

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 μ_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.¹ Recently they have been reported to exist in several other simple crystals, such as fluor-spar,² ammonium halides,³ and quartz.⁴

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 NH_4^+ ; M^{3+} is a trivalent cation such as Cr^{3+} , Fe^{3+} , Co^{3+} , or 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.⁵

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°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.⁶

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 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 kv, 15 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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¹ 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.

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

³ H. Rüchardt, *Z. Physik* **134**, 554 (1953).

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

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

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

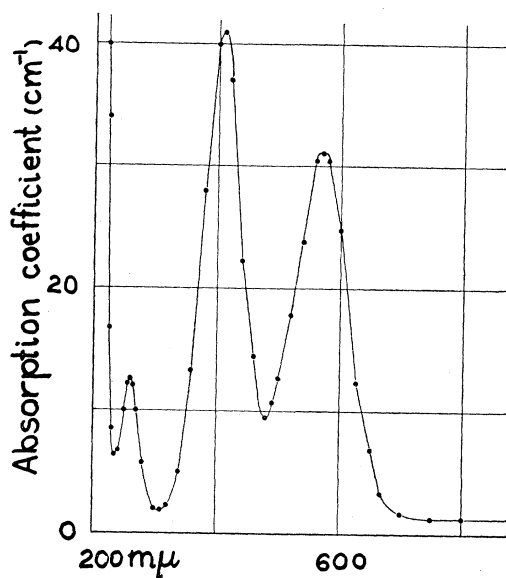


FIG. 1. Absorption spectrum of a potassium chrome alum crystal.

($\text{CuK}\alpha$) are given in Fig. 2. The changes in ultraviolet absorption are produced by the introduction of color centers. This may be more clearly seen by plotting the difference of absorption before and after x-ray irradiation against wavelength (Fig. 3). It should be noted that this band is rather wide. The apparent peak at $228 \text{ m}\mu$ may be erroneous, as it falls near the U.V. limit of sensitivity of the Beckman spectrophotometer.

The growth of the color band with x-ray irradiation ($\text{CuK}\alpha$) is shown in Fig. 4, where the increase of optical density is plotted against time of irradiation for three wavelengths inside the color band. (With "white" x-rays this buildup proceeds much more rapidly.) It will be observed that the curves tend to saturation values, indicating an upper limit to the number of color centers attainable by the method employed.

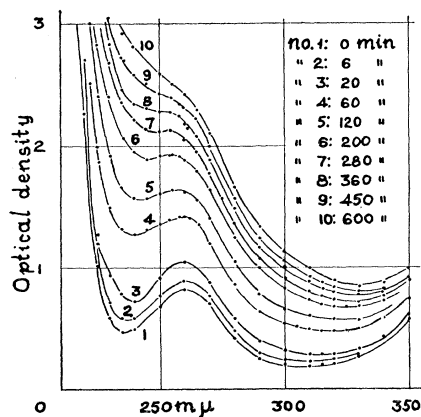


FIG. 2. Absorption spectra of a chrome alum crystal after various times of x-ray irradiation ($\text{CuK}\alpha$).

The apparently discontinuous drops in the curves of Fig. 4 are caused by the spontaneous decay of the color band during the interruptions of a few days between two successive x-ray irradiations. When the irradiated crystal is left at room temperature, the color band decays slowly with time, the half-life being of the order of a few weeks. At liquid air temperature no such decay occurs, which shows it to be of thermal origin. In Fig. 5, the color band absorption is plotted against time on a log-log scale for various wavelengths within the band. No reasonable decay law could be deduced from these experimental values.

The color band can be bleached by exposing the colored crystal to ultraviolet light. The bleaching was carried out both with filtered and unfiltered light and it was found that it may be obtained by light of any wavelength within the color band.

The ultraviolet light source was a 250-watt Hanovia high-pressure mercury arc lamp focused on the crystal

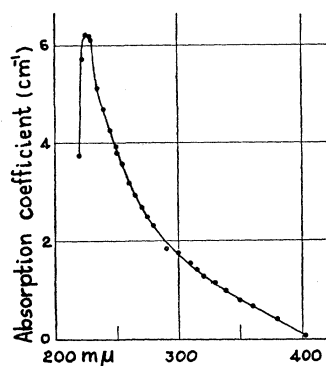


FIG. 3. Color band in chrome alum as obtained from the difference of absorption before and after x-ray irradiation.

from a distance of about 20 cm. Under these conditions, 45 minutes of irradiation with $360 \text{ m}\mu$ light reduced the intensity of the color band by about 10 percent. The whole band is bleached at approximately the same rate and no new absorption bands appear after bleaching.

PHOTOCONDUCTIVITY

The crystals were prepared for electrical measurements in the same manner as above. The usual method of evaporating contacts on the crystal for conduction measurements could not be employed, as the crystals are unstable in vacuum, and lose their waters of crystallization, and crumble to powder. Therefore, two thin metal strips were pasted on the crystal ends with conducting paint.

The conductivity was measured by a bridge method in which the null indicator employed a low grid-current electrometer tube.

The resistivity of the potassium chrome alum crystals thus obtained was of the order of $5 \times 10^{10} \text{ ohm-cm}$, but decreased with the time of application of the voltage, although the latter did not exceed 100 v.

No photoconductivity was observed either before or after x-ray irradiation. The sensitivity of the measurement was such as to allow the detection of a change in resistivity of less than 1 percent.

DISCUSSION

It is very difficult to reach any definite conclusion about the nature of the color centers described. First, alum crystals are much more complex than those treated hitherto, and, secondly, the experimental material is in sufficient. However, our results may be summed up and from this a few tentative suggestions may be given.

(a) In addition to the chrome alum crystals, the other alums at our disposal [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] were examined. The first two show no color centers, while the third is too unstable to give definite results.

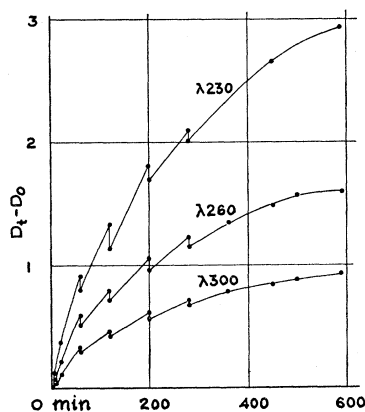


FIG. 4. Growth of color center absorption with time of x-ray irradiation, for three wavelengths within the band.

(b) The number of color centers obtainable by x-ray irradiation seems to have an upper limit (Fig. 4).

(c) The bleaching efficiency is low, and no photoconductivity was observed although the color band absorption is fairly high and comparable to that in the alkali halides.

(d) The color band has the same form and position in all the samples of chrome alum studied, although they come from different batches of material.

Impurities may play a role in the production of the color centers. This is unlikely in view of point (d) but not impossible, as all the batches examined may contain

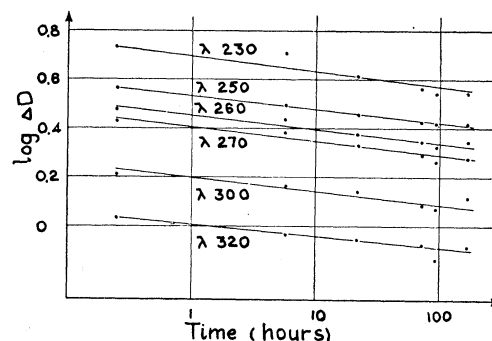


FIG. 5. Thermal decay of color centers at room temperature.

certain impurities which are unaffected by the standard purification procedures.

Another possibility is that the chrome ion is directly or indirectly involved in producing the centers. This follows from the fact that only the alum containing chrome ions showed color centers [point (a)]. In analogy with alkali halides, one can assume that the coloring can arise from ion vacancies, and only in the chrome containing alum are conditions correct for color centers to be stable enough to be observed at room temperature. Alternatively, one can assume that the chrome ion is more directly involved in the coloring through such a mechanism as the following: The x rays free an electron from the valence band and this becomes captured at a Cr^{3+} ion, thus changing it into a Cr^{2+} ion. The color absorption band would then correspond to transitions characteristic of Cr^{2+} . This assumption is supported by the fact that in the emission spectrum of Cr III many strong lines exist in the wavelength region of the color band. From the saturation of the coloring [point (b)] it follows that not all the chrome ions are able to become centers, but only a small proportion of them. This may be due to interaction among them as suggested by Rüchardt for ammonium halides,³ or due to impurities or vacancies playing a role.

A possible explanation of point (c) is that by the absorption of light quanta, the electrons in the centers are raised to an excited level, and from there most of them return to the ground level; only a small fraction of them reach the conduction band and subsequently drop to the valence band.

It is hoped that more definite conclusions will be reached by extending the measurements to low temperatures and by studying other alums, especially those containing chrome and other transition metals.