Color Centers in Alkali Halides at 5°K*

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This paper reports experimental data on the effect of x-raying NaCl, KCl, and KBr at 5°K (approximately liquid helium temperature). These crystals, grown by Harshaw, were exposed to x-rays (50 kv at 20 and 48 ma) at 5°K, and the absorption spectra were measured from 210 mμ to 1100 mμ. A large concentration of F-centers was produced after an exposure of 15 minutes. The F-center is narrower than those obtained in additively colored crystals at 20°K. This difference in width also occurs in crystals x-rayed at 78°K. The narrowing of the F-band does not seem to be due to the temperature difference, i.e., 5°K and 20°K. No bands were observed to the infrared with the exception of a small F'-band in NaCl and KBr. Bands which were not known previously were obtained to the ultraviolet. Some bands decrease on warming to 78°K while others grow.

INTRODUCTION

UNTIL recently color centers in alkali halide crystals were produced at high temperatures or by irradiating the crystals with x-rays or other high energy radiation at room temperature. By lowering the temperature at which the crystals are x-rayed, additional color centers appear, some of which are stable only at low temperatures. Considerable work has been done down to 78°K (liquid nitrogen temperature), and a number of absorption bands have been found. Pick[1] has studied the F'-bands which can be produced in additively colored KCl and KBr by irradiating with light in the F-band at low temperatures. Casler, Pringsheim, and Yuster[2] have produced additional bands by x-raying NaCl, KCl, and KBr at 78°K and at dry ice temperature. They have also shown that some of these bands are unstable when the temperature is raised. Dorendorf[3] has x-rayed KCl and KBr at several different temperatures ranging from −180°C to +75°C. He observed seven bands on the ultraviolet side of the F-band which are produced at various temperatures and have various ranges of temperature stability. Martienssen[4] has shown that KBr x-rayed at 20°K possesses a large α-band and an F-band. He has also reported the β-band in KBr which can easily be produced by x-raying KBr at 20°K. The properties of the α-band and β-band have been studied previously by Delbecq, Pringsheim, and Yuster[5] in KI.

In order to achieve a more complete understanding of color center formation at low temperature, it is desirable to extend these investigations to 5°K (liquid helium temperature).

This paper will report work on NaCl, KCl, and KBr x-rayed at 5°K. This is the measured temperature of the crystals within the low temperature cell. The work has been of a survey nature and many individual results remain to be fully explored. Since the work indicates important results, the authors deem it advisable to publish these data now, rather than to withold publication until such time as all the individual phenomena are fully explored. The experimental procedure will be described first, then results on the individual crystals will be given, and finally a summary will be made. No attempt will be made to give a theoretical interpretation of the results.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of four parts: obtaining the crystal, cooling it, x-raying it, and measuring its absorption spectrum. We shall now describe the parts in detail.

Some alkali halide crystals of unknown purity can be obtained from chemical companies. Pohl[6] has pointed out that for optical measurements crystals should have no more than 1 part per 10^5 or 10^6 of any one foreign element. A qualitative spectroscopic analysis of the impurities in several of the available alkali halides was made for us by Dr. S. Zerfoss of the Naval Research Laboratory and by Mr. B. F. Scribner of the National Bureau of Standards. The results are given in Table I. Unfortunately, the analysis gives information only about those elements listed. Thus, for example, we have no knowledge regarding the content of hydrogen which causes the U-band.[7] We would like to stress the fact that these figures are only qualitative and that further analysis is needed. Some estimates in the table may be changed upon improvement of the analytic technique. Table I indicates the following:

(1) The impurities in the samples tested are much higher than one would like for color-center work;

(2) Crystals from various chemical companies

† Part of a dissertation presented to the Faculty of the Graduate School of the University of Maryland as partial fulfillment for the degree of Doctor of Philosophy.

[1] H. Pick, Ann. Physik **31**, 365 (1938), **37**, 421 (1940).
[2] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 887, 1564 (1950).
[3] H. Dorendorf, Z. Physik **129**, 317 (1951).
[4] W. Martienssen, Z. Physik **131**, 488 (1952) and Naturwiss. **38**, 482 (1951).
[5] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951).
[6] R. W. Pohl, Proc. Phys. Soc. (London) **49**, extra part 4 (1937).
[7] R. Hilsch and R. W. Pohl, Nachr. Akad. Wiss. Göttingen Math.-physik. Kl. 2, 139 (1936–39).

TABLE I. Spectroscopic impurity analysis of several alkali halide crystals.*

Element	NaCl					KCl		KBr			NaF
	Har NRL	Har NRL	Har NBS	Har NBS	Opt NRL	Har NRL	Har NBS	Har NRL	Har NBS	Pil NRL	Zer NBS
Ag	T	—	T	—	—	—	—	T'	—	—	—
Al	W	W	T	T	W	VW	T	W	T	W	—?
As			—	—			—		—		—
Au			—	—			—		—		—
B			—	—			—		—		—
Ba			—	—			—		—		—
Be			—	—			—		—		—
Bi			—	—			—		—		—
Ca	—	—	VW	VW	M	VW	VW	—	VW	—	W
Cb			—	—			—		—		—
Cd			—	—			—		—		—
Ce	—	—	—	—	—	—	—	—	—	—	—
Co			—	—			—		—		—
Cr			—	—	W	T	—		—		—
Cs			—?	—?			—?		?		?
Cu	VW	—	—?	—?	VW	—	—?	VW	?	—	T
Fe	VW	W	T	T		VW	T	T	T	T	T
Ga			—	—			—		—		—
Ge			—	—			—		—		—
Hf			—	—			—		—		—
Hg			—	—			—		—		—
In			—	—			—		—		—
Ir			—	—			—		—		—
K	—	—	—	—	—	VS	VS	VS	VS	VS	W
Ka			—	—			—		—		—
Li	—	—	T	T?	T	—	—	—	T	—	T
Mg	—	—	T	T	T	—	T	—	T	—	T
Mn			—	—			—		—		—?
Mo			—	—			—		—		—
Na	VS	VS	VS	VS	VS	VW	W	T	W	W	VS
Ni			—	—	T	—	—		—		T
Os			—	—			—		—		—
P			—	—			—		—		—
Pb			—?	—?			—		—		—
Pd			—	—			—		—		—
Pt			—	—			—		—		—
Rb	—	—	—	—	—	—	T	—	T	—	—?
Rh			—	—			—		—		—
Ru			—	—			—		—		—
Sb			—	—			—		—		—
Sc			—	—			—		T		—
Si			T	T	VW		T		—		—?
Sn			—	—			—		—		—
Sr	—	—	—	—	—	—	—	—	—	—	—?
Ta			—	—			—		—		—
Te			—	—			—		—		—
Th			—	—			—		—		—
Ti			—	—			—		—		—
Tl			—	—			—		—		—
U			—	—			—		—		—
V			—	—			—		—		—
W			—	—			—		—		—
Y			—	—			—		—		—
Zn			—	—			—		—		—
Zr			—	—			—		—		—

* The terms or symbols used in the above table are as follows Har, Opt, Pil, and Zer, designate respectively, samples of the alkali halide obtained from the Harshaw Chemical Company, the Optovac Chemical Company, the Pilot Chemical Company, and Dr. Samuel Zerfoss of the Naval Research Laboratory, Washington, D. C.; NBS analysis made by the Spectrochemistry Section of the National Bureau of Standards, courtesy of Mr. B. Scribner; NRL analysis made by the Crystal Branch of the Naval Research Laboratory, courtesy of Dr. S. Zerfoss; VS—greater than 10 percent; M—0.1 to 1.0 percent; W—0.01 to 0.1 percent; VW—0.001 to 0.01 percent; T—0.0001 to 0.001 percent; —not detected.

generally have about the same order of magnitude of impurity content although variation in distribution occurs;

(3) There are considerable variations of the impurity content in samples of the same alkali halide obtained from any one company.

The justification for using these relatively impure crystals in the experiments is that they are the best obtainable at present. In order to produce purer crystals, two problems must be solved. First, exceptionally pure raw material must be obtained and second, the crystal must be grown from this material without introducing impurities. Impurity ions are rejected from the melt during the growth process,[8] but when a degree of purity of 1 part in 10^6 or better is required, injection of impurities from the crucible may occur unless exceptional care is taken to eliminate such contamination. In short, the acquisition of a highly pure crystal is in itself a major problem not fully solved as yet.[9]

The cell used in these experiments has been described elsewhere.[10]

The radiation sources were 50-kv Machlett C-524A molybdenum target x-ray tubes, one having maximum rating of 20 ma and the other 50 ma. The crystal was about 3 cm from the tube window, and the x-rays had to penetrate the beryllium window, 0.05 cm thick, of the cell.

The optical measurements were made on a Beckman Model Du Spectrophotometer adapted to be used with the cell. Before exposing the crystal to x-rays, a blank transmission run was made. The data will be reported in terms of k', which is defined as:

$$k' = \log_{10}(I_0/I),$$

where: I_0 = fraction of light transmitted before x-raying; I = fraction of light transmitted after x-raying. The quantity k' should be proportional to the absorption coefficient. Unfortunately, the depth of the color layer is unknown in these experiments and an absolute value of the absorption coefficient cannot be obtained. If the depth of coloration is assumed to remain constant during the x-raying, k' can be used to obtain the relative concentrations of color centers.[11] At present one can only obtain an order of magnitude of the number of color centers formed at low temperatures by assuming an average depth of coloration from measurements made with a travelling microscope on crystals irradiated at room temperature. Our measurements of this depth give values which are less than those of Dorendorf's.[3]

[8] R. McFee, J. Chem. Phys. 15, 856 (1947).
[9] The workers at Göttingen assumed that they were dealing with crystals of high purity; the authors, however, do not know of any spectroscopic test of crystals grown in Germany. The purity of the material used to grow the crystals is given in some of the papers, but the impurities introduced in growing the crystals is not known. The Applied Physics Laboratory is presently trying to obtain crystals of higher purities.
[10] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. 23, 421 (1952).
[11] A. Smakula, Z. Physik 59, 603 (1930).

TABLE II. Wavelengths of the maximum of various bands observed in NaCl.

Band name	U	V_3	V_2			V_1	F	F'	R_1	R_2	M
Wavelength, mμ	192[a]	210[b]	223[b]	260	330	345[b]	454[c]	510[d]	540[e]	595[e]	710[e]
Temperature	Room	Room	Room	5°K	5°K	80°K	20°K	140°K	90°K	90°K	90°K

[a] R. Hilsch and R. W. Pohl, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. 322 (1933).
[b] See reference 2.
[c] See reference 13.
[d] See reference 11.
[e] See reference 14.

EXPERIMENTAL RESULTS

In order to gain an over-all view of the color centers in the alkali halides, a tabular summary will be given of the major known bands (Table II–IV). We shall include the new bands found in this paper. These tables are extensions of summaries given by Ivey.[12] The reference given with each band is not meant to exclude the fact that other workers have observed it, but is intended to be a leading reference. Except for the V_0-band, no letter will be assigned to the new bands reported in this paper. The results and effects observed will be given in detail after each table.

NaCl

Careful measurements have been made on the F-band, so that the peak and half-widths are well known. For NaCl at 20°K, Mollwo[13] presents the following data:

$$\lambda_v = 426 \text{ m}\mu, \quad \lambda_m = 454 \text{ m}\mu, \quad \lambda_r = 482 \text{ m}\mu.$$

λ_m is the wavelength at the peak of the F-band. λ_v is the wavelength on the ultraviolet side of λ_m where $k' = 0.5k'_{max}$ (i.e., at λ_m) and λ_r is the wavelength on the infrared side where $k' = 0.5k'_{max}$. Mollwo's values at 90°K agree with the measurements at 90°K of Molnar.[14] Flechsig[15] has measured at 90°K the F-band produced at room temperature by x-rays in natural and synthetic NaCl. All values of λ_v agree very well; however, Flechsig's value of $\lambda_r(505 \text{ m}\mu)$ on synthetic crystals disagrees with the one given above.

Figure 1, curve 1, shows the absorption spectrum of a Harshaw NaCl crystal which has been exposed to x-rays (50 kv-48 ma) at 5°K for two hours. The spectrum which is found when the crystal is raised to 78°K after this exposure is also shown in this figure. The following conclusions seem justified:

(1) An F-band comparable in size with those produced at 78°K and higher temperatures appears with the following values:

$$\lambda_v = 426 \text{ m}\mu, \quad \lambda_m = 450 \text{ m}\mu, \quad \lambda_r = 471 \text{ m}\mu.$$

The values of λ_v and λ_m agree with previous measure-

[12] H. F. Ivey, Phys. Rev. 72, 341 (1947).
[13] The figure for the F-band was taken from a paper of E. Mollwo, Z. Physik 85, 56 (1933). The authors have been unable to find just how the F-bands were produced. In the paper he used both natural and synthetic crystals. Most probably the centers were produced by additive coloration.
[14] J. P. Molnar, unpublished thesis, Massachusetts Institute of Technology (1940). We would like to thank Dr. Molnar for a copy of his thesis.
[15] W. Flechsig, Z. Physik 36, 605 (1926).

ments, but λ_r disagrees. The difference is too large to be ascribed to experimental error. Four other separate runs also using Harshaw crystals produced spectra substantiating Fig. 1. On three of these, the x-ray tube was run at 50 kv-20 ma and in the other at 50 kv-48 ma. The variation of the λ's between the runs is less than 1 mμ and the average value has been given above.

(2) In Fig. 2, k' is plotted against time of exposure to x-rays. Similar data taken on other runs support these data. This curve should be compared with Harten's[16] data on KCl at higher temperatures.

(3) In NaCl the F'-band is difficult to detect since the F-band overlaps it. In three runs at 20 ma, no indication of an F'-band appeared. The runs at 48 ma, however, indicate a rise on the infrared side of the F-band. This is interpreted as an F'-band which appears when the intensity of x-radiation is high.

(4) The M- and R-bands do not appear.

(5) A broad well-defined band forms at 330 mμ which is not the V_1-band. The V_1-band is produced by x-rays at 78°K and is much narrower (see item 8 below).

(6) A band has been measured at 260 mμ. A second weak band may form at 230 mμ although the data do not establish this band conclusively. This structure appears on large-scale plots of the data and not in Fig. 1.

(7) The data suggest the possibility of a band between the F-band and the 330 mμ-band. The band would correspond to the V_0-band which will be described in KCl.

(8) Heating to 78°K caused the 330 mμ-band to disappear and the narrower V_1-band to appear at 345 mμ. When measured immediately after warming to 78°K, the V_1 absorption maximum is greater than the absorption maximum of the 330 mμ-band. During this
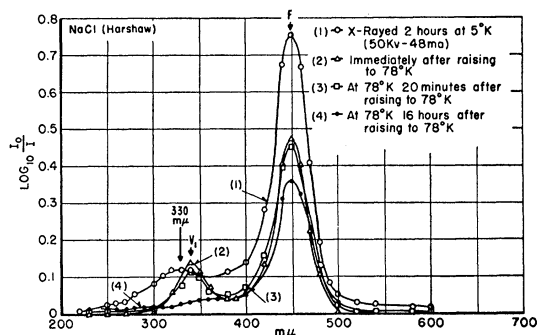

FIG. 1. Effect of x-raying NaCl at 5°K. The effect of warming to 78°K is also shown.
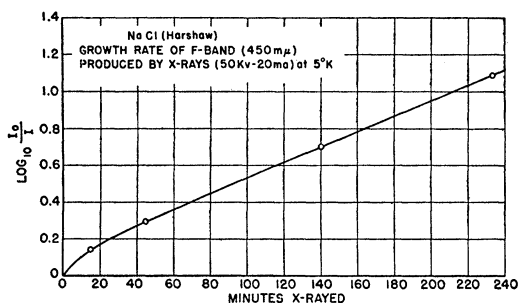
[16] H. Harten, Z. Physik 126, 619 (1949).

FIG. 2. Plot of the growth of the F-band
against time at 5°K.

heating the number of F-centers is reduced to about 60 percent of its previous value at 5°K (curve 2 of Fig. 1).

(9) The effect described in (8) occurs immediately after warming to 78°K and is followed by a gradual bleaching of both the V_1- and F-bands until the V_1-band is gone (curves 3 and 4 of Fig. 1), and the number of F-centers is reduced to about 48 percent of the previous value at 5°K. No further changes occur after this. The percentage changes are estimated with the use of Smakula's formula.[17] The effects of the band width are included.

(10) Warming to 78°K causes a small change in the width of the F-band, i.e.,

$$\lambda_v = 427 \text{ m}\mu, \quad \lambda_m = 451 \text{ m}\mu, \quad \lambda_r = 473 \text{ m}\mu.$$

Crystals x-rayed at 78°K have within our ability to measure them the same values of λ_v and λ_r. Mollwo's values at 90°K are:

$$\lambda_v = 426 \text{ m}\mu, \quad \lambda_m = 455 \text{ m}\mu, \quad \lambda_r = 483 \text{ m}\mu,$$

which disagree with our own values. Molnar's measurements at 90°K on F-centers produced at higher temperatures agree with Mollwo's values. X-raying these same crystals at room temperature gives:

$$\lambda_v = 422 \text{ m}\mu, \quad \lambda_m = 465 \text{ m}\mu, \quad \lambda_r = 506 \text{ m}\mu,$$

which is in excellent agreement with Mollwo's data.

Assuming the color layer in NaCl to be uniform and 0.07 mm thick, and an oscillator strength of 0.7, the F-center density after 4 hours of x-raying at 50 kv and 20 ma is 1.6×10^{18} per cm^3 at 5°K.

KCl

As can be observed in Table III the U-band and the V_3-band lie close together. Since we do not know the hydrogen content of the crystals, the V_3-band may be the same as the U-band.

Mollwo's[13] values for the F-band at 28°K are:

$$\lambda_v = 515 \text{ m}\mu, \quad \lambda_m = 540 \text{ m}\mu, \quad \lambda_r = 560 \text{ m}\mu.$$

The value of λ_m and λ_r shift to the infrared with rising temperature, but λ_v is apparently constant below 78°K.

The absorption spectrum of a Harshaw KCl crystal which was exposed to x-rays (50 kv–48 ma) at 5°K is shown in Fig. 3, curve 1. Curve 2 of this figure shows the effect of raising the crystal to 78°K, and curve 3 to room temperature. One other run was made with KCl at 5°K which substantiates the data. The following conclusions appear justified:

(1) An F-band comparable in growth rate with those produced at 78°K and higher temperatures appears with the following values:

$$\lambda_v = 518 \text{ m}\mu, \quad \lambda_m = 540 \text{ m}\mu, \quad \lambda_r = 557 \text{ m}\mu.$$

Unfortunately, only one run was made in which it was possible to obtain the half-width points.

(2) There are no indications of any band structure (F', R_1, R_2, and M) to the infrared side of the F-band.

(3) Two distinct V-bands are formed. The predominant band occurs at about 345 mμ. This band may correspond to the V_1-band which appears at 78°K. This rise, however, shifts with exposure from 355 mμ to 343 mμ. This suggests the possibility of a new band at about 340 mμ which forms at 5°K. Shortly we shall see that this is the case for KBr. The V_0-band appears here as it does at higher temperatures.[3] A very small band is indicated at about 255 mμ which is 20 mμ to the red side of the V_2-band. Our measurements did not extend far enough in the ultraviolet to measure V_3.

(4) On warming to 78°K, the 255 mμ-band apparently disappears and a band at 238 mμ appears, probably the V_2-band, with over twice the maximum absorption of the small 255 mμ-band it replaces. This same band (V_2) occurs when KCl is x-rayed initially at 78°K. Although the above values are only approximate, the authors believe that the difference between 255 mμ

TABLE III. Wavelength of the maximum of the various bands obtained in KCl.

Band name	V_5	V_3	U	V_2	V_4		V_7	V_6	
Wavelength mμ	<200[a]	212[a]	214[b]	230[a]	~254[a]	255	300[a]	334[a]	345
Temperature	90°K	90°K	Room	90°K	90°K	5°K	90°K	90°K	5°K

Band name	V_1	V_0	F	R_1	R_2	F'	M	N
Wavelength mμ	356[a]	455[c]	540[d]	680[e]	730[e]	750[f]	820[e]	980[g]
Temperature	90°K	5°K	28°K	Room	Room	170°K	Room	80°K

[a] See reference 3.

[b] See reference a of Table II.

[c] The V_0-band appears when KCl is x-rayed. It is not in Pick's curves on additively colored KCl crystals at 38°K although there is a band at this wavelength in the curves of F. G. Kleinschrod, Ann. Physik **27**, 97 (1936),

at room temperature which may be the V_0-band. The value of V_0 was obtained from the present set of measurements.

[d] See reference 13.

[e] See reference 14.

[f] See reference 1.

[g] E. Burstein and J. J. Oberly, Phys. Rev. **76**, 1254 (1949).

[17] A. Smakula, Z. Physik **59**, 603 (1930).

and 238 mμ is real. The authors' belief that the V_2-band appears on warming is based on the assumption that a band does not shift to the violet on heating. The V_0- and F-bands are reduced on warming, the F-band to about 45 percent of its value at 5°K. The maximum of the V_0-band shifts about 15 mμ to the red. The structure at 345 mμ (see item 3) bleaches, leaving the V_1-band.

(5) The F-band attains the following values on raising to 78°K:

$$\lambda_v = 516 \text{ m}\mu, \quad \lambda_m = 540 \text{ m}\mu, \quad \lambda_r = 563 \text{ m}\mu.$$

We have x-rayed KCl at 78°K. The values agree with those just given. Casler, Pringsheim, and Yuster's[2] curves give values at 78°K (514 mμ and 563 mμ) in close agreement with our data. There is only a very small variation in the half-width from run to run.

The values of λ_r are considerably less than values obtained by creating the F-band by x-raying at room temperature or heating in the alkali vapor and then cooling to 78°K. Mollwo's values at 90°K are:

$$\lambda_v = 515 \text{ m}\mu, \quad \lambda_m = 548 \text{ m}\mu, \quad \lambda_r = 571 \text{ m}\mu.$$

Molnar's values are in agreement with these values.

The above data seem to indicate that the F-band has a different half-width at 78°K for both NaCl and KCl, depending on whether it was created at high or low temperatures.

(6) Warming to room temperature bleaches the V_0- and V_1-bands and greatly reduces the F-band.

If the colored layer is assumed to be 0.08 mm thick, and the oscillator strength 0.81, the F-center density is 10^{18} per cm^3 after fifteen minutes of x-raying with 50 kv at 20 ma at 5°K.

KBr

From Table IV, the similarity between the U- and the V_3-bands should again be noted. Mollwo[18] obtained three bands at 430 mμ, 270 mμ, and 230 mμ at room temperature by heating KBr in Br vapor. These bands appear to be the V_1-, V_2-, and V_3-bands although considerable work is necessary before this statement can be confirmed.

Mollwo's data taken at 28°K on the F-band for synthetic KBr are:

$$\lambda_v = 570 \text{ m}\mu, \quad \lambda_m = 602 \text{ m}\mu, \quad \lambda_r = 628 \text{ m}\mu.$$
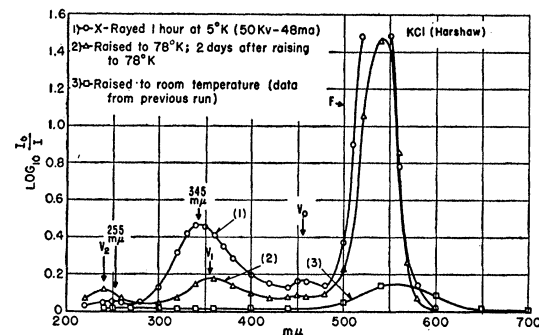

FIG. 3. Effect of x-raying KCl at 5°K. The effects of warming the crystal to 78°K and room temperatures are shown.

Further, λ_v does not change with temperature but λ_m and λ_r shift to the infrared with rising temperatures.

The absorption spectrum of a Harshaw KBr crystal x-rayed at 5°K is given in Fig. 4, curve 1. Curves 2 and 3 of this figure show the effects of raising the crystal to 78°K. The following conclusions appear justified:

(1) A large F-band appears at 5°K. Its growth rate at this temperature is comparable with that at 78°K. Our measurements on the F-band at 5°K give:

$$\lambda_v = 577 \text{ m}\mu, \quad \lambda_m = 601 \text{ m}\mu, \quad \lambda_r = 624 \text{ m}\mu.$$

These figures are an average of two runs. The band is narrower than Mollwo's value at 28°K. The difference between Mollwo's value of λ_v and the one given here seems to be due to the monochromator used. It does not seem to be due to the difference in temperature, since Mollwo's value of λ_v does not change between 28°K and 300°K.

(2) The R- or M-bands do not seem to appear. The F'-band does not appear for an exposure of 20 ma but seems to appear for an exposure of 28 ma for 50 kv x-rays.

(3) There are several bands to the ultraviolet of the F-band. At 230 mμ a band appears. It is well formed although it appears to the infrared side of another very large band (probably the α-band)[4] whose peak is beyond the Beckman range.

A band occurs at 380 mμ which does not correspond to any previously observed bands. We have x-rayed KBr at 78°K and produced a substantial V_1-band at 410 mμ. This band shifts less than 2 mμ on cooling to

TABLE IV. Wavelength of the maximum of various bands observed in KBr.

Band name	β	U'	α	U		V_3	V_2	U''	V_4		V_7
Wavelength, mμ	193[a]	200[b]	202[a]	224[c]	230	231[d]	265[d]	267[b]	275[d]	285	308[d]
Temperature	90°K	80°K	90°K	90°K	5°K	90°K	90°K	80°K	90°K	5°K	90°K

Band name	V_6		V_1	V_0	F	F'	R_1	R_2	M	N	
Wavelength, mμ	362[d]	380	410[d]	530	602[e]	700[f]	730[g]	790[g]	895[g]	1090[h]	
Temperature	90°K	5°K	90°K	5°K	28°K	170°K	90°K	90°K	90°K	Room	

[a] See reference 4.
[b] H. Thomas, Ann. Physik 38, 600 (1940).
[c] See reference a of Table II.
[d] See reference 3.

[e] See reference 13.
[f] See reference 1.
[g] See reference 14.
[h] J. J. Oberly, Phys. Rev. 84, 1257 (1951).

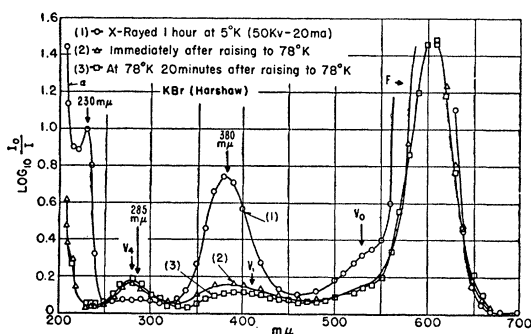[18] E. Mollwo, Ann. Physik 29, 394 (1937).

FIG. 4. Effect of x-raying KBr at 5°K. The effect of warming the crystal to 78°K is shown.

5°K and cannot be confused with the 380 mμ-band which forms at 5°K.

A slight rise at 530 mμ to the ultraviolet side of the F-band indicates a structure which may correspond to the V_0-band. This rise appears in additively colored crystals (see Martienssen, reference 4). At 285 mμ a weak band seems to form which is 10 mμ to the infrared of the V_4-band.

To summarize, two well-defined bands are resolved at 230 mμ and at 380 mμ, and one weak band at 285 mμ (V_4). Two other bands, one corresponding to V_0 and one beyond 210 mμ, are indicated to the ultraviolet of the F-band.

(4) On warming to 78°K, the V_0-, 380 mμ-, and F-bands decrease considerably. It cannot be determined whether the band to the ultraviolet of the 230 mμ-band (probably the α-band) changes. The 230 mμ-band bleaches out entirely. The 285 mμ-band seems to disappear and another band forms slightly to the ultraviolet. This new band is probably the V_4-band which by our measurements at 5°K and 78°K peaks at 277 mμ. The effect is much like that discussed above for KCl. The magnitude of the bands is small and this effect is difficult to measure accurately.

(5) A further phenomenon shown in Fig. 5 occurs at 78°K. The broad band at 380 mμ is not stable. Its ultraviolet side bleaches with time. This seems to indicate that the band is composed of two centers, one of which dissociates with time at 78°K. The remaining centers seem to be those associated with the V_1-band. As can be seen in Fig. 4, curves 2 and 3, the F-band continues to bleach with the decay of the 380 mμ-band at 78°K.

(6) The shape of the F-band when warmed to 78°K is close to what we have obtained when KBr is x-rayed initially at 78°K, the values being

$$\lambda_v = 576 \text{ m}\mu, \quad \lambda_m = 604 \text{ m}\mu, \quad \lambda_r = 632 \text{ m}\mu,$$

which again do not agree with Mollwo's values at 90°K, i.e.,

$$\lambda_v = 573 \text{ m}\mu, \quad \lambda_m = 609 \text{ m}\mu, \quad \lambda_r = 639 \text{ m}\mu.$$

Molnar's value does not agree with either set of figures.

(7) A very puzzling effect was observed at 5°K. After obtaining a spectrum, the sample was allowed to remain at that temperature for 4 hours and another spectrum obtained. Following the 4-hour measurement, it was again allowed to stay for another 4 hours and again measured. There was no difference between the spectra taken after the 4- and after the 8-hour period. There was a slight bleaching, however, of the bands to the ultraviolet side of the F-band between the first two measurements. The amount of bleaching to the ultraviolet side of the 380 mμ-band was very small and within the accuracy of our measurements. However, the effects on the F- and 380 mμ-bands seem measurable. It is to be stressed that only one set of measurements has been taken in KBr. However, many points were taken and the results look reliable. Obviously, more measurements are necessary.

If the depth of the color layer is assumed to be 0.06 mm, the number of F-centers produced at 5°K is 10^{18} per cm^3 after 15 minutes of x-raying at 50 kv and 20 ma.
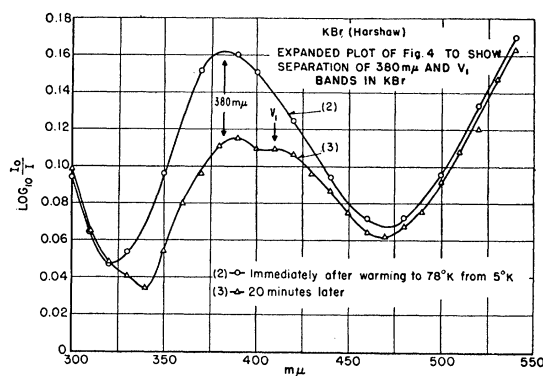

FIG. 5. The effect of time on the 380 mμ-band of KBr. Curve 2 shows the band immediately after warming to 78°K from 5°K. Curve 3 is 20 minutes later. Note the appearance of the V_1-band as the band at 380 mμ fades.

CONCLUSIONS AND DISCUSSION

Since most of the results are preliminary, no attempt to build a model will be made. Further, the impurity content of the crystals is relatively high. We shall attempt to summarize the results as far as possible and suggest lines along which further experiments could be carried out. It is to be stressed that the conclusions presented here are tentative, although the authors have tried as far as possible to report only those data which can be justified.

The general conclusions which apply to all the crystals are:

(1) The impurity content of the commercially available alkali halides is too high to consider the crystals fully suitable for optical work.

(2) The F-band forms easily by x-raying at 5°K. There appears to be a real difference between its shape when formed at low temperatures and when formed at high temperatures but measured at this low temperature.

(3) With the exception of possibly small F'-bands formed after high intensity x-raying in NaCl and KBr, no bands appear to the infrared of the F-band after x-raying at 5°K.

(4) New bands appear to the ultraviolet of the F-band after x-raying at 5°K. On warming to 78°K, these bands bleach, resulting in a reduction of the number of F-centers and the growth of certain of the V-bands normally produced by x-rays at higher temperatures.

The possible future experiments at 5°K are so large that it is difficult to list them. Some suggestions are:

(1) An attempt should be made to obtain very high purity material to use at these temperatures.

(2) Curves showing the rate of growth of the bands with time of x-ray exposure should be very valuable. It would be particularly interesting to see if the past

history of the crystal affects the growth-rate curves and what influence the x-ray intensities have.

(3) The optical and photoelectrical properties of the ultraviolet bands should be studied in detail.

(4) It will undoubtedly be necessary for a general understanding of the ultraviolet bands to measure the properties of these crystals between 5°K and 78°K. This will close the gap between Dorendorf's results and those given here.

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The Thermal Resistivity of Superconductors*

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The thermal resistance of tin, indium, and an alloy of tin with 0.134 percent bismuth have been measured as a function of transverse magnetic field strength from zero to values greater than critical at temperatures below their respective superconducting transition temperatures. Measurements have been carried out on tin at several temperatures and with polycrystalline and single-crystal specimens. In all cases a distinct maximum is found in the intermediate state thermal resistance of the pure metals, while no such anomaly is observed in the alloy. The probable origin of this phenomenon is discussed.

I. INTRODUCTION

IN general, at all temperatures below the zero-field superconducting transition temperature, two values are found for the thermal resistivity of a superconductor, one when the specimen is electrically superconducting, and a different one, usually higher, when superconductivity is destroyed by the application of a magnetic field greater than the critical field. This is in qualitative agreement with the assumption that when a metal is in the superconducting state a certain fraction of the conduction electrons are in their lowest energy state and not available for heat transport.

Until recently, very little information was available on the thermal resistivity of superconductors in the intermediate state since most of the measurements had been made on thin cylindrical specimens with the magnetic field applied parallel to the geometrical axis of the cylinder, in which case there is no intermediate

state. With the applied magnetic field normal to the axis of the cylinder, it would be reasonable to predice on the basis of the laminar structure of the intermediatt state[1-3] that the intermediate state thermal resistance (for $\frac{1}{2} H_c < H < H_c$ where H_c is the critical magnetic field) would vary linearly with magnetic field between the values characteristic of the superconducting and normal states, respectively, in analogy to the behavior of the electrical resistance.

Mendelssohn and Pontius[4] in 1937 did, indeed, find this intermediate state behavior for a lead-bismuth alloy (10 percent Bi) at about 5°K. However, in 1950, Mendelssohn and Olsen[5,6] made further measurements on niobium and a Pb-Bi alloy (0.1 percent Bi) and found a distinct maximum in the intermediate state resistance. More recently, a similar phenomenon has been reported in pure lead below about 4°K by Webber

[1] L. Landau, J. Phys. (U.S.S.R.) 7, 99 (1943).
[2] E. R. Andrew, Proc. Roy. Soc. (London) A194, 98 (1948).
[3] C. G. Kuper, Phil. Mag. 42, 961 (1951).
[4] K. Mendelssohn and R. B. Pontius, Phil Mag. 24, 777 (1937).
[5] K. Mendelssohn and J. L. Olsen, Proc. Phys. Soc. (London) A63, 2 (1950).
[6] K. Mendelssohn and J. L. Olsen, Phys. Rev. 80, 859 (1950).