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## Effect of Irradiation on Impurity-Vacancy Dipoles in KBr Crystals Doped with Strontium<sup>1)</sup>

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The concentration of impurity-vacancy dipoles in potassium bromide crystals doped with strontium bromide was measured using the ionic thermocurrent (ITC) technique. The parameters of the dipole relaxation are: fundamental relaxation time  $4 \times 10^{-14}$  s, activation enthalpy 0.66 eV. The effect of  $^{60}\text{Co}$   $\gamma$ -irradiation at room temperature was to reduce the number of dipoles and to increase the number of trapped holes and electrons, but the number of trapped holes and electrons, measured by optical absorption, was about 30 times smaller than the number of dipoles destroyed. It is proposed that the effect of irradiation is to increase the rate of aggregation of dipoles, primarily into trimer aggregates, through temporary electron trapping by strontium ions.

Mit der Ionen-Thermostrom(ITC)-Methode wurde die Konzentration der Störstellen-Leerstellendipole in Kaliumbromidkristallen, die mit Strontiumbromid dotiert waren, bestimmt. Die Parameter der Dipolrelaxation sind: Grundrelaxationszeit  $4 \times 10^{-14}$  s, Aktivierungsenthalpie 0,66 eV. Der Einfluß von  $^{60}\text{Co}$ - $\gamma$ -Bestrahlung bei Zimmertemperatur reduziert die Zahl der Dipole und erhöht die Zahl der angehafteten Löcher und Elektronen, jedoch war die Zahl der angehafteten Löcher und Elektronen, die durch optische Absorption gemessen wurde, etwa 30mal geringer als die Zahl der zerstörten Dipole. Es wird angenommen, daß der Einfluß der Bestrahlung in der Erhöhung der Geschwindigkeit der Aggregation der Dipole, hauptsächlich zu Trimer-Aggregaten, durch zeitweiliges Elektronenanhaften an Strontiumionen besteht.

### 1. Introduction

When strontium bromide is dissolved in potassium bromide crystals, divalent strontium ions substitute for potassium ions in the lattice and charge-compensating positive ion vacancies are introduced in equal number into the lattice. However, at room temperature such doped crystals are usually not in thermodynamic equilibrium, because the solid solubility of free strontium ions at that temperature is approximately  $10^{14} \text{ cm}^{-3}$ , or about  $10^{-8}$  mol fraction [1]. The strontium bromide will therefore eventually precipitate into a separate phase in the potassium bromide crystal, and for our purposes we may regard this precipitation as an aggregation that takes place in three stages: association into impurity-vacancy dipoles, aggregation to trimers consisting of three neighbouring dipoles, and aggregation into larger clusters eventually leading to a precipitated phase. The first stage, association, occurs at relatively high temperatures and

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has been extensively studied by ionic conductivity and diffusion methods [2]. The second stage, the aggregation of dipoles, has been studied by measurement of dielectric loss and ionic thermocurrent (ITC), which monitor the dipole concentration. The decrease in dipole concentration in the temperature range 20 to 150 °C was found to obey third-order kinetics, thus it has been postulated that a trimer of three dipoles is the first stable aggregation of dipoles [3]. The mechanism of further aggregation of the trimers until the final precipitated phase is reached is not nearly so well understood [4]; we shall not be concerned with it here.

When alkali halide crystals are irradiated at room temperature with X- or  $\gamma$ -rays a complex series of reactions takes place, and the final state of the crystal after such an irradiation is the relatively small resultant of a set of much larger forward- and back-reactions which take place during the irradiation [5]. The optical absorption bands which appear after irradiation are due to trapped electrons and trapped holes, and these bands appear relatively quickly during the "early stage" of irradiation and relatively slowly in the "late stage". In potassium bromide crystals doped with alkaline earth impurities the effects of early stage irradiation are particularly simple; the F-band and a V-band, at 269 nm, are the only absorption bands that appear [6].

We report here measurements of ionic thermocurrent and optical absorption, made at room temperature on crystals of KBr doped with varying amounts of  $\text{SrBr}_2$ , and the effect of  $\gamma$ -irradiation and subsequent optical bleaching on these properties. Similar measurements have been made on KCl crystals doped with strontium by Beltrami et al. [7], and on KCl and NaCl crystals doped with lead by Stott and Crawford [8]. Finally, Unger and Perlman [9] have made ionic thermoconductivity measurements, but not optical measurements, on KCl crystals doped with divalent rare earths. The measurements made on crystals doped with lead or rare earths are not directly comparable with ours, however, because the optical absorption bands caused by the impurities obscure V-bands formed by irradiation, and because the possibility of change of valence of these ions by hole or electron trapping is much greater than for alkaline earth ions.

## 2. Experimental Procedure

Single crystals of KBr doped with alkaline earth impurities were grown in our laboratory using a vertical-pull cooled-seed method in a dry nitrogen atmosphere. For ITC measurements, specimens were cleaved into blocks about 1 to 2 mm thick, with square cross-sections between  $4 \times 4$  and  $10 \times 10 \text{ mm}^2$ . Graphite electrodes were applied, and the dimensions of the specimen were measured in the manner described by Rolfe [1]. Strontium ion concentrations in the crystals were determined by atomic absorption analysis.

Optical absorption measurements were made with a Perkin-Elmer Model 350 recording spectrophotometer, either by using the same specimens as were used in ITC measurements, with an optical path passing between the graphite-coated surfaces, or by using clear specimens which had been cut from adjacent parts of the grown crystal and had been subjected to the same treatment as the specimen used for ITC measurement.

The ionic thermocurrent apparatus consisted of a variable temperature sample chamber with a specimen holder inside connected to a Cary Model 31 vibrating reed electrometer. The temperature of the specimen was measured with an in-

sulated junction sheathed chromel-alumel thermocouple located at the low-potential terminal of the specimen holder. An X-Y recorder was used to measure the depolarization current as a function of temperature, and a separate strip recorder was used to monitor the heating rate. The procedure used to measure ionic thermocurrent was as follows: a polarizing voltage of 500 to 2000 V was applied to the specimen at about 220 °K for a few minutes, the specimen was cooled to 120 °K with the field still on, the field was turned off and the electrometer connected, and finally the specimen was warmed to room temperature at a constant heating rate between 2.5 to 6.0 deg/min. The ITC spectrum is the depolarization current as a function of temperature measured during this final heating [10].

Specimens were irradiated with  $\gamma$ -radiation from  $^{60}\text{Co}$  at room temperature at an intensity of approximately  $4 \times 10^4$  R/h. Optical bleaching at room temperature was performed by exposing the specimens to daylight, or by using the unfiltered output of a 100 W mercury lamp from which the outer glass envelope had been removed.

### 3. Results

#### 3.1 Ionic thermoconductivity of quenched crystals

The first treatment given to all the crystals used in this investigation was to quench them to room temperature after annealing at 400 °C. This annealing temperature is high enough to cause any precipitated strontium bromide to dissolve [1], and to break up any dipole aggregations, but it is not high enough to break up impurity-vacancy dipoles (associated strontium ion-vacancy pairs); the calculated proportion of strontium ions associated into dipoles at 400 °C is about 80% [11]<sup>3</sup>).

The ITC spectra of three quenched crystals with different amounts of strontium are shown in Fig. 1. In the low temperature region, below that shown in the diagram, a small peak was detected similar to the one reported by Cappelletti and Fieschi [12], but the area under this peak was negligible in comparison with the main peak at 215 °K. The spectra in Fig. 1 follow very closely the form predicted by the simple theory [10] presented briefly below.

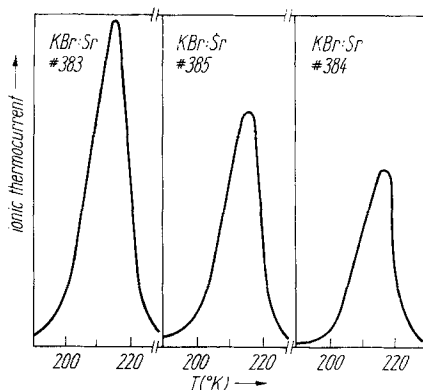


Fig. 1. Ionic thermocurrent spectra for three KBr:Sr crystals, strontium ion concentration given in Table 1. Current scale the same for all crystals

<sup>3</sup>) The association parameters for strontium in KBr are assumed to be equal to those quoted in [11] for calcium.

If the ITC spectrum is due entirely to one type of dipole with a relaxation time  $\tau(T)$  which is a function of the absolute temperature  $T$  given by

$$\tau(T) = \tau_0 \exp\left(\frac{E}{kT}\right), \quad (1)$$

where  $\tau_0$  is a fundamental relaxation time,  $E$  is the enthalpy for reorientation of the dipole and  $k$  is Boltzmann's constant, then the ionic thermocurrent  $i(T)$  as a function of temperature is given by

$$i(T) = \left[ \frac{Q_0}{\tau(T)} \right] \exp\left[ -\frac{F(T, E)}{b\tau_0} \right], \quad (2)$$

where

$$Q_0 = \frac{p^2 N_d V_p S}{3kT_p D} \quad (3)$$

and

$$F(T, E) = \int_{T_0}^T \exp\left(-\frac{E}{kT''}\right) dT''. \quad (4)$$

In these equations,  $Q_0$  is the total released charge,  $p$  the dipole moment,  $N_d$  the number of dipoles per unit volume,  $V_p$  the polarizing voltage,  $S$  the cross-sectional area,  $T_p$  the polarizing temperature,  $D$  the specimen thickness,  $T_0$  the temperature from which the specimen is warmed, and  $b$  is the heating rate.

We used this theory to calculate the parameters of the strontium ion-vacancy dipoles. First, we used the temperature of the maximum thermocurrent  $T = T_M$  at  $di(T)/dT = 0$  to calculate a set of pairs of  $E$ ,  $\tau_0$  values, and then found which pair produced the best fit to the experimental ITC spectrum with the minimum mean square deviation. Then we used (2) and (3) to calculate  $N_d$ . In all these calculations the approximation suggested by Squire [13] was used to calculate (4). This approximation is

$$F(T, E) = T \exp(-X) [(X + C_1)/(X^2 + C_2 X + C_3)], \quad (5)$$

where

$$X = E/kT, \quad C_1 = 3.0396, \quad C_2 = 5.0364 \text{ and } C_3 = 4.1916.$$

This approximation was in turn checked against the experimental results by calculation of  $Q_0$  from (2). The calculated values agreed within 5% with the value of  $Q_0$  obtained by graphical integration of the results in Fig. 1.

Finally, we compared experimental and calculated thermocurrents over the whole temperature range using a least squares fit of the ITC spectrum, with the results shown in Fig. 2. The deviations are random, except at the lowest temperatures, where a small contribution arises from the very small low-temperature ITC peak mentioned earlier.

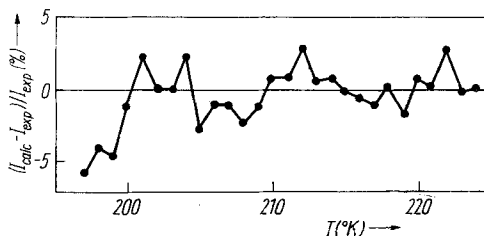


Fig. 2. Percentage difference between calculated and experimental ionic thermocurrent values as a function of absolute temperature

The relaxation parameters for strontium ion-positive ion vacancy dipoles were found to be  $E = 0.66 \pm 0.01$  eV and  $\tau_0 = (4 \pm 2) \times 10^{-14}$  s. The calculated dipole concentration  $N_d$  is listed in Table 1 for three different crystals, together with the strontium ion concentration determined by atomic absorption analysis.

No optical absorption bands were detected in the quenched crystals, in the wavelength range 2000 to 10000 Å.

Some quenched crystals were stored at room temperature for the same length of time as it took to perform the irradiation and bleaching experiments described below, and the ITC remeasured. No change in the ITC spectrum occurred during this time.

### 3.2 The effects of gamma-irradiation

After the initial measurement of ITC and optical absorption, crystals were gamma-irradiated, and the ITC and optical absorption measured as a function of irradiation time.

The effect of irradiation on the ITC spectrum was simply to cause a decrease in the thermocurrent, as shown in Fig. 3. No other ITC peaks were produced by irradiation, so that the effect of the irradiation is to reduce the number of impurity-vacancy dipoles. We define the loss of dipoles  $\Delta N_d$  caused by an irradiation for time  $t$  by the equation

$$\Delta N_d = N_d(0) - N_d(t). \quad (6)$$

After irradiation, the optical absorption spectrum consists of two absorption bands, as shown in Fig. 4, the F-band at 625 nm and an ultraviolet absorption band at 269 nm. The F-band is well-known to be due to electrons trapped at

Table 1  
Concentration  $N_d$  of impurity-vacancy dipoles determined by ITC measurements, and concentration  $N_{Sr}$  of strontium ions determined by atomic absorption analysis

crystal number	$N_d$ ( $\text{cm}^{-3}$ )	$N_{Sr}$ ( $\text{cm}^{-3}$ )
383	$4.4 \times 10^{18}$	$4.9 \times 10^{18}$
384	$2.4 \times 10^{18}$	$2.5 \times 10^{18}$
385	$3.3 \times 10^{18}$	$3.6 \times 10^{18}$

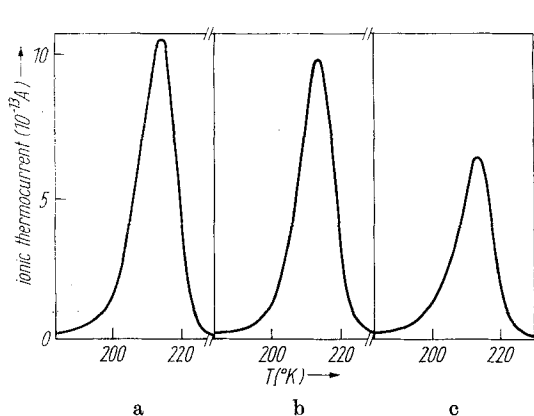


Fig. 3. Ionic thermocurrent spectra of a crystal irradiated for a) 2 h, b) 8 h, and c) 48 h

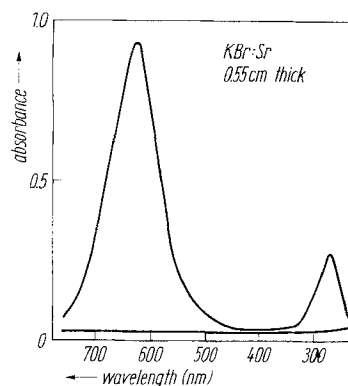


Fig. 4. Optical absorption spectrum of a crystal before irradiation (lower curve) and after 2 h of irradiation (upper curve)

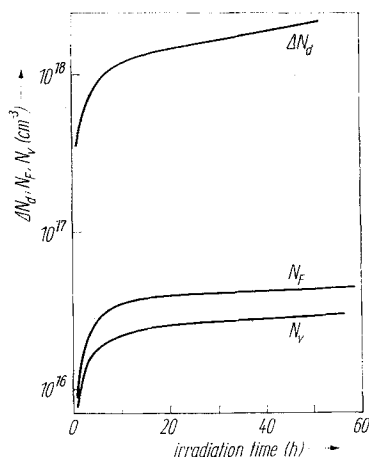


Fig. 5. The effect of time of irradiation on the dipole concentration  $N_d$ , the trapped electron concentration  $N_F$  and the trapped hole concentration  $N_v$ . The results were obtained by using adjacent crystals cleaved from the same boule

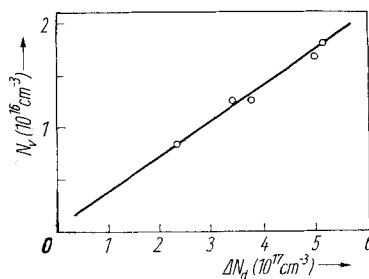


Fig. 6. Relation between the trapped hole concentration  $N_v$  and the loss of dipoles  $\Delta N_d$ , for early-stage irradiation

negative ion vacancies (F-centres), while the band at 269 nm was shown by Ishii and Rolfe [6] to be due to holes trapped near a divalent cation impurity. As the irradiation time increased, so did the height of these two absorption bands.

The number of F-centres, or trapped electrons, per unit volume, may be calculated from absorption band measurements. We used the Smakula equation for a Gaussian absorption band [14], with an oscillator strength of 0.75 [15], to calculate this number, which we call  $N_F$ , as a function of the time of irradiation.

The number of trapped holes cannot be so certainly calculated from the ultraviolet absorption band because the exact nature of the centre causing this absorption is not as well established as it is for the F-centre, and furthermore no measurements of oscillator strength have been made. So for an initial assumption we will set the oscillator strength at unity; in which case the Gaussian approximation of the Smakula equation can be used to calculate  $N_v$ , the number of centres per unit volume. If it is further assumed that each centre contains one trapped hole, then  $N_v$  is the concentration of trapped holes caused by the irradiation. In Fig. 5 are plotted  $\Delta N_d$ ,  $N_F$  and  $N_v$  as a function of irradiation time. The three curves have a similar shape, corresponding to the well-known [5] two stages of irradiation, an early fast stage, and a late slow stage. It will also be noted that the number of dipoles destroyed by irradiation is very much greater than the number of trapped electrons or holes. In the early stages of irradiation it was found that the loss of dipoles is proportional to the rise in the ultraviolet absorption band, as shown in Fig. 6, which refers to crystals with different strontium concentrations. In this graph the number of dipoles lost is about 30 times greater than the number of trapped holes.

In the late stage of irradiation the loss of dipoles proceeds at a greater rate than the trapping of electrons or holes, as seen in Fig. 5.

### 3.3 The effect of optical bleaching

The effect of optical bleaching was investigated by taking crystals which had been irradiated for a relatively short time, so that the irradiation was still in the

Table 2  
Effect of irradiation and optical bleaching

crystal number	treatment	$N_d$ ( $\text{cm}^{-3}$ )
383	4 h irradiation	$3.75 \times 10^{18}$
383	as above plus bleaching	$3.57 \times 10^{18}$
384	2 h of irradiation	$1.89 \times 10^{18}$
384	as above plus bleaching	$1.73 \times 10^{18}$
385	2 h of irradiation	$3.01 \times 10^{18}$
385	as above plus bleaching	$2.95 \times 10^{18}$

early stage, and bleaching them until the F-band absorption had completely disappeared. After such treatment some of the ultra-violet absorption band still remained, and the ITC intensity was further reduced. The results of these experiments are summarized in Table 2.

## 4. Discussion

### 4.1 ITC before irradiation

The large, isolated ITC peak in crystals before irradiation is simple to interpret: it is due to dipoles composed of strontium ions and positive ion vacancies, with a relaxation time having an enthalpy of  $0.66 \pm 0.01$  eV. This is in good agreement with the value of 0.65 eV found at higher temperatures and frequencies by means of dielectric loss measurements [16]. It is also equal to the enthalpy of motion of an isolated positive ion vacancy 0.65 eV, calculated from ionic conductivity measurements [11]. This shows that the jump frequency of a potassium ion into a positive ion vacancy is little affected by a nearby strontium impurity ion. However, the jump frequency of strontium ions into neighbouring positive ion vacancies is much slower, as shown by diffusion measurements, and this jump is the rate-determining process for dipole aggregation, where movement of the impurity ion is necessary. This explains why the aggregation of dipoles in unirradiated crystals at room temperature is such a slow process.

In order to determine the dipole concentration  $N_d$  from the ITC measurements we have to make an assumption about the effective dipole moment  $p$  before (3) can be used to calculate  $N_d$ . We assume that the dipoles consist entirely of nearest neighbour impurity-vacancy pairs, and also that corrections for local fields and other interactions with the surrounding lattice are negligible [17]. The results quoted in Table 1 give some support to this hypothesis. The degree of association of strontium ions, equal to the ratio  $N_d/N_{\text{Sr}}$  is about 90%, which is the degree of association to be expected at a temperature of 300 °C [11]. Though no measurements were made of the cooling rate during the quenching process from 400 °C, it is possible that the association equilibrium was fast enough that equilibrium was maintained during the first 100 deg of the quenching. The results in Table 1 may also be used to disprove the hypothesis that the dipoles consist entirely of next-nearest-neighbour pairs. In that case the dipole moment would be  $\sqrt{2}$  times greater, and the value of  $N_d$  calculated from (3) would be only half as great, making the degree of association approximately 45%. This is definitely much too small a degree of association to be expected at an equilibrium temperature of 400 °C.

#### 4.2 *The effect of irradiation*

We have observed three effects of irradiation: a decrease  $\Delta N_d$  in the dipole concentration, an increase from zero to  $N_F$  in the trapped electron concentration, and an increase in the trapped hole concentration from zero to a value  $N_v$  which is not precisely known. The number of dipoles lost is about 30 times greater than the increase in the number of trapped electrons. It is in this factor that we disagree with previously published results on similar systems. Beltrami et al. [7] found that the number of dipoles destroyed in irradiated KCl:Sr crystals was approximately equal to the number of trapped electrons, while Stott and Crawford [8] found that the number of destroyed dipoles in KCl:Pb was only about 15% of the number of F-centres formed. While it is clear that the behaviour of  $Pb^{++}$  is very different from the alkaline earth impurities like  $Sr^{++}$ , the difference in the behaviour of  $Sr^{++}$  in KCl and KBr is disturbingly large.

What is the mechanism which causes the decrease in dipole concentration on irradiation? One possible explanation, based on Fig. 6, might be that each dipole is destroyed by trapping a hole, and that the ultraviolet absorption band is caused by holes trapped at the dipole. This hypothesis cannot be true since the number of trapped holes would then be 30 times larger than the number of trapped electrons, leading to a very large charge unbalance, furthermore the oscillator strength of the ultraviolet absorption band would have to be fixed at an unreasonably low value of  $f = 0.03$ , if such a small absorption were to be due to such a large number of centres.

For another explanation of the mechanism of dipole destruction, we use the model of the ultraviolet absorption band which arose from the experiments of Ishii and Rolfe [6]. The model is that a trimer of dipoles has trapped a hole. If this is true, then dipole aggregation must have taken place before an absorption band could be formed, and since we know that dipole aggregation in unirradiated crystals is negligible, it follows that the effect of irradiation is greatly to increase the rate of aggregation. This means that the jump frequency of strontium ions into neighbouring vacancies ( $\omega_2$ ) which is the rate-determining step in aggregation, must also be greatly increased. The process responsible for this is, we suggest, the temporary capture of an electron by the strontium ion during the irradiation, when the crystal is flooded with free electrons, causing its temporary conversion to a singly charged cation. The jump frequency of the ion would immediately increase by several orders of magnitude towards the value ( $\omega_1$ ) of the jump frequency of a potassium ion into a neighbouring vacancy. After the irradiation ceases, electrons and holes rapidly recombine but some are left trapped at anion vacancies to form F-centres and some are trapped at trimers of dipoles to form the ultraviolet absorption band. If the number of trapped holes is assumed to be equal to the number of trapped electrons, then the oscillator strength of the ultraviolet absorption band can be calculated to be approximately 0.7, a reasonable value.

#### 4.3 *Effect of optical bleaching*

The primary effect of optical bleaching is to release electrons from F-centres, and on the basis of the above hypothesis we expect that some of these electrons will be temporarily trapped by strontium ions with a consequent enhancement of the aggregation rate. Thus the decrease of  $N_d$  shown in Table 2 is also explained by our hypothesis. A similar effect occurred in KCl:Pb, where optical bleaching caused complete disappearance of the ITC peak [8].



#### ***4.4 Other experimental consequences of the proposed mechanism***

One consequence of the proposed enhanced aggregation mechanism is that irradiation will increase the diffusion coefficient of strontium and other alkaline earth impurities in KBr. This might be detected by auto-radiographic techniques such as those reported by Beleites and Fröhlich [18]. The concentration gradients necessary for diffusion may already be present in crystals grown from the melt by the Kyropoulos method in the form of periodic concentration changes [18]. An irradiation at room temperature should smooth out such fluctuations by enhancing diffusion to the same extent that would only be possible by conventional diffusion at a much higher temperature.

It is possible that enhanced dipole aggregation leads also to an enhanced rate of precipitation. Precipitate phases can be detected by optical methods such as scattering, ultramicroscopy or impurity decoration [4]. Thus it might be possible to check our hypothesis by annealing two identical doped crystals to dissolve precipitates, and then to compare the rate of precipitation in irradiated and non-irradiated crystals.

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