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Electron paramagnetic resonance of Cu^{2+} and VO^{2+} ions in phosphate glasses

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Electron spin resonance (ESR) spectra of $x(CuO \cdot V_2O_5)$ $(1 - x)(Na_2O \cdot P_2O_5)$ and $x(CuO \cdot 2V_2O_5)(1 - x)(Na_2O \cdot P_2O_5)$ glasses for $0 \leqslant x \leqslant 40$ have been studied at the X-band and at 300 K. It is found that for $x \leqslant 5$, both Cu^{2+} and VO^{2+} are present, mostly as isolated species. For $x \geqslant 10$, broad resonance lines at $g = 2.1524$ for $x(CuO \cdot V_2O_5)(1 - x)(Na_2O \cdot P_2O_5)$ and at $g = 2.1448$ for $x(CuO \cdot 2V_2O_5)(1 - x)(Na_2O \cdot P_2O_5)$ are observed which may be mainly due to dipole–dipole type interaction between transition metal (TM) ions. Spin Hamiltonian parameters of TM ions have been calculated. Optical spectra of the sodium phosphate glasses doped with single TM ions have also been studied. The theoretical optical basicity, Λ_{th}, of these doped glasses has been calculated. It is found that for VO^{2+} ions $g_\parallel$, $g_\perp$ and k increase while $A_\parallel$, P and $\Delta g_\parallel / \Delta g_\perp$ decrease with increase in Λ_{th}. However, no significant change is observed in the spin Hamiltonian parameters of Cu^{2+} with the change in Λ_{th}.

1. Introduction

During the last few years many workers [1–10] have studied the oxide glasses containing mixed transition metal (TM) ions. Bogomolova and co-workers [5–7] have studied the P_2O_5–BaO–V_2O_5–CuO and P_2O_5–CaO–V_2O_5–CuO glasses and reported that a strong exchange interaction exists between Cu^{2+} and V^{4+} ions, leading to the mixed exchange Cu^{2+}–V^{4+} pairs formation. Bandyopadhyay [9] investigated the BaO–B_2O_3 glasses containing single and mixed transition metal oxides and suggested that out of various types of interactions taking place in the system, strong interaction between V^{4+} and Fe^{3+} or Cu^{2+} ions may result in the formation of V^{4+}–O–Fe^{3+} or V^{4+}–O–Cu^{2+} associates. This is thought [9] to be facilitated by the formation of less covalent $V^{4+}O_6$ units in the Fe–V or Cu–V mixed glasses. Ardelean *et al.* [10] studied $x(CuO \cdot 2V_2O_5)(1 - x)(2B_2O_3 \cdot K_2O)$ glasses and concluded that for $x < 10$ mol % both Cu^{2+} and V^{4+} ions are present mostly as the isolated species. They also reported that for $x \geqslant 10$ mol % the dipole–dipole and superexchange interactions occur between transition metal ions, which are manifest in EPR spectra by a broad line at $g = 2$. Therefore, we were interested to investigate ESR and optical spectra of V^{4+} and Cu^{2+} in sodium phosphate glasses.

2. Experimental details

The starting materials used in the present study were Analar grade reagents of $NaH_2PO_4 \cdot 2H_2O$, CuO and V_2O_5. Tables I and II give the composition in mol % of the glasses studied in the present paper. Each batch was melted in an electric muffle furnace at 700° C for about 3 h [11]. The melt was poured onto a carbon plate and pressed with a second plate.

The glasses were crushed for ESR measurement. The ESR spectra were recorded at 300 K on JEOL-FE3X spectrometer operating in the X-band. A magnetic field modulation of 100 kHz was applied. Diphenylpicryl hydrozyl (DPPH) with $g = 2.0036$ was used as a standard for the determination of the spin Hamiltonian parameters.

Optical absorption spectra of vanadyl and cupric ions in the glasses were recorded at 300 K using a

TABLE I Spin Hamiltonian parameters, P and k of VO^{2+} in $x(CuO \cdot V_2O_5)(1 - x)(Na_2O–P_2O_5)$ glasses. In glass 1 only CuO is added and in glass 2 only V_2O_5 is added

Glass no.	x	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ (10^{-4} cm^{-1})	$\lvert A_\perp \rvert$ (10^{-4} cm^{-1})	P (10^{-4} cm^{-1})	k	Λ_{th}
1	2	–	–	–	–	–	–	0.4678
2	2	1.9263	1.9696	176.3	65.3	120.42	0.8022	0.4665
3	1	1.9265	1.9697	175.8	65.8	119.35	0.8115	0.4687
4	3	1.9279	1.9700	174.4	66.2	117.57	0.8236	0.4698
5	5	1.9296	1.9703	172.7	66.7	115.45	0.8382	0.4709
6	10	–	–	–	–	–	–	0.4735
7	20	–	–	–	–	–	–	0.4778
8	30	–	–	–	–	–	–	0.4813
9	40	–	–	–	–	–	–	0.4843

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TABLE II Spin Hamiltonian parameters, P and k of VO^{2+} in $x(CuO \cdot 2V_2O_5)(1-x)(Na_2O\text{–}P_2O_5)$ glasses.

Glass no.	x	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ (10^{-4}cm^{-1})	$\lvert A_\perp \rvert$ (10^{-4}cm^{-1})	P (10^{-4}cm^{-1})	k	Λ_{th}
10	1	1.9289	1.9703	173.9	66.2	117.11	0.8261	0.4703
11	3	1.9305	1.9703	173.9	66.2	117.32	0.8251	0.4719
12	5	1.9316	1.9708	172.0	66.3	115.31	0.8352	0.4740
13	10	–	–	–	–	–	–	0.4786
14	20	–	–	–	–	–	–	0.4851
15	30	–	–	–	–	–	–	0.4896
16	40	–	–	–	–	–	–	0.4929

Unicam SP700 Spectrophotometer. Care was taken to keep the samples away from moisture before taking these measurements.

3. Results and discussion

The spectrum obtained for glass 1 exhibits a pronounced peak at $g = 2.0613$ and a broad and shallow quadruplet at $g = 2.4022$, the latter arising from the splitting of $g_\parallel$. Such spectral features are characteristic of the Cu^{2+} ions present in the axially distorted octahedral sites.

Figs 1 and 2 show the ESR spectra at 300 K of VO^{2+} and Cu^{2+} in $x(CuO \cdot V_2O_5)(1-x)(Na_2O \cdot P_2O_5)$ and $x(CuO \cdot 2V_2O_5)(1-x)(Na_2O \cdot P_2O_5)$ glasses, respectively, for $x = 1, 3, 5, 10$. The spectra obtained are modified with increasing content of Cu^{2+} and VO^{2+}. For $x \leqslant 5$, the ESR spectra are obtained in which hyperfine structure presumably due to VO^{2+} and Cu^{2+} ions is visible, whereas for $x \geqslant 10$, the hyperfine structure disappears completely. From these spectra, it can be suggested that there is a considerable interaction taking place between Cu^{2+} and VO^{2+} ions, simply because both these ions exhibit hyperfine spectra in the same region of the magnetic field. For $x \geqslant 10$ broad lines at $g = 2.1524$ for $x(CuO \cdot V_2O_5)(1-x)(Na_2O \cdot P_2O_5)$ and at $g = 2.1448$ for $x(CuO \cdot 2V_2O_5)(1-x)(Na_2O \cdot P_2O_5)$ appear which may be due to clustering of ions in the studied glasses. The dominant interaction between the TM ions may be that of the dipole–dipole type. The number of clustered ions may increase with increase in TM ions and for $x \geqslant 10.0$ the superexchange interaction may be prevalent. This leads to the formation of the mixed exchange $Cu^{2+}\text{–}V^{4+}$ in the present glasses. Similar behaviour was observed by Bandyopadhyay [9] in $2BaO \cdot 3B_2O_3$ glasses doped with Cu_2O and V_2O_5.

For VO^{2+} the solution [12] of the axial spin Hamiltonian [13, 14] given in Equations 1 and 2 is used for the parallel and perpendicular hf lines, respectively.

$$B_\parallel(m) = -A_\parallel m(1+P) + B_\parallel(0) \times \{1 - 4P[I(I+1) - m^2(1-p)]\}^{1/2} \tag{1}$$

$$B_\perp(m) = -A_\perp m(1+P_1) + B_\perp(0) \times \{1 - 4P_1[I(I+1) - m^2(1+P_1)]\}^{1/2} - \frac{(A_\parallel - A_\perp)^2}{8B_\perp(0)}[I(I+1) - m^2] \tag{2}$$

where

$$P = \frac{A_\perp^2}{4B_\parallel^2(0) - A_\parallel^2},$$

$$P_1 = \frac{(A_\parallel + A_\perp)^2}{4[4B_\perp^2(0) - A_\perp^2]},$$

and other symbols have their usual meaning. The spin Hamiltonian parameters are given in Tables I and II. The uncertainty in the value of g and A is ± 0.0010 and $\pm 0.6 \times 10^{-4}$ cm^{-1}, respectively. Relations given by Kivelson and Lee [15] were used to calculate P and k. P is the dipolar hyperfine coupling parameter and k is proportional to the amount of isotropic Fermi contact interaction. From the molecular theory we find that the components $A_\parallel$ and $A_\perp$ consist of the contributions $A'_\parallel$ and $A'_\perp$ of the 3dxy electron to the hyperfine structure and the Pk term arising due to the anomalous contribution of the s-electrons. Values of $A'_\parallel$, $A'_\perp$ and $\Delta g_\parallel/\Delta g_\perp$ were calculated and are given in Tables III and IV. The value of $\Delta g_\parallel/\Delta g_\perp$ is a measure of the tetragonality of the V^{4+} sites.

From Tables I to IV we see that spin Hamiltonian parameters change in the same way in both the systems. $A_\parallel$, P and $A'_\parallel$ decrease with increase in TM ion content but $g_\parallel$ and k increase with increasing TM ions.

TABLE III $A'_\parallel$, $A'_\perp$, Pk, $\Delta g_\parallel/\Delta g_\perp$ or VO^{2+} of $x(CuO \cdot V_2O_5)$ $(1-x)$ $(Na_2O \cdot P_2O_5)$ glasses

Glass no.	$\lvert A'_\parallel \rvert$ (10^{-4}cm^{-1})	$\lvert A'_\perp \rvert$ (10^{-4}cm^{-1})	Pk (10^{-4}cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$
2	79.70	31.30	96.60	2.3242
3	78.95	31.05	96.85	2.3251
4	77.57	30.63	96.83	2.3084
5	75.93	30.07	96.77	2.2718
6	–	–	–	–
7	–	–	–	–
8	–	–	–	–
9	–	–	–	–

TABLE IV $A'_\parallel$, $A'_\perp$, Pk, and $\Delta g_\parallel/\Delta g_\perp$ of VO^{2+} of $x(CuO \cdot 2V_2O_5)(1-x)$ $(Na_2O \cdot P_2O_5)$ glasses

Glass no.	$\lvert A'_\parallel \rvert$ (10^{-4}cm^{-1})	$\lvert A'_\perp \rvert$ (10^{-4}cm^{-1})	Pk (10^{-4}cm^{-1})	$\Delta g_\parallel/\Delta g_\perp$
10	77.16	30.54	96.74	2.2937
11	77.11	30.59	96.79	2.2437
12	75.65	30.05	96.35	2.2444
13	–	–	–	–
13	–	–	–	–
14	–	–	–	–
15	–	–	–	–
16	–	–	–	–

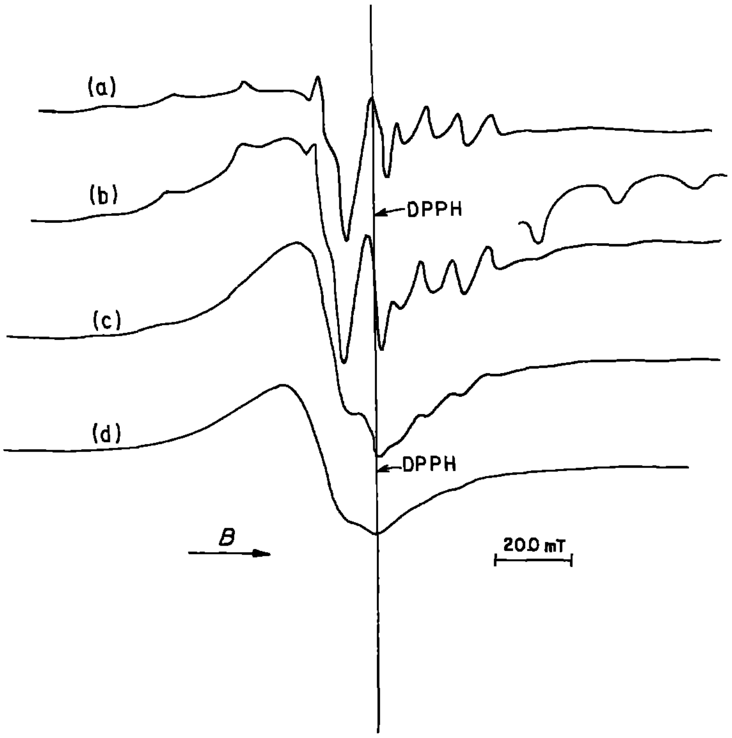

Figure 1 The ESR spectra of $x(\mathrm{CuO}\cdot\mathrm{V_2O_5})(1-x)$ $(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ glasses at the X-band ($\nu \sim 9.445$ GHz) and at 300 K. (a) Glass 3, (b) glass 4, (c) glass 5 and (d) glass 6. The spectrum below (a) is for glass 3 with a ten-fold increase in gain.

However, the variation in $g_\perp$, $A_\perp$ and $A'_\perp$ is within experimental uncertainty. From Tables I and II, we find that the $g_\parallel$ value of $x(\mathrm{CuO}\cdot 2\mathrm{V_2O_5})(1-x)$ $(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ is greater than the $g_\parallel$ value of $x(\mathrm{CuO}\cdot\mathrm{V_2O_5})(1-x)(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ for the same x, whereas the $A_\parallel$ value of $x(\mathrm{CuO}\cdot 2\mathrm{V_2O_5})$ $(1-x)(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ is smaller than the $A_\parallel$ value of $x(\mathrm{CuO}\cdot\mathrm{V_2O_5})(1-x)(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ for the same x. It seems that in the former glasses the strong co-ordinate oxygen atoms at $\mathrm{VO^{2+}}$ ions occur along the Ox and Oy axes in the xy plane. Consequently the V–O bonds along these axes become shorter to improve the octahedral symmetry.

The characteristic spectrum of $\mathrm{Cu^{2+}}$ ions is similar to those obtained for copper ions in other oxide glasses [9]. In the present study the perpendicular hyperfine lines are not resolved. A broad peak is obtained corresponding to which, $g_\perp$ is calculated. The values of spin Hamiltonian parameters characteristic of $\mathrm{Cu^{2+}}$ dispersed as isolated species are given in Tables V and VI.

Because $g_\parallel > g_\perp > 2.0023$ we can consider that the ground state for the paramagnetic electron is the $d_{x^2-y^2}$ orbital, the $\mathrm{Cu^{2+}}$ being deposited in the distorted octahedral sites (D_{4h}) elongated on the Oz axis [13]. It seems from Tables V and VI that the co-ordination structure of isolated $\mathrm{Cu^{2+}}$ complexes keeps approximately the same symmetry. Microenvironmental fluctuations around the $\mathrm{Cu^{2+}}$ may also exist, which together with the mututal dipolar interaction leads to the broadening of hyperfine lines.

The absorption spectra of $\mathrm{Cu^{2+}}$ and $\mathrm{VO^{2+}}$ in glasses

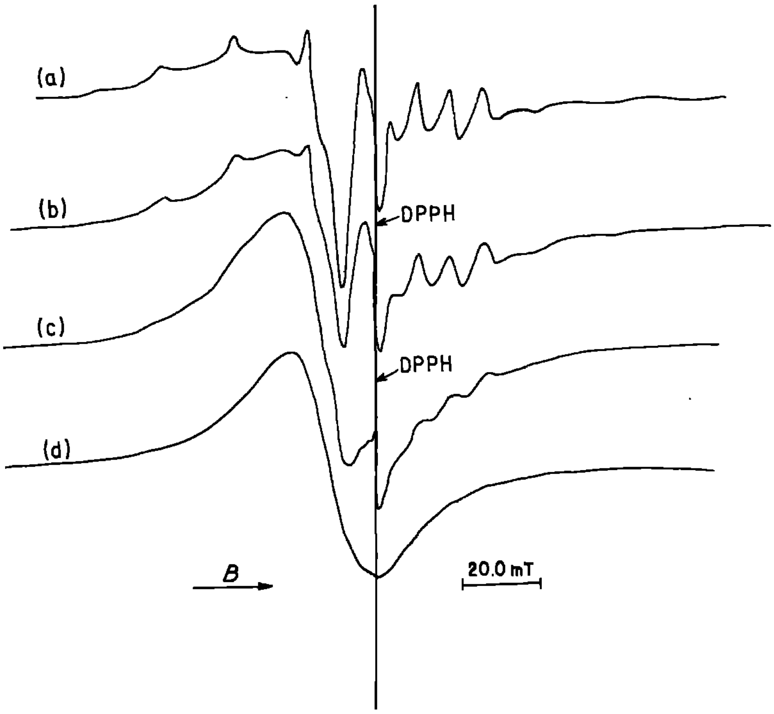

Figure 2 The ESR spectra of $x(\mathrm{CuO}\cdot 2\mathrm{V_2O_5})$ $(1-x)$ $(\mathrm{Na_2O}\cdot\mathrm{P_2O_5})$ glasses at the X-band ($\nu \sim 9.445$ GHz) and at 300 K. (a) Glass 10, (b) glass 11, (c) glass 12 and (d) glass 13.

TABLE V Spin Hamiltonian parameters of Cu^{2+} in $x(CuO \cdot V_2O_5)(1 - x)(Na_2O \cdot P_2O_5)$ glasses

Glass no.	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ ($10^{-4}cm^{-1}$)	$\lvert A_\perp \rvert$ ($10^{-4}cm^{-1}$)
1	2.4022	2.0613	112.1	–
2	2.4022	2.0561	112.1	–
4	2.4022	2.0561	112.1	–
5	–	–	–	–
6	–	–	–	–
7	–	–	–	–
8	–	–	–	–
9	–	–	–	–

1 and 2, respectively, are shown in Fig. 3. In optical absorption spectra of vanadyl, a broad band around 800 nm is observed. A single absorption peak around 892 nm is observed for Cu^{2+}.

ESR parameters and the position of the absorption band of Cu^{2+} are used [16] to evaluate Cu^{2+} bonding coefficients $\alpha^2 = 0.738$, $\beta_1^2 = 0.92$. The bonding coefficients α^2, β_1^2 and $\beta^2 (= 1.00)$ characterize, respectively, the in-plane σ bonding, in-plane π bonding and out-of-plane π bonding of the copper (II) complex; their values lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding. The β^2 value may be expected to lie sufficiently close to unity as to be indistinguishable from unity in the bonding coefficient calculations [17]. The α^2 value indicates an intermediate character for the in-plane σ bonding but the in-plane π bonding is significantly ionic.

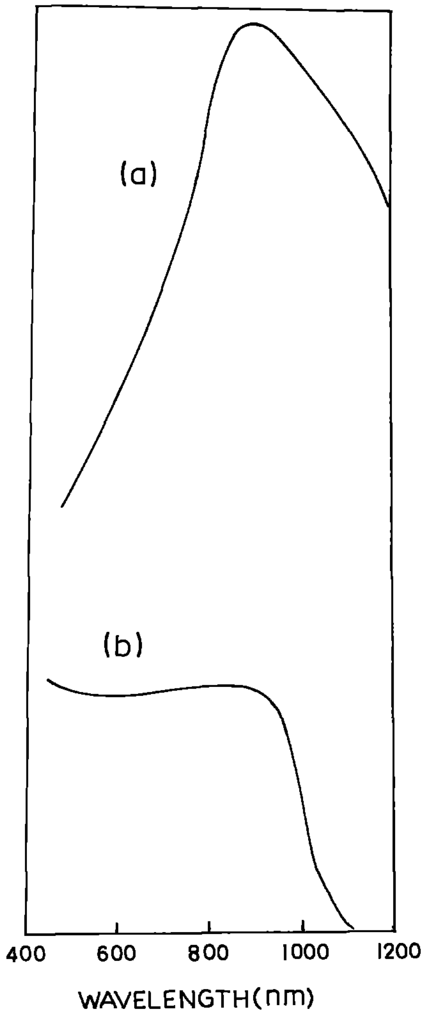

Figure 3 Optical absorption spectra of (a) Cu^{2+} and (b) VO^{2+} at 300 K in $Na_2O \cdot P_2O_5$ glasses 1 and 2, respectively.

TABLE VI Spin Hamiltonian parameters of Cu^{2+} in $x(CuO \cdot 2V_2O_5)(1 - x)(Na_2O \cdot P_2O_5)$ glasses

Glass no.	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$ ($10^{-4}cm^{-1}$)	$\lvert A_\perp \rvert$ ($10^{-4}cm^{-1}$)
10	2.4022	2.0613	112.1	–
11	2.4022	2.0561	112.1	–
12	–	–	–	–
13	–	–	–	–
14	–	–	–	–
15	–	–	–	–
16	–	–	–	–

It is also possible to calculate the theoretical optical basicity [18] given by:

$$\Lambda_{th} = \sum_i \frac{Z_i r_i}{2\gamma_i}$$

where Z_i is the oxidation number of the cation i, r_i is the ratio of cation i with respect to the total number of oxides and γ_i is the basicity moderating parameter. γ_i for the cation is given by

$$\gamma_i = 1.36(x_i - 0.26)$$

where x_i is the Pauling electronegativity [19] of the cation. The theoretical value of optical basicity thus calculated is also included in Tables I and II. It may be noted from Tables I to VI that in case of VO^{2+}, $g_\parallel$, $g_\perp$ and k increase while $A_\parallel$, P and $\Delta g_\parallel / \Delta g_\perp$ decrease with increase in Λ_{th}, while no significant change is observed in the spin Hamiltonian parameters of Cu^{2+} with the change in Λ_{th}. Klonkowski [20] also noted that ESR parameters of the Cu^{2+} spectra change insignificantly with increasing optical basicity.

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References

1. G. F. LYNCH and M. SAYER, *J. Phys. C.* **6** (1973) 3661.
2. M. SAYER and G. F. LYNCH, *ibid.* **6** (1973) 3774.
3. L. D. BOGOMOLOVA, V. N. LAZUKIN and N. V. PETROVYKH, *Sov. Phys. Solid State* **14** (1969) 243.
4. A. K. BANDYOPADHYAY and J. O. ISARD, *J. Phys. D.* **10** (1977) L 99.
5. L. D. BOGOMOLOVA, *J. Non-Cryst. Solids* **30** (1979) 379.
6. L. D. BOGOMOLOVA, M. P. GLASSOVA and V. A. SHMUDER, *Phys. Khim Stecla* **5** (1979) 26.
7. L. D. BOGOMOLOVA and M. P. GLASSOVA, *J. Non-Cryst. Solids* **37** (1980) 423.
8. L. D. BOGOMOLOVA, V. A. JACHKIN, M. P. GLASSOVA and S. N. SPASISKINA, *J. de Phys.* **42** (1981) C4-993.
9. A. K. BANDYOPADHYAY, *J. Mater. Sci.* **16** (1981) 189.
10. I. ARDELEAN, O. COZAR and Gh. ILONEA, *J. Non-Cryst. Solids* **57** (1983) 199.
11. J. A. DUFFY, *Phys. Chem. Glasses* **13** (1972) 65.

12. V. P. SETH, A. YADAV and R. S. BANSAL, *Phys. Status Solidi* (*b*) **132** (1985) 255.
13. A. ABRAGAM and B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions" (Clarendon, Oxford, 1970) p. 175.
14. V. P. SETH, V. K. JAIN and R. K. MALHOTRA, *J. Non-Cryst. Solids* **57** (1983) 199.
15. D. KIVELSON and S. K. LEE, *J. Chem. Phys.* **41** (1964) 1806.
16. D. KIVELSON and R. NEIMAN, *ibid.* **35** (1961) 145.
17. H. IMAGAWA, *Phys. Status Solidi* **30** (1968) 468.
18. J. A. DUFFY and M. D. INGRAM, *J. Inorg. Nucl. Chem.* **37** (1975) 1203.
19. L. PAULING, "The Nature of the Chemical Bond", 3rd Edn (Cornell University Press, New York, 1960) p. 93.
20. A. KLONKOWSKI, *Phys. Chem. Glasses* **22** (1981) 170.

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