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MICROSCOPIC IDENTIFICATION OF THE $F_2^+:O^{2-}$ CENTER FORMATION IN LiF:OH$^-$

ABSTRACT

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It has been stablished the model for the $F_2^+:O^{2-}$ formation in LiF:OH$^-$ irradiated based on a statistical distribution of the defects produced during the electron irradiation at - 30°C. These stabilized centers are formed during the thermal diffusion of the anionic vacancies in competition with the isolated F_2^+ centers. A critical distance of thirteen lattice parameters determined for the vacancy capture suggested that the O^{2-} - α dipole is the precursor entity responsible for the $F_2^+:O^{2-}$ creation.

A lot of efforts has been done by many authors to elucidate the mechanism of $F_2^+:O^{2-}$ center creation in LiF crystals doped with oxygen or hydroxyl ions[1]. By knowing this process one might find a way of increasing its maximum concentration which is currently in the order of magnitude of 7×10^{16} cm^{-3} [2]. One of the difficulties encountered in the increasing of this maximum level of concentration is the fact that the high energy irradiation produces primarily high concentration of F centers and electron traps centers (anionic vacancies, F center itself and impurities centers). These electron traps promove very efficiently the formation of isolated F_2^+ centers which competes very strongly with the formation of the $F_2^+:O^{2-}$ centers.

Until now, it is belived that the $O^{2-}-\alpha$ dipole center is the entity responsible for the creation of the $F_2^+:O^{2-}$ center after the irradiation and difusion of the anionic vacancies in LiF[3,4]. These dipole centers, $o^{2-}-\alpha$, are one of the secondaries products of the OH^- dissociation as a result of the F center capture by the substitutional O^- ion. The presence of this dipole centers in LiF:O and OH^- gama irradiated at 300K, has been reported[5]. Its absorption bands have maximuns at 113 nm and 190 nm according to reference 3. The higher energy absorption band in the near vacuum ultraviolet stays out of the measurable range of the conventional spectrophotomers. The near UV band overlaps with the intense absorption band of the F centers (with maximum at 250 nm). Considering these facts, this dipoles centers are almost impossible to be measured by absorption and emission techniques in irradiated crystals.

Besides that, no one has related before the production of $F_2^+:O^{2-}$ centers with the increasing of OH^- concentration for a fixed dose and temperature of irradiation. We did that for LiF crystals irradiated with electrons of 1.5 MeV at -30°C with a fixed dose of 45 Mrad.

Preliminaries studies of this center formation as function of the dose at three differents temperatures of irradiation showed that -30°C and 45 Mrad are the best conditions for the proposed study. Within these experimental conditions, is observed formation of $F_2^+:O^{2-}$ centers without the presence of F_4 centers with maximum absorption at 540 nm and overlaping with the stabilized F_2^+ absorption band at 600 nm. For higher doses of irradiation and higher temperatures one observes an increasing of F_4 concentration.

The minimum dose of radiation should be higher than 12 Mrad which is necessary to breaks 100% of the OH^- ions present initially in the crystals according to the observation of the absorption band of the OH^- ions at 2.68 µm. Always the $F_2^+:O^{2-}$ center concentration were measured after 24 hours of keeping the samples at room temperature, lack of time necessary to complete destroy all the unstable F_2^+ centers which are produced in competition with the stable ones.

The values of $F_2^+:O^{2-}$ concentration in the differents samples were measured by comparison of the $F_2^+:O^{2-}$ emission intensity at 900 nm with the intensity measured each time for a crystal pattern with a known $F_2^+:O^{2-}$ concentration. In order to have a normalized signal we used a mask of 0.5 nm wide in contact to the luminescence surface from where the emitted light should be collected.

Based on the observation of the optical transparency of fresh irradiated crystals during the warming up to room temperature we states that the electronic irradiation produces only F centers and anionic vacancies. In the first five minutes of thermal treatment, the crystal becomes blueish indicating the formation of F_2^+ centers. These centers are unstable at this temperature and decays with a half lifetime of 3.8 hours. At the expenses of the unstable F_2^+ centers occurs the formation of F_2 and F_3^+ centers making the crystal greenish, due to its strong absorption band at 441 nm and 458 nm respectively.

The production of $F_2^+:O^{2-}$ centers is relationed with the first step of centers aggregation during the diffusion of the vacancies. The experimental values of $F_2^+:O^{2-}$ concentration as function of the OH^- concentration is shown in figure 1. In this case, all the samples were irradiated together with electrons of 1.5 MeV (dose of 45 Mrad) at -30°C. The experimental points could be fitted by using a statistical model involving a critical radius for vacancy capture and the effective OH^- concentration in this process.

Our assumption is that the centers produced by the irradiation are statiscally distributed in the lattice. Also, we presume that most of the oxygen atoms produced in the OH^- dissociation stay negatively charged in the vacancies as O^- centers due to the small interstitial space available in this lattice. Of course, lets keep open the structure of the oxygen-type center which is responsible for the formation of $F_2^+:O^{2-}$ center. Lets represent this center with the symbol X and its concentration with N_X. The vacancies will be represented with the symbol α.

The fraction of α centers, $\frac{N(R)}{N\alpha}$, which will have a X center as the closest neighbor between distance R and R + dR is given by:

$$\frac{N(R)}{N\alpha} = \frac{4\pi R^2}{R_0^3}\,\frac{Nx}{N}\,\left(1 - \frac{Nx}{N}\right)^{\left(\frac{4\pi R^3}{3R_0^3} - 2\right)} \qquad (1)$$

with $R_0^3 = \frac{a^3}{4} = \frac{1}{N}$ (a denotes the lattice parameter). Interating Eq. (1) yields

$$\frac{N(R)}{N\alpha} = \frac{Nx}{N}\,\frac{1}{\ln(1 - \frac{Nx}{N})}\left[(1 - \frac{Nx}{N})^{\left(\frac{4\pi R^3}{3R_0^3} - 2\right)}\right]$$

Lets assume now that the X center capture a vacancy with an efficiency η_0 constant up to some critical distance R_c. For larger distance the capture efficiency, $\eta(R)$ is zero. In this model, the total efficiency of $F_2^+:O^{2-}$ formation is obtained by the summation over all the pairs (X,α) in the crystal yielding:

$$\eta = \eta_0 \sum_{0}^{R_c} \frac{N(R)}{N\alpha} = \eta_0\left(1 - \sum_{R_c}^{\infty} \frac{N(R)}{N\alpha}\right)$$

It is known that $\sum_{R_c}^{\infty} \frac{N(R)}{N\alpha} = \exp(-\frac{4\pi}{3} R_c^3\,Nx)$. So, the concentration of stabilized F_2^+ is given by:

$$N(F_2^+:O^{2-}) = Ns\left(1 - \exp(-\frac{4\pi}{3} R_c^3\,Nx)\right) \qquad (2)$$

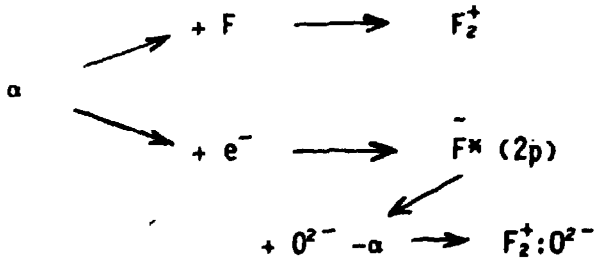
where $Ns = \eta_0 N$.

To test this model, we plot ΔN defined as $\frac{(N(F_2^+:O^{2-}) - Ns)}{Ns}$, in a logarithmic scale as function of the OH^- concentration. The result is presented in figure 2. The obtained fitting is quite good form where we extracted the critical radius for capture $R_c = (13 \pm 0.1)a$ and

$N_s = 2.74 \times 10^{16}\ cm^{-3}$.

It can be noted that there are two mechanisms of $F_2^+:O^{2-}$ formation: one below and the other above N_0, the starting value of OH^- concentration which validates the proposed model. By using $N_x = N_{OH^-} - N_0$ in equation 2 we plotted the predicted curve (solid line in figure 1) from the model. The critical radius of thirteen lattice parameter found for the distance of vacancy capture by the X-center reveals an interaction of the same type as exists between two neighboring F centers being one in the ground state (1s) and the other in the relaxed electronic excited state (2p)[6]. This means that the X center must include one anionic vacancy in its structure. Also this center must have an electronic character similar to the F center ground state in order to trap 2p electrons in a metastable state as an F′ center (one F center with two electrons) and capture the correlationed vacancy to form the $F_2^+:O^{2-}$ center.

Considering the qualities required for the X center, we conclude that this center must be the $O^{2-}-\alpha$ dipole center. The following mechanism of formation is proposed:



We conclude directly from the model that the concentration of $O^{2-}-\alpha$ dipoles is smaller than the N_{OH^-}. By computing the necessary $O^{2-}-\alpha$ dipoles concentration to fit the experimental values of $F_2^+:O^{2-}$

by using the fitted parameters R_c and N_s, we could plot the $N(O^{2-}-\alpha)$ versus the N_{OH^-} as is shown in figure 3. The results can be explained with base on a equilibrium equation between the formation of $O^{2-}-\alpha$ dipoles (rate A) and its destruction (rate B) during the 1.5 MeV electron irradiation. This yields the following equation of dipoles formation:

$$N(O^{2-}-\alpha) = N(O^-)\,\frac{A}{B}\left[1 + \frac{A}{B}\right]^{-1}$$

For low OH^- concentrations, $\frac{A}{B}$ is 0.086 and for higher concentrations than N_0, $\frac{A}{B}$ is the unity. For the last case ($\frac{A}{B} = 1$), the $O^{2-}-\alpha$ dipoles concentration follows the concentration difference between the N_{OH^-} and the N_0. These two regions of $O^{2-}-\alpha$ dipoles formation indicates that for low N_{OH^-} (consequently low O^- concentration) the destruction of dipoles are more efficient than is for the case where $N_{OH^-} > N_0$. This may be correlated with the fact for that such level of O^- concentration a second O^- ion can capture the unbonded vacancy and electron produced in the dissociation process.

One question still remains about the low efficiency of $F_2^+:O^{2-}$ formation. This fact may be due to the enviromental condition that the $O^{2-}-\alpha$ centers have for capturing vacancies in competition with the F centers present in much higher concentrations than the capturer centers. The efficiency of vacancy capture, η_0, by the dipoles can be estimated by the ratio between the initial vacancies concentration N_α and N_s. N_α is obtained by the summation over all types of F aggregated centers produced in the equilibrium at room temperature (F_2, F_3^+ and $F_2^+:O^{2-}$ centers), which was estimated to be in the order of 3×10^{18} cm^{-3}. So, $n_0 \approx 0.01$.

In conclusion, one may increase the saturation concentration of $F_2^+:O^{2-}$ centers if can increase the vacancy concentration presents before the thermal activation process. This may be possible by bleaching some effective amount of F centers at low temperature (below 200 K) with intense laser light.

It was noted that the initial amount the $F_2^+:O^{2-}$ centers produced during the thermal diffusion of the vacancies, increases in the samples stored at room temperature for several mounths. This results are shown in figure 1 (dotted line). This effect probably is due to the small thermal diffusion of the remaining O^{2-} - α dipoles at room temperature which reacts with a neighboring F center. Actually not all the dipoles can be transformed into stable F_2^+ centers but only a small fraction of 1% is obtained after completing the thermal activation process in eight mounths. The remaining dipole centers may aglomarates in a more stable configuration inhibiting the recovery of OH^- ions.

We found that the saturation concentration of stabilized F_2^+ centers initially obtained can be increased by a factor of 1.7 reirradiating the samples with a small dose of gamma rays at 77 K. The results are exhibited in figure 1 (broken line). It is clear that the mechanism of $F_2^+:O^{2-}$ formation after the gamma irradiation still remains inalterable (same R_c).

The results we presented clearly demonstrated the microscopic process of $F_2^+:O^{2-}$ formation and some improvement for increasing its final concentration. This study constitutes an important step for the understanding the role of the OH^- impurity in the stabilization process of laser active centers like F_2^+.

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FIGURE CAPTIONS

Figure 1. Formation of $F_2^+:O^{2-}$ in LiF crystals with variable OH^- concentration. The solid line represents the formation curve measured after remaining the samples 20 hrs at 300 K well after the e^- - irrad. at -30°C (40 Mrad). The broken line shows the effects of a small dose of gamma irradiation at 77 K (0.7 Mrad) and the dotted line the time effect after 8 months at 300 K.

Figure 2. Logarithmic plot of the ΔN defined as $\left(\frac{N(F_2^+:O^{2-})-N_S}{N_S}\right)$, as a function of ΔN_{OH^-}, $N_{OH^-} - N_0$, the displaced OH^- concentration. The use of a simple step function for the vacancy capture gives a good fitting with $R_c = (13 \pm 0.1)a$.

Figure 3. The predicted O^{2-} $-\alpha$ dipoles concentration formed during the e^- - irradiation at -30°C (45 Mrad) by using the fitted parameters R_c and N_s. Towards high OH^- concentration the ratio $\frac{A}{B}$ goes from 0.086 to unity. The A and B represents the rates of formation and destruction of O^{2-} $-\alpha$ centers respectively.

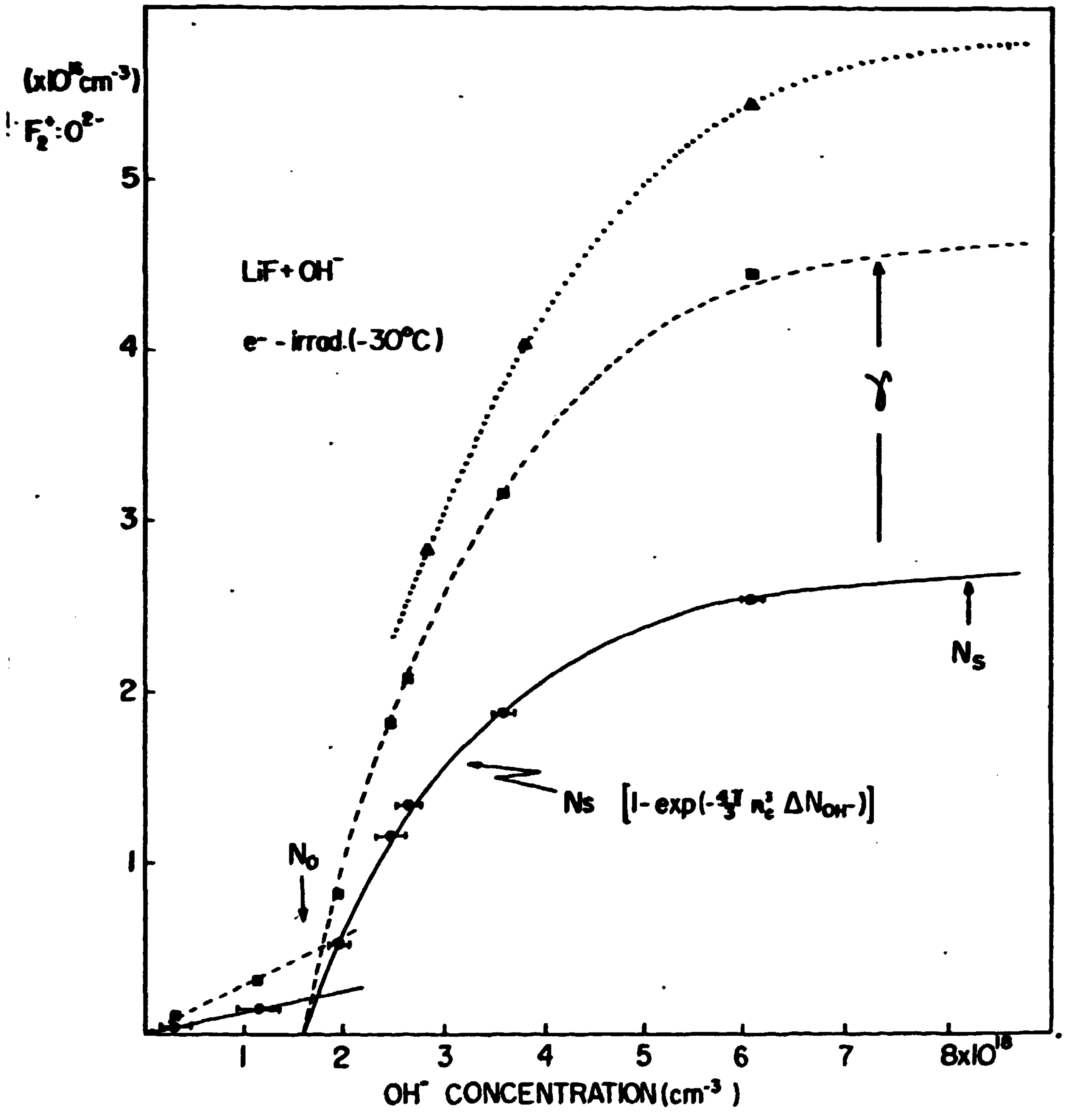
(x10^18 cm^-3)
F2+:O2-
5
4
3
2
1
LiF+OH-
e- - irrad.(-30°C)
γ
Ns
Ns [1-exp(-4π/3 rc^3 ΔNOH-)]
N0
1
2
3
4
5
6
7
8x10^18
OH- CONCENTRATION (cm-3)

figura 1

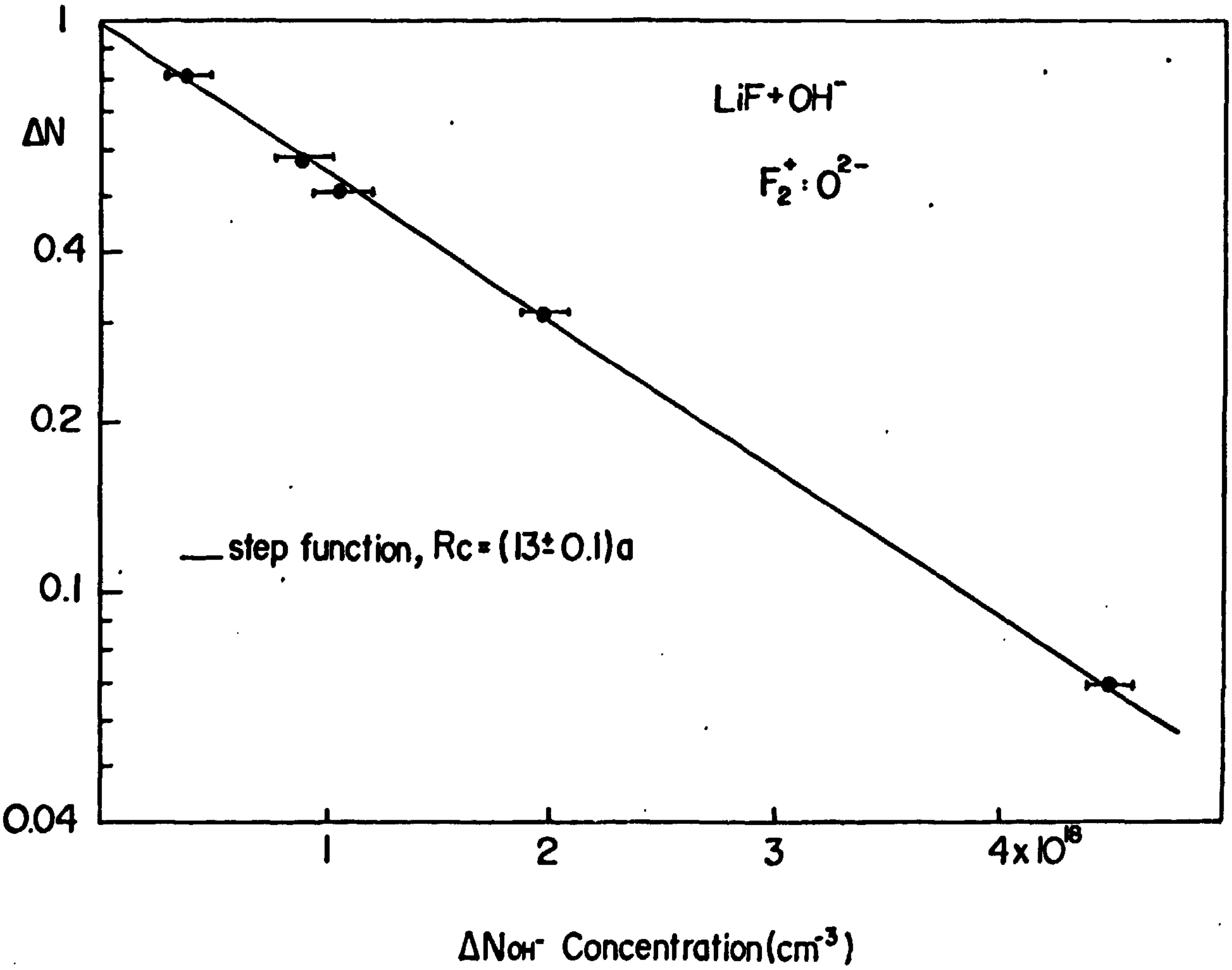
1
ΔN
0.4
0.2
0.1
0.04
LiF+OH⁻
F₂⁺:O²⁻
step function, Rc=(1.3±0.1)a
1
2
3
4x10¹⁸
ΔNOH⁻ Concentration(cm⁻³)

figure 2

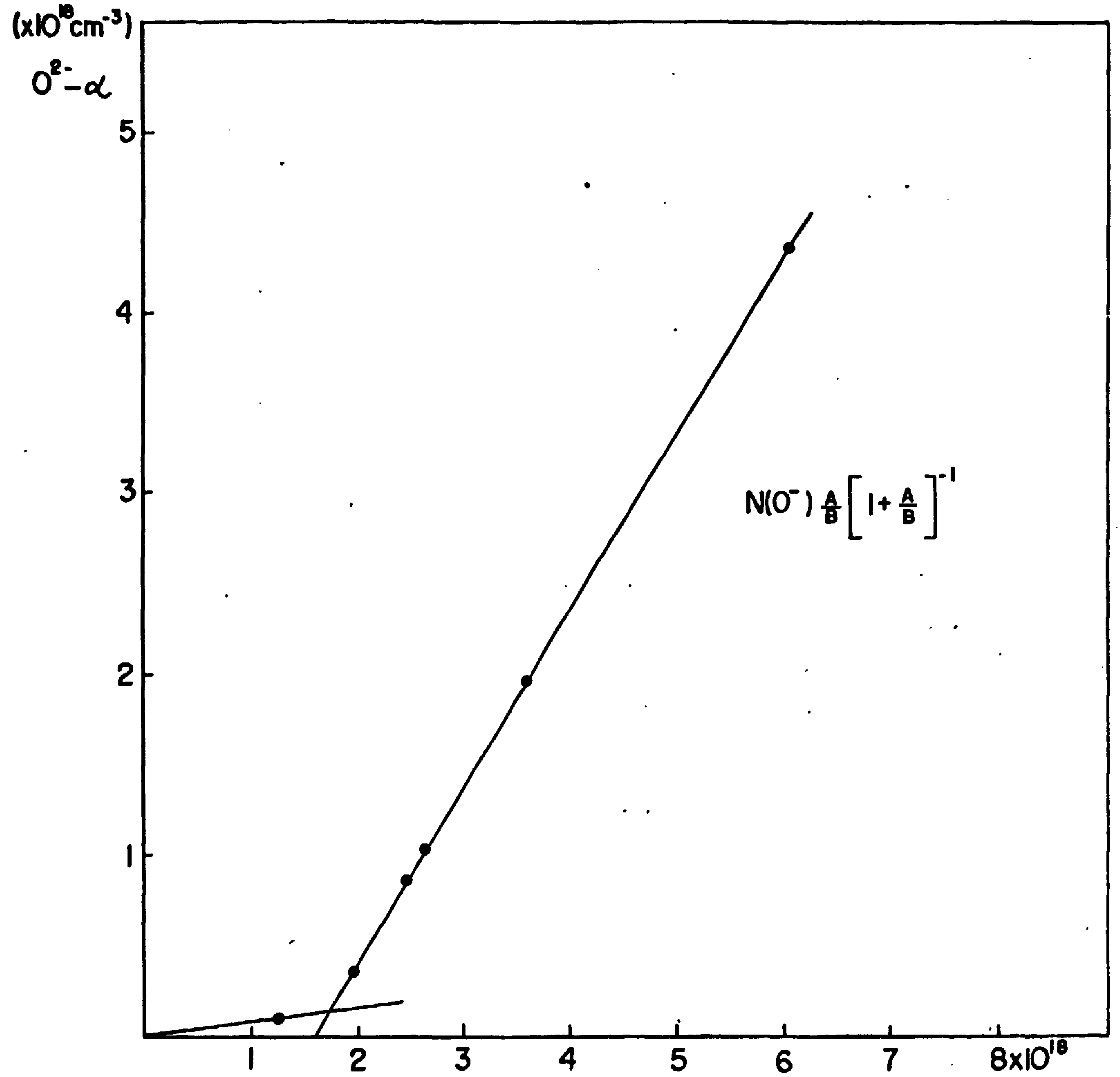
(x10^18 cm^-3)
O^2- - α
5
4
3
2
1
N(O^-) A/B [1 + A/B]^-1
1
2
3
4
5
6
7
8x10^18
OH^- CONCENTRATION (cm^-3)

Figure 3