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DECAY KINETICS STUDY OF  $Ag^0$  IN SILVER DOPED  
BARIUM ALUMINOBORATE GLASSES

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# DECAY KINETICS STUDY OF $Ag^0$ IN SILVER DOPED BARIUM ALUMINOBORATE GLASSES

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**ABSTRACT**

EPR measurements of  $30BaO.50B_2O_3.20Al_2O_3$  at. % glasses containing different amounts of silver impurity, X- and  $\gamma$ -irradiated at room temperature, showed the presence of  $Ag^0$  and  $Ag^{++}$  centers. Decay kinetics of  $Ag^0$  was determined for different temperatures in glass containing 0.1% of silver. We show that our model of stabilization energy of  $H^0$  in B-O rings through van der Waals forces is not applicable to  $Ag^0$ . Thus, we propose the model of reduction of  $Ag^0$  to  $Ag^+$  as the mechanism of the  $Ag^0$  decay kinetics.

**Keywords:** Kinetics,  $Ag^0$ , Barium Aluminoborate Glasses

## I. INTRODUCTION

Silver doping is frequently applied to the preparation of pyroceramics, photosensitive glass and colored glass. Ionizing irradiation effects have been reported by 1950 on phosphate glasses activated by silver<sup>1-3</sup>.

A great deal of knowledge on borate glasses was achieved from EPR studies of boron-oxygen hole centers (BOHC)<sup>4-7</sup> boron electron centers (BEC)<sup>8,9</sup> and atomic hydrogen (H<sup>0</sup>)<sup>9,10</sup>.

In this work we report the EPR study of atomic silver Ag<sup>0</sup>, in barium aluminoborate glasses. Our purpose is mainly to analyse the microscopic mechanism of the thermal kinetic decay of Ag<sup>0</sup> in these glasses.

The single ionized silver atom Ag<sup>+</sup> has been studied by optical absorption spectroscopy<sup>11</sup>, showing that silver appears in this ionizing state in aluminoborate glasses. The silver states Ag<sup>0</sup> and Ag<sup>2+</sup> are generated by ionizing irradiation. The silver ions in several glassy matrices have been subject of many studies<sup>12-16</sup>.

The Ag<sup>0</sup> is classified as a ns<sup>1</sup> defect center<sup>17</sup> (similar to atomic hydrogen H<sup>0</sup>), with an unpaired electronic spin of the 5s orbital of the atomic silver in the glass. This center has nuclear spin I = 1/2 for both isotopes <sup>109</sup>Ag (51%) and <sup>107</sup>Ag (49%). The small difference in nuclear gyromagnetic ratio produces a slight difference in the line separations of the two concentric doublets. The Ag<sup>0</sup> interaction with the glass network is expected to be similar to that observed for H<sup>0</sup> in the same glassy matrix.

## II. EXPERIMENTAL PROCEDURE

Samples of barium aluminoborate glasses containing silver were prepared and kindly furnished by Prof. A. Bishay of the Cairo American University. The experiments were

carried out using samples of 30BaO.50B<sub>2</sub>O<sub>3</sub>.20Al<sub>2</sub>O<sub>3</sub> at. % glasses with 0.1 and 5.0 at. % of Ag. The details of the sample preparation, EPR measurements and temperature control conditions are explained elsewhere<sup>10</sup>. The  $\gamma$ -irradiations were done using a <sup>60</sup>Co source of EMBRARAD S.A.. The X-irradiations were done using an apparatus (Philips Electronic Instruments, Mahwah, NJ) operating at 40kV and 20mA.

## III. RESULTS

Barium aluminoborate glasses with 0.1 at. % of silver, X-irradiated at room temperature, exhibit the characteristic EPR spectrum shown in Fig. 1. In the spectrum

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### INSERT FIG. 1

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we see a strong line of BOHC at the center and four additional <sup>107</sup>Ag<sup>0</sup> and <sup>109</sup>Ag<sup>0</sup> lines originating from silver impurity in the sample. The small satellite lines around the strong BOHC spectrum are BEC lines.

Barium aluminoborate glasses with 5 at. % of silver,  $\gamma$ -irradiated at room temperature, exhibit the characteristic EPR spectrum shown in Fig. 2. In the spectrum we

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### INSERT FIG. 2

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see only one pair of Ag<sup>0</sup> lines because the <sup>107</sup>Ag<sup>0</sup> and <sup>109</sup>Ag<sup>0</sup> spectra are not resolved due to the strong line broadening. The remaining lines are attributed to Ag<sup>2+</sup> and BEC. The additional broad bump superposed on the spectrum is probably a small BOHC line or a g = 2.0 resonance attributed to iron clusters of paramagnetic ions containing two or more ions<sup>18,19</sup>. The BOHC line is almost suppressed by silver doping because it is a good hole scavenger. The capture of a hole by Ag<sup>+</sup> gives Ag<sup>2+</sup> shown in the spectrum.

The line broadening of the  $\text{Ag}^0$  EPR lines is due to the dipole-dipole interaction which is very strong for glasses within 1 and 5 at. % of silver. Otherwise, glasses with 0.1 at. % of silver showed an almost unchanged linewidth through the kinetic decay measurements. As the  $\text{Ag}^0$  concentration is small, the dipole-dipole broadening is now strongly reduced. Our measurements of the decay kinetics of  $\text{Ag}^0$  were carried out with the glass sample having 0.1 at. % of silver.

The relative concentrations of  $\text{Ag}^0$  were evaluated from the p-p (peak to peak) amplitudes of the EPR first derivative curves. As the line width did not change in the temperature range of the measurements, the number of spins was assumed to be proportional to the p-p amplitude.

To perform isochronal temperature pulse annealing experiments, the following procedure was applied: the sample was X-irradiated at room temperature for 8 h. The sample was heated to temperature  $T_1$ , held for 10 minutes, lowered to temperatures between 38 and 44°C where  $\text{Ag}^0$  is stable for EPR measurements, raised to a second temperature  $T_2 = T_1 + 10^\circ\text{C}$ , held for 10 minutes, returned to 38–40°C for EPR measurements, etc..

The thermal bleaching behavior of  $\text{Ag}^0$  is represented by the isochronal decay curve of Fig. 3. The  $\text{Ag}^0$  decay extends over a wide temperature range (330 to 550K).

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INSERT FIG. 3

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A series of measurements was carried out to obtain the isothermal annealing of the  $\text{Ag}^0$  centers using the following procedure: the same sample was X-irradiated at room temperature for 8 h. The temperature was raised to a given value  $T_1$  and held constant within  $\pm 0.2\text{K}$ . The series of EPR measurements started immediately after reaching the chosen temperature. After the series of measurements at  $T_1$  was completed, the sample

was annealed at 500°C for 30 to 40 minutes and X-irradiated again. The process was repeated at a second temperature and so on.

The isothermal decay of  $\text{Ag}^0$  is plotted in Fig. 4. The points are experimental data and the full lines are the best fits with the microscopic model developed herewith.

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INSERT FIG. 4

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#### IV. DISCUSSION AND CONCLUSIONS

Here we analyse two models for the explanation of the thermal decay kinetics of  $\text{Ag}^0$  in barium aluminoborate glass. The first one is the diffusion model (proposed for  $\text{H}^0$  in barium aluminoborate glass<sup>10</sup>, where  $\text{Ag}^0$  is trapped by van der Waals attractive forces in the B-O ring structure and the oxygen atoms occupy the corners of polygons. After this model, on heating  $\text{Ag}^0$  is released from the ring structure and then can be either retrapped in another ring structure or recombined in sites in which  $\text{Ag}^0$  converts into  $\text{Ag}^+$  by the loose of one electron.

Another model is the ionization model where, on heating,  $\text{Ag}^0$  loses one electron to the conduction band which can be retrapped by  $\text{Ag}^+$  ions forming  $\text{Ag}^0$  or recombined with another center. In both cases we have untrapping, retrapping and recombination processes. Thus, we write the rate equations for the ionization model, keeping in mind that the same equations are also applicable to the diffusion model.

In order to write the coupled differential rate equations describing the proposed reactions which took part in the thermal annealing process, the following statements were considered:

- a) The empty electron trapping sites are identified as silver impurity ions  $Ag^+$ . Each trapped electron corresponds to an  $Ag^0$  center. Let  $[e_t^-]$  be the concentration of trapped electrons and  $[E]$  the concentration of empty traps.
- b) On heating, the trapped electrons are released from their traps through the first order reaction  $Ag^0 \rightarrow Ag^+ + e^-$  and moves almost freely throughout the extended levels of the conduction band. Let  $[e_f^-]$  be the concentration of free electrons.
- c) The electron retrapping rate is proportional to  $[E]$  and  $[e_f^-]$ .
- d) The recombination rate is proportional to the product  $[e_f^-][R]$ , where  $R$  is the concentration of the hole centers or electron scavengers where the electrons can recombine.
- e) The coupled equations must satisfy the conservation equations:

$$[R] = [e_f^-] + [e_t^-] \quad (1a)$$

$$[N] = [E] + [e_t^-] \quad (1b)$$

where  $N$  is the total concentration of electron traps ( $Ag^+$ ) before irradiation.

From the above considerations we obtained the following coupled equations:

$$\frac{d}{dt} [e_f^-] = -\alpha [e_f^-] + \gamma [e_f^-] \{N - [e_t^-]\} \quad (2a)$$

$$\frac{d}{dt} [e_t^-] = \alpha [e_f^-] - \gamma [e_f^-] \{N - [e_t^-]\} - \beta [e_f^-] \{[e_f^-] + [e_t^-]\} \quad (2b)$$

The above equations were normalized assuming that all electron traps ( $Ag^+$ ) are filled. The initial conditions are given by:  $N = 1$ ,  $[e_f^-]_0 = 1$  and  $[e_t^-]_0 = 0$ . The coupled differential equations (2) were solved using the numerical method of Runge-Kutta<sup>20-22</sup>.

The best fit untrapping  $\alpha$ , recombination  $\beta$  and retrapping  $\gamma$  parameters are shown in Table I.

INSERT TABLE I

The Arrhenius law applied to  $\alpha$  parameter is shown in Fig. 5. The electron untrapping activation energy is  $E_\alpha = (0.45 \pm 0.03) \times 10^{-19}$  J.

INSERT FIG. 5

In diffusion model, silver is stabilized at particular sites of the glassy network, by van der Waals forces. In order to the attractive forces of the van der Waals interaction be efficient to trap an  $Ag^0$ , it is necessary to the kinetic energy of  $Ag^0$  be sufficiently small in order to be retained inside the ring structures, where the oxygen atoms occupy the corners of polygons as shown in Fig. 6. These polygons may be not necessarily as regular as we are going to assume, for sake of simplicity.

INSERT FIG. 6

The binding energy of  $Ag^0$  center shown in Fig. 6 is determined by calculating the O-Ag dispersion energy in a similar way to the O-H dispersion energy, as it was first suggested by Adrian<sup>23</sup>, and multiplying by the number  $n$  of polygon vertices.

The radial distance  $R_n = \ell / [2 \sin(\pi/n)]$  was evaluated from the geometry of Fig. 6, where  $\ell$  is the O-O distance, equal to the polygon edge. The length of  $\ell$  is obtained multiplying by  $\sqrt{3}$  the B-O distance in  $BO_3$  planar unit, known to be  $1.39 \text{ \AA}$ <sup>24</sup>.

The interaction energy between each oxygen and the  $Ag^0$  was evaluated with the aid of London dispersion energy<sup>25</sup>:

$$\varphi = \frac{c}{R_n^6} - \frac{c'}{R_n^8} - \frac{c''}{R_n^{10}} \quad (3)$$

where

$$c = \frac{3h \mu_a \mu_b \alpha_a \alpha_b}{2(\mu_a + \mu_b)}$$

$$c' = \frac{45}{8} \frac{h^2 \mu_a \mu_b \alpha_a \alpha_b}{e^2} \left[ \frac{\alpha_a \mu_a}{2\mu_a + \mu_b} + \frac{\alpha_b \mu_b}{\mu_a + 2\mu_b} \right]$$

$$c'' = \frac{315}{16} \frac{h^3 \mu_a^2 \mu_b^2 \alpha_a^2 \alpha_b^2}{e^4 (\mu_a + \mu_b)}$$

It was first assumed here that  $h\mu_a$  and  $h\mu_b$  are the ionization energies of  $\text{Ag}^0$  and O, respectively,  $12.06 \times 10^{-19}$  J and  $21.76 \times 10^{-19}$  J. The polarizability  $\alpha_a$  and  $\alpha_b$  were assumed to be the cube of the atomic radii, respectively,  $2.96 (\text{A}^\circ)^3$  and  $2.74 (\text{A}^\circ)^3$ . The binding energies calculated for  $\text{Ag}^0$  trapped at the center of oxygen ring structures having different number of  $n$  vertices is given in Table 2.

The ionization energy used here for oxygen is almost certainly inappropriate, because the oxide ion in the glass has a different electronic structure than atomic oxygen. Because of this difference in electronic structure, the polarizability of oxygen used here is probably too low, as also will be the polarizability used for  $\text{Ag}^0$ . The 5s wavefunction should be more diffuse in the glass leading to a larger value of  $\alpha_{\text{Ag}}$ . The deficiency in the method used to extract the values of ionization energies and polarizabilities probably leads to lower values of  $c$ ,  $c'$  and  $c''$ . The discrepancy between the calculated and the experimental  $c$  was noted by Hirschfelder et al.<sup>26</sup> to be 1.5 to 2.5 (depending on the species). Although the discrepancy is now believed to lie within the choice of experimental data, and the methods used to extract the  $C_{\text{visc}}$  from them, rather than a deficiency in

the theory<sup>25</sup>, the Hirschfelder correlation can be applied to estimate by what magnitude  $c$  is lowered by the use of smaller values of ionization and polarizabilities. Thus we compare the activation energy obtained from the analysis of the kinetic decay of  $\text{Ag}^0$  with the binding energies from Table II within the interval  $1.5 n\phi$  and  $2.5 n\phi$ , where  $\phi$  is the potential energy (see equation 3) calculated for an oxygen- $\text{Ag}^0$  pair.

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INSERT TABLE II

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The above analysis shows that for the diffusion model the  $\text{Ag}^0$  trap would be a B-O ring structure with of about 10 vertices. The crystalline  $\text{B}_2\text{O}_3$  is composed by B-O rings with 6 vertices. As the glassy structure of our sample is rather expected to be composed by B-O rings having 5, 6 and 7 vertices, it is concluded, therefore, that the diffusion model does not gives binding energies for  $\text{Ag}^0$  consistent with the expected number of vertices of B-O rings.

From the above considerations we conclude that the best model for the kinetic decay of  $\text{Ag}^0$  is the ionization model, where  $\text{Ag}^0$  is thermally oxidized to  $\text{Ag}^+$  by the release of one electron into the conduction band.

## REFERENCES

- 1) J.H. Schulman, R.J. Ginther, C.C. Klick, R.S. Alger and R.A. Levy, "Dosimetry of X-Rays and Gamma-Rays by Radiophotoluminescence", *J. Applied Phys.*, 22[12] 1479-87 (1951).
- 2) J.H. Schulman, W. Schurcliff, R.J. Ginther and F.H. Altix, "Radiophotoluminescence Dosimetry System of the U.S. Navy", *Nucleonics*, 11[10] 52-56 (1953).
- 3) H.W. Etzel and J.H. Schulman, "Silver-Activated Alkali Halides", *J. Chem. Phys.*, 22[9] 1549-54 (1954).
- 4) P.C. Taylor and P.J. Bray, "Structural Properties of Glasses Inferred from Computer Simulations of Magnetic Resonance Spectra", *Am. Ceram. Soc. Bull.*, 51[3] 234-39 (1973).
- 5) D.L. Griscom, P.C. Taylor, D.A. Ware and P.J. Bray, "ESR Studies of Lithium Borate Glasses and Compounds - Irradiated at 77K: Evidence for New Interpretation of Trapped-Hole Centers Associated with Boron", *J. Chem. Phys.*, 48[11] 5158-73 (1968).
- 6) P.C. Taylor, "Resonance Effects in Glasses", pp. 223-81 in *Treatise on Materials Science and Technology*, Vol. 12, Glass I. Edited by M. Tomozawa and R.H. Doremus. Academic Press, New York, 1977.
- 7) E.J. Friebele and D.L. Griscom, "Radiation Effects in Glass", pp. 257-351 in *Treatise on Materials Science and Technology*, Vol. 17, Glass II. Edited by M. Tomozawa and R.H. Doremus. Academic Press, New York, 1979.
- 8) D.L. Griscom, "ESR Studies of an Intrinsic Trapped-Electron Center in X-Irradiated Alkali Borate Glasses", *J. Chem. Phys.*, 55[3] 1113-22 (1971).
- 9) W.M. Pontuschka, S. Isotani and A. Piccini, "Optical and Thermal Bleaching of X-Irradiated Barium Aluminoborate Glasses", *J. Am. Ceram. Soc.*, 70[1] 59-64 (1987).
- 10) W.M. Pontuschka, S. Isotani and A. Piccini, "EPR and Kinetic Studies of Hydrogen Centers in Aluminoborate Glasses", *J. Am. Ceram. Soc.*, 65[10] 519-23 (1982).
- 11) A.K. Ghosh, "Optical Properties of Electron and Hole Traps in Ag-Doped Aluminoborate Glass", *J. Phys. Chem. Solids*, 30 2385-94 (1969).
- 12) L. Shields, "Ag I and Ag III from Solvated Ag II by Radiation - Chemical Conversion in  $\gamma$ -Irradiated Solutions at 77°K", *J. Chem. Phys.*, 44 1685-89 (1966).
- 13) R.A. Zhitnikov and A.L. Orbeli, "Paramagnetic Resonance of Free Silver Atoms Formed in Frozen Solutions of Silver Salts Irradiated at 77°K", *Soviet Physics - Solid State*, 7[7] 1559-71 (1966).
- 14) T. Feldman and A. Treinin, "Inorganic Radicals Trapped in Glasses at Room Temperature. IV. Silver Radicals in Metaphosphate Glass", *J. Chem. Phys.*, 47 2754-58 (1967).
- 15) R.A. Zhitnikov and N.I. Mel'nikov, "Silver Atoms Stabilized in Inorganic Glasses", *Soviet Physics - Solid State*, 10[1] 80-88 (1968).
- 16) F. Seitz, "Speculations on the Properties of the Silver Halide Crystals", *Rev. Mod. Phys.*, 23[4] 328-52 (1951).
- 17) D.L. Griscom, "Electron Spin Resonance in Glasses", *J. of Non-Crystalline Solids*, 40 211-72 (1980).
- 18) E.J. Friebele, L.K. Wilson, A.W. Dozier and D.L. Kinser, "Antiferromagnetism in an Oxide Semiconductor Glass", *Phys. Stat. Sol.*, B45 323-31 (1971).
- 19) H.O. Hooper, G.B. Berad, R.M. Catchings, R.R. Bukrey, M. Forrest, P.F. Verhelst, "Magnetic Order in Alkaliborate and Aluminosilicate Glasses Containing Large Concentrations of Iron-Group Ions", pp. 47-63. Edited by H.O. Hooper and A.M. de Graaf, Plenum, New York, 1972.
- 20) W.E. Milne, "Numerical Solution of Differential Equations", Dover Publications, Inc., New York, 1970.

- 21) L. Brand, "*Differential and Difference Equations*", John Wiley & Sons, Inc., New York, London, Sydney, 1966.
- 22) W.E. Boyce and R.C. DiPrima, "*Elementary Differential Equations and Boundary Value Problems*", John Wiley & Sons, Inc., New York, London, Sydney, 1977.
- 23) F.J. Adrian, "*Matrix Effects on the Electron Spin Resonance Spectra of Trapped Hydrogen Atoms*", *J. Chem. Phys.*, 32[4] 972-81 (1960).
- 24) J. Bischof and B.E. Warren, "*X-Ray Diffraction Study of Soda-Boric Oxide Glass*", *J. Am. Ceram. Soc.*, 21 287-93 (1938).
- 25) H.F. Hornig and J.O. Hirschfelder, "*London Dispersion Forces Between Unlike Molecules*", *J. Chem. Phys.*, 20[11] 1812 (1952).
- 26) J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "*Molecular Theory of Gases and Liquids*", John Wiley & Sons, Inc., New York (1954).
- 27) J.C. Antonio, "*The Dipole-Dipole Dispersion Forces for Small, Intermediate and Large Distances*", *Rev. Bras. Fis.*, 17[4] 628-39 (1987).

Table 1 - Best fit untrapping  $\alpha$ , recombination  $\beta$  and retrapping  $\gamma$  parameters for the  $\text{Ag}^0$  thermal decay (ionization model).

T (K)	$\alpha$ (s <sup>-1</sup> )	$\beta$ (s <sup>-1</sup> )	$\gamma$ (s <sup>-1</sup> )
473	5.8	18.8	1.3
493	7.0	22.0	1.6
513	10.6	19.2	1.7
523	12.0	30.0	10.5



Table 2 - Binding energies calculated for  $\text{Ag}^0$  trapped in B-O rings having different numbers  $n$  of vertices (diffusion model).

$n$	$R_n$ (Å)	$\varphi$ ( $10^{-19}$ J)	$n\varphi$ ( $10^{-19}$ J)	$1.5 \times n\varphi$ ( $10^{-19}$ J) <sup>(*)</sup>	$2.5 \times n\varphi$ ( $10^{-19}$ J) <sup>(*)</sup>
7	3.1	0.22	1.54	2.29	3.82
8	3.5	0.09	0.72	1.08	1.80
9	3.9	0.04	0.36	0.54	0.90
10	4.3	0.02	0.20	0.30 <sup>(**)</sup>	0.50 <sup>(**)</sup>
11	4.7	0.01 <sub>0</sub>	0.11	0.17	0.28
12	5.1	0.00 <sub>6</sub>	0.07	0.11	0.18
13	5.6	0.00 <sub>3</sub>	0.04	0.06	0.10

<sup>(\*)</sup>Lowest and highest empirical factors (1.5) and (2.5) from Hirschfelder et al.<sup>26</sup> to account for the correct values of  $\alpha$  and  $\mu$ .

<sup>(\*\*)</sup>The experimental value of activation energy  $E_a = (0.45 \pm 0.03) \times 10^{-19}$  J corresponds to the  $\text{Ag}^0$  binding energy at the center of a ring structure of 10 oxygens.

#### FIGURE CAPTIONS

Fig. 1. EPR spectrum of  $30\text{BaO} \cdot 50\text{B}_2\text{O}_3 \cdot 20\text{Al}_2\text{O}_3$  (at. %) glass doped with 0.1 at. % of silver, X-irradiated at room temperature.

Fig. 2. EPR spectrum of  $30\text{BaO} \cdot 50\text{B}_2\text{O}_3 \cdot 20\text{Al}_2\text{O}_3$  (at. %) glass doped with 5 at. % of silver,  $\gamma$ -irradiated at room temperature.

Fig. 3. Isochronal decay curve of the high-field  $\text{Ag}^0$  normalized EPR line intensity measured at 38-40°C. Each temperature pulse was held for 10 minutes.

Fig. 4. Isothermal decay curves of  $\text{Ag}^0$  at the temperatures of 473, 493, 513 and 523K. The continuous lines were adjusted by the method of Runge-Kutta of numerical solution of the coupled system of differential equations (2a) and (2b).

Fig. 5. Arrhenius plot of the electron untrapping parameter  $\alpha$ , giving the activation energy  $E_a = (0.45 \pm 0.03) \times 10^{-19}$  J.

Fig. 6. An atomic silver atom stabilized by van der Waals forces at the center of a polygonal oxygen ring structure, as described in the diffusion model.

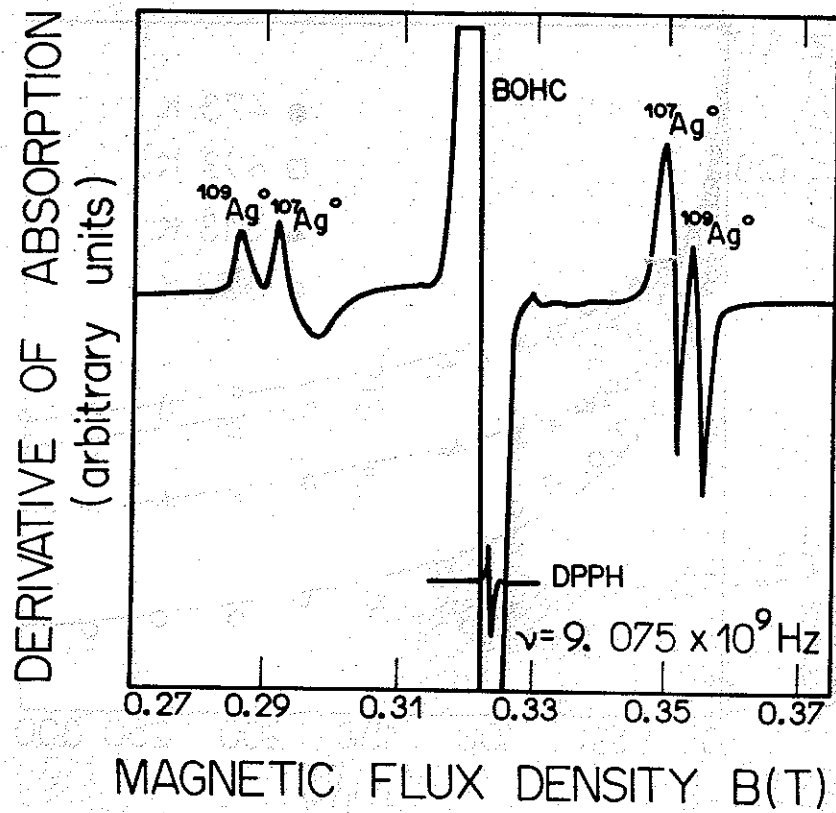


Figure 1

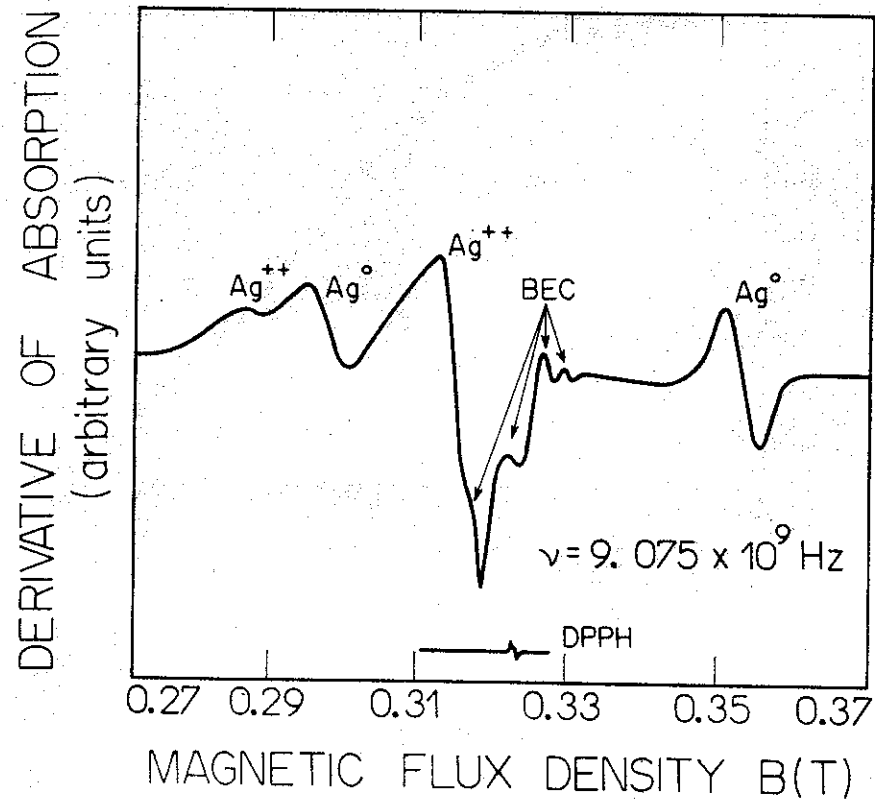


Figure 2

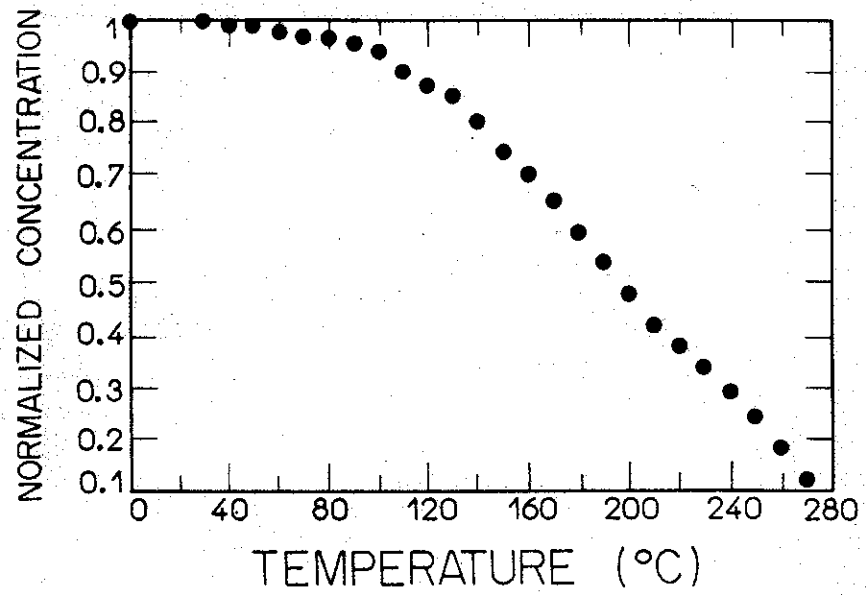


Figure 3

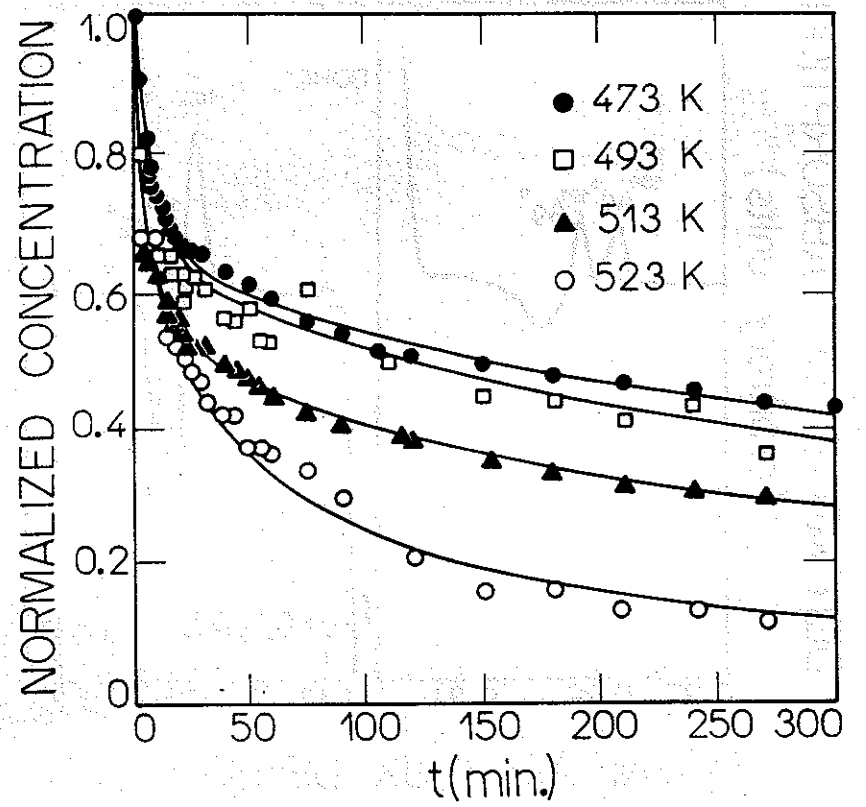


Figure 4

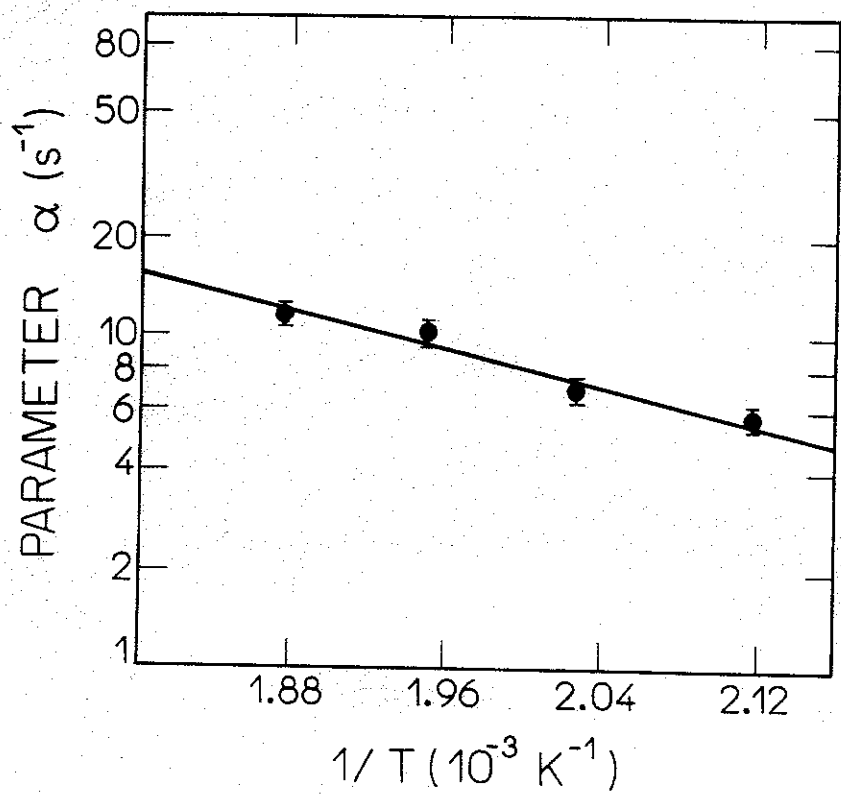


Figure 5

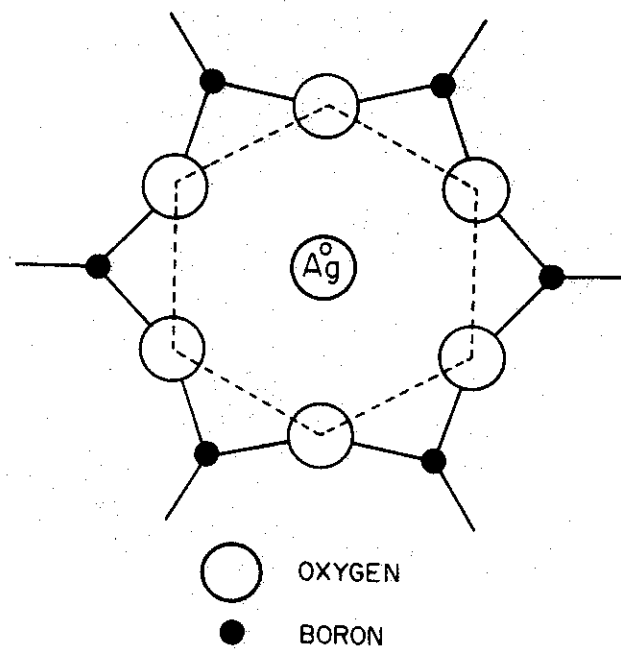


Figure 6