorless. It might prove fruitful to investigate specimens of colorless and blue sodalite as found in the natural state and to correlate this difference in terms of temperature histories.

The temperature scheme for the artificial substances is as follows:

For Synthetic Sodalite



For Synthetic "Hackmanite"



The irreversible loss in sensitivity to U.V. of natural hackmanite and the concomitant loss in mass upon heating may be due to a loss of the activating compounds which produce the U.V. sensitive centers. The shift in the F-band of natural hackmanite under heating and the discrepancies between the behavior of the natural sodalite-hackmanite system and the artificial sodalite-hackmanite system indicate that we have not duplicated the natural substances exactly.

We found that the substitution or addition of the following elements in varying amounts did not introduce the necessary U-levels into pure sodalite.

Sm, Cu, Ti, Ni, Mg, Ca, Cd, Mn, Pb,
Sn, Mo, Zn, Y, Cs, Ce, Ba, Ge, La,
Sr, Ag, Bi, Hg, Co, S

Firing the pure sodalite in atmospheres of nitrogen, air, oxygen, steam, and CO₂ also gave no additional levels although darkening was still possible with x -rays.

However, if the sodalite were fired in a reducing atmosphere of hydrogen or in a carbon crucible with limited access to the atmosphere, the specimens became strongly sensitized to 2537 Å U.V., i.e., the required U-levels appeared. However, although natural hackmanite shows a fair response to 3600 Å U.V., the synthetic form had only weak sensitivity at this wavelength. The characteristic salmon-orange fluorescence was also observed although somewhat weaker than in the natural substance.

It seems very tempting to identify these U-levels and the corresponding absorption band, with the U-bands observed by Hilsch and Pohl in

KBr which has had some of the Br^- lattice sites replaced by H^- (25). The electronic transition can be considered as one in which an electron is raised from the H^- into a state extending over the neighboring metal ions. This condition is similar to the excited state of a halogen ion in the pure crystal which gives rise to the intrinsic absorption band. However, the formation of the F-band is not clearly understood. Mott and Gurney (26) believe it forms when the excited electron leaves a hydrogen atom behind which diffuses away at room temperature. The electron then falls back into the vacated lattice site and forms an F-center. However, this theory when applied to hackmanite has its shortcomings.

In our investigations, we have implicitly assumed that the basic $(\text{NaAlSiO}_4)_6$ lattice of sodalite is relatively stable and optically inert. Thus, it is in the $\cdot 2\text{NaCl}$ part that we seek our explanations. If Cl^- is replaced by H^- then $\text{NaCl} = > \text{NaH}$ is analogous to $\text{KBr} = > \text{KH}$. However, the present theory of U-center transformation to F-centers is unsatisfactory if we consider the activating reaction as being $\cdot \text{NaCl} \rightarrow \cdot \text{NaC}$, when we consider the more immobile carbon atom.

We have used the band theory of color centers to help elucidate the peculiar properties of hackmanite. On the other hand, further investigations of the hackmanite-sodalite materials may prove of importance in our basic ideas of color centers.

V. SUMMARY

The unique optical properties of hackmanite have been explained in a phenomenological manner, utilizing the present role of color centers in the band theory of solids. We have found that pure bleached sodalite will darken to a magenta coloration only under x -rays. The darkening is considered to take place in two stages, (1) Electrons are promoted from the filled band to the conduction band by the highly energetic x -ray photons, and (2) These conduction band electrons are trapped at negative ion vacancies (in this case considered to be Cl^-) forming F-centers. Absorption measurements give 2.34 electron volts as the F-level depth. When exposed to visible light, the specimen appears colored since quanta corresponding to this energy are being absorbed. The process is analogous to writing with a pencil on a sheet of white paper; light is absorbed at the graphite trace. The color is observed to fade under a bright light since the F-centers are eventually emptied. This represents erasure or bleaching.

Hackmanite darkens to the same magenta coloration, but only long wavelength ultra-violet is needed. Thus, some type of electron donor levels arising from a substitutional or interstitial impurity in sodalite are needed. The existence of these donor levels lowers the energy required to

excite electrons into the conduction band. This is stage (1) which can be carried out with 2537 Å or 3600 Å quanta. Stage (2) proceeds as before and the specimen has thus been darkened with ultra-violet. The absorption maximum is also at 5300 ± 50 Å (about 2.34 e.v.).

In synthetic hackmanite which was prepared by heating sodalite in a reducing atmosphere, we can identify these donor levels as U-centers. A U-center is formed in KBr when a Br^- ion is replaced by a hydride ion, H^- . If the Mott-Gurney mechanism for the U-center to F-center transformation is correct, then the following hypothesis can be applied to formation-transformation of a generalized U-center.

(1) A U-center is formed whenever an ion is substituted for the normal lattice negative ion, the substituted ion having a considerably lower electron affinity than the lattice ion (cf. hydride or carbide ion with chloride ion electron affinity).

(2) The transformation to an F-center only occurs when the substituted ion (H^- or C^-) has a small ionic radius and a low mass number so that atomic diffusion through the lattice is facilitated.

ACKNOWLEDGMENT

I wish to thank Mr. W. E. Bradley for his continuing guidance and stimulation through every phase of this work. I am indebted to Mr. H. A. Affel, Jr., for his patience, forbearance, and help in his capacity as project engineer with a study whose electronic potentialities were not always evident, to Mr. R. E. Waggener for his fruitful discussions and suggestions, and to Miss Sally Kerr for her able technical assistance.

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Manuscript received May 5, 1953.