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ELECTRICAL TRANSPORT AND POLARIZATION IN DEFORMED ALKALI HALIDES

by

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Introduction. — In recent times there has been renewed interest concerning the creation of point defects in deformed alkali halides. Earlier experiments [1] on the so-called Gyulai-Hartly effect (excess conductivity) have been re-examined, in the light of new experimental results. Different interpretations have been proposed, some of which are in definite contrast to Seitz's original idea, based on positive-ion vacancy production.

Fishback and Nowick [2] suggest, for instance, that the enhancement of ionic conductivity during deformation is sufficiently explained in terms of pre-existing vacancies, which are set free in large numbers when the vacancy clusters surrounding dislocations are broken up. According to them, fresh vacancies are probably also formed: their mobility, however, is not in accordance with the observed size of the excess conductivity, unless an unreasonable rate of production is postulated. Other authors [3] claim that the very existence of the G.-H. effect is still open to question; indeed, the entire field is so deeply complicated by the potential effects of the moving dislocations, to justify the question whether a true conductivity increase has ever been determined. Accepting completely this line, all speculations about the production of defects would be idle; the argument, however, underlines correctly the present situation, and the need for more basic experiments.

Recently, the authors have published the first results of d. c. conductivity measurements performed during steady-state deformation [4]. From a study of the enhancement which is observed in these conditions, it was possible to establish a picture, whereby the role of very mobile defects — other than vacancies — was motivated. These carriers were tentatively identified as excess anion interstitials, since there are hints in

Résumé. — Lorsqu'on mesure la relaxation diélectrique de cristaux d'halogénures alcalins en cours de fluage uniforme, on trouve des caractéristiques très différentes de celles des mêmes cristaux non déformés ou pré-déformés. La réponse en c. c. des échantillons montre une nouvelle composante, plus importante que la relaxation naturelle du diélectrique normal; la cinétique du phénomène est aussi différente. Cette relaxation «anomale» est accompagnée par la formation de charges localisées: l'importance de ces charges correspond au courant de relaxation intégré. A partir de ce fait, ainsi que de la loi temporelle et du comportement en fonction de la température, on peut formuler l'hypothèse que la relaxation anomale est un processus composé, dans lequel un mécanisme essentiellement dipolaire (déplacement des charges liées aux dislocations) est activé et contrôlé par les porteurs en excès introduits par la déformation plastique.

Summary. — Measurements of electric relaxation have been performed in alkali crystals that were undergoing steady-state deformation, and the relaxation behaviour was found to be remarkably different from that of undeformed or predeformed crystals. The observations, based on the d. c. response of the specimens, have shown the presence of a new component in the relaxation current, which predominates at finite times over the natural relaxation of the unstrained dielectric, and follows a different kinetics. The enhanced relaxation is associated, in the end, with the formation of a space-charge, and the size of this charge corresponds closely to the time-integral of the relaxation current. This fact, together with the results on the time-law and temperature dependence of the phenomena, seems to suggest that the anomalous relaxation is a composite process, whereby an essentially dipolar mechanism (displacement of dislocation-bound charges) is activated by the presence of excess carriers due to deformation.
the literature that this species may have a very high mobility in alkali halides [5]. However, the alternative of pre-existing vacancies could not be ruled out entirely.

The developments described here are parallel to the previous d.c. measurements; they are aimed to complete the informations obtained from the study of conductivity. In this direction there remained two major points to be checked:

1) the possibility that sustained dielectric changes, due to deformation, be responsible for the apparent conductivity, hitherto ascribed to defect transport.

2) the entity of space-charge formation (if any) in the deformed crystals, and its relationship to the presence of true point defects.

The following is a description of the results obtained so far in this line.

**Experimental.** — In our experiments the d.c. response (relaxation) of a simple circuit is observed, following sudden application or withdrawal of a finite e.m.f. The circuit (see Figure 1) contains a capacitor DD, and the crystal under examination is mounted between the capacitor plates. Insofar as the conductive losses of the crystal remain negligible, charge and discharge of the capacitor are governed by a time-constant $RC$, i.e. by the resultant capacity and by the external resistor alone. When, however, the conduction loss is increased, for instance by acting on the crystal with plastic flow, one expects charge and discharge currents to follow a different time-law. Now the process is controlled also by the leakage conductance of the «imperfect» dielectric, and eventually by the kinetics of charge relaxation within the sample.

The aim of the present experiments was to determine the relaxation behaviour of non-deformed vs. deformed samples, in order to have a further check on the *excess conductivity* induced by deformation. The experimental set-up, shown schematically in figure 1, was essentially the same [4] used for d.c. measurements.

In a typical experiment the crystal is placed inside the vacuum-tight compression cell, where it is mounted between two massive metal plates (acting at the same time as the squeezing device, and as capacitor plates). The compression movement is provided by coupling to an Instron Tensile Machine. Before any deformation starts, a charging run is performed, by

![Fig. 1. — Experimental set-up (schematic).](image)
closing suddenly the capacitor plates over a dry-cell battery, in series to the external resistor. The charging current $I_c(t)$ is measured and recorded. After that, a discharge run is performed, by excluding the battery and shunting the charged crystal over the resistor. Now, the discharge current $I_d(t)$ is measured and recorded. After observing the behavior of the non-deformed sample, a continuous cycle of deformation at constant speed is started; then further observations are performed, by repeating charging and discharging experiments at regular intervals, as deformation proceeds. A record of the stress acting on the sample is also taken, in order to link the electrical phenomena with the mechanical history.

**Results.** — Fig. 2 illustrates the scheme of our procedure, and gives a qualitative summary of the results obtained on KBr and KCl. This figure emphasizes what happens following the application of on-off voltage steps to the same crystal, under different conditions corresponding to:

- a) no deformation of the crystal,
- b) only elastic deformation in progress,
- c) plastic deformation in progress.

In case b) (i.e. during the short stage of elastic deformation) charge and discharge currents were seen to have the same features as in the undeformed case a), namely a single «fast relaxation» tail, of time constant $\sim 0.5$ s., matching the original RC constant of the external circuit.
In case c) (i.e. during deformation) two additional features stand out. The first is the enhancement of the asymptotic current $I_\infty$: obviously, this effect shows up only in the charging run, when a quiescent electric field is present. It corresponds to the well known excess conduction, studied in a previous work [4]. The second, and new effect is a modification in the net charging current $[I_e(t) - I_\infty]$, or in the discharging current $I_d(t)$. This effect takes the form of an appreciable slow-decaying tail, which is superposed on the fast $RC$-relaxation of the undeformed case, and dominates at times larger than a few seconds.

A direct illustration of these phenomena is given for KBr by figures 3 and 4. The first shows the record of a charging run, performed before deformation of the sample: the response here is very fast, having decayed completely within about 4 seconds. The second shows the record of a charge/discharge run, performed when continuous deformation was acting on the sample: an appreciable relaxation takes place in this case, and can be followed for times of the order of 30 seconds after each application of the field.

It must be re-emphasized that the anomalous relaxation tails are associated with the presence of plastic flow. No trace of these phenomena appears when the voltage steps are applied in the absence of deformation. In this sense, as-received samples and pre-deformed samples are perfectly similar.

The analysis of the relaxation currents was usually made starting from plots of log $[I_e(t) - I_\infty]$ or log $I_d(t)$ vs. time. The experiments were repeated at several temperatures in the range from R. T. to $\sim 110$ °C. Some plots obtained in this way, and referring to KBr, are shown in figure 5; the different curves are taken from experiments which were performed at the same rate of strain (approx. $2 \times 10^{-4}$/s). These results illustrate the typical behaviour of KBr, and can be summarized as follows:

- the relaxation of anomalous charge and discharge currents follows an exponential time law, with a definite time constant, over a range extending to $30 \sim 50$ s.
- at fixed strain rate, the time constant is independent of temperature (in the experiments of figure 5 its value was for instance $\sim 18$ s at all temperatures explored).

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**Fig. 4.** — Current relaxation in the same sample of fig. 3, following application or withdrawal of the same field. Record taken in the presence of uninterrupted deformation at constant rate (approx. $6 \times 10^{-4}$/s). The current scale is identical to that of fig. (3).
charging currents in KBr during deformation at rate of $-2.5 \times 10^{-4} \text{sec}$

![Graph showing charging currents in KBr](image)

**Fig. 5.** — Plots of anomalous relaxation currents vs. time, in KBr at several temperatures. Independent cycles performed under the same strain rate. The R. T. data refer to a charge-discharge cycle on the same specimen. The currents are reduced to conductivity dimensions.

— the time constant is the same in charging as in discharging cycles (see the R. T. data). The size of the relaxation currents increases with temperature.

A similar illustration is given for KCl in figure 6. Again, one observes that the relaxation current, in the presence of continuous deformation, follows an exponential decay, with a time constant sensibly independent of temperature. The size of the relaxation current increases with temperature.

**Strain dependence and temperature dependence of relaxation currents.** — A series of experiments was performed on KBr in order to establish the effects of strain and temperature. These experiments were carried out, for the sake of consistency, on specimens of the same origin (Harshaw) and of rigorously equal size, normalized by controlled amounts of pre-deformation. The same strain rate ($\sim 2.5 \times 10^{-4} \text{sec}^{-1}$) was used during the different runs.

(*) The absolute size of charge and discharge currents is not, however, always the same: in many cases the values of $I_d(t)$ were found to lie below the values of $[I_e(t) - I_s]$ from the preceding cycle. In other words, the superposition was not fulfilled as closely as in the particular case shown in the figure. This is connected with the strain dependence of our phenomena, discussed in the text.

Figure 7 is an illustration of the results. Here the logarithm of the charging-current-density/electric field is plotted as a function of reciprocal temperature. The curves refer to the following conditions of measurement:

- **Curve a)**: values of net charging current, taken 8 seconds after application of the electric field.
- Set of samples with 1-2 % pre-deformation.
- **Curve b)**: similar to a), from another set of samples with 3 % pre-deformation.
- **Curve c)**: similar to b), from the same set of samples with 5 % pre-deformation.
- **Curve d)**: similar to b), from the same set of samples with $\sim 8$ % deformation.

As a preliminary comment, one can say that the absolute size of the relaxation currents depends markedly on the strain history. In other words, the total charge transported during successive relaxation cycles decreases steadily, with increasing the level of strain at which the experiments are performed. It must be emphasized that this is just the opposite of what happens to the steady-state excess conductivity: this quantity is known to be independent of the strain, within large limits [4].

The strain dependance obviously carries a big complication, and sets a limit to the reproducibility of
the present experiments. There is a minimum time required for the observation of a charge transient, and during that time, deformation continues to operate. Thus the state of the sample changes continuously, and the results of successive cycles cannot be compared on a rigorous scale, since they refer to different strain levels. For this reason it is preferable to work on a large number of independent samples, which have been pre-deformed to a standard strain, and to perform separate runs at different temperatures.

In spite of the above limitations, the experiments of figure 7 seem to prove adequately that the anomalous relaxation currents are thermally activated; the activation law appears to be always the same, irrespective of the particular level of strain at which one operates.

From the plots of figure 7, an average value was derived for the heat of activation, which turned out to be \( Q \approx 0.11 \text{ eV} \). This figure appears to be quite low, and its significance will be discussed later.

Evidence for charge separation. — It is obvious that the enhanced relaxation currents observed during charging or discharging runs must be associated with a relevant separation or recombination of charge. In order to prove charge separation, experiments of the type schematized on the right side of figure 2

**Fig. 6.** — Same as fig. (5), for KCl. The steeper curve illustrates normal relaxation in the absence of plastic flow.

**Fig. 7.** — Temperature dependence of the anomalous relaxation current in deformed KBr. The plotted quantity is \( I(t_0) - I_0 \), taken at fixed time \( (t_0 = 8 \text{ s}) \) after each application of the field. The curves refer to different sets of specimens (see text).
(cycle $d$) have been performed. A crystal is first subjected in the usual way to a charging cycle during deformation. Correspondingly, anomalous relaxation is observed. Then, deformation is arrested, and the crystal short-circuited: no anomalous relaxation is observed at this stage, comparable to that of the charging cycle. In other words, the discharge characteristic of the polarized crystal has apparently reverted to the predeformation behaviour. When, however, deformation of the short-circuited crystal is resumed (even after a waiting time of $1/2$ hour at R. T.) an appreciable back-current is seen to reappear (see final curve of case $d$, Fig. 2). This deformation-induced relaxation in zero field is seen to match approximately, apart from the initial build-up, the magnitude and the decay law of the net charging current observed during the previous run.

Figure 8 is a direct reproduction of these phenomena, as observed in KBr at R. T. In this case, the total charge given back during the «forced» relaxation, as estimated from the area under curve $b$, was $\sim 4 \times 10^{-11}$ Coul/cm$^2$. It is interesting to observe that this figure fits closely the net charge transported during the previous experiment: the latter quantity, extrapolated for a comparable period from curve $a$ (after subtraction of the ordinary relaxation current at short times) was only $\sim 10\%$ higher.

**Discussion.** — From the phenomenological standpoint, the behaviour described in the last Sections can be interpreted in a simple way.

Clearly, «free» charges are made available during deformation of the specimen. Upon application of the field these charges are separated, according to a certain kinetics, giving rise to a characteristic relaxation. The nature of these charges, however, is open to question, and cannot be completely clarified with a study of relaxation kinetics. They might be point-charges; they might equally be bound charges, associated with a bulk-polarization field.

The existence of relaxation in both directions, during experiments of uninterrupted deformation, certainly means that the charges are not transported out of the crystal, nor locally compensated. On the other hand, the polarized charges are unable to relax spontaneously, and their separation becomes semi-permanent when the action of plastic flow is arrested: this means that the charges are easily trapped in the accumulation regions. In view of these facts, two alternative models can be defined:

1) Excess carriers are produced by deformation, and transported by the field; eventually they accumulate at the surface, or in localized regions within the crystal, where they are trapped giving rise to a true space-charge. In this case, relaxation reflects the change of the effective field from the external value to the polarized value or viceversa. When deformation

![Figure 8](image-url)

**Fig. 8.** — *a*) Record of charging cycle on a KBr sample undergoing deformation.

*b*) Record of the following deformation-induced discharge in zero field.

In the interval between the two runs, deformation was arrested and the crystal short-circuited, to allow the «fast» components of polarization to discharge. After 5 mm, deformation was resumed.

Charging e.m.f.: 270 V. Dimensions: .831 cm x .286 cm$^2$. Strain rate: $6 \times 10^{-4}$/s. Scale sensitivity: $8 \times 10^{-12}$ A full scale.
is arrested, anomalous relaxation disappears, since no fresh carriers are available.

2) Deformation perturbs the equilibrium of charged defect clouds surrounding dislocations. This is equivalent to induce a change of the bulk polarizability, and gives rise to displacement currents in the presence of a field. Relaxation in this case reflects the build-up kinetics of the excess polarization. When deformation ceases, the source of polarizability is removed and relaxation disappears. 

Let us suppose, for instance, that mobile defects are produced by deformation: in this case relaxation ceases, the source of polarizability is removed and relaxation disappears. 

Either hypothesis is faced with the following facts, waiting for explanation:

— Relaxation follows a law of the type 

\[ [L(t) - L_a] \sim e^{-t/\alpha}, \]

where \( \alpha \) is independent of temperature.

— The size of relaxation currents, in KBr, is thermally activated with a very low value of the activation energy (\( \sim 0.1 \) eV).

— Spontaneous back-relaxation of the polarized charges is forbidden.

The discussion will be limited here to a simple model based on assumption 2), namely on a bulk polarization mechanism. The reason for this choice is twofold. First, the case is very interesting in itself, since it represents an alternative to the production of excess defects. Secondly, any interpretation based on the exclusive role of mobile defects is unpractical at this stage: even if such carriers were present, it would be difficult to prove directly — at least, in the frame of existing space-charge theories [6] — that a simple exponential relaxation should follow.

The dipolar mechanism can be associated, for instance, with the equilibrium defect clouds existing around dislocation arrays, or dislocation walls. It is known that these clouds are associated with strong local fields [7]. It is conceivable, therefore, that the clouds will normally be rigid and very stable, unless some external perturbation (such as plastic flow) unlocks them: in these conditions, they might become polarizable and acquire a dipole moment.

Let us assume, that, when the electric field is applied, a number of these «potential» dipoles are ready, as a result of progressive flow. At any later time, the net rate of orientation of these dipoles, under the combined action of electric field (tending to polarize them) and plastic deformation (tending to destroy the resultant alignment) can be described, if one assumes: a) a «thermal» orientation time \( \tau \), and b) an average time \( \tau' \) after which an induced dipole is forcibly «depolarized» by mechanical disorder. 

In the simplest hypothesis, the thermal time \( \tau \) will depend on the mobility of the clouds, i.e. on the mobility of the constituent defects. Therefore we consider \( \tau \) as a thermally activated quantity. On the other hand, we expect \( \tau' \) to be dependent from the strain rate, but sensibly independent of temperature.

By means of simple considerations [8] the charging current density, following application of the field, becomes 

\[ I(t) = \frac{N_0 p}{\tau} e^{- \left( \frac{1}{\tau} + \frac{1}{\tau'} \right) t}, \]

where \( p \) is the dipole moment per cm² of a dipole layer, induced by the actual field; \( N_0 \) is the number of dipole layers per unit length in the direction of the field.

It must be observed that expression (1) goes to zero asymptotically: therefore, it accounts only for the transient relaxation stage, and not for the excess steady-state conduction observed at later times. In other words, expression (1) must be identified with the net charging current \( (I(t) - I_\infty) \). In this sense, the presence of the factor \( 1/\tau \) in the pre-exponential agrees very well with our observations on the temperature-activated character of the relaxation currents. Furthermore eq. (1) appears to give a correct prediction of the experimental time-law: the identification is complete, if the quantity 

\[ (1/\tau + 1/\tau') \]

is set equal to the empirical time constant \( 1/\alpha \). But \( \alpha \) was seen to be independent of temperature, whereas the relaxation time \( \tau \) is an activated quantity: therefore it is necessary that \( \tau \geq \tau' \), or \( \tau \geq \alpha \). Referring to the data of sect. 3 on KBr, it follows \( \tau \geq 18 \) s. It is interesting to observe that such a long relaxation time fits in nicely with the observed lack of spontaneous relaxation.

There is, however, a serious difficulty. This is found in the low value of the activation energy for the relaxation currents in KBr, \( Q \simeq 0.11 \) eV. In the present picture, one would expect this quantity to coincide with the migration energy of the individual defects forming the polarizable clouds. Such defects are admittedly vacancies: therefore the figure obtained is much too low.

A detailed appreciation of this problem is premature. The authors suggest that the difficulty might be removed, if it were accepted that mobile carriers, not only dislocation clouds, have a part in these phenomena. Let us suppose, for instance, that mobile defects are produced by deformation:
the polarization of the perturbed clouds would be free to develop, in principle, even if the constituent vacancies were completely immobilized. The new carriers, not the old vacancies, would now provide the vehicle for the displacement currents, thus determining the temperature dependence. On the other hand, the rate of perturbation of the polarizability (due to plastic flow) would remain the controlling agent of the kinetics.

A different view could be taken, opposite to the above suggestion. Let us imagine that the cloud vacancies are always sufficiently mobile to allow unrestricted polarization of the perturbed clouds. In this case, the displacement currents are no longer limited by carriers mobility, and their size must reflect only the size of dislocation charges. According to this view, the heat of activation found here might be checked directly against some recent results [9] on the temperature dependence of dislocation charges.

A critical evaluation of these points is presently being attempted by the authors, in conjunction with new experiments on space-charge polarization and associated internal fields.

Bibliographie

[8] CAMAGNI (P.), MANARA (A.), to be published.