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Abstract. The Kerr constants $(R_{1111} - R_{1122})$ and R_{1212} of KCl containing Cd^{2+} ions in the concentration range from 10^{-2} to 10^{-1} mol% and KCl containing 10^{-1} mol% of Br^- ions, $KCl_{0.8}Br_{0.2}$ and $KCl_{0.4}Br_{0.6}$ have been determined. In $KCl:Cd^{2+}$ the state of the Cd^{2+} ions has been investigated using the ionic thermoconductivity (ITC) technique and the volume change brought about by these impurities has been studied using powder, x-ray diffractograms. The processes by which the Kerr effect is produced in alkali halides containing different classes of defects have been discussed. We conclude that the observed Kerr effect is due to (i) the polarisability anisotropy of the ions (chiefly of impurities) and (ii) the electrostrictive elasto-optic effect which coexist in a crystal when a high electric field is applied. The relative importance of the two processes mentioned above, in alkali halides containing different classes of defects, has also been discussed.

1. Introduction

Impurities and lattice point defects have been given attention by workers in solid state physics with regard to the local distortion caused by a defect or an impurity atom. An anisotropic point defect in an alkali halide crystal generates an anisotropic elastic strain field. Phenomenologically, the defect can be described as an anisotropic elastic dipole [1]. Two classes of such defects in alkali halides which are known to produce birefringence are as follows.

(1) Defects without an electric dipole: $KCl:Br^-$ is an example of this class. The introduction of monovalent substitutional defects leads to a change in the macroscopic volume due to the size mismatch together with an inhomogeneous strain field falling away from the site of the defect in the crystal. The anisotropy due to the strain field will, in general, be non-vanishing. As the concentration of Br^- ions increases the volume increases and this change in volume follows Vegard's volume law closely [2]. Since the polarisability of Br^- ions is greater than that of Cl^- ions, we can expect an increase in the refractive index of the crystal and the change becomes appreciable at high defect concentrations [3].

(2) Defects with an electric dipole moment: these defects have necessarily an anisotropic elastic dipole. In this class of defects there are three categories. They are systems like:

(a) $KCl:Li^+$ and $KCl:Cu^+$, where the equilibrium positions of the substitutional impurities are off-centre, hence the electric dipole;

(b) $KCl:OH^-$ and $KCl:CN^-$ where the intrinsic electric dipole moment adds to the off-centre electric dipole moment;

Table 1. Concentration of Cd^{2+} in KCl in various samples (determined by polarography) expressed in mol % with errors in parentheses. (In the second column the concentration is expressed in number per cm^3 obtained using the relation $N_0 = NC/2Nr^3$ where $2r^3$ is the volume of the unit cell obtained from x-ray diffractograms, C is in mol fraction and N is Avagadro's number.)

C (mol%)	$N_0 \times 10^{19}$ (cm^{-3})
0.013 74 ($\pm$0.000 98)	0.2225
0.032 57 ($\pm$0.000 45)	0.5275
0.059 61 ($\pm$0.001 10)	0.9655
0.101 69 ($\pm$0.002 75)	1.6472
0.130 21 ($\pm$0.002 41)	2.1093
0.171 64 ($\pm$0.001 81)	2.7791
0.197 54 ($\pm$0.002 78)	3.1980

(*c*) KCl containing divalent impurities such as Pb^{2+} and Cd^{2+}, where impurity–vacancy (I-V) dipoles are present.

In this class of defects also, a volume change occurs due to the mismatch of the substitutional impurity ions. With respect to orientations, it is worth noting that asymmetric molecules like CN^- have, perhaps, the maximum number of orientations possible, followed by off-centre systems and I-V dipole systems. In the case of divalent impurities, the volume change occurs due both to the mismatch of impurities and the presence of charge-compensated vacancies equal in number to the impurity ions. Also, if one succeeds in producing a preferred orientation of these defects an appreciable dimension change along the orientation axis and consequently perpendicular to the alignment axis is likely to occur. At high concentrations aggregation takes place due to the interactions among the defects through their strain fields.

Birefringence measurements have been performed only on systems containing defects belonging to class (2) mentioned above [4–7].

The purpose of this paper is thus to investigate in detail the process by which birefringence is produced in alkali halides doped with monovalent defects (without electric dipole moments) and also that produced in divalent doped alkali halides.

The systems that have been examined are KCl in which Cd^{2+} and Br^- ions are introduced to replace K^+ and Cl^- ions respectively. While volume change measurements, ionic thermoconductivity (ITC) measurements and birefringence studies have been performed on KCl:Cd^{2+}, birefringence measurements have been carried out for KCl containing 10^{-1} mol% of Br^- ions, $KCl_{0.8}Br_{0.2}$ and $KCl_{0.4}Br_{0.6}$.

2. Experiment

The KCl:Cd^{2+} samples were grown from the melt in our laboratory by the Kyropoulos technique in a dry nitrogen atmosphere to minimise contamination by OH and oxygen. Analar grade KCl powder was taken as the starting material and controlled amounts of impurities in the form of cadmium chloride ($CdCl_2.2\frac{1}{2}H_2O$) were added. After annealing at 650 °C for about 10 h, the crystals were cooled slowly to room temperature in 48 h. The actual amounts of cadmium present in the crystal were determined by polarography and are given in table 1. The sample of KCl containing 10^{-1} mol% of KBr was grown in

a similar manner and the samples of $KCl_{0.8}Br_{0.2}$ and $KCl_{0.4}Br_{0.6}$ were supplied to us. The samples were cut along the desired orientations, after which they were annealed at 250 °C in vacuum and quenched to room temperature prior to the electro-optical measurements.

X-ray powder diffractograms of samples containing different concentrations of Cd^{2+} ions were taken using Cu Kα radiation. Then the volume of the unit cell was calculated using the observed value of the lattice parameter at each concentration.

ITC measurements were performed on $KCl:Cd^{2+}$ by the method developed by Bucci and Fieschi [8] and Bucci *et al* [9]. The cryostat in which the measurements were made in vacuum ($\sim 10^{-3}$ Torr) can be operated in the range from liquid-nitrogen temperature (LNT) to 523 K. The samples were annealed at 523 K in vacuum for 2 h and cooled down to 240 K in 5 min. Then they were polarised by a static electric field (E_p) of 6 kV cm^{-1} for 5 min at 240 K (T_p) and then cooled down to 100 K (T_0), after which the field was switched off. Thus the dipoles become polarised and remain aligned in the same configuration obtained at T_p. The crystal was then heated at a constant rate of 5 K min^{-1}. The dipole relaxation time for orientation gets shorter and the dipoles lose their preferred orientation, giving rise to a depolarisation current. This was detected with a Keithley electrometer (model 610 C) and was recorded. The minimum current that can be measured is 10^{-15} A. The reproducibility of measurements was within 3%.

A static compensator method was employed to determine the Kerr constants at $\lambda = 632.8$ nm at room temperature, using a He–Ne laser for the two field configurations, $E\|$ (100) and $E\|$ (110). The experimental procedure is the same as that described in [6]. A Soleil–Babinet compensator was introduced between the two crossed polarisers and was adjusted to a position corresponding to $\frac{1}{4}\lambda$ retardation. This bias enables us to work at the optimum point of the arrangement, i.e. at the midpoint of the linear part of the change in intensity (ΔI) against $\sin^2(\Delta n)$ curve. With this $\frac{1}{4}\lambda$ compensation technique the Kerr effect was measured with maximum accuracy, thus eliminating errors from the possible birefringence that may be present due to the strain introduced in the crystal during the growing, cutting and polishing processes. Since all the doped systems belong to the NaCl structure, the only non-vanishing Kerr constants are R_{1111}, R_{1122} and R_{1212} and these can be determined from the relations

$$\Delta n = -\tfrac{1}{2}n_0^3(R_{1111} - R_{1122})E^2 \qquad \text{for } E \| (100) \qquad (1)$$

and

$$\Delta n = -n_0^3 R_{1212} E^2 \qquad \text{for } E \| (110) \qquad (2)$$

where Δn is the birefringence ($n_\| - n_\perp$), $n_\|$ and $n_\perp$ are the refractive indices of the crystal for the two polarisations of the electromagnetic wave with respect to the external DC electric field E and n_0 is the refractive index of the crystal in the field-free condition. The signs of the Kerr constants reported here are arbitrary. The estimated error in measuring the Kerr constants is 1%.

3. Results and discussion

3.1. Measurements on volume change

Using the x-ray diffractograms of $KCl:Cd^{2+}$ the relative changes in volume ΔV_R of the crystal have been calculated and the variation of ΔV_R with concentration C of Cd^{2+} ions
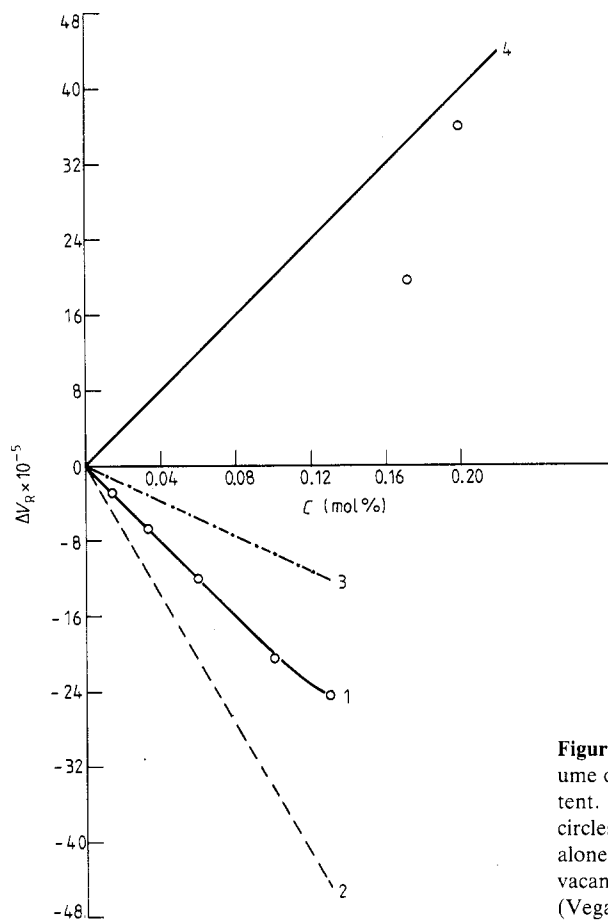
Figure 1. Variation of the relative change in volume of the unit cell of $KCl:Cd^{2+}$ with Cd^{2+} content. 1, x-ray diffraction measurements (open circles); 2, theoretical estimation (size misfit alone); 3, theoretical estimation (size misfit and vacancy contribution); 4, theoretical estimation (Vegard's volume law).

in KCl is represented as curve 1 in figure 1. We have made estimates for the change in volume of the samples and these are also shown in figure 1. Curve 2 represents the relative change in volume due solely to the size mismatch of Cd^{2+} ions in K^+ ion sites. Curve 3 shows the variation of the relative change in volume with concentration when the volume change produced by the equal number of vacancies is also considered together with that produced due to the size mismatch. It is observed from the above results that, at low concentrations, the lattice parameter decreases on substitution of Cd^{2+} as reported in references [10] and [11]. The relation between the relative change in volume ΔV_R and the concentration C of Cd^{2+} ions expressed as mol fraction can now be written as

$$\Delta V_R = -0.1988C \qquad \text{(curve 1)}$$

$$\Delta V_R = -0.3432C \qquad \text{(curve 2)} \qquad\qquad (3)$$

$$\Delta V_R = -0.0932C \qquad \text{(curve 3)}.$$

Curve 4 in figure 1 represents the relation to be expected if the volumes were simply additive [12]. At high concentrations such as 0.17164×10^{-2} and 0.19754×10^{-2} mol fraction an increase in lattice parameter is observed and these two points are also plotted
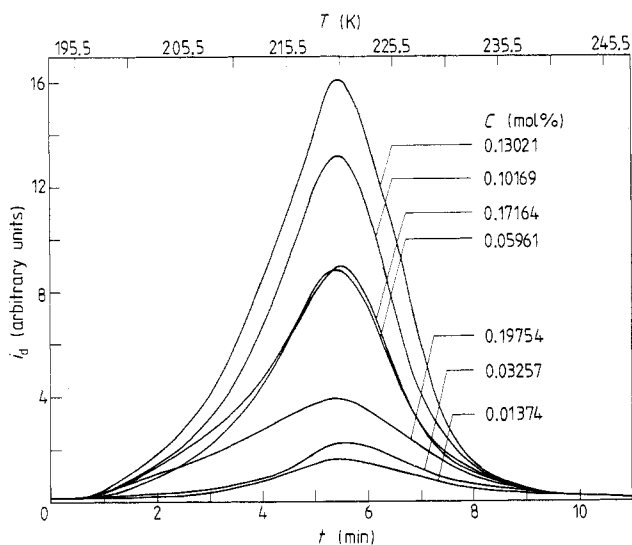
Figure 2. ITC curves of samples containing different concentrations of Cd^{2-} in KCl.

in figure 1. It is interesting to note that the two points lie closer to the curve 4. Though the situation here at high concentrations is not clear, it should be mentioned that precipitation of the compound $CdCl_2.6NaCl$ occurred in the mixed crystal NaCl: $CdCl_2$ containing a few mol % of $CdCl_2$ [13].

3.2. ITC measurements

The ITC curves of samples containing different amounts of Cd^{2+} are shown in figure 2. The peak at 220 K is due to the I–V dipoles. The ITC curves were analysed to calculate E_a and τ_0 using the method of Bucci *et al* [8, 9]; here E_a is the activation energy for the reorientation of the I–V dipoles and τ_0 is the inverse frequency factor associated with it. The calculated values are $E_a = 0.61$ eV and $\tau_0 = 8.01 \times 10^{-13}$ s. The area delimited by the dipole peak is proportional to the total number of isolated dipoles, assuming that a cluster of two or more dipoles has a negligible dipole moment. The number of free non-interacting dipoles N_d at each concentration is given by

$$(Q/A)_{100} = N_d p_0 f_{(100)}(p_0 E_p/kT_p)$$

and

$$(Q/A)_{110} = N_d p_0 f_{(110)}(p_0 E_p/kT_p)$$

(4)

where Q is the total charge released, determined from the area enclosed by the ITC curve, A is the electrode area, p_0 is the electric dipole moment and f is the alignment function. It is found that the alignment function $f_{(110)}$ is twice $f_{(100)}$. This clearly indicates that the number of dipoles alignable when the field is applied along (110) is twice the number alignable when the field is along (100). The variation of N_d with concentration N_0 (figure 3) shows that N_d increases linearly with N_0 at low concentrations and decreases at high concentrations.

It is known that the divalent cations and vacancies associate together to form higher-order complexes than dipoles and this has been the subject of many investigations [13–
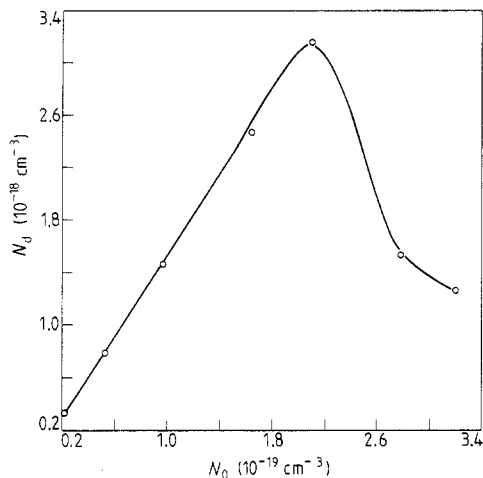
Figure 3. Variation of the total number of non-interacting dipoles with Cd^{2+} content in KCl.
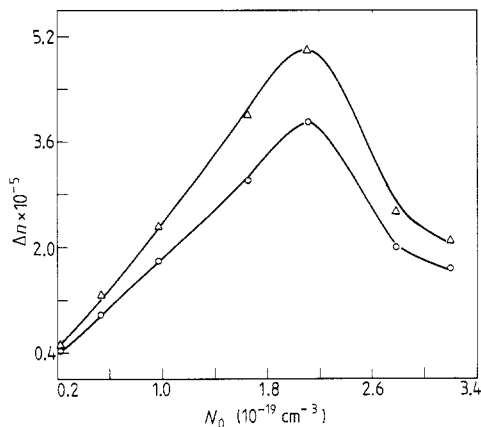

Figure 4. Variation of the birefringence with Cd^{2+} content in KCl for $E = 6\,kV\,cm^{-1}$ at $\lambda = 632.8$ nm for the two field configurations $E \parallel (100)$ (○) and $E \parallel (110)$ (△).

16]. Suzuki [13] examined the mixed crystal $NaCl:CdCl_2$ containing a few mol % of $CdCl_2$ using an x-ray method and concluded that the diffused reflections are due to precipitation of the compound $CdCl_2 . 6NaCl$. Others [14–16] studied the decay of I-V dipole concentration in KCl and NaCl with time, either by dielectric absorption or by the ITC method, fitted the experimental data with a chemical rate equation and concluded that the aggregation consists of the growth of higher-order complexes. Thus at high concentrations the dipole–dipole interactions can lead to the formation of dimers, trimers and higher-order complexes and consequently N_d, the number of free dipoles, decreases.

3.3. Kerr effect measurements

The variations of the observed birefringence Δn with the concentration of the impurity N_0 in $KCl:Cd^{2+}$ when the external field is applied along the (100) as well as along the (110) direction are shown in figure 4 and the following features are observed.

Table 2. The Kerr constants $(R_{1111} - R_{1122})$ and R_{1212} of KCl containing different concentrations of impurity Cd^{2+} and Br^- ions at $\lambda = 632.8$ nm.

System	Impurity concentration (mol%)	$(R_{1111} - R_{1122})$ $(10^{-17} \text{ m}^2 \text{ V}^{-2})$	R_{1212} $(10^{-17} \text{ m}^2 \text{ V}^{-2})$
$KCl: Cd^{2+}$	0.013 74	0.6763	0.4428
	0.032 57	1.6118	1.0507
	0.059 61	2.9504	1.9206
	0.101 69	5.0194	3.2792
	0.130 21	6.4080	4.2013
	0.171 64	3.2800	2.0940
	0.197 54	2.7665	1.7822
$KCl: Br^-$	0.1	0.0608	0.0425
$KCl: KBr$	20.0	0.1414	0.0988
$KCl: KBr$	60.0	0.2356	0.1531

(1) The measured birefringence is three orders of magnitude greater than that observed in pure alkali halides, though the applied electric field is one order smaller.

(2) At low concentrations the birefringence Δn increases linearly with defect concentration N_0, goes through a maximum and at high concentrations starts decreasing.

(3) When the applied electric field E is along the (110) direction, the observed birefringence is different and greater than that observed when E is applied along the (100) direction.

The Kerr constants are calculated using the relations (1) and (2) and are given in table 2. The Kerr constants of KCl containing three different concentrations of Br^- ions studied are also given in table 2 and it is observed that the magnitude of the Kerr constants is about two orders less than that of $KCl: Cd^{2+}$ but it is, however, greater than that of pure KCl by three orders.

It is interesting to note that the three features mentioned above have also been observed in the case of $KCl: CN^-$ [4].

Except at low concentrations, where Δn decreases with concentration initially, the other two features above have been observed in $KCl: Cu^+$ [5, 7].

Now consider figure 5, where Δn is plotted against N_d for both $E \parallel (100)$ and $E \parallel (110)$. It is clear that Δn is linear in N_d in the low-concentration regime and at high concentrations, as N_d decreases, the values of Δn do not fall on the same line and are actually above it.

The observed birefringence can be attributed to the following two processes that occur under the external electric field.

(1) *Polarisability anisotropy of the ions.* The electronic polarisability α of an ion depends upon the environment in which it is situated. The introduction of defects into alkali halides removes the cubic symmetry of the lattice at and around each defect site. The local electric fields present now introduce a tensorial nature to the polarisability of the ions. The external applied field enhances the local electric fields, which in turn cause distortion of the electron clouds of the ions. Then each ion can be characterised by an electronic polarisability tensor. Consequently, the anisotropy in these microscopic polarisabilities of the ions will lead to the development of a macroscopic birefringence
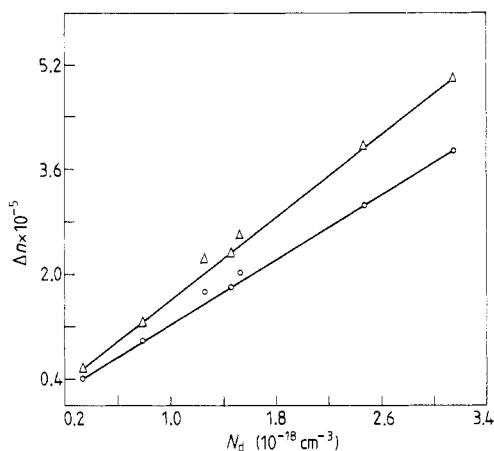
Figure 5. Variation of the birefringence with the total number of non-interacting dipoles available at each concentration of Cd^{2+} in KCl for the two field configurations $E \parallel (100)$ ($\bigcirc$) and $E \parallel (100)$ ($\triangle$).

in the crystal. In the absence of the external field the defects are oriented randomly and therefore the crystal is optically isotropic and no birefringence is observed.

(2) *Deformation of the crystal.* Deformation of the crystal occurs when an electric field is applied due to electrostriction. This means that in the description of the electro-optical effect we must allow for the change in the optical constants due to the deformation, caused here by the electrostrictive effect.

In the case of pure alkali halides the electrostrictive elasto-optic contribution possesses the same order of magnitude as the effect arising from the polarisability anisotropy [17]. Theoretical work on the basis of the shell model [18] applied to NaF and NaI shows that the sign of the Kerr effect is governed by the electrostrictive elasto-optic contribution.

Studies [19] on the electrostriction of alkali halides containing substitutional impurities such as KCl: Li^+, RbCl: Ag^+ and KCl: OH^- show that there are three independent contributions to the field-induced macroscopic strain and that the electrostrictive effect in RbCl: Ag^+ is about two orders larger than that in the pure crystal.

In reference [4] the authors attributed the measured Kerr effect to the anisotropy $(\Delta\alpha = \alpha_\parallel - \alpha_\perp)$ of the CN^- polarisability tensor and calculated $\Delta\alpha$ using the Lorentz–Lorenz relation

$$(n^2 - 1)/(n^2 + 2) = \tfrac{4}{3}\pi \, \alpha N \tag{5}$$

where n is the refractive index of the system of N randomly oriented non-interacting dipoles each with average polarisability α. The fact that CN^- has an intrinsic electric dipole moment allows one to calculate the anisotropy $\Delta\alpha$ from the measured Kerr effect in KCl: CN^-. But in other systems, namely KCl: Cu^+, KCl: Pb^{2+} etc, the electric dipole moments attached to the defects cannot in any way contribute to the change in the refractive index other than through electrostriction.

Hence, in conclusion, the enhancement of the Kerr constants of KCl: Cd^{2+} is from two contributions, namely

(i) the polarisability anisotropy (chiefly of impurities) and

(ii) the electrostrictive elasto-optic effect; these two effects coexist in the system under high electric fields.

At low concentrations the birefringence increases linearly with defect concentration since the two processes by which birefringence is produced increase in proportion to the concentration in the low-concentration regime.

The birefringence observed when the electric field is applied along (110) is greater than that observed when the field is along (100) because of the tensorial nature of the electronic polarisability of the ions and also due to the alignment of a greater number of I-V dipoles (as revealed by the ITC results) contributing to the electrostrictively induced birefringence. However, the relative importance of one over the other is still not clear.

In addition to these studies on divalent impurities in KCl, more experiments are being performed on KCl: Mn^{2+} in order to understand completely the relative importance of either of the two processes which lead to the Kerr effect under high electric fields.

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