

Symmetry Properties of the  $V_1$  Center\*

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The symmetry of the  $V_1$  center was studied using a technique of bleaching with polarized light. The  $V_1$  band in KCl and KBr produced by x-rays and 2-Mev electron bombardment was examined. In addition, the effect of bleaching with polarized light on the phosphorescent emission of KCl was observed. It is concluded that the center responsible for the  $V_1$  absorption band in KCl and KBr has cubic symmetry insofar as its optical absorption is concerned. The phosphorescent emission of KCl became anisotropic under polarized bleaching light, indicating the presence of a center of noncubic symmetry. This second center has a [011] axis of symmetry.

## I. INTRODUCTION

RECENTLY spin resonance experiments have been carried out by Känzig<sup>1</sup> on alkali-halide crystals which had been x-rayed at liquid-nitrogen temperature. At this temperature he finds a paramagnetic resonance absorption spectra showing fine structure and which appears to be related to a center of noncubic symmetry which has an axis of symmetry along the [011] direction. If the crystal showing such resonance is warmed up from 77°K, the resonance center is thermally bleached. From this fact, and the known thermal-bleaching properties of the  $V_1$  center,<sup>2</sup> it was concluded that the paramagnetic center involved is the same center that gives rise to the  $V_1$  absorption band.

This result is of interest because it has been proposed<sup>3</sup> that the  $V_1$  center may be the antimorph of the  $F$  center; that is, a hole trapped at a positive-ion vacancy. Such a center should have cubic symmetry however, in contrast to the [011] symmetry which Känzig associates with the  $V_1$  center. Since thermal-bleaching properties are involved in Känzig's result, it is of interest to examine the symmetry of the  $V_1$  center using methods which do not involve this aspect. In the present work optical methods are used to study the symmetry of the  $V_1$  center.

This experiment utilizes a method similar to that used by Ueta<sup>4</sup> for the  $M$ -center symmetry studies. In this technique, one bleaches in the absorption band with polarized light. If the centers responsible for the absorption are anisotropic, preferential bleaching occurs along the direction of polarization of the bleaching light. The crystal then shows dichroic absorption and from this type of measurement symmetry features can be established.

In addition to the above type of measurement, it was found useful to observe the phosphorescent emission from crystals being studied. After KCl or KBr have

been x-rayed or bombarded with electrons at 77°K, a phosphorescence is observed. Such emission has been studied by Dutton and Maurer<sup>2</sup> in connection with thermal-glow curves. In the present work, the effect of bleaching with polarized light on this phosphorescence was examined.

## II. EXPERIMENTAL METHODS

Crystals of KCl and KBr were colored at 77°K by x-raying (45 kvp) or bombardment with 2-Mev electrons. The crystals were maintained at 77°K during the course of subsequent measurements.

Optical absorption measurements were made with a Beckman monochromator modified for work at 77°K. Glan-Thompson prisms were inserted between the crystal and detector such that the optical absorption could be studied as a function of the polarization of the light as seen in Fig. 1. A 1P21 photomultiplier was used to measure the transmitted light with the sample in and out of the light beam. Phosphorescence induced by x-rays or by 2-Mev electron bombardment was also observed with the photomultiplier through the same Glan-Thompson prisms. In this case, the exit shutter was closed on the monochromator. This phosphorescence persists for several hours after high-energy irradiation.

After the crystals had been irradiated, the optical absorption and the total phosphorescent emission was

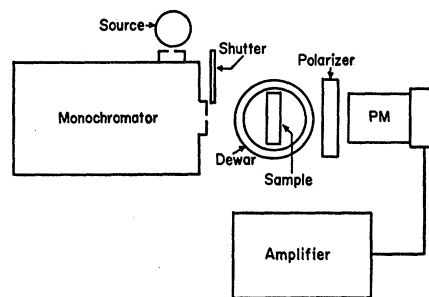


FIG. 1. Apparatus used to measure optical absorption as a function of polarization of absorbed light and to measure polarization of phosphorescent emission. The  $PM$  is a 1P21 photomultiplier. For phosphorescent emission measurements, the shutter is closed. The Dewar is of clear Pyrex.

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<sup>1</sup> W. Känzig, *Phys. Rev.* **99**, 1890 (1955).

<sup>2</sup> D. Dutton and R. J. Maurer, *Phys. Rev.* **90**, 126 (1953).

<sup>3</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

<sup>4</sup> M. Ueta, *J. Phys. Soc. Japan* **7**, 107 (1952).

measured as described above. The crystals were then bleached with polarized light in their respective  $V_1$  bands (Hg 3650 Å line used for KCl, 4360 Å line used for KBr), using an  $H-4$  mercury lamp with an appropriate filter. The mercury lamp for purposes of bleaching, was placed in the position of the photomultiplier. After bleaching, the photomultiplier was returned to position and measurements made.

### III. EXPERIMENTAL RESULTS

#### A. KCl and KBr X-Rayed at 77°K

These materials were x-rayed for about 4 hours. Subsequent bleaching with polarized light was carried out for periods of 5 minutes to an hour. Experiments were done with the bleaching light polarized along the  $[011]$  crystal direction and the  $[001]$  direction. Figure 2 shows a typical run for KCl. Results indicate that no dichroism was induced although substantial bleaching of the  $V_1$  band occurred. Similar results were obtained for KBr.

It must be established in bleaching experiments of this type that the bleaching occurs directly by the action of the light on the center under consideration and not by some indirect process. For example, when bleaching in the  $V_1$  band in KCl, it must be ascertained that the bleaching effect is not a result of ejecting electrons from  $F$  centers by absorption of light in the high-energy tail of the  $F$  band. Such electrons could annihilate  $V_1$  centers and no dichroism would be observed. To check this possibility, 4360 Å light of intensity equal to the 3650 Å light normally used, was used to bleach the  $V_1$  band in KCl. The rate of bleach

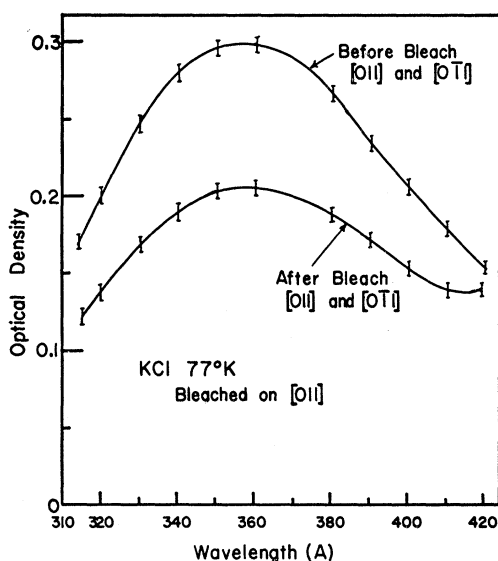


FIG. 2. The effect on the  $V_1$  absorption band of bleaching with polarized 3650 Å light. The  $V_1$  band is produced by exposure to x-rays at 77°K. The figure shows the absorption as measured with polarized light. The bleaching light was polarized parallel to the  $[011]$  crystal direction.

TABLE I. Effect of bleaching on phosphorescence and optical density in KCl. The crystals were bleached for about 2 minutes at 3650 Å.

	Before bleach		After bleach on $[011]$	
	$[011]$	$[0\bar{1}1]$	$[011]$	$[0\bar{1}1]$
Optical density at 3650 Å	0.30	0.30	0.28	0.28
Phosphorescence	10	10	3	6

of the  $V_1$  band was much less under these conditions. If  $F$ -band absorption had been significant the 4360 Å should presumably have had a larger effect than the 3650 Å.

The observations on phosphorescence are as follows. Immediately after high-energy irradiation a phosphorescence was observed which decreased slowly with time. Using filters it was determined that this emission was apparently the same as that observed by Dutton and Maurer.<sup>2</sup> After the crystals were bleached with polarized light for a few minutes, it was observed that the phosphorescent emission had decreased and was anisotropic. The emission was partially polarized with the maximum occurring in a direction oriented at 90° to the direction of the plane of polarization of the bleaching light. This effect was observed for bleaching light polarized along  $[011]$  and  $[001]$  crystal directions. A typical result is shown in Table I for bleaching along  $[011]$ .

Upon warming it was found that the polarized emission persisted to about  $-140^\circ\text{C}$ . At this temperature the emission was swamped out by the large thermally stimulated emission as has been reported.<sup>2</sup> This emission is not polarized, and with continued warming to  $-120^\circ\text{C}$  all emission ceased. It was determined by using filters that the thermal-glow emission was of different spectral quality than the low-temperature phosphorescence. Thus, the phosphorescence is removed by warming.

#### B. KCl 2-Mev Electron Bombardment at 77°K

Crystals were colored at 77°K by bombardment with 2-Mev electrons. Temperature was maintained by immersing the sample just below the level of liquid nitrogen. Very large absorption in the  $V_1$ -band region could be induced as compared to that obtained in exposure to x-rays. The same type of optical experiments were carried out, but the results obtained showed some difference from the x-rayed case.

In these experiments it was possible to observe a small induced dichroic absorption in the region of the  $V_1$  band, definitely indicating the presence of some anisotropic center. For example, Fig. 3 shows the dichroism induced by bleaching with light polarized along the  $[011]$  direction. Similar results were obtained when bleaching was along  $[001]$ . In each case the absorption was less for light polarized in the same direction as the bleaching light. The amount of dichroism, the difference in optical density between the

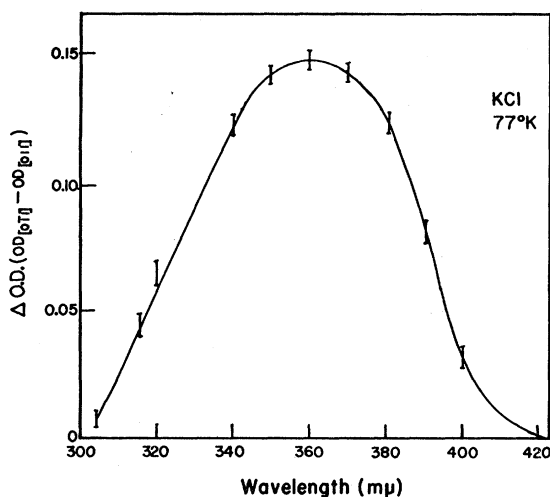


FIG. 3. The effect of polarized 3650 Å bleaching light on the absorption of electron-bombarded KCl crystal. The ordinate shows the difference in optical density for light polarized along  $[0\bar{1}1]$  and  $[011]$ . The bleaching light was polarized along  $[011]$ . The optical density at 3650 Å was 1.7 along  $[011]$ .  $T = 77^\circ\text{K}$ .

parallel and perpendicular direction, was about 10% at most. This dichroism could be removed by warming the crystals to  $-120^\circ\text{C}$ . The temperatures at which it disappeared could not be accurately determined in our apparatus.

The phosphorescent behavior of these crystals was the same as that found for x-rayed samples. That is, bleaching with polarized light caused the phosphorescence to become polarized just as for the x-rayed case. Similarly this polarized emission was removed by warming the crystal to its first glow peak. Figure 4 shows the time dependence of the phosphorescence and the effect of bleaching with polarized light.

### C. KCl(Tl)

It has been reported<sup>6</sup> that when thallium or silver is added to KCl, exposure to x-rays at  $77^\circ\text{K}$  produces a center which shows a very strong spin resonance absorption. This resonance is very similar to that observed by Känzig for the  $V_1$  center. Experiments were therefore carried out to determine what similarities might exist in the optical experiments.

KCl crystals prepared with 1 mole percent thallium added to the melt were x-rayed at  $77^\circ\text{K}$  and optical measurements were then made. These crystals showed a strong phosphorescence which differed somewhat in spectral quality from the pure material in that the emission was shifted toward longer wavelength. The optical absorption is of course different than for the pure material,<sup>5</sup> several other bands being present.

For such crystals, bleaching with polarized light did induce dichroic absorption in the region around 3650 Å.

<sup>5</sup> Delbecq, Smaller, and Yuster, Color Center Symposium, Argonne National Laboratory, 1956 (unpublished).

In addition the phosphorescence became polarized. These effects were found for bleaching along the  $[011]$  and  $[001]$  crystal directions. It should be noted that the phosphorescent polarization is not a trivial effect due to self-absorption of the dichroic crystal since the maximum in the phosphorescence is in the same direction of polarization as the maximum absorption.

In this material the induced dichroism and the anisotropic phosphorescence persisted as the crystal was warmed to appreciably higher temperatures than for the pure crystal. The anisotropic phosphorescence persisted until the onset of a large thermal glow emission at about  $-75^\circ\text{C}$ . This thermal glow peak was of different spectral quality than the phosphorescence and was not polarized. The dichroic absorption was also removed by warming through this temperature region.

### IV. DISCUSSION

Since the results of Känzig<sup>1</sup> on resonance apply to x-rayed KCl, we will focus our attention on this case first. Those results have been interpreted in terms of a center like a  $\text{Cl}_2^-$  molecule ion.<sup>1,6</sup> This center is taken to have an axis of symmetry along the  $[011]$  direction. It might be expected that such a center should have anisotropic absorption. Our results indicate that insofar as optical bleaching is concerned the  $V_1$  center has cubic symmetry in agreement with the model of Seitz.<sup>4</sup> This leads to two possibilities: (a) the  $V_1$  center displays cubic symmetry in optical absorption but not in spin resonance; (b) the spin resonance results apply to a center other than the center which gives rise to the  $V_1$  center absorption. The first possibility would have to be examined in terms of a more detailed analysis of ground and excited states of the proposed  $\text{Cl}_2^-$  model. Case (b), however, has aspects which are born out by

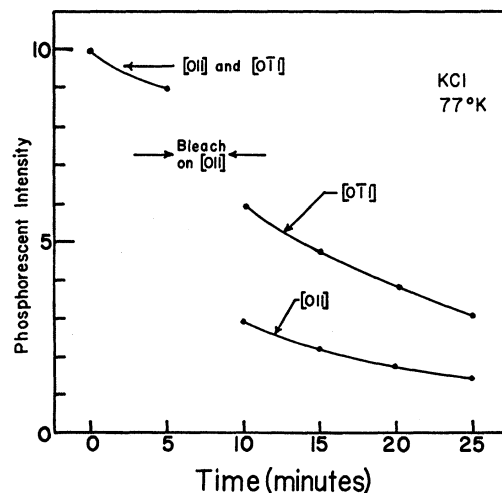


FIG. 4. The effect of polarized bleaching light at 3650 Å on the phosphorescent emission of electron-bombarded KCl. The bleaching light was polarized along  $[011]$ .  $T = 77^\circ\text{K}$ .

<sup>6</sup> T. Inui and S. Harasawa, J. Phys. Soc. Japan 11, 612 (1956).

present results on phosphorescence so that it may well represent the true situation.

The examination of anisotropic phosphorescence indicates that there is certainly a center other than the  $V_1$  center present in KCl x-rayed at 77°K which has an axis of symmetry along [011]. Moreover, this center can absorb light at 3650 Å and can be bleached anisotropically. Its absorption properties are therefore anisotropic even though this could not be observed directly in x-rayed KCl but is implied by the phosphorescent behavior. Further, the anisotropic phosphorescence disappears in the same temperature region as the  $V_1$  center so that the center responsible for the phosphorescence may also disappear in this region. Thus, this center would have thermal-bleaching properties very similar to the  $V_1$  center.

The results on electron-bombarded crystals are in agreement with the above findings. The same anisotropic phosphorescence is found and in this case the small induced dichroism indicated the presence of an anisotropic center. The fact that dichroism could be observed directly in electron-bombarded crystals is

probably due to the higher coloration obtained which makes the experimental observation simpler.

The results of KCl(Tl) are rather suggestive. It was noted that for KCl(Tl)<sup>5</sup> one observes an x-ray induced resonance signal quite like that reported by Känzig. It is much more intense than in pure KCl for the same amount of x-raying. Our results show that one can easily find induced dichroism and anisotropic phosphorescence in this case. Thus, it is possible that the center in KCl(Tl) which shows noncubic symmetry in resonance is also manifested in the observed dichroism and anisotropic phosphorescence. It should be noted that phosphorescence in KCl(Tl) is shifted in wavelength from that found in pure KCl. This indicates that the centers involved are not identical.

#### ACKNOWLEDGMENTS

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## Problem of Spin Arrangements in MnO and Similar Antiferromagnets\*

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The magnetic dipolar energy is computed for ordering of the second kind with the four antiferromagnetic sublattices of a face-centered cube making arbitrary spin directions with respect to one another, and this energy is shown to be of the same form in the sublattice direction cosines as is the calculated powder neutron-diffraction pattern. (The dipolar energy is also calculated for ordering of the third kind and shown to lead to a spin arrangement in disagreement with powder neutron-diffraction results on  $\beta$  MnS.) The observed neutron patterns in MnO and  $\alpha$  MnS agree with minimum dipolar energy, but many spin arrangements can satisfy this and the spins are constrained only to certain regions. Other sources of anisotropy in  $Mn^{++}$  salts are shown to be much weaker. A model is introduced in which the spins are constrained by dipolar

and exchange forces to point parallel to (111) planes and constrained by the weaker anisotropy to a threefold set of easy axes within these planes. Nagamiya's small-field approximation for the field dependence of the powder susceptibility of a uniaxial antiferromagnet is extended to all values of the applied field, and a similar calculation is made for the powder susceptibility of our MnO model. Comparison with experimental data indicates that the weak within-plane anisotropy is  $\sim 3 \times 10^4$  ergs/cm<sup>3</sup> which is to be contrasted with the theoretical out-of-plane dipolar anisotropy of  $10^7$  ergs/cm<sup>3</sup>. A rough theory of antiferromagnetic resonance for our model seems to explain the partial paramagnetic-like absorption observed below the Néel point.

### I. INTRODUCTION

THE problem of the arrangement of spins in antiferromagnetic MnO, and in the similar crystals  $\alpha$  MnS and  $\alpha$  MnSe, is not simple, and it will most likely remain somewhat unsettled until good single crystals are available for experimental study.

Neutron diffraction experiments give unquestioned evidence that the ordering in MnO is of the second kind,

that is, coordination of next-nearest neighbors.<sup>1,2</sup> However, the problem of the direction in which the spins point (or multidirections, since the system can be divided into many sublattices) remains entirely open. The original neutron evidence<sup>1</sup> suggested an arrangement in which all spins pointed along [100] directions. Subsequently Kaplan<sup>3</sup> showed that in ordering of the

<sup>1</sup> Shull, Strauser, and Wollan, *Phys. Rev.* **83**, 333 (1951).

<sup>2</sup> For an excellent review of antiferromagnetism, which we shall quote throughout this paper, see Nagamiya, Yosida, and Kubo, in *Advances in Physics* (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

<sup>3</sup> J. I. Kaplan, *J. Chem. Phys.* **22**, 1709 (1954).

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