

## Atomic Center Interactions in BaO; Al<sub>2</sub>O<sub>3</sub>; B<sub>2</sub>O<sub>3</sub> Glasses Containing Silver\*

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Recebido em 23 de Fevereiro de 1978

The EPR study of borate glasses, with 30% of BaO and 5% mole of silver, X-irradiated at 77°K, showed Ag<sup>0</sup> and Ag<sup>++</sup> centers. In addition were detected the boron electron center (BEC) and the boron hole center. The silver centers and BEC were studied in detail and the spin Hamiltonian parameters are given. The different AR<sub>2</sub>O<sub>3</sub> concentrations exerted only little influence on the tabulated constants. The Ag<sub>2</sub><sup>+</sup> center was not observed, indicating that the collisions between Ag atoms are not very frequent in these glasses, even during the process of thermal bleaching. The hfs of the boron electron center suffers severe variation as one compared the spectra of base glasses and those containing silver. This is an evidence of the action of silver as a glass modifier like the alkali atoms.

O estudo de EPR dos vidros com boratos, contendo 30% de BaO e 5% mol de prata, irradiados com raios X a 77°K, revelou a presença dos centros Ag<sup>0</sup> e Ag<sup>++</sup>. Foram também observados o centro do elétron do boro (BEC) e o centro de buraco do boro. Os centros de prata e o BEC foram estudados em detalhe, sendo obtidos os parâmetros da Hamiltoniana de spin. As diferentes concentrações de AR<sub>2</sub>O<sub>3</sub> exerceram apenas uma pequena influência sobre as constantes expressas nas Tabelas. O centro de Ag<sub>2</sub><sup>+</sup> não foi observado, indicando que as colisões entre os átomos de Ag não são muito frequentes nestes vidros, mesmo durante o processo de decaimento térmico. A constante de interação hiperfina do centro de elétron do boro sofreu acentuada variação quando da comparação dos espectros dos vidros-base

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\* This work was partially supported by FAPESP and CNPq (Brazil).

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com os que contêm prata. Este fato torna evidente a atuação da prata como modificadora do vidro, à semelhança dos átomos alcalinos.

## 1. INTRODUCTION

The study of atomic centers in glassy matrices has received increasing attention in the last decade.

In this work, we intend to add more data about the silver interactions in  $BaO$ ;  $Al_2O_3$ ;  $B_2O_3$  glasses. The silver centers were already investigated in several amorphous matrices, being related to the EPR spectra of  $Ag^0$ ,  $Ag^{++}$  and  $Ag_2^+$  centers. These centers were induced by X-irradiation at liquid nitrogen temperature. During irradiation, electrons and holes are liberated in the sample, both being trapped by the  $Ag^+$  ion, which is present in the sample in its original state. The production of the centers is as follows:



The paramagnetic resonance lines of each center are well known. The  $Ag^+$  ion is not paramagnetic.

The interest of the study of these centers in different matrices rests in the interpretation of the quantitative data, which are sensible to the nature of the site where the silver ion is stabilized.

In addition, two more kinds of EPR lines were detected:

- a) boron hole centers<sup>2</sup>
- b) boron electron centers (BEC)<sup>1</sup>.

The  $Ag_2^+$  centers were not detected, even with subsequent thermal bleaching.

## 2. EXPERIMENTAL

The samples were X-irradiated at 77°K during 8 hours, with 45 KV and 35 mA beam using a Phillips unity, type 1008/65, with tungsten target.

The glass samples were given by A. Bishay during his permanence in the Instituto de Física of University of São Paulo. The details of sample production are given in Ref. 3. All the glasses studied contain 30% of BaO and silver enters in the composition with 5% mole. The Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> content is variable from sample to sample, as indicated in the tables.

The EPR spectra were obtained with X-band reflection homodyne spectrometer, using rectangular cavity which operates in the H<sub>102</sub> mode. The temperature control was done using a Varian unity, model V-4540.

## 3. TYPICAL SPECTRUM OF BaO; Al<sub>2</sub>O<sub>3</sub>; B<sub>2</sub>O<sub>3</sub> GLASSES CONTAINING SILVER

In Fig.1 there is a typical spectrum of atomic centers of silver induced by radiation. Care was taken, during the transfer of the sample to the spectrometer, to prevent temperature raising, avoiding the recombination of the more unstable centers.

The assignment of the lines located respectively in 2920 Oe and 3500 Oe to Ag<sup>0</sup> centers needs a careful verification on account of the similarity in position and shape with the EPR lines of the Ag<sub>2</sub><sup>+</sup> center discovered by Mel'nikov *et al.*<sup>4</sup> in glassy B<sub>2</sub>O<sub>3</sub> containing silver impurity.

The Ag<sup>++</sup> center presents EPR lines with noticeable local anisotropy verified by means of the separate values of  $g_{||}$  and  $g_{\perp}$  of the splitting factor. To each anisotropic g-factor component corresponds a non-resolved doublet, their positions being in agreement with those studied by Shields<sup>5</sup> in X-irradiated frozen silver salts. In Fig. 1 the  $g_{\perp}$  doublet corresponds nearly to the values between 3080 Oe and 3100 Oe. The  $g_{||}$  doublet is situated in the region of 2800 Oe.

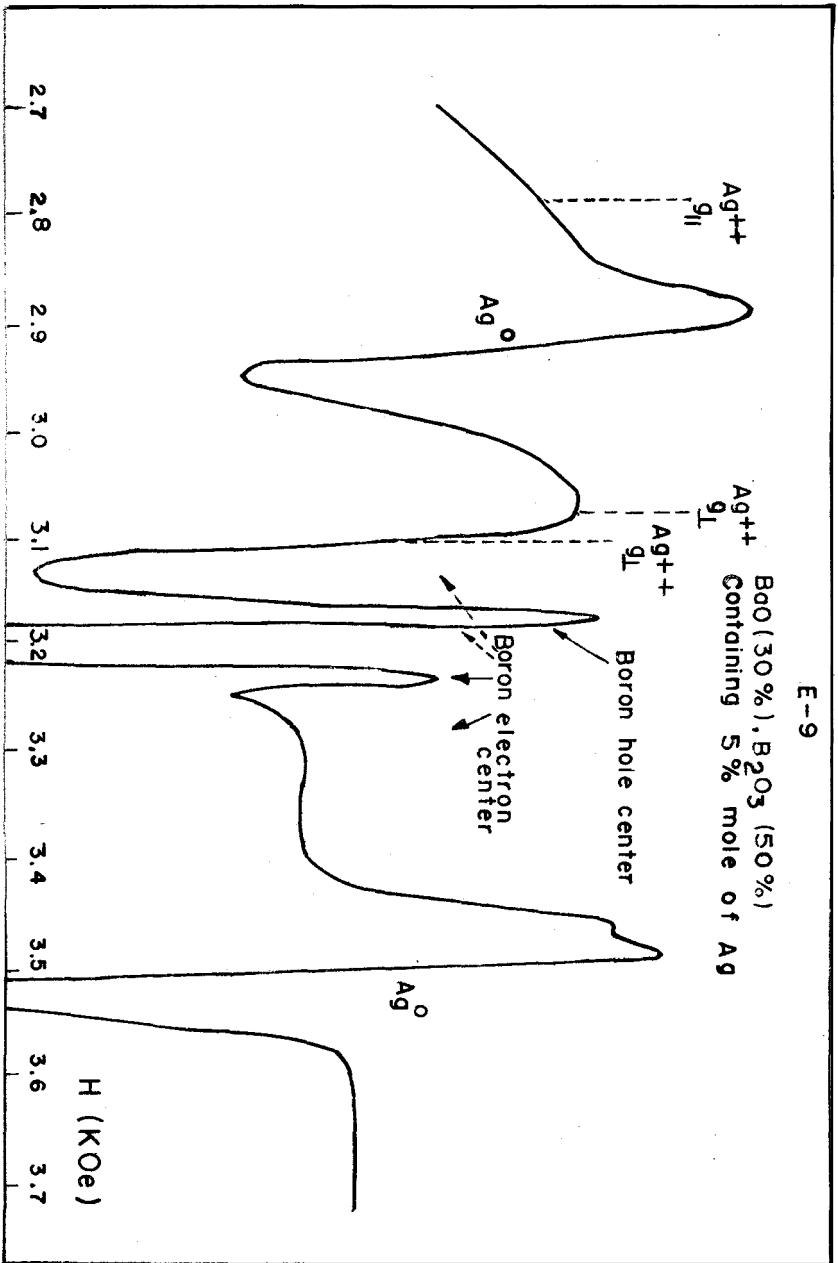


Fig. 1 - Typical EPR spectrum of borate glass containing 30% BaO and 5% mole of silver, X-irradiated at 77°K.

In 3.2 kOe a superposition of EPR lines appears whose centers are not attributable to silver ions. These centers were identified respectively as boron hole center and boron electron center.

#### 4. ATOMIC CENTER OF $\text{Ag}^0$

There are two types of silver isotopes with almost the same relative abundance. Both isotopes, 48.1% of  $^{107}\text{Ag}$  and 51.9% of  $^{109}\text{Ag}$ , have the nuclear spin  $I = 1/2$ , giving a doublet of each of them. Both doublets are observable in a lot of materials containing silver, giving four resolved EPR lines. The internal pair is related to  $^{107}\text{Ag}$  isotope and the external to  $^{109}\text{Ag}$ .

The energy levels (see Fig.2) are calculated using the Breit-Rabi formula<sup>6</sup> which, applied to  $\text{Ag}^0$ , is

$$W_{(F,m)} = -\Delta W/4 - \mu_I(\beta_N) \beta_N H_0^m \pm (\Delta W/2) \sqrt{1 + 2mx + x^2} \quad (4.1)$$

where

$$x = \left( g_J - \frac{\mu_I(\beta_N)}{I} \frac{\beta_N}{\beta_0} \right) \frac{\beta_0 H_0}{\Delta W} ;$$

$$\Delta W = A = \hbar \Delta \nu ;$$

$$\mu_I(\beta_N) = \text{nuclear magnetic moment in nuclear magnetons};$$

$$\beta_N = \text{nuclear magneton} ;$$

$$\beta_0 = \text{Bohr magneton} ;$$

$$H_0 = \text{applied magnetic field in Oe};$$

$$F = 1, 0 ;$$

$$m = 0 \text{ for } F = 0 \text{ and } m = -1, 0, +1 \text{ for } F = 1 ;$$

$$g_J = - \frac{\mu_J}{J \beta_0} .$$

The constants  $\mu_I(\beta_N)$ ,  $g_J$ ,  $\beta_0$  and  $\beta_N$  are found in tables of Ref. 7. The transitions corresponding to the observed  $\text{Ag}^0$  lines in the spectra are respectively  $(F = 1, m = 1) \rightarrow (F = 0, m = 0)$  and  $(F = 1, m = 0) \rightarrow (F = 1, m = +1)$ .

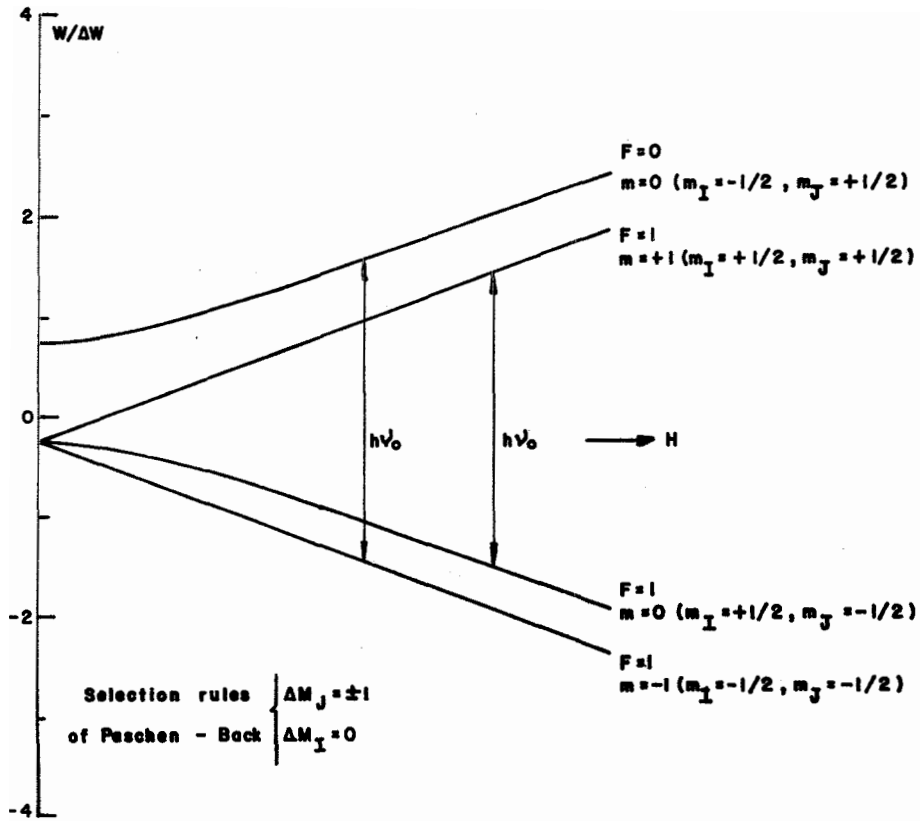


Fig.2 - Sketch of  $Ag^0$  center energy levels calculated from the formula of Breit-Rabi<sup>6</sup>.

For these transitions, using the formula of Breit-Rabi, we get

$$\nu = -\Delta\nu \left( \frac{1}{2} (1 + x_1^2)^{1/2} + \frac{1}{2} (1 - x_1) + \frac{2\mu_I(\beta_N)\beta_N H_1}{h\Delta\nu} \right) \quad (4.2)$$

$$\nu = -\Delta\nu \left( \frac{1}{2} (1 + x_2^2)^{1/2} - \frac{1}{2} (1 + x_2) + \frac{2\mu_I(\beta_N)\beta_N H_2}{h\Delta\nu} \right) \quad (4.3)$$

where  $\nu$  is the klystron frequency.

The values of  $\overline{g_J}$  and  $\overline{\Delta\nu}$  which satisfy simultaneously the equations (4.2) and (4.3) (using the constant  $\overline{\mu_I(\beta_N)}$  equal to the arithmetic mean between the respective values of nuclear magnetic moment of each silver isotope) are expressed in Table 1, where the line width of each transition is included.

Table 1

Sample	%Al <sub>2</sub> O <sub>3</sub>	%B <sub>2</sub> O <sub>3</sub>	$\delta(\overline{\Delta\nu})/\overline{\Delta\nu}_{\text{free}} \%$	$\overline{\Delta\nu} \cdot 10^9 \text{ Hz}$	$\overline{g_J}$	Line width, Oe	
						(1,-1)→(0,0)	(1,0)→(1,1)
E-9	-	70	- 14.6 ± .1	-1.618 ± .022	1.9997 ± .0015	64	52
(a) E-9	-	70	- 18.7 ± .1	-1.670 ± .022	1.0015 ± .0017	57	52
E-7	5	65	- 15.7 ± .1	-1.597 ± .022	1.9888 ± .0015	64	48
(b) E-3	20	50	- 19.7 ± .1	-1.522 ± .021	1.9838 ± .0014	64	52
E-2	20	50	- 18.7 ± .1	-1.536 ± .022	1.9811 ± .0014	68	56
(a. t.) E-2	20	50	- 22.2 ± .2	-1.474 ± .029	1.9853 ± .0025	60	48

(a) Repetition of the measure 2 days after, in the same conditions. (b) Sample produced in oxidizing conditions. Very pure Al<sub>2</sub>O<sub>3</sub> content. (a. t.) Measured at ambient temperature.

The spectrum in Fig. 1 is very similar to the spectrum of  $Ag_2^+$  obtained by Mel'nikov *et al.*<sup>4</sup>, mainly because of the overlapping of the central line of  $Ag_2^+$  triplet with a lot of lines originated from boron centers.

In order to eliminate the doubt whether the line located in 2920 G and 3500 G are associated to  $Ag_2^+$  centers, we observe in detail the central region located in the range of 3080 G to 3220 G (see Fig. 3). There is a superposition of the spectra of the BaO (30%);  $B_2O_3$  (70%) glass containing 5% mole of silver and of the respective base glass. The lines situated in the central part are due to the boron hole center. In the spectrum of glass containing silver the only additional lines are due to the  $Ag^{++}$  center and the boron electron center assigned as  $e_t^-$ . In base

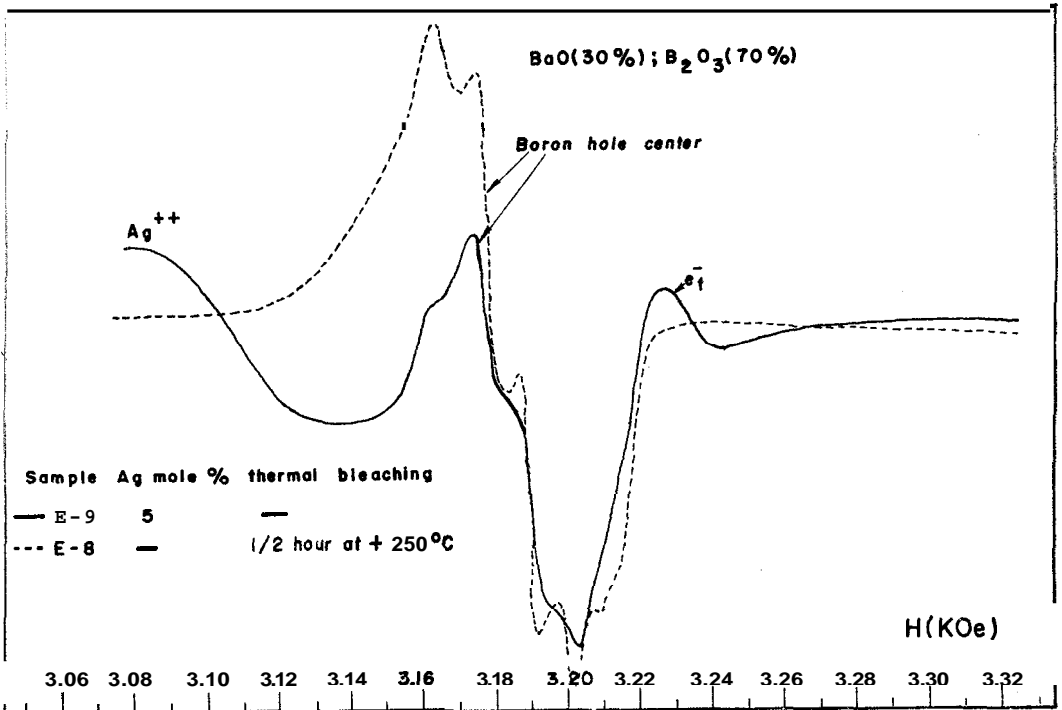


Fig.3 - Central region viewed in detail of the EPR spectra of the samples E-8 and E-9 of BaO(30%);  $B_2O_3$ (70%) glasses put together in order to compare X-irradiated sample containing silver with base glass. All the lines present were identified being evidenced the absence of the third line of  $Ag_2^+$  center which might be present.



glass the line corresponding to  $e_t^-$  by boron atom were bleached out. It is evident, therefore, the absence of any possible EPR line attributable to  $Ag_2^+$  center in the central part of the spectrum.

The factors governing the width and the separation of the  $Ag^0$  EPR lines are;

- a) concentration of the alkali modifier
- b) concentration of silver impurity

The values of the Table 1 are in excellent agreement with the results of Asabghy et al.<sup>8</sup>, who plotted the hfs constants and the line widths in function of the concentration of alkali oxide in the composition of borate glasses containing sodium oxide.

## 5. ATOMIC CENTER OF $Ag^{++}$

The  $Ag^{++}$  centers are formed by hole trapping of  $Ag^+$  ions. The interactions of  $Ag^{++}$  ions are studied by means of the spin Hamiltonian with axial symmetry<sup>5,9</sup> in first approximation

$$H = g_{||} \beta_0 H_z S_z + g_{\perp} \beta_0 (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y) \quad (5.1)$$

where A and B are the hfs constants,  $g_x = g_y = g_{\perp}$  and  $g_z = g_{||}$ .

Taking  $\theta$  as the angle between the local symmetry axis and the direction of applied magnetic field and  $g_0 = (g_{||} + 2g_{\perp})/3$ , it follows:

$$H_{(\theta=0)} = (g_0 H_0 / g_{||}) - (m_I A / \beta_0 g_{\perp}) ; \quad (5.2)$$

$$H_{(\theta=\pi/2)} = (g_0 H_0 / g_{\perp}) - (m_I B / \beta_0 g_{\perp}) ; \quad (5.3)$$

where  $H_0 = h\nu / g_0 \beta_0$ .

The  $Ag^{++}$  EPR lines of borate glass containing 30% BaO and 5% mole of silver are indicated in Fig. 1, corresponding to non-resolved doublets for each  $g_{\perp}$  and  $g_{||}$ . In Fig. 4 the doublet corresponding to  $g_{||}$  is

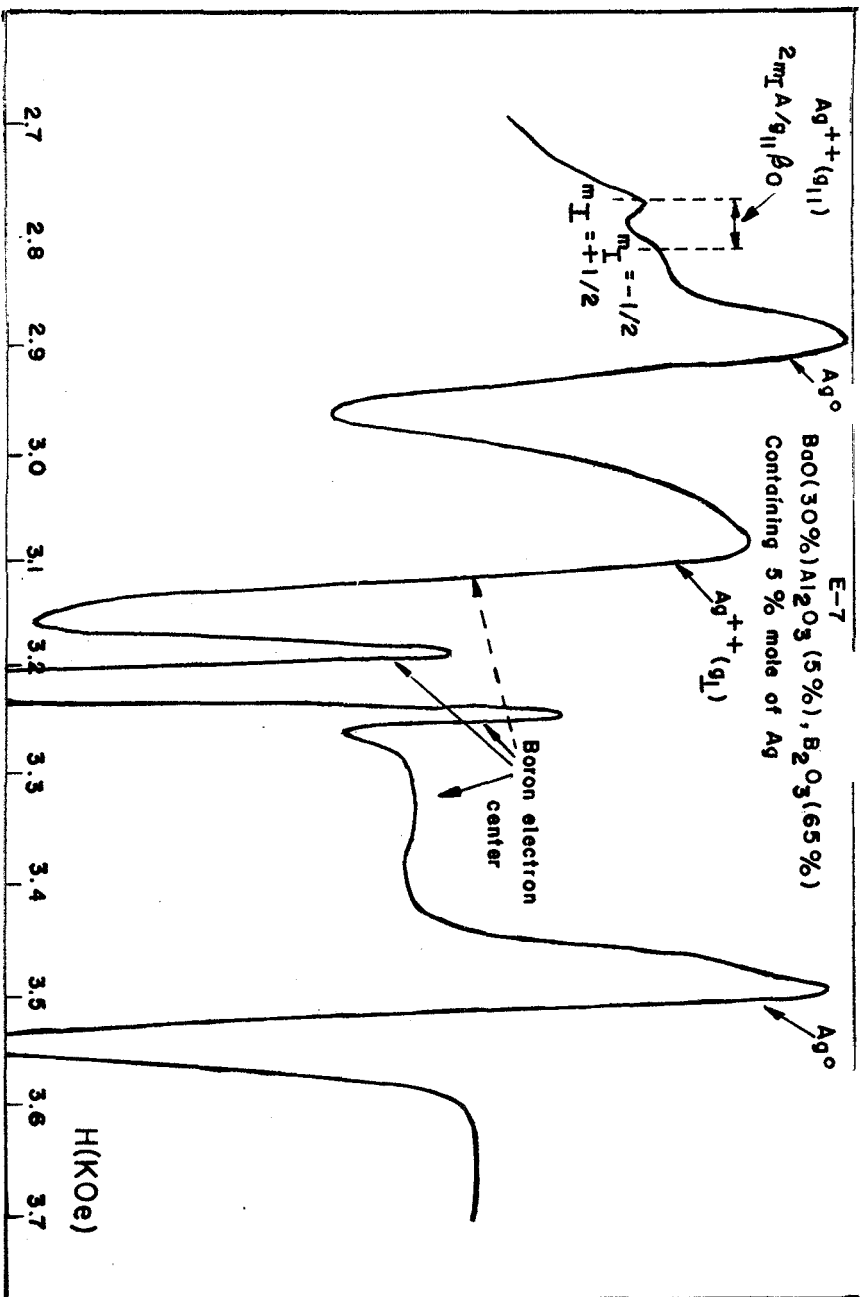


Fig. 4 - EPR spectrum of BaO(30%); Al<sub>2</sub>O<sub>3</sub> (5%); B<sub>2</sub>O<sub>3</sub> (65%) containing 5% mole of Ag showing the partial resolution of Ag<sup>++</sup> (g<sub>||</sub>) doublet.

partially resolved. The set of resolved EPR lines of  $\text{Ag}^{++}$  were obtained by Shields<sup>5</sup> using frozen  $\text{D}_2\text{O}$  matrix. The same transitions were observed by Yokota et al.<sup>9</sup> after thermal bleaching in Li - Al - metaphosphate glass containing Pb and Ag. In the last case the resolution of doublets was not achieved on account of the multiplicity of types of  $\text{Ag}^{++}$  sites in the glass structure.

The partial resolution of the doublet of  $g_{||}$  in Fig. 4 is very unstable and readily disappears at a temperature of about  $-100^\circ\text{C}$  during 10 minutes. It was not possible to evaluate the hfs constants  $A$  and  $B$  of spin Hamiltonian because of the lack of resolution of these doublets. The values of  $g_{||}$  and  $g_{\perp}$  could be evaluated writing the equations (5.2) and (5.3) in the reduced form:

$$H_{0||} = \frac{h\nu}{g_{||}\beta_0} \quad (5.4)$$

$$H_{0\perp} = \frac{h\nu}{g_{\perp}\beta_0} \quad (5.5)$$

where  $H_{0||}$  and  $H_{0\perp}$  correspond to the mean position of the central positions of  $\text{Ag}^{++}$  doublets.

The values of  $g_{||}$  and  $g_{\perp}$  evaluated for the samples are listed in Table 2.

Table 2

Sample	% $\text{Al}_2\text{O}_3$	% $\text{B}_2\text{O}_3$	$g_{  }$	$g_{\perp}$
E-9	—	70	$2.327 \pm .017$	$2.108 \pm .013$
(a) E-9	—	70	$2.328 \pm .017$	$2.108 \pm .013$
E-7	5	65	$2.308 \pm .016$	$2.079 \pm .013$
(b) E-3	20	50	$2.301 \pm .016$	$2.062 \pm .013$
E-2	20	50	$2.301 \pm .016$	$2.062 \pm .013$
(a.t.) E-2	20	50	$2.273 \pm .016$	$2.064 \pm .013$

The separation of the lines of the  $g_{\parallel}$  doublet of Fig. 4 gives an estimate of hfs constant A which is of the order of

$$A/g_{\parallel} \beta_0 = 44 \pm 4 \text{ Oe} \quad (5.6)$$

## 6. BORON ELECTRON CENTER (BEC)

The EPR lines related with electrons trapped  $e_t^-$  by boron atoms are indicated in Figures 1, 4 and 5. These centers were first described by Griscom<sup>1</sup> in recent work using EPR study of borate glass with potassium oxide. The observed lines are part of 4 transitions from the interaction between <sup>11</sup>B nucleus, more abundant, with the trapped electron. The <sup>11</sup>B nucleus has the spin  $I = 3/2$  and the equal separation between adjacent lines gives the hfs constant A.

The hfs constant of BEC is very sensitive to the local dimension of the site where the electron was trapped. In Table 3 is apparent the difference between the interactions in glasses containing about 5% mole of silver and the base glass. We conclude that the presence of silver impurity atoms exerts great influence on the glass structure, whose boron and oxygen chains are destroyed, giving origin to greater rings, where the electron center suffers a smaller interaction.

Table 3

Sample	%Al <sub>2</sub> O <sub>3</sub>	%B <sub>2</sub> O <sub>3</sub>	%Ag	<A> (BEC) (Oe)
E-9	—	70	5	56 ± 4
(a) E-9	—	70	5	56 ± 4
E-7	5	65	5	56 ± 4
(b) E-3	20	50	5	50 ± 4
E-2	20	50	5	60 ± 4
E-8	—	70	—	96 ± 4
E-1	20	50	—	96 ± 4

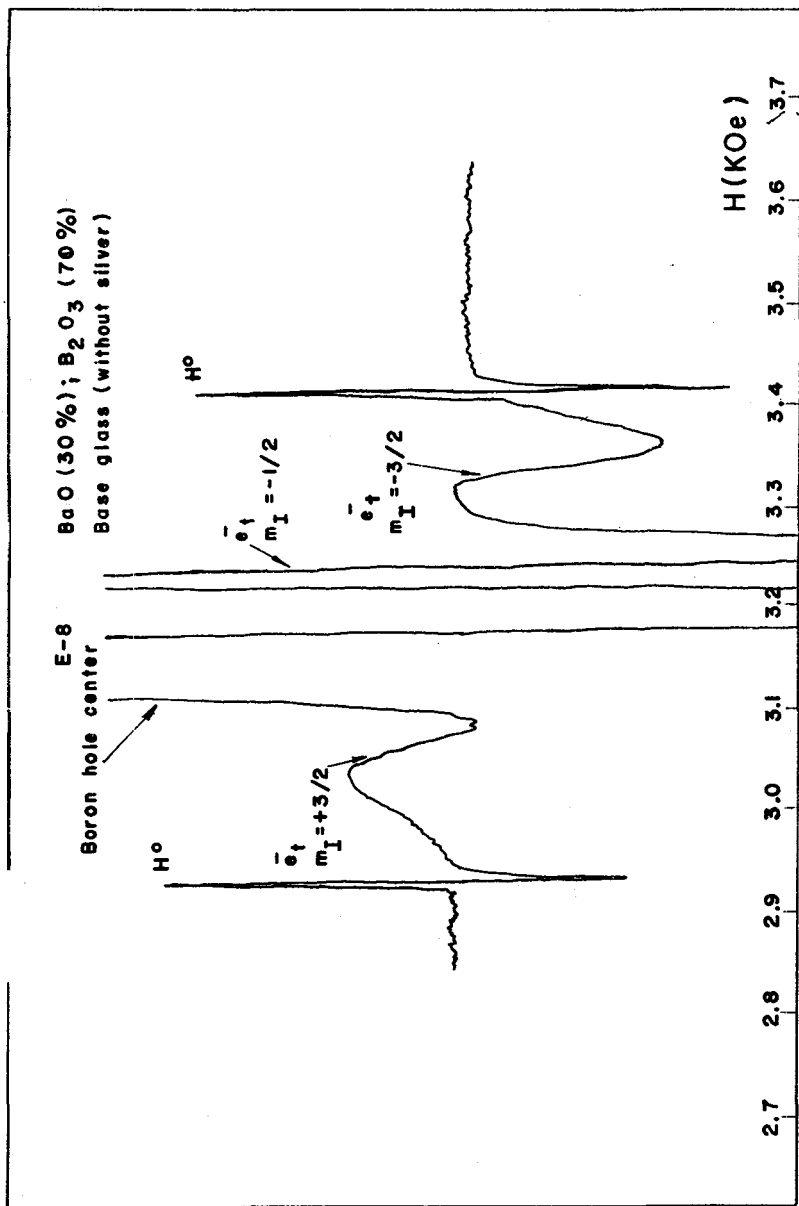


Fig 5 - EPR spectrum of BaO(30%);  $B_2O_3$ (70%) base glass showing three of the furthest boron electron center (BE0). The line of BE0 for  $m_I = +\frac{1}{2}$  was obscured by the boron hole center.

Looking at the Table 3, it is apparent that the concentration of  $Al_2O_3$  exerts only a weak influence on the BEC.

The evaluation of the mean value of hfs constant  $\langle A \rangle$  of BEC was done measuring the separation of the lines corresponding to  $m_I = -1/2$  and  $m_I = +1/2$  in the glasses containing Ag and between the lines corresponding to  $m_I = -3/2$  and  $m_I = +3/2$  in the base glasses.

The comparatively greater value of  $\langle A \rangle$  for the base glasses indicates that the boron-oxygen rings have respectively smaller size.

## 7. DISCUSSION

The relatively high concentrations of alkali oxide (30% of BaO) and Ag (5% mole) favours the formation of an  $Ag^0$  center with great line width and without isotopic resolution. Asabghy *et al.*<sup>8</sup> designated this center as  $Ag_N^0$  and showed that the line width is associated to the non-bridging oxygen content in the matrix.

The occurrence of the  $Ag_N^0$  center and the increment of its concentration is nearly proportional to the silver content in the sample as shown by these authors, who proposed that the  $Ag_N^0$  center results from the association of  $Ag^0$  with a metal atom to form a binary compound.

Since the  $Ag_2^+$  centers are absent in the samples with relatively high concentration of alkali oxide and silver, it is to be also expected the absence of  $Ag_2^0$ , because in both cases collisions must occur between silver atoms. This would be possible only in favorable conditions for the migration of silver atoms or ions in these materials. So we conclude that in these samples the migration of silver atoms, if any, is very reduced.

The reduced influence of  $Al_2O_3$  concentration on the spin Hamiltonian parameters is due probably to the little ionic radius of aluminium.

The observed  $Ag^{++}$  centers gave parameters in good agreement with the values found in literature, related to different matrices.

The drastic variation of hfs constant of boron electron center showed that the glass structure was affected severely by the presence of 5% mole of silver, possibly by the cracking of the boron-oxygen rings in the matrix chain, opening greater places in similar fashion as the effect of the addition of alkali oxide modifier.

The authors are grateful to Prof. A. Bishay for introducing them to the study of glass during his permanence in the Instituto de Física of the University of São Paulo. We acknowledge also helpful discussions with Prof. C. Quadros and M.L. de Siqueira.

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