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Radiation-induced Schottky defects in NaCl

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Abstract. It has been found in nominally pure NaCl single-crystal samples that have been either gamma irradiated, plastically deformed or quenched into liquid nitrogen from 700 °C, that an additional quenching with a short residence time at the quenching temperature reveals the presence of dipolar defects by means of ionic thermocurrent (ITC) measurements. This procedure does not induce ITC signals in untreated samples. Since the occurrence of divacancies and divacancy clusters in plastically deformed or quenched samples is expected, it is pointed out that gamma irradiation may also form divacancies. The fact that all the ITC spectra of the samples treated in the above-indicated ways exhibit peaks at similar temperatures also supports this view.

The parallelism observed between the stored energy spectra of these samples and the evolution of the ITC areas against the quenching temperature indicates that the two phenomena are related. The occurrence of dipolar defects is consistent with a previous proposal: that the stored energy release is due to the recombination of divacancies with alkali halide molecules.

1. Introduction

Damage induced by ionizing radiation in alkali halides has been a very active research subject in the past few decades. The photolytic mechanism leading to the formation of F centres and interstitial halogen atoms as well as the tree of lattice defects derived from these primary defects are now well understood phenomena (see, for example, Itoh 1982, 1989). To detect the occurrence of parallel damage in the cation sublattice has always been a rather elusive experimental task and it has received little attention. The group led by Professor Ch Lushchik has devoted much effort in the study of, mostly by optical techniques, the formation of defects in the cation sublattice (Lushchik *et al* (1991) and references therein). Their study includes the optical detection of divacancies (Schottky defects) induced by treatments such as quenching, plastic deformation and irradiation.

The thermal recovery of the ionic conductivity of alkali halides, that have been either x-irradiated, thermally quenched or plastically deformed, exhibit rather similar features, which led us to propose that the formation of dipolar defects occurs in alkali halides irradiated even at a low dose (Vignolo and Alvarez Rivas 1980). The induction period observed in the formation of colloids in alkali halides irradiated above room temperature also indicates that some structural changes, which might be divacancy clustering, have to take place before colloid formation occurs (Hodgson *et al* 1983, Hughes and Lidiard 1989). On the other hand, from a series of studies of the stored energy in alkali halides, that have been either irradiated, quenched or plastically deformed, it was concluded that similar lattice defects are induced by these three types of treatment, and that in irradiated samples most

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of the observed energy release does not involve the thermal annealing of lattice defects related to the formation of F centres (Jiménez de Castro and Alvarez Rivas 1985, hereafter paper I). Further studies of the lattice defects related to the stored energy release indicate that in irradiated samples they coalesce near the crystal surfaces. It was again proposed that clusters of divacancies could account for the stored energy (Jiménez de Castro and Alvarez Rivas 1990). It is worth noting that stored energy induced by ionizing radiation in MgO and Al_2O_3, in which a photolytic mechanism is not known to occur, has also been observed (Jiménez de Castro *et al* 1987).

The purpose of this paper is to present some results obtained by ionic thermocurrent (ITC) measurement, a technique developed by Bucci *et al* (1966), which show the dipolar character of the defects involved in the stored energy release of alkali halide crystals after the above-indicated treatments. The results again suggest that Schottky defects might well be directly induced by ionizing radiation in alkali halides. Previous ITC results in electron irradiated KCl by Stott and Crawford (1972) led them to propose the formation of lattice defects involving the cationic sublattice also.

2. Experimental

Nominally pure Harshaw NaCl single-crystal samples have been used in this work. A block $3.4 \times 2.1 \times 2$ cm^3 was irradiated in Co^{60} gamma source up to 5.7 Grad after being annealed at 700 °C for 30 minutes in dry nitrogen. To avoid contributions from the surface (Jiménez de Castro and Alvarez Rivas 1990) slabs about 1 mm thick were removed from all the block faces after irradiation. Samples cleaved from the irradiated crystal core did not exhibit any ITC signals.

The quenched samples were prepared by heating up to 700 °C in air and after 10 minutes at this temperature they were dropped into liquid nitrogen. In the as-quenched condition a very small ITC signal was observed. It faded away in a few hours. To study the effect of plastic deformation the samples were deformed in a hand vice. As-deformed samples show a rather unstable ITC spectrum (see below) which could be related to well known conductivity transient effects (Whitworth 1976). This mostly disappears a few hours after deformation.

Since it is assumed that the divacancies, which are supposedly involved in the stored energy release of samples that have been either irradiated, quenched or plastically deformed (paper I), are aggregated forming dimers, trimers or even microcavities, no ITC signals should be expected, in agreement with the experimental results indicated in the above paragraphs. By trial and error it was found that a convenient procedure to provoke at least a partial dissociation of these aggregates is to quench the sample into liquid nitrogen after a short residence time (2 minutes) at each temperature. This procedure shall be called flash quenching hereafter. It was also checked that this flash quenching does not induce ITC signals in samples which had not been previously either irradiated, plastically deformed or quenched from 700 °C.

The ITC measurements were made with samples about 1 mm thick on which silver electrodes were painted. The samples were mounted in an Oxford cryostat model CF1204 and cooled down to liquid nitrogen temperature with a 700 V polarization from 270 K. After removing the polarization field, the sample was connected to a Keithley 617 electrometer and heated at 3.5 K min^{-1}. The experimental installation was checked with a NaCl:Ca (80 ppm) sample for which ITC signals in agreement with reported results (Bucci *et al* 1966) were obtained. It is worth noting that the intensity of the ITC signal in the calcium doped sample is several times lower than the intensity of the ITC spectra of the irradiated or deformed samples here presented.

3. Results

The ITC measurements have been made in samples irradiated at 5.7 Grad, samples quenched from 700 °C to liquid nitrogen temperatures, and samples plastically deformed. More details have already been indicated in the experimental section. These treatments were as close as possible to those used on the NaCl samples, to obtain the stored energy spectra reported in paper I.

It has been found in treated samples that in two consecutive ITC runs after a flash quenching the intensity of the second ITC spectrum is less than half the intensity of the first one. This was found to be a serious problem when applying the usual techniques to isolate the ITC peaks, in order to obtain their thermal activation energies and frequency factors, because to apply these techniques several consecutive measurements have to be made. This fast decrease of the ITC signal also indicates that in addition to the thermally induced dipole reorientation there is a fast diffusion process leading to dipole aggregation. This process is somewhat faster than that found for the impurity-cation vacancy dipoles in NaCl samples doped with divalent cation impurities, where the level of the ITC signal is well observed for several days after the disaggregation quenching process (Cussó *et al* 1978, Unger and Perlman 1974). This fact is consistent with the already noted difficulty of detecting free dipoles in as-treated samples. On the other hand this fast aggregation process poses some problems in the application of ITC models in which only dipole reorientation is taken into account. It can affect, for example, the shapes of the ITC peaks.

The results for each treatment shall be presented under separate headings.

3.1. Irradiated samples

Platelets of size 8×6 mm^2 and thickness ranging between 0.6 and 1.1 mm were cleaved from the central region of an irradiated single-crystal block. Figure 1(*a*) shows the ITC spectra of samples flash quenched at temperatures between 175 and 320 °C. In spite of some scatter it can be seen that the main ITC peaks occur at about 190, 210 and 220 K. Figure 1(*b*) shows the value for P_0/E_p (P_0 being the total sample polarization, that is the area under the ITC spectrum, and E_p the polarization field), versus the quenching temperature. P_0/E_p is proportional to the sum of the products of the concentration of each dipolar species times the square of the corresponding dipolar moment. The evolution of P_0/E_p follows fairly well the thermal release (or spectrum) of the stored energy reported by Jiménez de Castro and Alvarez Rivas (1990) for similar samples irradiated at 15 Grad. The shape of the stored energy spectrum does not depend markedly on the irradiation dose as can be seen by comparing it with the results in paper I, where the stored energy spectra of samples irradiated at 7.5 Grad are also reported. It should be noted that the samples in paper I had irradiated surfaces and therefore their stored energy spectra exhibit, in addition to peaks at 140 and 260 °C (bulk), the surface contribution reflected by peaks above 400 °C.

3.2. Plastically deformed samples

NaCl platelets were strained along their shortest dimension between 15 and 45% in a hand vice. In the as-deformed condition these samples exhibit the ITC spectra present in figure 2. These spectra are rather unstable as can be seen from the figure, where they are obtained

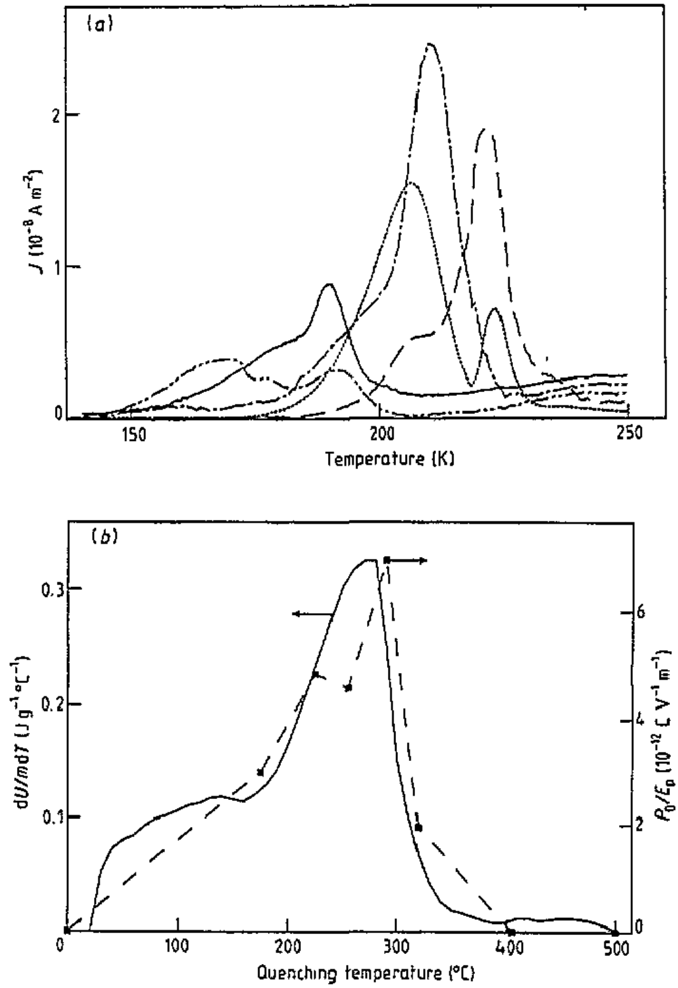

Figure 1. (*a*) ITC sprectra for NaCl samples gamma irradiated up to 5.7 Grad and quenched from: 175 (——), 225 (– – –), 255 (— —), 290 (— · —) and 320 (— · · —) °C. (*b*) The dependence of P_0/E_p (P_0 being the ITC area and E_p the polarization field) on the flash quenching temperature for a gamma irradiated sample (squares) and its corresponding stored energy spectrum (full curve, taken from Jiménez de Castro and Alvarez Rivas (1990)).

at twenty hour intervals. The ITC signal above 230 K clearly depends on the polarization temperature, thus it may arise from space–charge polarization (Kessler 1976), which is also consistent with the large ionic conductivity increase observed in strained samples (Vignolo and Alvarez Rivas 1980). Three peaks at around 170, 190 and 215 K appear. The last two peaks are not observed in a second run made just after the first one. To avoid this unstable situation the flash quenching procedure in the deformed samples was delayed at least five days after deformation.

Figure 3(*a*) shows the ITC spectra obtained for increasing quenching temperatures in samples strained between 20 and 30% (several samples have had to be used because they are rather brittle). These spectra exhibit, besides a small peak at 165 K, two main peaks at about 195 and 210 K. Since the maxima of the peaks above 225 K depend on the polarization temperature, these are likely due to space–charge effects also. Figure 3(*b*) shows the value

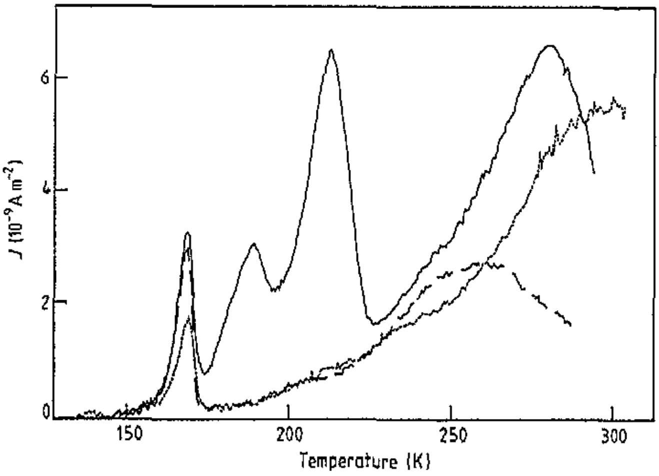

Figure 2. ITC spectra after deforming a NaCl sample up to 44%, obtained at twenty hour intervals for the following polarization temperatures: 270 (——), 286 (- - -) and 250 (— —) K.

for P_0/E_p as a function of the quenching temperature. The trend of the P_0/E_p values roughly follows, up to 600 °C, the stored energy spectrum of a NaCl sample deformed at 40%, which was reported in paper I.

3.3. Thermally quenched samples

As was mentioned in the experimental section the quenching treatment used, in which the samples are heated at 700 °C for 10 minutes and then dropped into liquid nitrogen, induces a barely detectable ITC signal. However if the flash quenching procedure is afterwards applied to these samples, ITC spectra are clearly observed, as shown in figure 4(a). These spectra, which correspond to different quenching temperatures, present neat peaks at temperatures around 170, 185, 195 and 220 K. It should be noted that the ITC signals for quenched samples are smaller than in samples that are either irradiated or plastically deformed. The values for P_0/E_p versus the quenching temperature are presented in figure 4(b). They recall the stored energy spectrum of samples equally quenched (paper I), which is also shown in this figure.

4. Discussion and conclusions

It has been noted that the flash quenching procedure is not able to produce a measurable amount of dipolar defects in the as-cleaved samples of nominally pure NaCl. Dipolar defects are however produced by this procedure in samples that have been previously either thermally quenched, plastically deformed or irradiated with gamma rays. Hence it has to be concluded that these three treatments are able to produce some precursors from which dipoles are released by the flash quenching procedure. The occurrence of ITC peaks at close temperatures (table 1) for these three treatments indicates that the treatments produce the same types of dipoles.

Over the years it has been recognized that both thermal quenching and plastic deformation are processes in which divacancies and divacancy clusters or even microcavities are produced (Kear and Pratt 1959). Thus it is not at all surprising that divacancies could

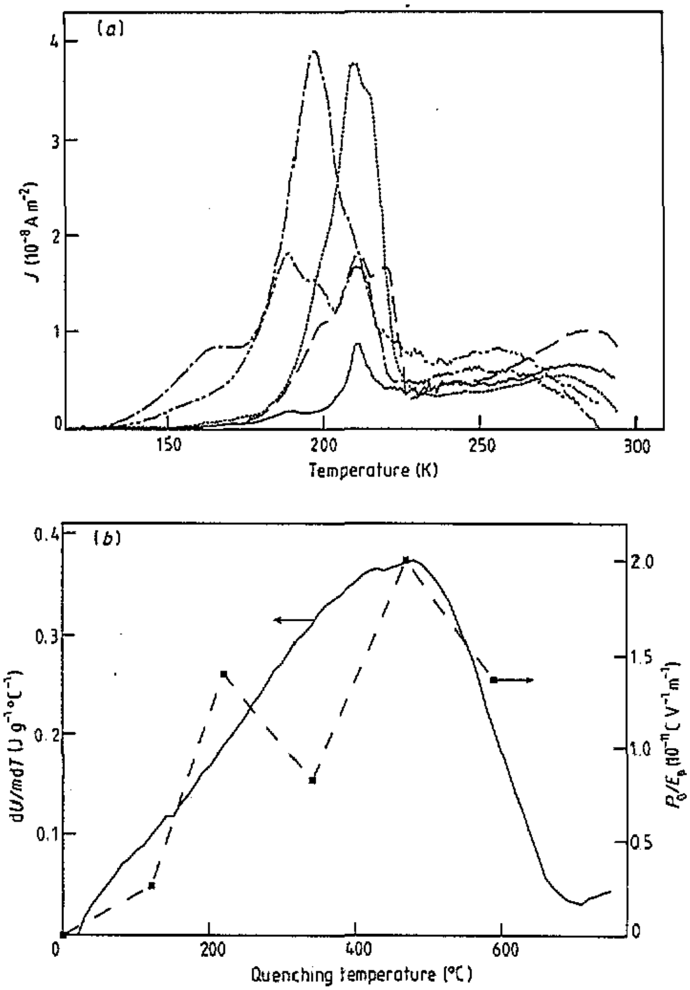

Figure 3. (*a*) ITC spectra for NaCl samples plastically deformed (22–30%) and quenched from: 120 (——), 220 (- - -), 340 (— —), 470 (— · —) and 590 (— · · —) °C. (*b*) As figure 1(*b*) for deformed samples (stored energy spectrum taken from paper I).

be thermally released from these precursors. The most important point to be noted here is that gamma irradiation induces the same ITC pattern as plastic deformation or quenching. This strongly suggests that ionizing radiation also induces divacancies which mostly form clusters. The occurrence of several ITC peaks reveals that the disaggregation of clusters induced by flash quenching does not produce a single type of dipole, say nn divacancies. Other species with a different dipolar moment or even free anion and cation vacancies may be released by the flash quenching. Their reorientation as well as the observed fast diffusion process can contribute to the ITC spectrum.

Finally, it should be pointed out that the parallelism between the area below the ITC spectra versus the quenching temperature and the corresponding stored energy spectrum indicates that they are related phenomena. This lends support to the proposal of ascribing the stored energy release to the recombination of divacancies, either free or clustered, with alkali halide molecules (Jiménez de Castro and Alvarez Rivas 1985, 1990).

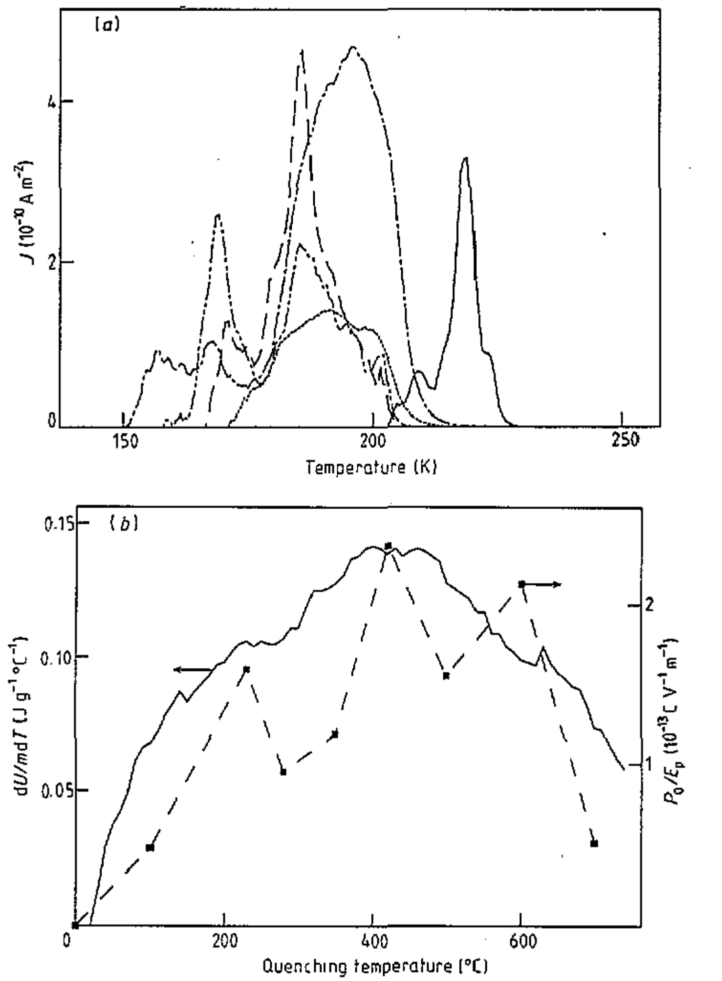

Figure 4. (*a*) ITC spectra for NaCl samples quenched from 700 °C and quenched again from: 100 (——), 280 (- - -), 350 (— —), 420 (— · —) and 500 (— · · —), °C. (*b*) As figure 1(*b*) for quenched samples (stored energy spectrum taken from paper I).

Table 1. ITC peak temperatures for irradiated, deformed and quenched samples.

Sample treatment	ITC peak temperatures (K)				
Irradiation			190	210	220
Plastic deformation	165		195	210	
Quenching	170	185	195		220

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