20th Annual Meeting of the
Radiation Research Society,
Portland, Oregon, May 14-18-1972

CONF-720530--6
Appendix III

THERMAL ANNEALING OF RADIATION DAMAGE IN
NaCl CRYSTALS STUDIED BY POSITRON ANNIHILATION TECHNIQUES¹

J. Blair Nicholas, Charles S. Tumosa, and Hans J. Ache
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

MASTER

The thermal annealing of radiation damage induced by gamma radiation in NaCl crystals is studied by positron annihilation techniques. The results show that the concentration of positron annihilation centers (A-center) decreases quickly at first upon heating, but then more slowly until a very slowly decreasing region, a "pseudo plateau" is reached. The A-center concentrations at which these "pseudo plateaus" are obtained depend on the temperatures at which the annealing processes are carried out.

The kinetics of the annealing as observed by the positron annihilation technique is consistent with a bimolecular reaction model. The experimentally obtained activation energy for this process is about 1.2 eV, which suggests the elimination of positive ion vacancies aggregates, which act as positron annihilation centers, by migrating anion vacancies at elevated temperatures.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Introduction

Several studies have been made of the properties of ionic crystals such as NaCl which were irradiated with ionizing radiations.² These investigations showed that the effect of irradiation on the ionic structure, which leads to distinct changes of the optical, mechanical, thermal or electrical properties of the crystals, is determined by the kind, the density, and the state of the defects, formed during the irradiation.

Recently Ache et al.³⁻⁴ and Brandt et al.⁵ found that another property, namely the progress of the positron annihilation process in ionic crystals is also greatly affected when the crystals are subjected to ionizing radiations. The experimental results suggested that positron annihilation centers (A-centers)^{3,5-7} are responsible for the observed changes of the positron lifetimes in the irradiated crystals.

Valuable information about the nature of the radiation damage which is present, e.g. in the form of excess vacancies or interstitials or clusters of such defects in the irradiated crystals, can usually be obtained upon thermal annealing. Thus the study of the kinetics of damage recovery, as observed by the positron lifetime measurements, should reveal further details about the species acting as positron annihilation centers and should allow an assessment of their interactions with other defects during the annealing process in gamma irradiated NaCl crystals.

Experimental

Single crystals of NaCl (obtained from Harshaw Co.) were irradiated with the 30 MeV proton beam of the 60 in. BNL cyclotron.³⁻⁴ The ^{22}Na formed in the reaction $^{23}\text{Na}(p,pn)^{22}\text{Na}$ was believed to be homogeneously distributed in the crystal and provided the source of the positrons. Crystal size was about 4 x 4 x 20 mm with ^{22}Na activity of about 50 μCi . The crystals were thoroughly annealed at 400°C and subsequently subjected to ^{60}Co γ -irradiation in the irradiation facilities at BNL. Total dose was 150 Mrad at a dose rate of 1.25×10^4 rad sec⁻¹. The thermal annealing was carried out by heating the crystals in vacuum to the desired temperature. They were rapidly cooled back to room temperature before each lifetime measurement. The positron lifetime measurements followed the standard procedure using delayed coincidence techniques as previously described.^{3,4,5} The optimum resolving time of the fast-slow timing equipment was 0.35 nsec. The best lifetime values were obtained by decomposing the positron lifetime spectrum into two components. Computational methods developed by Cumming⁹ and Tao¹⁰ were used.

Results and Discussion

Positrons, after being slowed to nearly thermal energies in crystalline NaCl, can annihilate either in the bulk of the crystals at a rate λ_0 or are captured by A-centers at a rate κ , which is proportional to the number of A-centers n_v :⁷

$$\kappa = \text{const} \times n_v \quad (1)$$

The positrons trapped in these A-centers may annihilate as such at a (slower) rate λ_1 , where $\lambda_0 > \lambda_1$, or escape from these traps and annihilate in the bulk of the crystal.³

The capture rate, κ , is related to the observable parameters λ_A , λ_B , and I_B (at moderate defect concentrations) by the equation:

$$\kappa = I_B(\lambda_A - \lambda_B) \quad (2)$$

where $\lambda_A = 1/\tau_A$ and $\lambda_B = 1/\tau_B$. τ_A and τ_B are the lifetimes of the short- and longlived components respectively in the observed positron lifetime spectra. I_B is the intensity of the longlived component.³

In Fig. 1 the observed annihilation rates λ_A and λ_B of the shortlived and longlived component in the positron lifetime spectra are shown as a function of annealing time and temperature. From these experimental data κ , the capture rate, has been calculated using eq. (2).

In Fig. 2 κ is plotted vs. the annealing time at various temperatures. Since κ is proportional to the concentration of A-centers, n_v (Eq. 1), the resulting curve should also reflect the dependence of the latter on the above experimental parameters. It can be seen in Fig. 2 that the A-center concentration decreases quickly at first, but then more slowly until

a very slowly decreasing region, a "pseudo plateau", is reached. Further annealing at an elevated temperature causes again an initial rapid decrease in the A-center concentration followed by a second "pseudo plateau". It should be pointed out that the same second (or third) plateau is obtained when the sample is subjected to the elevated temperature at the start of the annealing procedure (not shown in Fig. 1 or 2).

In previous work evidence was presented which suggested that positive ion vacancies act as A-centers.^{3,5-7} It was pointed out, that the number of effective A-centers, as calculated from the observed maximum κ -value exceeds by far the number of available free cation vacancies present under these experimental conditions.^{5,11}

On the other hand measurements of density changes and of coloration which occur when crystals are irradiated with radiation doses comparable to those absorbed in the present investigation clearly indicate the creation of new vacancies.^{2,12} Ionic conductivity measurements,¹³ however, have shown that the conductivity, which is widely believed to be due to the presence of mobile or free cation vacancies does not show any simultaneous increase upon irradiation. From these findings one might want to conclude that although massive radiation increases undoubtedly the total number of vacancies present in the irradiated crystals they become subsequently immobilized by formation of clusters and aggregates with other defects. Thus the observed increase of κ (or n_v , see eq.1) upon irradiation provides additional evidence for the previously made contention⁵ that the positron annihilation centers are not single free cation vacancies. They are probably made up of aggregates or clusters of cation vacancies, carrying

an overall positive charge, which have become bound to other defects most likely dislocations.

The fact that upon heating κ (Fig. 2) decreases may then be explained by interactions of the A-centers with other defects (A-center traps). As a result of this interaction the capability of the A-center to trap positrons is destroyed and it ceases to function as an annihilation center. If one assumes that the "A-center traps" diffuse randomly and interact when they come accidentally within some distance with the A-centers, the elimination of the latter can be treated as a diffusion limited bimolecular chemical reaction, in which the reacting species are A-centers and "A-center traps".

Waite¹⁴ has analyzed the diffusion controlled reaction rigorously. In the present investigation, however, where relatively long annealing times are involved, a simplified approach originally applied by Ingham and Smoluchowski¹³ in the study of ion conductivity of gamma irradiated NaCl crystals may be used.

It leads to the following equation for n_v , the number of A-centers present after a given time, t , of isothermal anneal:

$$1 - (n_{v\infty}/n_v) = C_0 \exp (-K_e t) \quad (3)$$

$$\text{and } K_e = n_{v\infty} K \quad (4)$$

where $n_{v\infty}$ represents the number of A-centers available after a long time of anneal; K is the rate constant of the bimolecular reaction between A-center and "A-center trap". C_0 is a function of n_{v1} and n_{T1} , the initial concentrations of A centers and "A-center traps" at time t_0 ,

$$C_0 = (n_{T1}/n_{v1}) \exp (-K_e t_0) \quad (5)$$

By keeping in mind that n_v is related to κ by eq. 1 the above model can be tested by plotting $\ln(1-\kappa_\infty/\kappa)$ as a function of annealing time.

This has been done in Fig. 3, where $\ln(1-\kappa_\infty/\kappa)$ is plotted vs. t at three different annealing temperatures, 100° , 150° and 250° . The resulting straight lines support the applicability of the bimolecular model of annealing during the time period under investigation. Exceptions would be the final values of $\ln(1-\kappa_\infty/\kappa)$ observed towards the end of the annealing, when the number of A-centers and "A-center traps" in the crystal is determined by the equilibrium state, in which the rate of A-centers formed is equal to the rate of trapping.

K_e , which can be directly extracted from the graph, remains constant at the various annealing temperatures used in this study. From equations 1 and 4 it follows immediately that K , the reaction rate constant at a given temperature, is reciprocal to κ_∞ observed at the same temperature.

Fig. 4 shows the usual Arrhenius plot where κ_∞ is plotted ^{vs} $1/T$, the reciprocal of the annealing temperature (in $^\circ K$), for various samples of ⁱⁿ gamma or proton irradiated NaCl crystals. The computation results ^{an average} activation energy for the A-center elimination process of about 1.2 eV. A comparison with the known activation energies for motion of simple defects in NaCl shows that the observed activation energy corresponds most closely to that observed for anion vacancy motion, which is about 1.1-1.3 eV.¹⁴ We thus would like to suggest that the positron annihilation centers are aggregates of cation vacancies possibly locked at dislocation which are eliminated at elevated temperatures by migrating anion vacancies. More experimental results are certainly necessary to provide us with a more detailed description of the

annealing behavior of cation vacancy aggregates. The present study, however, seems to confirm the usefulness of the positron annihilation technique as a tool in radiation damage studies.

REFERENCES

1. Work supported by the U. S. Atomic Energy Commission.
2. For a general review on radiation effects in solids, see for example:
 - a) G. J. Dienes and G. H. Vineyard, "Radiation Effects in Solids", Interscience Publ. Inc., New York, 1957.
 - b) B. V. Budylin and A. A. Voreb'ev, "Effect of Radiation on Ionic Structures" Report OTS 64-11095 (1964).
3. C. S. Tumosa, J. B. Nicholas and H. J. Ache, J. Phys. Chem., 75, 2030 (1971). Additional references on the positron annihilation process in ionic solids can be found in this article.
4. T. L. Williams and H. J. Ache, J. Chem. Phys., 51, 3536 (1969).
5. W. Brandt, H. F. Waung and P. W. Levy, Phys. Rev. Lett. 26, 496 (1971).
6. W. Brandt, H. F. Waung and P. W. Levy, in "Proceedings of an International Symposium on Color Centers in Alkali Halides", Rome, Italy, Sept. 1968, p. 48.
7. W. Brandt and H. F. Waung, Phys. Rev. B 3, 3432 (1971).
8. T. L. Williams and H. J. Ache, J. Chem. Phys., 50, 4493, (1969).
9. J. B. Cumming, BNL Reports 6470.
10. S. J. Tao, IEEE Trans. Nucl. Sci., 1968, p. 175.
11. In ref. 3 the authors of this paper calculated a vacancy fraction of about 2.6×10^{-7} on the basis of a model of weak interaction between positrons and lattice, which is considerably smaller than that reported in ref. 5. (2×10^{-5}) (The experimental capture rates were approx. the same in both investigations). It seems that the latter figure, based on a strong interaction and random walk model⁷ is more realistic.
12. Optical measurements in the present investigation have shown no correlation between F-centers and κ . Complete bleaching of the F-centers was accompanied only by an insignificant change of the lifetimes and the corresponding intensities.

The reduction of κ upon thermal annealing was accompanied by a reduction of absorption in the V-band. However, no quantitative correlation between κ and V center concentration could be established.
13. J. S. Ingham and R. Smoluchowski, Phys. Rev. 117, 1207 (1960).
14. T. R. Waite, Phys. Rev. 107, 463 (1957).
15. G.A. Ermakov and E.M. Nadgornyi, Soviet Phys. Solid State, 13, 550 (1971)

Captions

Fig. 1 Positron annihilation rates λ_A and λ_B and the intensity of the longlived component vs annealing time at various temperatures

Fig. 2 Capture rate κ vs. annealing time at various temperatures

Fig. 3 $\ln(1 - \kappa_\infty/\kappa)$ vs annealing time

Fig. 4 $\ln 1/\kappa_\infty$ vs $1/T$ for various irradiated NaCl crystals

- Radiation dose 100 Mrad γ -irradiation
- Radiation dose 150 Mrad γ -irradiation
- Crystals were irradiated with the 30 MeV proton beam of the 60 in. BNL cyclotron³. Total proton dose approx. 10^{17} protons.

Fig. 1 -- Nicholas

2

Fig. 2 -- Nicholas