

## PARAMAGNETIC PROPERTIES OF THE DIVALENT NICKEL IONS IN SOME ALKALI BORATE GLASSES

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### ABSTRACT

Paramagnetic properties of some alkali borate glasses containing nickel oxide were studied to throw some light on the equilibrium between the octahedral and the tetrahedral states of the divalent nickel ions.

The experimental results obtained indicated that all the glasses studied are paramagnetic and  $\text{NiO}_2/\text{NiO}_4$  equilibrium depends on several factors such as the polarizability of the oxygen ligands surrounding the nickel ions, mobility of the alkali ions, field strength and the ability of some divalent, trivalent and tetravalent metal oxides as network forming units.

### INTRODUCTION

The magnetic susceptibility measurements of coloured glasses have been found to be of particular interest to follow the different forms in which the elements of the transition metals group can exist in glass<sup>1</sup>. According to the earlier works in this subject, it was found that the magnetic properties of different compounds are influenced with the change in their chemical combination and this was completely explained in the work of Pascal<sup>2</sup>. From the other hand, Selwood<sup>1</sup> had summarized the earlier works on the transition elements compounds in his monograph. Consequently, other studies have been published concerning the magnetic properties of some glasses containing different transition metal elements<sup>1</sup>. Briet and Juza<sup>1</sup> studied the magnetic properties of nickel ions in glass of tertiary system, boric oxide-alkali oxide-nickel oxide. Juza and et al<sup>1</sup> measured the magnetic properties of nickel ions in different types of glasses and attributed the colour changes to the change

in the coordination number of nickel. The magnetic measurements of nickel ions in glasses of different compositions have been explained on the basis of the ligand field theory<sup>1</sup>.

In the present work, the effect of different factors such as the glass composition and the nickel ion concentration in some selected alkali borate glasses were studied.

#### Experimental details and calculations

All the glass batches, after pulverization, were melted in Pt-2 % Rh crucibles in an electrically heated furnace at a temperature of 1100-1250 °C, depending on the glass composition, for 4 hr. The molten glass samples were then poured as rods of ten cm long and of one cm<sup>2</sup> cross-sectional area. The glasses, after setting, were annealed to give strain free samples as could be detected by the polarized light. Grinding and polishing were carried out with minimum amount of water. The magnetic measurements for all the glass samples were determined following the Gouy method<sup>1</sup> using an electromagnet of approximately 14700 Gauss field strength. The volume susceptibility for each glass sample was determined using the equation:

$$K_1 = K_2 + 2 \Delta mg / aH^2 \dots \text{where,}$$

$K_1$  is the volume susceptibility of the glass sample;

$K_2$  is the volume susceptibility of the air (approximately Zero);

$\Delta m$  is the weight difference due to the magnetic pull;

$g$  is the gravity acceleration;

$a$  is the cross sectional area of the glass sample; and

$H$  is the magnetic field strength.

The value of the mass susceptibility of each glass sample was then calculated using the equation:

$$\varnothing = K_1 / \rho \dots \text{where,}$$

$\varnothing$  is the mass susceptibility of the glass sample; and

$\rho$  is the glass density.

Similar measurements were also carried out on the base glass (free from nickel) for each glass composition, and the difference gives the mass susceptibility values for the nickel ion.

## RESULTS

The experimental results obtained for the glasses studied can be summarized in the following:

1. Fig. (1) represents the experimental results obtained for the binary lithium-borate, sodium-borate and potassium-borate glasses. Each glass sample contains a constant amount of nickel oxide (0.25 g NiO / 100 g glass). It can be seen from the above figure that the values of the paramagnetic susceptibility increased as the alkali oxide was gradually increased in these glasses. In the glasses containing low and moderate proportions of the alkali oxide content, the values of the paramagnetism for lithium borate glasses are higher than those for sodium borate glasses and the latter values are higher than those for potassium borate glasses; while in the glasses containing high proportions of the alkali oxide content, the values of the paramagnetism are in the following order: potassium borate > sodium borate > lithium borate

2. The values of the paramagnetic susceptibility for the sodium borate glasses of the same base composition  $B_2O_3$  80 % -  $Na_2O$  20 % containing different proportions of nickel oxide are linearly increased with the gradual increase of the nickel oxide content, Fig. (2).

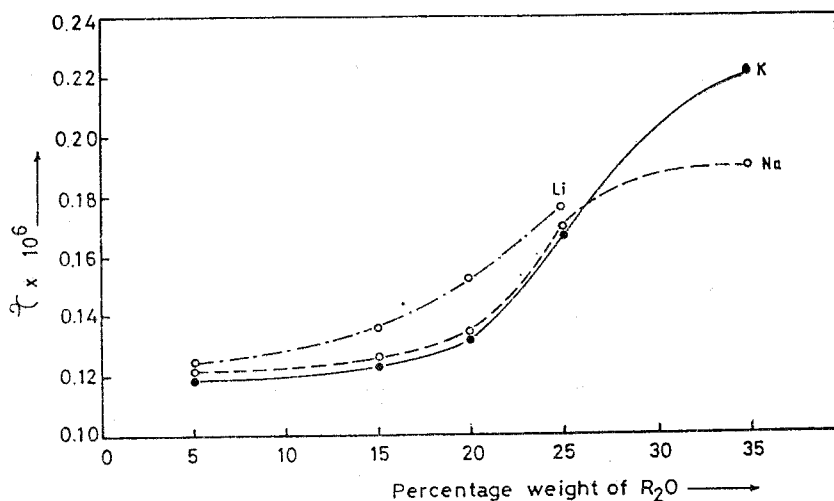


Fig. 1. The relation between the mass susceptibility and the alkali oxide content in alkali borate glasses containing 0.25 gm. NiO/100 gm. glass.

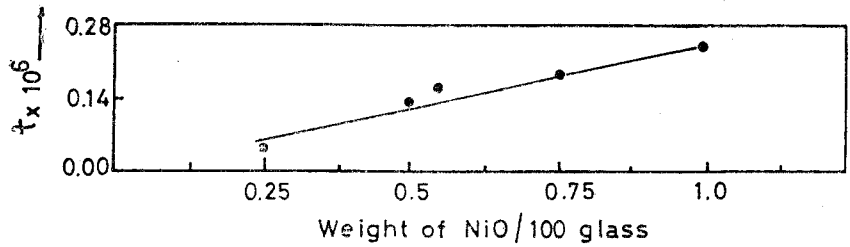


Fig. 2. The relation between the mass susceptibility and the concentration of nickel oxide in the glass of the composition  $B_2O_3$  80 % -  $Na_2O$  20 %.

3. The replacement of soda in the glass of the base composition  $B_2O_3$  80 %- $Na_2O$  20 % containing 0.25 g NiO/100 g glass by one of the divalent metal oxides, magnesia, cadmium oxide, zinc oxide, lime, strontium oxide or barium oxide increases the values of the paramagnetic susceptibility of these glasses as shown in Fig. (3). Also it can be seen that the values of the paramagnetism follow the order:

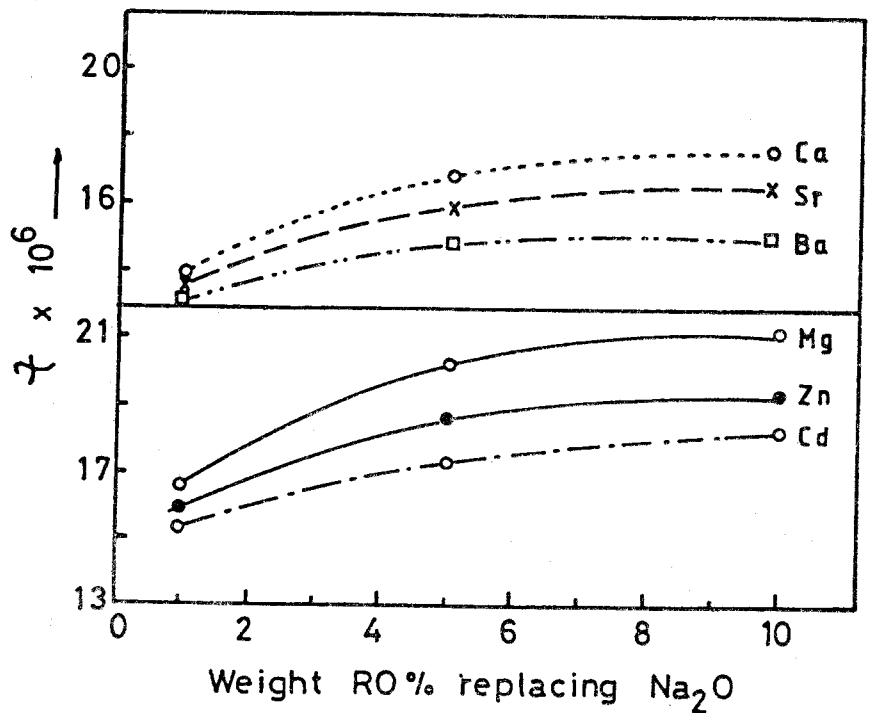


Fig. 3. The relation between the values of the mass susceptibility and the parts of soda replaced by one of the divalent metal oxides in the glass of the composition  $B_2O_3$  80 % -  $Na_2O$  20% containing 0.25 gm. NiO/100 gm. glass.

- i.  $\text{MgO} > \text{ZnO} > \text{CdO}$  for the glasses containing magnesia, cadmium oxide or zinc oxide.
- ii.  $\text{CaO} > \text{SrO} > \text{BaO}$  for the glasses containing lime, strontium oxide or barium oxide.

4. The replacement of boric oxide by alumina, titania or zirconia increases the values of the paramagnetic susceptibility as tabulated in table(1).

Table 1. Compositions and values of mass susceptibility for sodium borate glasses of the base composition  $\text{B}_2\text{O}_3$  80 % -  $\text{Na}_2\text{O}$  20 % containing 0.25 g NiO / 100 g glass, with parts of boric oxide replaced by alumina, titania or zirconia.

Glass No.	Class composition wt %			Values of $-\chi \times 10^3$
	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{R}_2\text{O}_3$ or $\text{RO}_2$	
1	80	20	—	0.1339
2	79	20	$\text{Al}_2\text{O}_3$	0.1692
3	75	20	= 1 % $\text{B}_2\text{O}_3$	0.2222
			= 5% $\text{B}_2\text{O}_3$	
4	79	20	$\text{TiO}_2$	0.1428
			= 1% $\text{B}_2\text{O}_3$	
5	79.9	20	$\text{ZrO}_2$	0.1375
			= 0.1% $\text{B}_2\text{O}_3$	

## DISCUSSION

It is well known that the paramagnetism introduced into a glass by the incorporation of the transition metal ions arises from the unpaired electrons of the unfilled 3d-subshell of these metals. The d-shell contains five orbitals, each of which may be occupied by one or two electrons. On considering the outer electronic configuration of nickel, it is appeared that nickel has paramagnetic properties in either the atomic or the ionic form. It will be also paramagnetic when it exists either in the octahedral or in the tetrahedral field<sup>1</sup>. Accordingly, the experimental results obtained for our glass samples can be discussed as follows:

1. The values of the paramagnetic susceptibility for the glasses containing soda, lithia or potash show a progressive increase as the alkali oxide is increased, Fig. (1). According to Moore et al<sup>1</sup>, the change exhibited in the value of the paramagnetism takes place at about the same content of the metal alkali oxide as the colour of the glasses change which can be related to the change in the coordination number of nickel ion from octahedral to tetrahedral state. Hence, it can be concluded that the equilibrium between octahedral and tetrahedral coordinations of the

nickel ion shifts towards the formation of more tetrahedral and less octahedral forms as the alkali oxide content increases. The relative effect of soda, lithia and potash can be explained when we realise that the lithium ion can fill the spaces in the alkali borate glasses without distorting the structure itself, and hence facilitating the formation of the nickel ion in the octahedral coordination<sup>11</sup>; also the oxygen ion in proximity to a sodium or a potassium ion must be more polarized than an oxygen in proximity to a lithium ion, hence in the glasses containing sodium or potassium ions the presence of the relatively easily polarizable oxygen ions shift the equilibrium between the octahedral and the tetrahedral coordinated nickel ion to the formation of more tetrahedral and less octahedral states with the gradual increase of the alkali oxide content, soda or potash. This is in complete agreement with the work of Berkes et al<sup>11</sup> on some alkali borate glasses containing nickel from which they concluded that there is a continuous increase in the proportion of the tetrahedral coordinated nickel ion as the atomic number of the alkali is raised.

2. The increase of the values of the paramagnetic susceptibility as the nickel oxide content was gradually increases in the same base glass of the composition  $B_2O_3$  80 %- $Na_2O$  20 %, can be attributed to the paramagnetic character of the divalent nickel ion itself due to its two unpaired electrons.

3. In the same base glass of the composition  $B_2O_3$  80 %- $Na_2O$  20 % containing 0.25 g NiO / 100 g glass, when magnesia, cadmium oxide or zinc oxide was introduced replacing soda, Fig. (3), a considerable proportion of these different divalent oxides will form  $MgO_4$ ,  $CdO_4$  or  $ZnO_4$  groups, while the rest ions remain enclosed in the glass structure interstices. The oxygen ions which are deformed by one of the divalent cations are found to be less polarizable than those which are deformed by the sodium ions and this can be due to the relatively small size and the high field strength of the group II-A metal ions. Thus, on replacing more soda by one of these divalent metal oxides, in the base glass of the composition  $B_2O_3$  80 %- $Na_2O$  20 % which contains high proportions of nickel ions mainly in the octahedral state, the amount of  $MgO_4$ ,  $CdO_4$  or  $ZnO_4$  are reduced and some of these divalent metal ions act as bridges between the network forming units. Consequently, the proportion of the nickel ion in the octahedral coordination tend to increase. The relative effect of these oxides may be due to the higher tendency of magnesia form  $MgO_4$  groups than zinc oxide or cadmium oxide<sup>10</sup>.

4. In the same sodium borate base glass, if soda is gradually replaced by lime, strontium oxide or barium oxide, Fig. (3), these ions will act partly as bridges between the glass forming groups and partly enclosed in the interstices of the glass structure. Since the oxygen ions around the divalent cations are strongly held and less polarized than with sodium ions, thus the proportion of the nickel ions in the octahedral coordination will tend to increase with the gradual increase of one of the divalent metal oxides replacing soda. The relative of these oxides may be due to their relative sizes and their ionic potentials<sup>11</sup>.

5. When alumina is introduced into the same base glass replacing boric oxide, Table (1), it will exist as  $AlO_4$  groups separated from each other by  $BO_3$  triangles. However, each tetrahedron would require an alkali ion in its immediate vicinity. Hence, the number of singly bonded oxygen ions would be large giving a considerable flexibility in the glass structure. Thus, it can be expected that the proportion of the nickel ion in the octahedral form would be also increased as more boric oxide was replaced by alumina.

6. The resulting effect of adding titania or zirconia replacing boric oxide in the same base glass, Table (1), depends partly on the strength of the linkages of the oxygen at the corners of the adjoining units. However, in these glasses the polarizability of the oxygen ligands will decrease. Then, the nickel ions would be expected to be found in the octahedral coordination.

All the above conclusions are in complete agreement with the experimental results obtained.

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