

## Magnetic and Crystalline Behavior of Certain Oxide Systems with Spinel and Perovskite Structures

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A series of substitutions have been performed on nickel ferrite where the  $\text{Fe}^{3+}$  is replaced, by varying amounts, with  $\text{In}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{La}^{3+}$ .  $\text{In}^{3+}$  went into solid solution with the nickel ferrite to form a spinel structure whose lattice constant  $a_0$  increased linearly with increasing amounts of  $\text{In}^{3+}$  to a maximum value of 8.708 Å for 1.5  $\text{In}^{3+}$  ions per molecule. At greater concentration of  $\text{In}^{3+}$ , the starting materials appeared as a mixed phase with  $\text{NiO} \cdot \text{Fe}_{0.5}\text{In}_{1.5}\text{O}_3$ . The saturation magnetization ( $\mu_0$ ), obtained by extrapolation to absolute zero, increased with increasing amounts of  $\text{In}^{3+}$ , in a manner indicating that the  $\text{In}^{3+}$  ions preferred the A sites. In the case of  $\text{Sc}^{3+}$ , an increased cell size was found which "leveled off" at  $a_0=8.41$  Å for 0.75

$\text{Sc}^{3+}$  ions per molecule.  $\mu_0$  decreased with increasing  $\text{Sc}^{3+}$  content and approached a compensation point similar to that found previously for the  $\text{Al}^{3+}$  substitution. It is concluded that trivalent metal ions having a rare gas electronic structure, by showing a preference for the B sites, give rise to compensation points and the Néel  $P$ -type curves. The Curie temperatures for the substitution of  $\text{In}^{3+}$  and  $\text{Sc}^{3+}$  show a nearly linear decrease with concentration but with slopes greater and less, respectively, than the slope of the single curve found previously to represent both the  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  substitutions. The  $\text{Y}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{La}^{3+}$  substitutions resulted in a mixed solution of nickel ferrite and corresponding perovskite structures formed with  $\text{Fe}^{3+}$ .

### I. INTRODUCTION

WHEN trivalent aluminum is substituted in nickel ferrite, the  $\text{Al}^{3+}$  ions move into the B sites in such a manner as to produce a compensation point<sup>1,2</sup> at a composition of approximately 0.7 of an aluminum ion per molecule; the Néel  $P$ -type curve [Fig. 5(a) of reference 1, curve for  $t=0.63$ ] occurs when the concentration of  $\text{Al}^{3+}$  is slightly less than 0.7. In the case of the nickel ferrite-gallates, no compensation point was found;<sup>1</sup> the preference of  $\text{Ga}^{3+}$  for the A sites results in a maximum in the saturation magnetization near the compensation point found for the nickel ferrite-aluminates. Maxwell and Pickart<sup>1</sup> found that the nickel ferrite-aluminates and nickel ferrite-gallates have a common Curie temperature, for equal numbers of nonmagnetic ions per molecule, that decreases nearly linearly with increasing amounts of the nonmagnetic ion.

The present paper will report on a continuation of the above type of substitution experiments to ions having greater ionic radii.

### II. EXPERIMENTAL RESULTS AND DISCUSSION

The method used for the preparation of the materials and the measurement of their magnetic properties has been described previously.<sup>1</sup> All of the materials were slow-cooled from approximately 1400°C at an average rate of 1° per minute.

#### A. Nickel Ferrite-Indates $(\text{NiO} \cdot \text{Fe}_{2-t}\text{In}_t\text{O}_3)$

##### 1. Crystal Structure

Powder x-ray diffraction examination showed that  $\text{In}_2\text{O}_3$  went into solid solution with NiO to form a

homogeneous spinel whose length of edge of unit cell ( $a_0$ ) increased linearly with  $t$  up to  $t=1.5$ , as illustrated by Fig. 1. Chemical analysis made of the material formed for the substitution at  $t=1.5$  showed that  $\text{Ni}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{O}^{2-}$  were present in the proper amounts to give the spinel  $\text{NiO} \cdot \text{Fe}_{0.5}\text{In}_{1.5}\text{O}_3$ . For values of  $t$  between 1.5 and 1.875,  $a_0$  remained constant at a value of 8.71 Å; within this region there appeared diffraction lines from NiO and  $\text{In}_2\text{O}_3$ , which showed that there existed a mixture of  $\text{NiO} \cdot \text{Fe}_{0.5}\text{In}_{1.5}\text{O}_3$  and the starting materials. At  $t=2.0$ , we found diffraction patterns from only NiO and  $\text{In}_2\text{O}_3$  even when the sample was quenched after prolonged heating.

##### 2. Magnetic Properties

The variation of saturation magnetization ( $\mu$ ) normalized with respect to the saturation magnetization at absolute zero ( $\mu_0$ )—obtained by extrapolation—is shown as a function of the normalized temperature in Fig. 2(a) for values of  $t$  from 0 to 1.0. The curves are similar to those found for the gallium substitution<sup>1</sup> and appear to be characteristic of the magnetic behavior of those trivalent ions that prefer the four coordination positions. The  $\mu$  vs temperature relationship for  $t=1.5$  did not show a constant slope over a

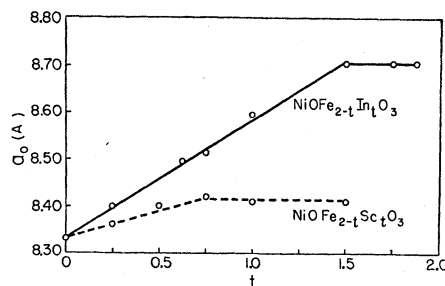


FIG. 1. Variation of unit cell size ( $a_0$ ) with composition for nickel ferrite-indates and nickel ferrite-scandates.

<sup>1</sup> L. R. Maxwell and S. J. Pickart, Phys. Rev. **92**, 1120 (1953).

<sup>2</sup> E. W. Gorter, Ph.D. Thesis, University of Leyden, 9 June 1954 (to appear in Phillips Research Reports).

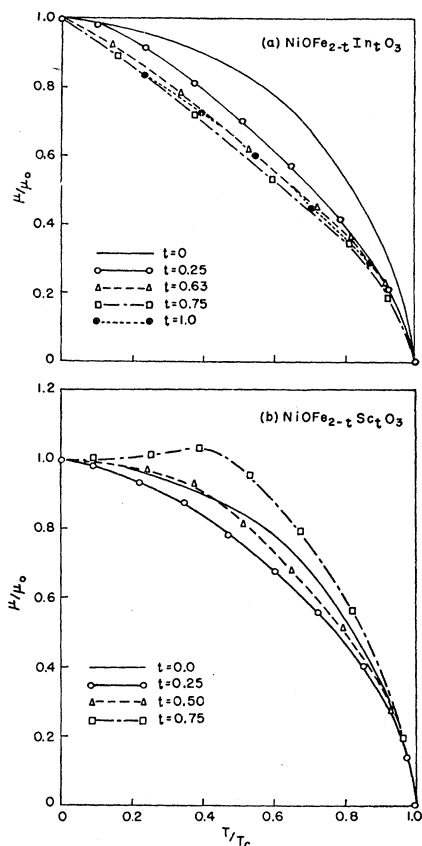


FIG. 2. Normalized thermomagnetization curves for (a) nickel ferrite-indates and (b) nickel ferrite-scandates.

sufficient range to warrant the development of a normalized curve.

$\mu_0$  was found to increase with  $t$  starting at  $t=0$  (Fig. 3) with an initial slope calculated for all of the  $\text{In}^{3+}$  ions going preferentially into the  $A$  sites, an action that is expected in view of the fact<sup>3</sup> that  $\text{In}^{3+}$  is known to prefer the  $A$  sites. The departure of  $\mu_0$  from this linear increase, which results in a maximum occurring at about  $t=0.5$ , is attributed to a certain fraction of the  $\text{In}^{3+}$  ions going into the  $B$  sites or to the predominance of the negative  $B$ - $B$  interaction.

The  $\text{In}^{3+}$  substitution in this respect is similar to the  $\text{Ga}^{3+}$  substitution;<sup>1</sup> since these ions have filled  $4d$  and  $3d$  shells, respectively, there is apparently a correlation between this magnetic behavior and the electronic configuration.

The Curie temperature decreased nearly linearly with increasing indium content (Fig. 4) and at a greater negative slope than that found for the aluminum and gallium substitutions,<sup>1</sup> which are represented by a common curve.

<sup>3</sup> E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.* **15**, 174 (1947).

## B. Nickel Ferrite-Scandates ( $\text{NiO} \cdot \text{Fe}_{2-t}\text{Sc}_t\text{O}_3$ )

### 1. Crystal Structure

In the case of the scandates, the initial increase of  $a_0$  (Fig. 1) was less than that observed for the indates yet it flattened off earlier, at  $t=0.75$ , where  $a_0=8.41\text{\AA}$ . For values of  $t$  greater than 0.75, the diffraction lines of the starting oxides begin to appear, and for  $t=2.0$  we find only lines from  $\text{NiO}$  and  $\text{Sc}_2\text{O}_3$  that again persisted when the material was quenched after prolonged heating.

### 2. Magnetic Properties

The thermomagnetic properties of the scandates are shown in the normalized form in Fig. 2(b). For  $t=0.75$ , we find an increase in the normalized magnetization similar to the  $P$ -type curve predicted by Néel<sup>4</sup> and similar to the one observed<sup>1,2</sup> for the aluminum substitution at a value ( $t=0.63$ ) slightly less than that corresponding to the compensation point.

$\mu_0$  decreased with increasing  $t$  (Fig. 3) with an initial negative slope indicating that all of the  $\text{Sc}^{3+}$  is going preferentially to the  $B$  sites. The decrease in  $\mu_0$  continues at a lesser rate but approaches a compensation point in a manner similar to that<sup>1,2</sup> for the substitution of  $\text{Al}^{3+}$ . However, the crossover is not reached because, for values of  $t$  greater than 0.75, the spinels would not form under conditions of preparation used.

It becomes apparent from both the scandium and aluminum substitutions that there is a definite correlation between the Néel  $P$ -type curves and the existence of a compensation point. In both instances, the  $P$ -type curves appeared for a  $t$  value slightly less than that which corresponds to the compensation point. The

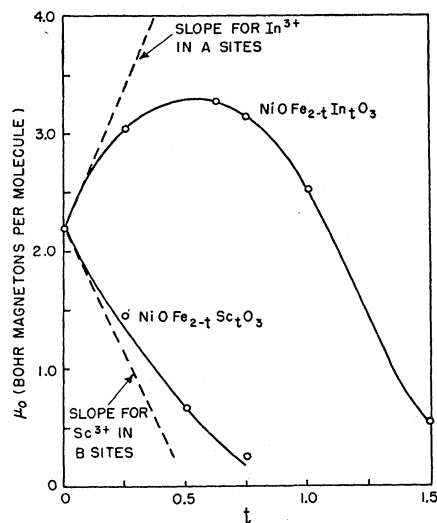


FIG. 3. Variation of  $\mu_0$  with composition for nickel ferrite-indates and nickel ferrite-scandates.

<sup>4</sup> L. Néel, *Ann. phys.* **3**, 137 (1948).

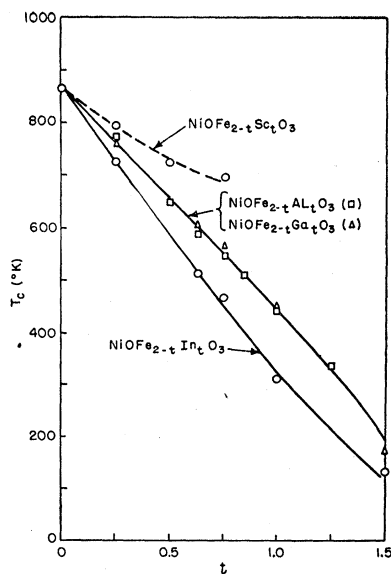


FIG. 4. Variation of Curie temperature ( $T_c$ ) with composition for nickel ferrite-indates and nickel ferrite-scandates, including previous data (see reference 1) for nickel ferrite-aluminates and gallates.

fact that the  $P$ -type curve should occur in the vicinity of the compensation point has been explained by Gorter<sup>2</sup> by the Néel theory as formulated for one type of magnetic ion ( $\text{Fe}^{3+}$ ).

It was found that the Curie temperature decreased with  $t$  (Fig. 4) at a slower rate than for all of the previous substitutions.

### C. Nickel Ferrite-Yttrates (Spinel-Perovskite Phases)

#### 1. Crystal Structure

Another type of reaction appeared when an attempt was made to replace trivalent iron by  $\text{Y}^{3+}$ . As  $\text{Y}^{3+}$  was added, it combined with an equal amount of  $\text{Fe}^{3+}$  to form  $(\text{YFe})\text{O}_3$ ,<sup>5</sup> which has a distorted perovskite structure classified by Keith and Roy as the  $(\text{YCr})\text{O}_3$  structure. At  $t=0.25$  there appears the prominent perovskite reflection at a spacing of 2.69Å. For increasing values of  $t$ , this reflection increases in intensity and NiO appears. At  $t=1.0$ , all of the iron has combined with all of the yttrium to yield the deformed perovskite structure; the reflections due to NiO are prominent, indicating that it exists as a separate phase. When more yttrium is added, the excess  $\text{Y}_2\text{O}_3$  begins to show and at  $t=2.0$ , we end up with only the starting materials, i.e., NiO and  $\text{Y}_2\text{O}_3$ .

#### 2. Magnetic Properties

The thermomagnetic data indicate that the only magnetic phase present is the nickel ferrite. This can be seen from Fig. 5(a) where we plot the intensity of

<sup>5</sup> M. L. Keith and R. Roy, *Am. Mineralogist* **39**, 1 (1954).

magnetization ( $I$ ) per gram as a function of temperature. There is a continuous decrease in  $I$  with increasing  $t$  roughly proportional to the amount of nickel ferrite remaining as a separate phase, in a manner expected on the basis of the x-ray diffraction results. Furthermore, all of the curves give approximately the same Curie temperature (about 600°C).

At  $t=1.0$ , we find [Fig. 5(a)] essentially a paramagnetic material,  $(\text{YFe})\text{O}_3$ , whose susceptibility is decreasing gradually with increasing temperature without a break at the Curie temperature for nickel ferrite.

### D. Nickel Ferrite-Gadolinates (Spinel-Perovskite Phases)

#### 1. Crystal Structure

Substitution of trivalent gadolinium through  $t=1.0$  showed that, as in the case of the substitution of  $\text{Y}^{3+}$ , the  $\text{Gd}^{3+}$  prefers to combine with  $\text{Fe}^{3+}$  to form a distorted perovskite structure whose lattice parameter  $a^*$  is 3.45Å. The diffraction pattern of NiO appeared with increasing intensity as  $t$  increased while the intensity of the lines due to the nickel ferrite decreased correspondingly.

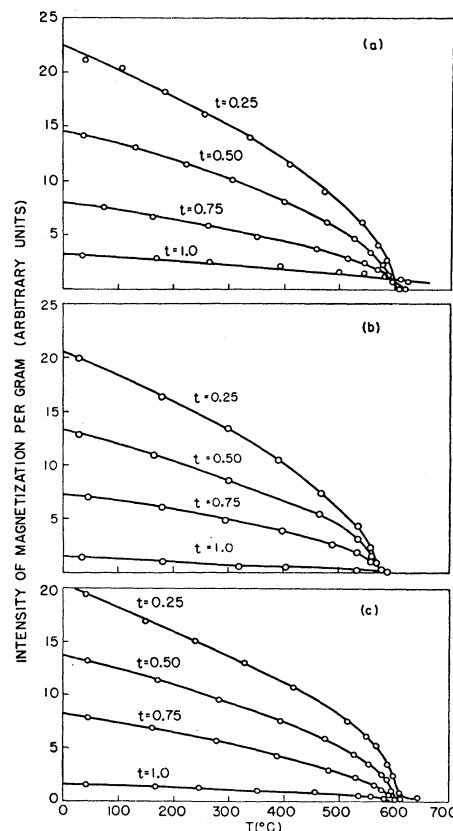


FIG. 5. Thermomagnetization curves for (a) nickel ferrite-tytrates, (b) nickel ferrite-gadolinates and (c) nickel ferrite-lanthanates.

## 2. Magnetic Properties

The thermomagnetic data [Fig. 5(b)] show a variation of the intensity of magnetization with temperature characteristic of nickel ferrite. There is a continual decrease of  $I$  with increasing  $t$  roughly proportional to the amount of nickel ferrite present.

At  $t=1.0$ , where we have only  $(\text{GdFe})\text{O}_3$  and  $\text{NiO}$ , the combined material has only a trace of a paramagnetic response.

## E. Nickel Ferrite-Lanthanates (Spinel-Perovskite Phases)

### 1. Crystal Structure

For the lanthanum substitution, the phase relationships follow a behavior (Fig. 6) similar in part to that observed for the yttrium substitution; for values of  $t$  up to and including  $t=1.0$  the  $\text{La}^{3+}$  combines with  $\text{Fe}^{3+}$  to form a very nearly cubic perovskite structure.<sup>5</sup> At  $t=1.5$ , there appears to be a shift in the reflections of the perovskite structure to slightly smaller Bragg spacings with the appearance of a new phase. At  $t=2.0$ , the former perovskite structure is gone—since there is no more iron present—and an apparently homogeneous system exists through a combination of  $\text{NiO}$  and  $\text{La}_2\text{O}_3$  (Table I).

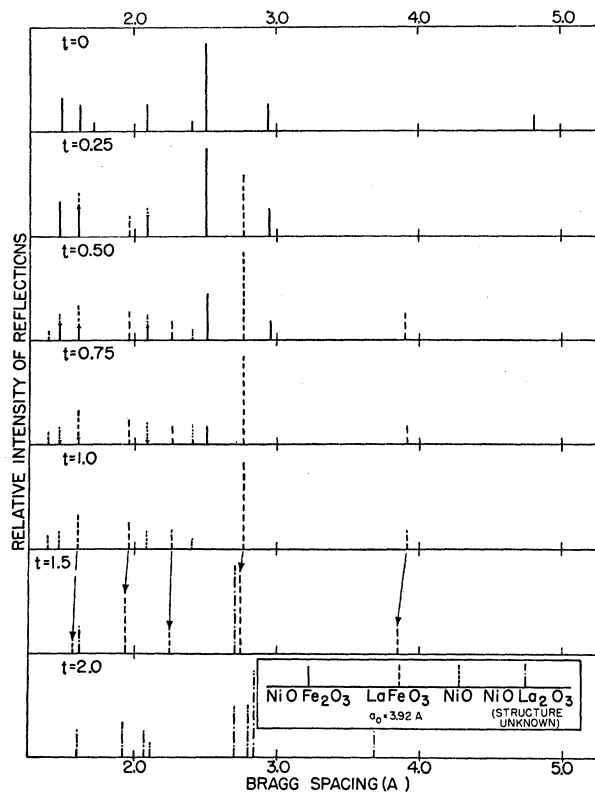


FIG. 6. Relative intensities of x-ray diffraction patterns of the system  $\text{NiO} \cdot \text{Fe}_{2-t}\text{La}_t\text{O}_3$  for various values of  $t$ .

## 2. Magnetic Properties

The thermomagnetic behavior of the lanthanate series is almost identical to that found for the yttrium and gadolinium substitutions as illustrated in Fig. 5(c). Similarly, we find only the presence of nickel ferrite since the Curie temperatures all equal the value for nickel ferrite. The intensity of magnetization also decreases with increasing  $t$  in a way that indicates simply a dilution of the magnetic constituent. At  $t=1.0$ , we have a mixture of  $\text{NiO}$  and  $(\text{LaFe})\text{O}_3$  whose intensity of magnetization is considerably less than that found for  $(\text{YFe})\text{O}_3$ .

## F. Spinel-Perovskite Phase Relationships

When the nonmagnetic ion has a radius greater than  $0.92\text{Å}$  ( $\text{In}^{3+}$ ), it has a greater tendency to combine with the trivalent iron ion to form the perovskite structure than to make a spinel. This action is in agreement with the following relationship<sup>6</sup> required for the formation of the perovskite structure:

$$r_A + r_O = \tau\sqrt{2}(r_B + r_O),$$

where  $r_A$ ,  $r_B$ , and  $r_O$  are the ionic radii for the two metallic ions in order of decreasing radii and the radius of the oxygen ion, respectively.  $\tau$  is a parameter that varies between approximately 0.8 and 1.0 and permits a certain amount of deformation of the cubic structure. In the present case,  $\tau=0.85$ ,  $0.86$  and  $0.90$  for  $(\text{YFe})\text{O}_3$ ,  $(\text{GdFe})\text{O}_3$ , and  $(\text{LaFe})\text{O}_3$ , respectively.

## III. CONCLUSIONS

The behavior of nonmagnetic trivalent ions as replacements for  $\text{Fe}^{3+}$  in nickel ferrite can be adequately described as follows:

a. Those ions whose radii are less than  $ca$   $0.9\text{Å}$ , (except  $\text{B}^{3+}$ ), form a homogeneous spinel, with certain limitations upon the maximum number of ions that can be substituted per molecule.

b. Trivalent ions having radii greater than  $ca$   $0.9\text{Å}$  combine with  $\text{Fe}^{3+}$  to form a perovskite structure existing as a separate phase. The ferrimagnetic properties in these instances are those of the remaining nickel ferrite.

TABLE I. X-ray diffraction pattern of  $\text{NiOLa}_2\text{O}_3$ .

Bragg spacing $d$ (Å)	Relative intensity
3.68	40
2.85	100
2.81	50
2.73	90
2.11	20
2.07	20
1.93	20
1.60	30

<sup>6</sup> A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1950), p. 376.

c. When the electronic configuration has the rare gas structure a ferrimagnetic compensation point is either reached or closely approximated, and the Néel  $P$ -type curves occur for a concentration of the trivalent ion slightly less than that required for the compensation point.

d. Those ions with filled  $d$  shells yield a maximum  $\mu_0$  greater than that for nickel ferrite and show no  $P$ -type curves.

e. The Curie temperatures vary with the number of

nonmagnetic trivalent ions per molecule in a manner that bears no simple relationship with the distance between magnetic ions.

#### IV. ACKNOWLEDGMENTS

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### Color Centers in Chrome Alum Crystals

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Color centers have been observed in chrome alum crystals following their irradiation by x-rays. The absorption band thus produced has an apparent peak at  $228\text{ m}\mu$ , and its intensity increases with the time of irradiation, tending to saturation. The color band decays spontaneously with time, the half-life time at room temperature being several weeks. The band can be bleached by exposure to light of any wavelength within the band ( $215$  to  $400\text{ m}\mu$ ). The crystals do not exhibit photoconductivity either before or after x-ray irradiation.

#### INTRODUCTION

COLOR centers have been extensively studied in alkali halides.<sup>1</sup> Recently they have been reported to exist in several other simple crystals, such as fluor-spar,<sup>2</sup> ammonium halides,<sup>3</sup> and quartz.<sup>4</sup>

In this paper, results are described which indicate that color centers can be produced in potassium chrome alum single crystals [ $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ].

The general chemical formula of the alums is  $M^+M^{3+} \times (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , where  $M^+$  is any alkali metal ion or a radical like  $\text{NH}_4^+$ ;  $M^{3+}$  is a trivalent cation such as  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , or  $\text{V}^{3+}$ . The chemical bonds in the alums are of a mixed nature, some being ionic while others are covalent. The water molecules serve as packing water.<sup>5</sup>

The alum crystals belong to the cubic system and are usually easily crystallized from aqueous solution in the form of octahedra. The common alums melt at low temperatures (usually below  $100^\circ\text{C}$ ) and decompose easily at even lower temperatures by losing part of their water. It should be mentioned that alum crystals

are of special interest in low-temperature technique, where use is made of their adiabatic demagnetization.<sup>6</sup>

#### OPTICAL INVESTIGATION

##### Experimental Procedure

The potassium chrome alum crystals used were "Baker's chemical pure" or "Baker's analyzed;" some specimens have been additionally recrystallized from aqueous solution. As the crystals exhibit poor cleavage, the specimens measured were ground with fine carborundum suspended in alcohol. In this way, flat pieces down to  $0.4\text{ mm}$  thick were obtained. The absorption spectra were measured with a Beckman D.U. quartz spectrophotometer in the range from  $210\text{ m}\mu$  to  $1200\text{ m}\mu$ . The x-ray irradiation was carried out on a crystallographic x-ray set ( $45\text{ kv}$ ,  $15\text{ ma}$ ) with copper target and beryllium window.

#### Results

Figure 1 shows the absorption spectrum of a typical potassium chrome alum crystal. The bands at  $410$  and  $560\text{ m}\mu$  and the absorption edge at  $215\text{ m}\mu$  appear in approximately the same positions in the spectrum of the aqueous solution (not shown); only the band at  $260\text{ m}\mu$  is characteristic of the crystal.

The absorption spectra of a chrome alum crystal after various times of exposure to filtered x-rays

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<sup>1</sup> See for example F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954); N. F. Mott and R. W. Gurney, *Electronic Processes In Ionic Crystals* (Clarendon Press, Oxford, 1950), second edition.

<sup>2</sup> F. Lüty, *Z. Physik* **134**, 596 (1953); A. Smakula, *Phys. Rev.* **91**, 1570 (1953).

<sup>3</sup> H. Röchardt, *Z. Physik* **134**, 554 (1953).

<sup>4</sup> E. W. J. Mitchell and E. G. S. Paige, *Proc. Phys. Soc. (London)* **67**, 262 (1954).

<sup>5</sup> F. Ephraim, *Inorganic Chemistry* (Gurney and Jackson, London, 1943), fourth English edition.

<sup>6</sup> C. Kittel, *Introduction To Solid State Physics* (John Wiley and Sons, Inc., New York, 1953).