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Positron annihilation in colourless centres in heavily gamma-irradiated NaCl

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Abstract. A detailed study of positron lifetimes in heavily gamma-irradiated NaCl single crystals, which undergo a pulsed thermal annealing treatment up to 740 °C, is presented. Above 300 °C, at which temperature the samples are completely bleached, two exponential terms suffice to fit the lifetime curve. While the shortest lifetime τ_1 does not depend upon the annealing temperature and has a value close to that found in unirradiated samples, the other lifetime τ_2 exhibits a monotonic increase with annealing temperature and two recovery stages at about 340 and 540 °C. This pattern parallels the thermal recovery of the ionic conductivity of irradiated NaCl. It is suggested that τ_2 reflects the annihilation of positrons at cation vacancies thermally released from radiation-induced divacancies. The τ_2 evolution with the annealing temperature has been analysed in terms of a trapping model and a value of 1.96 ± 0.08 eV for the divacancy formation enthalpy is obtained.

1. Introduction

A great deal of both experimental and theoretical work on positron annihilation in alkali halides has been carried out since the beginning of the seventies (Dupasquier 1979). However, the positron states in these materials are not yet well understood. In lifetime measurements with nominally pure specimens, there are discrepancies between different results not only in the number of resolved exponential decay components but also on their origin. In particular, for NaCl the presence of two lifetimes is generally accepted; the shortest is assigned to the annihilation of the positron in a free state, while the second one corresponds to positrons trapped at some kind of defect (Linderoth *et al* 1986, Pareja 1988).

The complication increases when defects are introduced either by doping, irradiation, plastic deformation or quenching. The effect of cation additive colouration is the appearance of an additional long-living component which has been attributed to the annihilation of positrons at F-centres (Dupasquier 1979, Ramasamy *et al* 1980). It is known that colour centres, colloids, interstitial aggregate centres and other complex lattice defects are produced by irradiation in alkali halides. Since a large variety of such defects can be effective as positron traps, it is difficult to identify their corresponding effects on the lifetime spectrum. In consequence, there is not much agreement between different authors on the effects of irradiation on the positron states in alkali halides (Brandt *et al* 1971a, b, Brandt and Paulin

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1973, Nicholas *et al* 1973, Dannefaer *et al* 1978, Dedoussis *et al* 1985, Annenkov *et al* 1986). It seems clear that such a complex situation can not be unravelled by only studying the exponential decays occurring in the positron decay curve: firstly because the sensitivity of the method is limited and secondly because the coalescence and recombination of different defect species might preclude the observation of single exponential decays corresponding to each type of defect.

A large variety of techniques have been applied to the study of radiation-induced defects in alkali halides. Stored energy measurements in gamma-irradiated NaCl single crystals have shown that the F-centres and other related defects (vacancy and interstitial centres) might be a small part of the total number of lattice defects induced by irradiation in this material (Jiménez de Castro and Alvarez Rivas 1985). They found that during the thermal annealing of heavily irradiated NaCl samples there is a thermal energy release even at temperatures above 300 °C at which all the colour centres and colloids have already disappeared (Ausín and Alvarez Rivas 1974). Guided by the fact that the thermal recovery of the radiation effects on the ionic conductivity also occurs at temperatures at which colour centres have already been annealed (Vignolo and Alvarez Rivas 1980), it has been proposed that the stored energy observed in these materials is also due to the thermal annealing of radiation-induced divacancies. The presence of radiation-induced dipolar defects in NaCl identified by means of ionic thermocurrent measurements has been recently reported (Mariani *et al* 1994).

We present here positron lifetime measurements on unirradiated and heavily gamma-irradiated NaCl single crystals and the evolution of their lifetime parameters as the samples are thermally annealed from room temperature up to 740 °C. The main purpose of this work is to observe the existence of radiation-induced defects affecting the positron annihilation lifetime in the temperature range where the colourless centres (divacancies) are thermally annealed.

2. Experimental details

Conventional fast–fast lifetime equipment with two BaF_2 detectors has been used. The time resolution (FWHM) was 250 ps for ^{60}Co and the time calibration was 18.7 ps/channel. The source, $^{22}NaCl$ (about 10 μCi) sealed in a Kapton foil (1.42 g cm^{-3}), was sandwiched between two samples.

Sets of two NaCl Harshaw samples were cleaved from a single-crystal block (1 cm^3) which was previously gamma irradiated in a ^{60}Co source (dose: 5.7 Grad), and from an as-received block.

The samples were annealed at increasing temperatures from 200 to 740 °C with a residence time of 10 min and then measured at room temperature; each spectrum has about 10^6 counts. The spectra were analysed by the POSITRONFIT program (Kirkegaard *et al* 1981) without constraints. No source correction was made.

3. Results and discussion

The time spectrum of unirradiated samples has been fitted with two exponential decay components; the values obtained agree with those reported for this material by Linderoth *et al* (1986). A three-terms fit, as suggested by other authors (Kerr *et al* 1978) yields a very low value for I_3 (less than 1%) and does not substantially improve the variance of the fit. However, for irradiated samples a third component ($\tau_3 = 1000$ ps, $I_3 = 6\%$) has

been necessary in order to fit the data. Table 1 shows the values obtained for unirradiated samples with two components as well as two- and three-component fits for the irradiated samples. The presence of this new long-living component is well known in both additively coloured and irradiated alkali halides and it has been associated with F-centres (Dupasquier 1979, Dannefaer *et al* 1978).

Table 1. Lifetime positron parameters for unirradiated and gamma-irradiated NaCl.

NaCl	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	χ^2
Unirradiated	236_5	47_2	458_4	53_2	—	—	1.176
As-irradiated	297_2	85_1	738_{12}	15_1	—	—	1.364
	262_{19}	58_{18}	424_{70}	37_{16}	1000_{150}	6_2	1.265

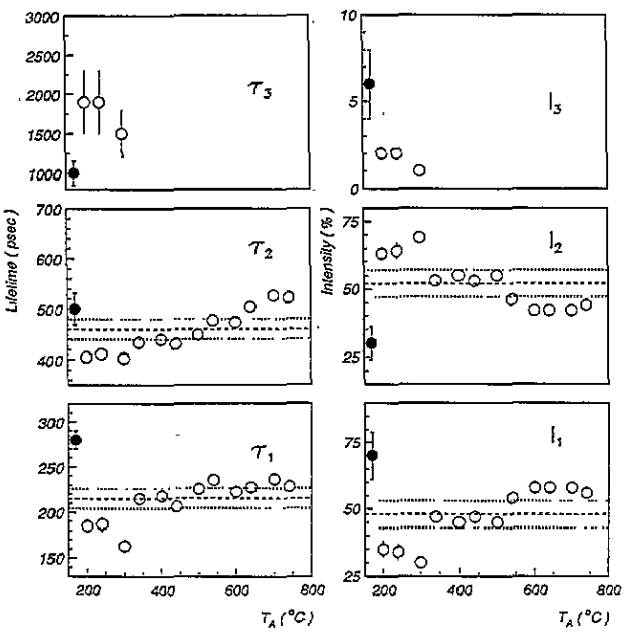

Figure 1. Lifetime parameters versus the annealing temperature. Open symbols correspond to irradiated samples during thermal annealing. Filled symbols correspond to samples in the as-irradiated condition; therefore the temperature reading for these full circles is actually room temperature. The horizontal dashed and dotted lines represent the mean values and their corresponding statistical errors of unirradiated samples respectively.

Figure 1 shows the corresponding lifetime parameters versus the annealing temperature obtained for both unirradiated and irradiated samples. The horizontal dashed and dotted lines represent the mean values and the statistical error band of the parameters (τs, Is) obtained in unirradiated samples respectively. It can be concluded that the isochronal annealing treatment does not affect positron annihilation in unirradiated samples. The empty and full circles correspond to irradiated samples. Error bars are included when they are larger than the circle size. Full circles correspond to samples in the as-irradiated condition and they are plotted at an arbitrary temperature.

For irradiated samples (open symbols) three zones can be clearly distinguished: from

RT to 300 °C, from 340 °C to 500 °C and above 540 °C. The results are reproducible for the different sets of irradiated samples used.

In the first region, below 300 °C, the results are better described by a three-terms fit. This third component can be attributed to F-centres created by irradiation (Dannefaer *et al* 1978) as indicated above. It should nevertheless be noted that F-aggregate centres are also formed by irradiation and that, moreover, during the thermal annealing process new aggregate centres and even colloids are formed by the accretion of F-centres. All these defect species disappear at 300 °C (Ausín and Alvarez Rivas 1974). It seems plausible to assume that the value of τ_3 reflects an average value of the positron annihilation lifetime in this class of centres. This is consistent with the fact that above 300 °C a third component is not necessary. In this region a drastic decrease in τ_1 and τ_2 is also observed, while τ_3 increases after the first annealing at 200 °C. The intensities also show significant variations. Since the correlation of positron annihilation with colour centres is not the purpose of this work, this point is not analysed any further.

Through the rest of the temperature range the time spectra are analysed in terms of two lifetime components. After heating at 340 °C the four fitting parameters exhibit steps and the material seems to recover the unirradiated condition, but this is not the case. The fitted parameters τ_2, I_1, I_2 are nearly constants from 340 to 500 °C, while τ_1 is essentially constant up to 740 °C. However, above 500 °C it is found that τ_2 monotonically increases; this trend in the value of τ_2 indicates that some thermally induced defects appear. Since this trend in τ_2 is not observed in unirradiated samples, these new defects have to be originating from radiation-induced defects other than the colour centres mentioned above, which are already annealed at these high temperatures.

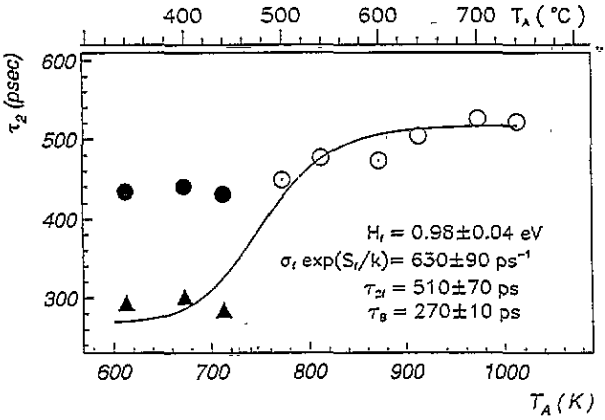

Figure 2. τ_2 versus the annealing temperature. Open circles are the fitted values for τ_2 for the irradiated samples above 500 °C. The triangles are the bulk lifetime values obtained using equation (3). Full circles are the values for τ_2 before radiation-induced traps are thermally released. The full line is the result of a least-squares fitting using equation (1) (see the text).

The above considerations lead us to conclude that there are, at least, two processes involved in the sample recovery starting around 340 and 540 °C.

The variation of the second lifetime, τ_2, has been analysed with a trapping model (West 1979), which essentially assumes that there are different types of traps in the solid and that the escape rate of positrons from these traps is negligible compared to the decay rate. Using these reasonable hypotheses one can define an independent lifetime, τ_{2f}, for the positron annihilation in a new kind of trap, which in this case are thermally released above 500 °C

from some radiation-induced precursors. These traps compete with other positron traps in the trapping process from the bulk state, τ_B. Figure 2 displays the thermal evolution of τ_2 from 340 °C. If we assumed that the experimental values above 500 °C for the second lifetime are mean values between two different states (the positron bulk state (full triangles) and the radiation-induced trap state (open circles)), we can write:

$$\tau_2 = \tau_B[(1 + K_f\tau_{2f})/(1 + K_f\tau_B)] \tag{1}$$

where K_f is the rate of transition between the bulk state and the τ_{2f} traps. This rate is given by

$$K_f = \sigma_f \exp(S_f/k)\exp(-H_f/kT) \tag{2}$$

where σ_f is the trapping rate per unit concentration of defects; S_f and H_f are the defect formation entropy and enthalpy respectively; k is the Boltzmann constant and T the annealing absolute temperature. The bulk lifetime values used in the fit (full triangles) are calculated using the trapping model. This time is expressed as

$$\tau_B^{-1} = I_1\tau_1^{-1} + I_2\tau_2^{-1} \tag{3}$$

where I_1, I_2, τ_1, τ_2 are the experimental values for each temperature between 340 and 440 °C. Fitting the data on the basis of equation (1) using a non-linear least-squares fitting program the following values were obtained (solid line in figure 2): $\tau_B = 270 \pm 10$ ps, $\tau_{2f} = 510 \pm 70$ ps, $\sigma_f \exp(S_f/k) = 630 \pm 90$ ps^{-1} and $H_f = 0.98 \pm 0.04$ eV. The determination of the τ_{2f} value is not accurate because few points have been measured in the high-temperature region due to the proximity of the melting point. The value obtained here is nevertheless consistent with an estimation by Brandt (1967) for the positron annihilation time (500–650 ps) at a cation vacancy. It does not agree with the value of 340 ps reported by Dannefaer *et al* (1976) but such a low value of τ_{2f} is not consistent with the nearly constant values of τ_1 obtained in this work as is shown in figure 1.

The electric carriers in the ionic conductivity of alkali halides are the cation vacancies. The ionic conductivity of these materials is depressed by irradiation with x- and γ-rays and the thermal recovery of the free cation vacancy concentration in NaCl exhibits a small step at 320 °C; about 90% of the recovery occurs between 400 and 550 °C (Vignolo and Alvarez Rivas 1980). These authors ascribe these two steps to the release of cation vacancies from the divacancies associated with radiation-induced dislocation loops and from small radiation-induced divacancy clusters. Since cation vacancies are favourable sites for positron trapping it seems sensible to point out that the trend of the sigmoidal curve in figure 2 might well reflect the above-mentioned release of cation vacancies found by ionic conductivity measurements at about 400 °C. In this case, since positrons are not trapped at anion vacancies, H_f may be associated with the cation vacancy formation enthalpy. In pure stoichiometric alkali halides the enthalpy of formation of Schottky defects (an anion (a) plus a cation (c) vacancy), H_S, is given by $H_S = H_a + H_c = 2H_f$ (Allnatt and Lidiard 1993). Then the following divacancy formation enthalpy results: $2H_f = 1.96 \pm 0.08$ eV, in reasonable agreement with the value 2.1 eV reported by Dannefaer *et al* (1976).

It has to be noted that quite close effects on the ionic conductivity were also observed in plastically deformed and quenched samples (Vignolo and Alvarez Rivas 1980). Positron lifetime studies on quenched and deformed NaCl samples are in progress in order to obtain additional support on the nature of these colourless centres by means of their effects on the lifetime parameters.

4. Conclusions

The evolution of the positron lifetime in heavily gamma-irradiated NaCl single crystals, which are thermally annealed up to 740 °C, is presented. The long-living component $\tau_3 \simeq 1000$ ps, which is ascribed to F-centres, vanished above 300 °C. This is consistent with the annealing of all colour centres at 300 °C in these samples.

Above this temperature two exponential decays suffice to fit the decay curves. The shortest lifetime τ_1 is practically constant through the whole annealing temperature range and its value is close to that observed in unirradiated samples. On the other hand τ_2 shows an overall increasing trend as the annealing temperature increases. At about 340 °C it exhibits a step and gets to a value close to that in unirradiated samples. From 500–540 °C τ_2 shows a monotonic increase with the annealing temperature which is not observed in unirradiated samples. It has to be concluded that radiation creates some precursors from which defects suitable for positron annihilation are thermally released. The parallelism between the τ_2 evolution curve and the thermal recovery of the ionic conductivity of irradiated NaCl suggests that the precursors might be radiation-induced divacancies from which cation vacancies are thermally released.

By fitting the experimental τ_2 values above 500 °C with the trapping model, we obtained reasonable values for the positron lifetime at a cation vacancy and for the formation enthalpy of a divacancy.

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