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LETTER TO THE EDITOR

The surface effect on the stored energy in gamma-irradiated NaCl and LiF

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Abstract. Stored energy measurements of NaCl and LiF single crystals gamma-irradiated at 15 Grad have shown that the energy release occurring at high temperatures is due to the annealing of radiation-induced damage located near the sample surfaces. The low temperature energy release corresponds to damage uniformly distributed within the sample. Although the total energy stored in NaCl samples either by irradiation or thermal quenching or plastic deformation can be close to or even larger than the solution heat of NaCl in water, it has been found that this solution heat is not affected by such treatments. It is proposed that the stored energy spectrum reflects the thermal annealing of radiation-induced divacancies.

It has been shown in a series of papers that ionising radiation induces a relatively large amount of stored energy in alkali halides (Delgado and Alvarez Rivas 1979, 1980, Jiménez de Castro and Alvarez Rivas 1985) and in other insulator materials as MgO and Al₂O₃ (Jiménez de Castro *et al* 1987). Uniaxial plastic deformation and thermal quenching from high temperature also induce stored energy as has been reported in the above references.

This letter is intended to present experimental evidence which indicates that a sizable part of the storing of energy induced by gamma irradiation in alkali halide samples occurs in a region near the sample surface. It is also reported that the large stored energy observed in NaCl does not affect its solution heat in water (Jenks and Bopp 1977).

NaCl and LiF samples with sizes of about $4 \times 2 \times 2$ mm³ and cubes with ridges about 1 cm long were cleaved from pure Harshaw single-crystal blocks. After thermal annealing *in vacuum* at 700 °C, they were simultaneously irradiated at room temperature in a ⁶⁰Co gamma source at 4.3 Mrad h⁻¹ up to 15 Grad. Some samples were kept unirradiated to be used as references to obtain the stored energy spectrum of the irradiated samples with a SETARAM, M-5 model, differential thermal analyser (DTA) operated at 10 °C min⁻¹ with high-purity argon in the sample chamber.

Figure 1 shows the results obtained for NaCl. The full curve corresponds to the spectrum of a small as-irradiated sample. The energy release occurs in two main regions, respectively peaked at about 260 °C and 570 °C. The total stored energy in this sample is about 240 J g⁻¹ of which 60 J g⁻¹ are released below 400 °C. This is consistent with the results for lower doses previously reported (Jiménez de Castro and Alvarez Rivas 1985). It is worth noting that the energy release occurring below 400 °C saturates at about

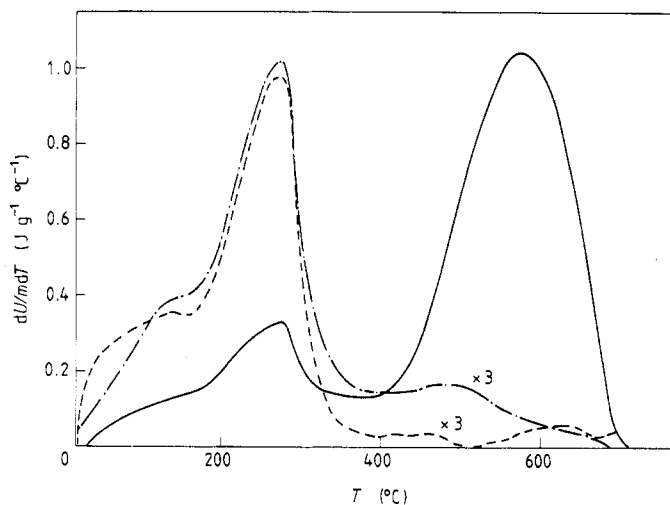


Figure 1. Stored energy spectra of NaCl samples gamma-irradiated at 15 Grad. Full curve, as-irradiated sample; broken curve, sample cleaved from the interior of an irradiated cube; chain curve, sample cleaved from the surface of an irradiated cube.

4 Grad, while that taking place above this temperature does not exhibit saturation up to 15 Grad at least.

The stored energy spectrum of a sample cleaved from the central zone of an irradiated cube is also shown in figure 1 (broken curve). It can be seen that while the energy release below 400 °C (50 J g^{-1}) is similar to that of an as-irradiated sample (full curve), the release above this temperature is irrelevant. It has been found that samples cleaved from irradiated cubes after removal (cleavage) of 0.2 mm thick slabs from the surfaces show a negligible energy release above 400 °C. Furthermore, in small as-irradiated samples dipped in an ethanol–water mixture to remove material from the surface it was found that the high temperature energy release decreases as the removal of material proceeds, and after removal of a layer of thickness about 0.1 mm (as calculated from the decrease in sample weight) the energy release above 400 °C practically vanishes. Infra-red spectroscopy of powder scratched from the surface of as-irradiated samples did not show any presence of nitrates.

Figure 1 also shows the stored energy spectrum (chain curve) of a sample cleaved from the surface of an irradiated cube. A release of energy is clearly observed above 400 °C (15 J g^{-1}), while below this temperature the energy release is about 50 J g^{-1} . The small dispersion in the values obtained for the energy release below 400 °C for these three samples reflects the reproducibility of this DTA procedure. This pattern is also observed in figure 2, where the results for LiF samples corresponding to those for the above-described NaCl samples are presented. It was also found that LiF samples cleaved from irradiated cubes after removing surface slabs of 0.2 mm thickness do not exhibit energy release above 470 °C. The energy release below this temperature is about 200 J g^{-1} , while the total energy release in the as-irradiated sample is about 650 J g^{-1} .

An obvious conclusion from these results is that the defects annealed at low temperatures are uniformly distributed within the sample while those annealed at high temperatures are formed near the sample surface.

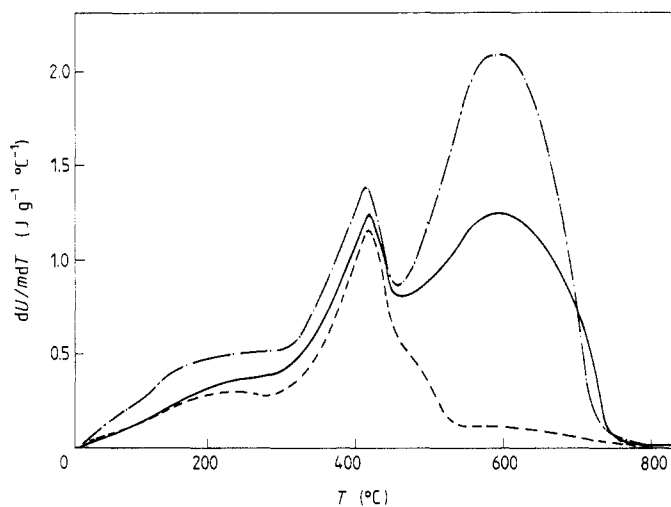


Figure 2. As figure 1 but for LiF samples.

A rather different type of result will now be presented. Jenks and Bopp (1977) reported an extensive study of the stored energy in NaCl mostly gamma-irradiated at dose rates and total doses comparable to those used in this work. They report results obtained with a drop-calorimeter, using analytical chemistry techniques and using a calorimetric method that measures the difference between the heats of solution of irradiated and unirradiated salts. No more specific information on this calorimetric method is reported. The stored energy values obtained by this method were about half of those resulting from the drop-calorimeter.

Measurements of the heat of solution of NaCl samples either irradiated or quenched or plastically deformed were also made. It was noted that the stored energy in pure gamma-irradiated Harshaw NaCl (about 12 cal g^{-1} for a dose of 5.6 Grad), as well as the values obtained in quenched or plastically deformed samples (Jiménez de Castro and Alvarez Rivas 1985) are close to or even larger than the heat of solution of NaCl in water, i.e. 15.88 cal g^{-1} . The heat of solution is the difference between the lattice electrostatic (Madelung) energy and the energy of solvation of the lattice ions in water. It seems sensible to expect that although the variation in the lattice energy (3.12 kcal g^{-1}) produced by the stored energy resulting from the above-indicated treatments is rather small, it should nevertheless affect the solution heat of treated NaCl samples. The heats of solution of a set of samples including some irradiated at 5.6 Grad, some quenched from $650 \text{ }^\circ\text{C}$ to room temperature, some plastically deformed up to 25% and some as-cleaved were measured. For this set of samples the average value of the heat of solution obtained is $16.06 \pm 0.6 \text{ cal g}^{-1}$, compared with the tabulated value of 15.88 cal g^{-1} . This result seems to disagree with that reported by Jenks and Bopp (1977) for the stored energy obtained by heat of solution measurements.

In the discussion of these results it should first be noted that the energy release occurring in the low-temperature regions of the stored energy spectra, which seems to be related to damage uniformly distributed in the sample, has values of $8 \times 10^{20} \text{ eV g}^{-1}$ and $3 \times 10^{21} \text{ eV g}^{-1}$, respectively, for NaCl and LiF samples irradiated at 15 Grad. Since the estimated F centre–interstitial recombination energy is quite a way below 10 eV per

recombination, an unexpectedly high concentration of vacancy centres, based upon F centres and their corresponding interstitial halogen atoms, should have occurred in these samples if their recombination is to account for such an energy release. It can therefore be concluded, as was also the case for the whole energy spectrum (Delgado and Alvarez Rivas 1980, Jiménez de Castro and Alvarez Rivas 1985), that even this energy release taking place at low temperatures is *not* mainly due to the annealing of F centre related defects.

The storage of energy through thermal quenching and through plastic deformation, as well as the fact that the effect of irradiation on the ionic conductivity of NaCl and KCl (Vignolo and Alvarez Rivas 1980) only vanishes after thermal annealing at temperatures at which the stored energy is completely released, led to the proposal that radiation-induced divacancies (a vacancy pair) might be involved in the stored energy effect (Jiménez de Castro and Alvarez Rivas 1985).

Evidence has been presented that there is a large damage build-up near the surface where the formation of divacancies might be easier than in the bulk. No saturation of this damage has yet been observed. On the other hand, it has also been found that NaCl samples either irradiated or quenched or plastically deformed do not show any variation in their heat of solution in water, although they stored energy to values similar to and even larger than this heat of solution. This is consistent with the formation by irradiation (as by the other treatments) of microcavities (divacancy clusters) and some surface roughening or reconstruction, but it is not consistent with the formation of Frenkel-type defects that are effective in varying the electrostatic energy. These results allow us to insist on the previous proposal, namely that the observed stored energy originates from the thermal annealing of radiation-induced divacancies.

It is plausible that exciton recombination, in addition to the well established F centre-interstitial production in alkali halides (Itoh 1982), might also generate divacancies when it occurs at dislocations (surfaces) according to a forty year old proposal by Seitz (1946, 1954) which, to our knowledge, has not yet received clear experimental support.

Interference effects between both branches of defect formation might well occur in the radiation-induced dislocations (Hobbs *et al* 1973) and in the induction period observed in the formation of colloids in alkali halides irradiated above room temperature (Hughes and Lidiard 1989 and references therein). This induction period indicates that some structural changes, which might be divacancy clustering, have to take place before colloid formation. It has been reported by Swyler *et al* (1979) that the induction period is reduced by prior plastic deformation and prior irradiation followed by annealing and that it increases again to the as-cleaved value when the sample is annealed, after irradiation, at temperatures at which the radiation-induced stored energy is completely released (Hodgson *et al* 1983).

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