Fission damage detection and investigation of the annealing behavior in apatite by absorption spectroscopy

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A new method for fission-track detection by means of absorption spectroscopy is presented. Application of the method to the investigation of the annealing behavior shows the following result: Annealing of fission tracks in apatite crystals containing fossil tracks causes a decrease of the characteristic absorption due to a diffusion process. In crystals with freshly induced tracks, however, the absorption fading is partly due to bimolecular recombination.

I. INTRODUCTION

In pure fossil fluor-apatite crystals from Durango, Mexico, the intrinsic absorption at room temperature rises from about 430 nm. As in other materials[1] the position of the absorption edge is slightly dependent upon the concentration of lattice defects, for instance, vacancies[2] and interstitials. Absorption bands due to reactor-neutron-induced atomic displacement have been investigated recently,[3] but so far nothing has been reported about fission-track detection using such absorption bands.

Fission tracks in solids are regions of intense damage created along the path of high-energy-fission fragments (cf. Fleischer *et al.*[4]). Thus, absorption spectroscopy may provide a valuable method to determine the degree of lattice destruction caused by fission tracks. In case of the presently investigated Durango apatite the fission tracks are produced either by spontaneous fission of ^{238}U (fossil tracks) or thermal-neutron-induced fission of ^{235}U.

In the present study, absorption spectroscopy was applied to perform experiments on fission-track annealing in apatite. The time dependence of the reduction of either fossil or freshly induced tracks has been investigated at various constant annealing temperatures.

II. EXPERIMENTAL METHOD

Natural apatite crystals from Durango, Mexico, were cut parallel to the optical axis, ground to slices of about the same thickness (i.e., 190–230 μm), and the surface polished carefully. Afterwards pairs of slices which had exactly the same thickness were inserted into a PYE-UNICAM UV-VIS double-beam spectrophotometer, one piece serving as sample to be studied (test sample), the other (either thermally untreated or preannealed, i.e., stored for 48 h at 733 K, thus containing no etchable fission tracks) serving as comparison blank. (No absorption difference was observed between such preannealed samples which after the annealing process were cooled down either within a few minutes or with a cooling rate of less than 5 K/h.) The logarithmic ratio of the intensities transmitted by each of the two samples ($\log I_1/I_2$) has been recorded at room temperature as a function of wavelength from 290 up to 500 nm (an example is given in Fig. 1). For convenience we shall call this in the following the "absorption difference spectrum" because it indicates the difference of the absorption coefficients of the two samples. The behavior of the characteristic absorption difference (CAD) has been studied as a function of both annealing temperature and annealing time of samples which contained either only fossil or only freshly induced tracks. In the case of fossil tracks the annealing temperatures for the isothermal annealing have been 646, 673, 703, 713, 728, 743, and 758 K, whereas annealing of the freshly induced tracks has been performed until now at 633, 663, and 713 K.
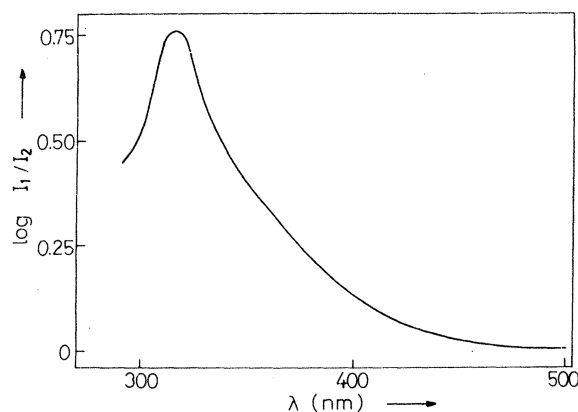
Fresh fission tracks have been induced by ther-

FIG. 1. Absorption difference spectrum of a fossil crystal with a preannealed sample serving as comparison blank.

mal-neutron irradiation in the ASTRA reactor in Seibersdorf, Austria. The neutron fluxes ranged from 1.6×10^{14} up to 1×10^{16} $n\,cm^{-2}$ and were determined by Co monitors. The irradiation was performed without cooling the samples in order to have similar conditions as in fossil track formation.

To check the influence of surface effects the CAD spectrum has also been recorded using a heavily etched (65-vol.% HNO_3, 60-sec, 20 °C) test sample. With exception of a generally reduced transmittance no changes of the CAD have been observed.

III. RESULTS

Absorption difference spectra of thermally untreated fossil samples relative to preannealed samples as comparison blanks show a characteristic broad absorption peak at about 318 nm. This peak is diminished if the test sample has been stored at increased temperatures for a certain time interval. The peak height is reduced further and finally vanishes if this procedure is repeated, whereas the halfwidth of the peak remains quite constant. The annealing behavior is characterized by annealing curves such as given in Fig. 2, showing the CAD peak-height reduction as observed in four isothermal annealing experiments. Attention must be drawn to the fact that annealing experiments at the same temperature, but with different slices, yielded different annealing curves even if the slices were cut from the same crystal.

After thermal-neutron irradiation of preannealed test samples the CAD peak is found to reappear. The freshly induced absorption is less stable under thermal treatment. This can be seen from Fig. 3,

FIG. 3. Isothermal annealing of the CAD in crystals with freshly induced tracks at three different annealing temperatures. Reduction of the CAD peak height as a function of annealing time. There is also shown for comparison an annealing curve of fossil CAD.

where annealing curves of samples with fossil CAD and samples with freshly induced CAD, both for isothermal annealing at 713 K are shown for comparison. Also shown in this figure are annealing curves of samples with freshly induced CAD, which have been annealed at 633 and 663 K, respectively. It can be seen, that the shape of the annealing curves strongly depend on the respective annealing temperature.

The response of the CAD to thermal-neutron irradiation in both, fossil as well as preannealed samples, is shown in Fig. 4 (preannealing has been performed at 743 K for 48 h and the cooling down rate between 743 and 513 K did not exceed 5 K/h). In both cases there seem to be two stages in the increase of absorption: A fast linear rise of the
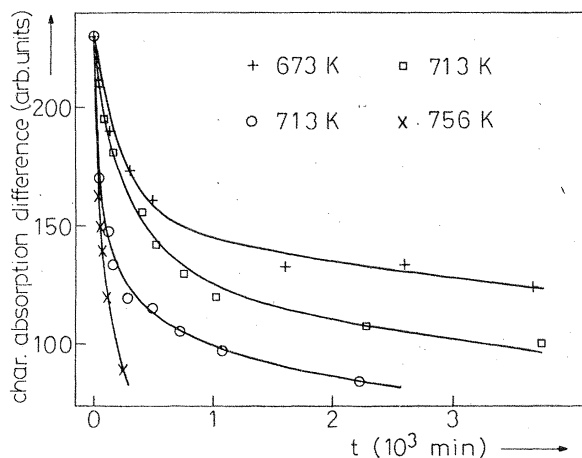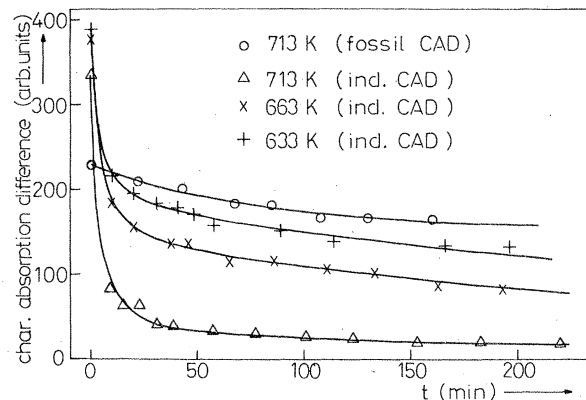

FIG. 2. Isothermal annealing of the CAD in crystals with fossil tracks at three different annealing temperatures. Reduction of the CAD peak height as a function of annealing time.
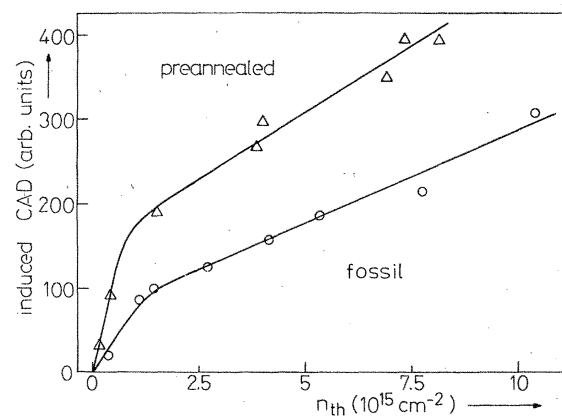

FIG. 4. CAD response to thermal-neutron irradiation. Peak height of freshly induced CAD as a function of the integrated thermal neutron flux in preannealed and fossil samples, respectively.

CAD for neutron doses up to about 1×10^{15} $n\,cm^{-2}$ and a moderate one for higher doses, but also linear. The rate of CAD increase in fossil samples is significantly lower than in preannealed samples.

IV. DISCUSSION

A. Origin of the CAD

It is quite obvious that radiation damage must be the source of the CAD. Let us consider various possibilities of radiation damage: Damage due to α-radiation can be excluded in the case of annealed and subsequently neutron irradiated crystals taking into account that the total number of α-decays arising from (n, α) reactions in apatite at neutron fluxes of 10^{15} $n\,cm^{-2}$ is about 8×10^9 g^{-1}. The only α-source in the crystals under natural conditions is the uranium[5] ($\sim$10 ppm[5]) and its product nuclei contained in the Durango apatite. The number of α-decays during geological periods (i.e., 30×10^6 yr, the age of the Durango apatite determined by the K-Ar and by the fission-track method[6] is about 10^{15} g^{-1}. Thus, the number of α-decays in fossil samples and samples with freshly induced tracks differs by a factor of about 10^5, whereas the observed CAD is of the same order in both cases. Thus, at least in crystals with freshly induced tracks α-radiation damage cannot contribute to the CAD.

The possible influence of β-radiation on the CAD was tested by means of a 68-mC ^{90}Sr source, which was brought into contact with samples containing fossil tracks as well as with samples containing only freshly induced tracks. Only after an irradiation time of about 10 min is a slight increase of the CAD observed. We may expect a comparable β-radiation dose—mainly due to activated ^{32}P—in samples with freshly induced tracks only after a neutron irradiation which exceeds 2×10^{15} $n\,cm^{-2}$. Thus, damage due to β-radiation cannot account for the CAD in total.

The possible influence of γ-radiation was tested with a ^{60}Co source. An irradiation dose of 30 krad caused no observable change in either fossil or induced CAD. Damage caused by atoms knocked on by neutrons in irradiated samples can be ruled out considering that the energy distribution of the neutrons corresponds to temperatures of 350–380 K.

Thus, the only source of radiation-induced disorder in preannealed samples which still can provide an explanation for the CAD is the induced uranium fission. The possibility, however, should be pointed out, that α-radiation may contribute considerably to absorption in fossil thermally untreated samples.
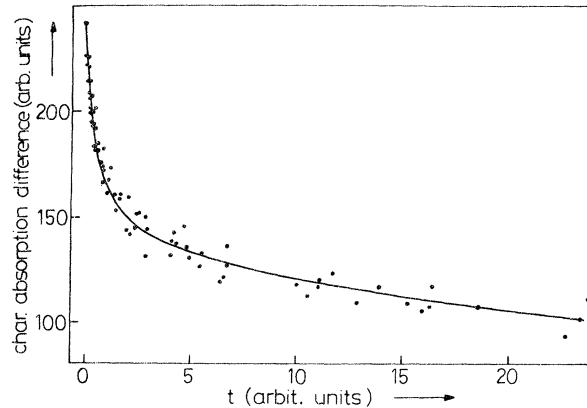

FIG. 5. Combined results of eight annealing experiments at 646, 673, 703, 713, 728, 743, and 758 K on crystals with fossil tracks. Reduction of the CAD peak height as a function of annealing time. The solid line gives a two-component approximation according to (1).

B. Annealing of fossil CAD

According to Smakula[7] and taking into account the quite constant half width of the CAD peak, the peak height can be considered as being proportional to the number of induced defects. This fact has been used in the annealing experiments. The combined data of eight annealing experiments on the CAD in samples with fossil tracks are shown in Fig. 5. (The mode of data dressing will be explained below.) The (measured) points represent the time-dependent decrease of the CAD peak at 318 nm due to annealing as described above. Summarizing the experimental observations the annealing behavior of the CAD in fossil samples can be characterized by the following statements.

(i) Each of the originally different annealing curves can be represented by a function

$$y(t) = \sum_i a_i \exp(-\alpha_i t). \tag{1}$$

(In all cases, a two-component approximation yielded satisfying results.)

(ii) An analysis of the experimental data using the automatic computer program "Discrete Version 1A" by Provencher[8] showed, that the coefficients α_i are not independent but all exhibit the same dependence on the temperature. Thus, it is possible to superimpose the annealing curves for different temperatures by properly adjusting the time scale. This is done in Fig. 5, where the results of eight isothermal annealing experiments have been matched by expanding the respective time scales with appropriate time scaling factors $s(T, \Lambda)$, T being the temperature, Λ an additional parameter, which will be shown below to be the characteristic diffusion length.
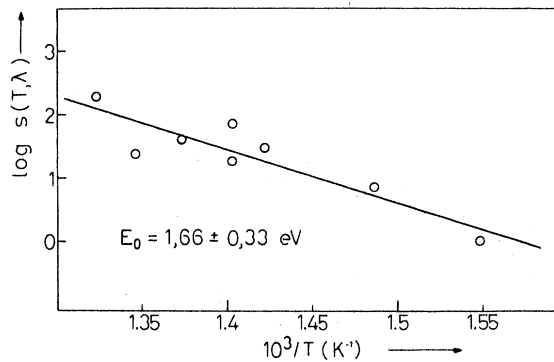
FIG. 6. Arrhenius plot of the time scaling factor $s(T, \Lambda)$ for isothermal annealing of the CAD in crystals with fossil tracks.

(iii) The temperature dependence of the coefficients α_i (or the time scaling factors, respectively) is on the whole given by

$$d \log \alpha_i / d(1/T) = \text{const}, \tag{2}$$

but the points show considerable scatter in an Arrhenius plot $\log \alpha_i$ vs $1/T$ (see Fig. 6).

(iv) The time scaling factors for annealing curves measured at the same temperature were found to be quite different (300%). This permits the conclusion, that the scatter mentioned in (iii) is not due to inaccuracy but should be regarded as a significant fact: Besides time and temperature there must be an additional parameter governing the annealing behavior of the CAD in fossil samples.

Exactly the same characteristics are expected for a diffusion-governed process. The solution of the diffusion equation (cf. Seitz and Koehler[9] and Fletcher and Brown[10]) consists of a sum of (or integral over) exponential decay functions, the time-dependent terms given as $a_i \exp[-D(T)\Lambda_i^{-2}t]$, $D(T)$ being the diffusion coefficient and Λ_i only depending upon geometric factors such as distribution of vacancy and interstitial sinks in the crystal or the macroscopic shape of the sample, respectively. Thus, the annealing of the CAD can be explained in fossil samples as a diffusion process in accordance with the results outlined above.

(i) The time decay is represented by a sum of exponential decay functions. It is true that the theory yields an infinite sum, but it is no surprise that it can be approximated by a two-component function: The annealing time as well as the accurateness of the collected data are finite. Moreover, it is a matter of fact, that a sum of exponential decay functions can be well approximated by a single function of this type (for a detailed discussion of this subject cf. Cukier and Hynes[11]).

(ii) The temperature dependence of the single terms is given by the diffusion coefficient only and

is therefore the same for all.

(iii) Equation (2) represents a temperature dependence as it would be expected for the diffusion coefficient.

(iv) The additional parameter responsible for the deviations mentioned above is provided by the geometric factor Λ_i.

Due to the fact that the parameter Λ_i was not under sufficient control in the experiments, quantitative statements must be treated with caution. Nevertheless a rough estimate of the activation energy may be made from Fig. 6 yielding

$$E_0 = 1.66 \pm 0.33 \text{ eV}. \tag{3}$$

The preexponential coefficients a_1, a_2 in a two-component approximation were found to be of the same order of magnitude a_1—the coefficient of the short-lived component—being about $0.6 a_2$.

C. Annealing of freshly induced CAD

Results for the annealing of the CAD with freshly induced tracks are given in Fig. 3. The samples have been preannealed as described above and were cooled down with a cooling rate of about 4.5 K/h. The main features of the annealing behavior of the freshly induced CAD are the following.

(i) It cannot be described by a function of the type given by Eq. (1), but the annealing at 713 K fits well into the function

$$1/y(t) = 1/y(0) + \beta t, \tag{4}$$

(β being 6.5×10^{-4} min^{-1}).

(ii) The annealing curves of different samples for the same temperature yield the same β value even for different initial amounts $y(0)$ of the induced CAD. Thus, the curves can be matched easily in contrast to the behavior of fossil CAD (see Fig. 7, where the results of three annealing experiments are displayed). The appropriate transformation calibrating the curves to an initial value $ky(0)$, k being an arbitrary constant, results also in a change of the independent variable t into t/k as can be seen from dividing Eq. (4) by the constant k.

(iii) At lower temperatures only the initial part of the annealing curves fit into a function of type (4). Later on, the decay rate is much less and the CAD-decay function seems to approach that of samples with fossil tracks.

Equation (4) represents exactly the time dependence expected for a bimolecular recombination process (cf. Ref. 10). According to the theory the recombination coefficient β in a given type of crystal should only depend upon the diffusion coefficients of the recombining point defects and not upon the geometric features of the sample. This is in good agreement with the experimental result
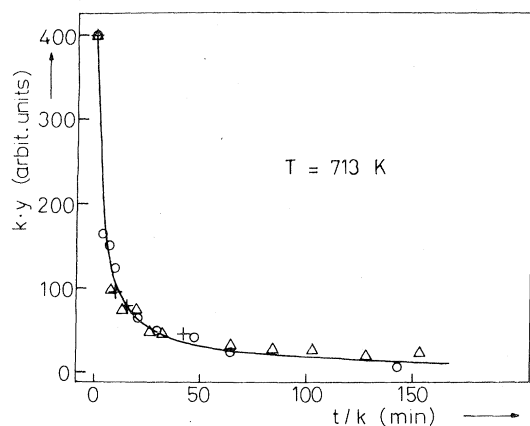
FIG. 7. Combined results of three annealing experiments at 713 K on crystals with freshly induced tracks. The solid line gives an approximation according to Eq. (4).

given in point (ii).

From this the conclusion may be drawn, that at higher temperatures the centers responsible for the freshly induced CAD are annealed by bimolecular recombination with complemental defects. Furthermore, from point (iii) it may be argued that a competing process consuming these complemental defects becomes the more important the lower the temperature is.

D. CAD response to thermal-neutron irradiation

The response curve of the CAD to fission-track production by thermal-neutron irradiation (see Fig. 4) is nonlinear, but it does not exhibit saturation. Thus, it is quite unlikely that a simultaneous "ionic" annealing process (i.e., an annealing of the atomic defects) is responsible for the nonlinearity because all these processes should result in saturation. A resonable explanation for the re-

duced increase rate of the CAD at higher neutron doses might be that the CAD production in this second stage is no longer controlled by the increase of atomic displacement but by another process (perhaps carrier production or annihilation at other atomic defects). Such a process could also account for the difference in the CAD response of fossil and preannealed samples to neutron irradiation. But at the present state of investigations this should be regarded rather as a conjecture than a positive conclusion.

We should also be cautious in applying the above results to etchable fission tracks, because the CAD and the etchability may be due to different defect structures both occurring in the disordered lattice region which is referred to as "fission track." Nevertheless, it should be mentioned that the explanation of diffusion-governed annealing may also apply to the etchable fission tracks, thus revealing that the dependence of activation energies upon the annealing stages commonly found (cf. Ref. 4) is not a physical reality but only a consequence of high-order diffusion modes.

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