JOURNAL OF MATERIALS SCIENCE 9 (1974) 1057-1063

Optical absorption of nickel (II) in Na_2O-NaCl-B_2O_3 and Na_2O-NaBr-B_2O_3 glasses

A. PAUL, A. N. TIWARI*
Department of Glass Technology, University of Sheffield, UK

The optical absorption spectra of nickel(II) have been studied in Na_2O–NaX–B_2O_3 glasses X = Cl or Br); the absorption bands have been interpreted in terms of Ligand Field Theory. In halide-free B_2O_3-rich glasses nickel(II) is octahedral, and halide substitution is accompanied by the formation of a tetrahedral nickel(II)–oxide–halide complex. In alkali-rich glasses nickel(II) is square planar and/or tetrahedral and no halide substitution can be observed. It is suggested that the halide ions are unable to substitute for oxygen in the predominantly covalent nickel(II)–oxygen bonds of the complex formed in basic glasses.

1. Introduction

Use of nickel as a colourant in glass is common; sometimes a small concentration of nickel is also used as decolourizer in glass industry. The colour of nickel containing glasses is known to be critically dependent on the composition and the thermal history of the glass. In this paper we present experimental evidence that the colour of nickel containing glass can also be altered by making small additives with the batch.

Nickel usually occurs in glass as nickel(II) in octahedral, square planar and tetrahedral symmetry depending upon the composition of the glass [1]. High-spin octahedral nickel(II) which occurs in low-alkali borate glasses is olive green; square planar nickel(II) is usually greyish brown and occurs in Na_2O–SiO_2 and high-alkali Na_2O–B_2O_3 glasses, whereas in high-alkali K_2O–SiO_2 and K_2O–B_2O_3 glasses nickel(II) is tetrahedral and imparts a pink colour. Numerous investigations on mixed ligand nickel(II) complexes have been reported in molten salt and in co-ordination compounds. When alkali halides or alkali sulphides are added to a glass containing a transition metal ion, anionic substitution around the transition metal ion takes place with a subsequent change in symmetry of the complex [2]. In this paper we report the chloride and bromide substitution around nickel(II) and the subsequent changes in symmetry of the complex in Na_2O–B_2O_3 glasses.

2. Experimental

All the raw materials (Na_2CO_3, NaCl, NaBr and H_3BO_3) were of "analar" quality; 0.50 wt % nickel was added as green NiO powder to the batch. Ten grammes of glass were melted at a time in a Pt + 2% Rh crucible at 1000° C in an electric furnace for four hours. Halide containing glasses were melted by partially substituting Na_2CO_3 by NaCl or NaBr in the batch; these glasses were stirred with a thick platinum wire for uniform distribution of halide throughout the melt.

All the constituents of the glass were estimated chemically. Nickel was estimated colorimetrically with dimethyl glyoxime [1]. Absorption spectra of 0.5 to 0.05 cm thick polished samples were measured on a Cary 14 spectrophotometer. In every case a blank glass of corresponding composition and thickness but without nickel was prepared and its absorption spectrum measured. In all the reported spectra of nickel(II) the blank absorption was subtracted.

3. Results

The composition of glasses studied in this investigation is shown in Table I. Absorption spectra of nickel(II) in Na_2O–NaCl–B_2O_3 glasses are shown in Fig. 1a and b. Nickel (II) in $16Na_2O,84B_2O_3$ glass is octahedral with three main absorption bands at 7200, 13 200 and 24 100 cm^{-1}. On small (up to 0.17 mol NaCl per litre

---

*Department of Metallurgical Engineering, Kanpur IIT, India.

TABLE I Composition of glasses (after chemical analysis)

Glass no.	Mol % B_2O_3	Density (g cm^{-3})	Moles per litre glass		
			Total Ni	NaCl	NaBr
1	84	1.7631	0.151	0.000	—
2	84	1.7620	0.143	0.126	—
3	84	1.7621	0.139	0.164	—
4	84	1.7600	0.147	0.169	—
5	84	1.7521	0.148	0.881	—
6	84	1.7001	0.138	2.486	—
44	92	1.9838	0.148	—	0.000
45	92	1.9854	0.137	—	0.042
46	92	1.9879	0.137	—	0.060
47	92	1.9878	0.137	—	0.073
48	92	1.9853	0.139	—	0.086
49	92	1.9869	0.147	—	0.179
50	92	1.9888	0.147	—	0.224
51	92	1.9887	0.143	—	0.231
52	84	2.0801	0.143	—	0.000
54	84	2.0754	0.143	—	0.092
56	84	2.0673	0.147	—	0.125
58	84	2.0711	0.148	—	0.204
76	75	2.2300	0.129	—	0.000
78	75	2.2360	0.117	—	0.769
83	75	2.2287	0.147	—	1.874

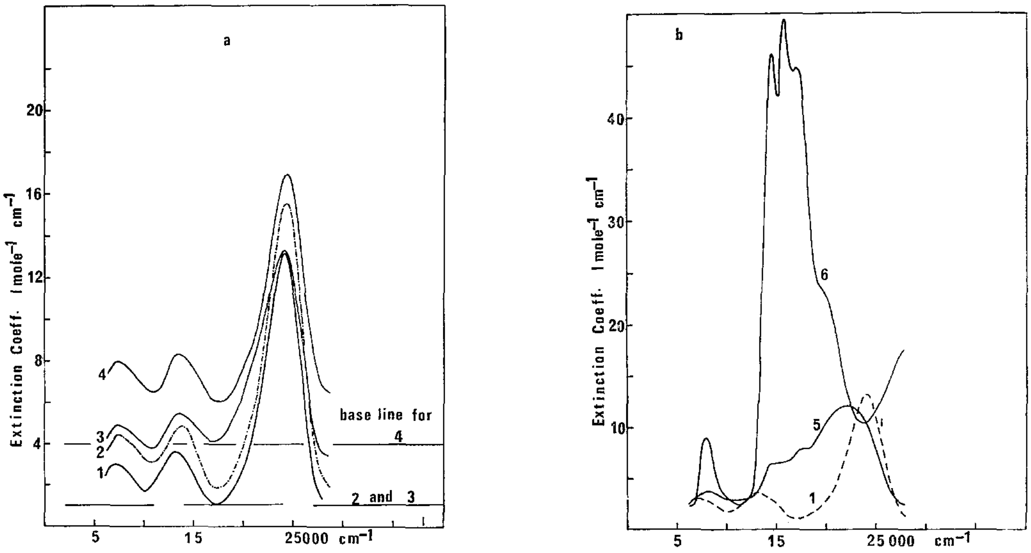

Figure 1 (a) and (b) Optical absorption spectra of nickel(II) in $(16 - x)Na_2O$, $2xNaCl$, $84B_2O_3$ glasses.

glass) substitution of NaCl for Na_2O in the glass, a shoulder is developed on the low energy side which may be represented as a separate set of bands buried in the more intense neighbouring band; the other bands at 13 200 and 7200 cm^{-1} do not show any significant change. With larger amounts of NaCl in the glass (Fig. 1b) an altogether new set of bands are developed

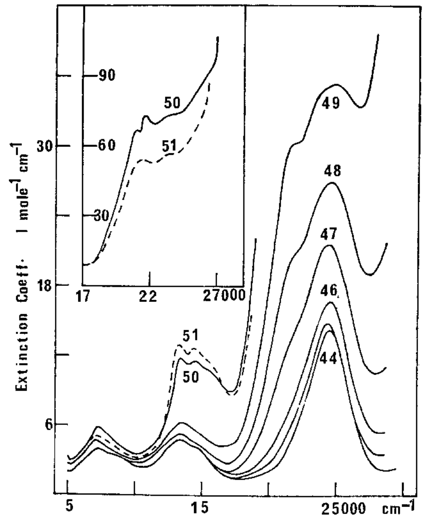

Figure 2 Optical absorption spectra of nickel(II) in $(8 - x)Na_2O$, $2xNaBr$, $92B_2O_3$ glasses.

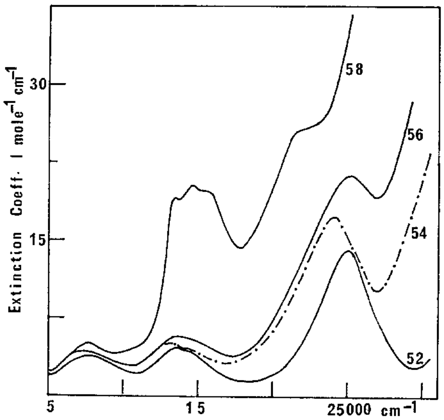

Figure 3 Optical absorption spectra of nickel(II) in $(16 - x)Na_2O$, $2xNaBr$, $84B_2O_3$ glasses.

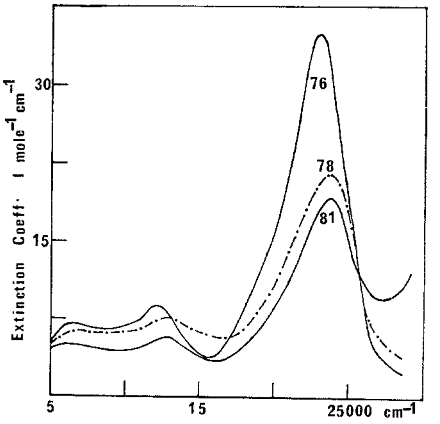

Figure 4 Optical absorption spectra of nickel(II) in $(25 - x)Na_2O$, $2xNaBr$, $75B_2O_3$ glasses.

around 7900, 15 800 and 21 000 cm^{-1} characteristic of square planar and tetrahedral nickel(II) complexes.

Absorption spectra of nickel(II) in different Na_2O–$NaBr$–B_2O_3 glasses are shown in Figs. 2 to 4. In the glass $8Na_2O.92B_2O_3$ (Fig. 2) a very small amount of bromide ($\geqslant 0.08$ mol NaBr per litre glass) produces the absorption bands around 7000 and 14 000 cm^{-1} characteristic of tetrahedral nickel(II); the intensity of all the tetrahedral bands increase with increasing amounts of bromide in the glass. With larger amounts of bromide ($\geqslant 0.8$ mol NaBr per litre glass) in these glasses, a strong tail of charge transfer bands due to nickel(II) tetrahedral complex intrudes into the visible region increasing the blue end absorption of the glass. The effect of bromide substitution in $16Na_2O,84B_2O_3$ glass containing nickel(II) is very similar; only a larger amount of bromide is necessary to produce the tetrahedral bands. In $25Na_2O$, $75B_2O_3$ glass no tetrahedral nickel(II) is formed even with 1.87 mol bromide/litre glass (Glass 83). Fig. 5 shows the absorption bands of tetrahedral nickel(II) in different glasses with oxide and oxide-halide coordination; and Fig. 6a and b show the absorption spectra of crystallines $NiCl_2$ and $NiBr_2$ respectively.

4. Discussion

Nickel(II) is $3d^8$; the relevant part of the energy level diagram for a d^8 system is shown in Fig. 7a and b. Both in octahedral and in tetrahedral

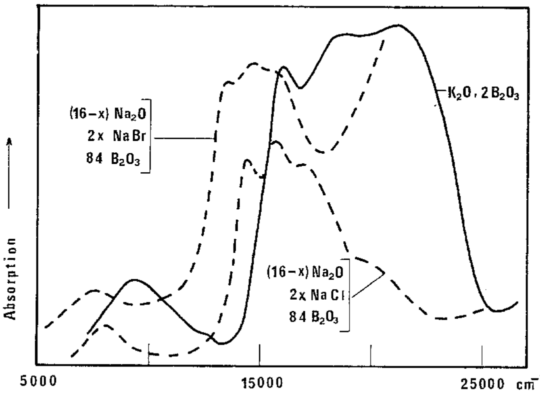

Figure 5 Optical absorption spectra of tetrahedral nickel(II) in different glasses with oxide and oxide-halide co-ordination.

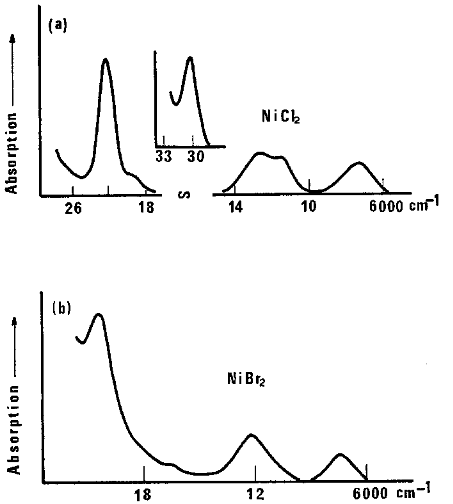

Figure 6(a) Optical absorption spectra of crystalline $NiCl_2$. (b) Optical absorption spectra of $NiBr_2$ (crystalline).

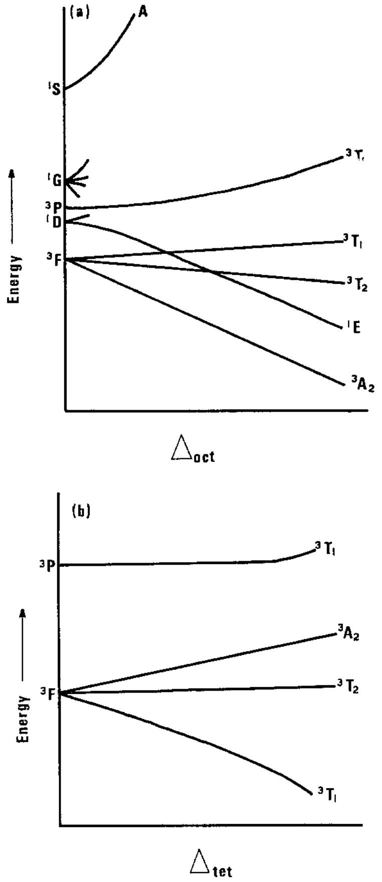

Figure 7 (a) Energy level diagram of d^8 system in octahedral field. (b) Energy level diagram of d^8 system in tetrahedral field.

symmetry three spin-allowed transitions are expected with the following energies [3]:

Octahedral

$$^3A_2(F) \rightarrow {}^3T_1(F) = \frac{15}{2} B + 15Dq - \tfrac{1}{2}(225B^2 + 180BDq + 100Dq^2)^{\frac{1}{2}}$$

$$\rightarrow {}^3T_1(P) = \frac{15}{2} B + 15Dq + \tfrac{1}{2}(225B^2 + 180BDq + 100Dq^2)^{\frac{1}{2}}$$

$$\rightarrow {}^3T_2(F) = 10Dq$$

Tetrahedral

$$^3T_1(F) \rightarrow {}^3T_1(P) = (225B^2 + 180BDq + 100Dq^2)^{\frac{1}{2}}$$

$$\rightarrow {}^3A_2(F) = \frac{15}{2} B + 15Dq + \tfrac{1}{2}(225B^2 + 180BDq + 100Dq^2)^{\frac{1}{2}}$$

$$\rightarrow {}^3T_2(F) = \frac{15}{2} B + 5Dq + \tfrac{1}{2}(225B^2 + 180BDq + 100Dq^2)^{\frac{1}{2}}$$

Glasses 1, 44 and 52 are green; from Figs. 1a, 2 and 3 it can be seen that three absorption bands are obtained around 7000, 13 000 and 24 000 cm^{-1} and these are assigned to $^3A_2(F) \rightarrow {}^3T_2(F)$, $^3A_2(F) \rightarrow {}^3T_1(F)$, and $^3A_2(F) \rightarrow {}^3T_1(P)$ transitions respectively. With these assignments the appropriate algebraic equations have been solved to get ligand field parameters (Δ_0 and B) in different glasses and crystals, and these are given in Table II along with those for $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ complexes in aqueous solution. Δ_{oct} in $25Na_2O,75B_2O_3$ glass apparently seems to be smaller than that in $8Na_2O,92B_2O_3$ and $16Na_2O,84B_2O_3$ glasses. It may be that the symmetry of nickel(II) complex in $25Na_2O$, $75B_2O_3$ glass is D_{4h} rather than C_{3v}; this will be discussed in a later section.

The middle absorption band of octahedral nickel(II) around 13 000 cm^{-1} corresponding formally to the transition: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ is double peaked. According to Jøorgensen [4] this is due to the closeness of a ^1E state coming from ^1D; spin-orbit coupling mixes the $^3T_1(F)$ and ^1E states and splits the band. Ballhausen *et al* [5] have calculated the complete energy level diagram for $3d^8$ system with spin-orbit coupling included and shown that the ^1E level never does approach "very closely" to any triplet level

TABLE II Optical transitions and ligand field parameters of some octahedral nickel(II) complexes

Complex	Optical transitions (cm^{-1})			Δ_{oct} (cm^{-1})	B (cm^{-1})
	$^3A_2 \rightarrow {}^3T_2$	$^3A_2 \rightarrow {}^3T_1(F)$	$^3A_2 \rightarrow {}^3T_1(P)$		
$[Ni(H_2O)_6]^{2+}$	8 500	14 000	25 000	8 500	940
$[Ni(en)_3]^{2+}$	11 500	18 500	30 000	11 500	850
Nickel(II) in $8Na_2O, 92B_2O_3$ glass	7 200	13 200	24 100	7 200	1 047
Nickel(II) in $16Na_2O, 84B_2O_3$ glass	7 700	14 000	25 000	7 700	1 060
Nickel(II) in $25Na_2O, 75B_2O_3$ glass	6 500	12 900	23 800	6 500	1 146
$NiCl_2$	7 720	12 400	22 065	7 720	750
$NiBr_2$	7 420	12 820	20 290	7 420	650

However, it must be pointed out that the calculations of Ballhausen are strongly dependent upon the choice of the values of Racah parameters, B and C, and the spin-orbit coupling parameter, λ.

In $8Na_2O,92B_2O_3$ and $16Na_2O,84B_2O_3$ glasses containing halides, in addition to octahedral bands two sets of new major bands are developed around 8000 and 15 000 cm^{-1}; the intensity of these two band systems increases with increasing halide content of the glass. These two bands were assigned to $^3T_1(F) \rightarrow {}^3A_2$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions respectively. With these assignments the appropriate algebraic equations have been solved for Δ_{tet} and B, and these are shown in Table III. Δ_{tet} which turns out to be around 4000 cm^{-1} is about 4/9 Δ_{oct} in these glasses; unfortunately this region of spectrum is masked by strong hydroxyl absorption in these glasses (due to residual water in the glass from batch materials) and thus this transition could not be experimentally identified. It is clear from Table III that Δ_{tet} is larger and B is smaller in bromide containing glasses than those in pure oxide or oxide-chloride containing glasses. This decrease in B indicates that nickel(II)—bromide bonds are more covalent that the corresponding nickel(II)—chloride or nickel(II)—oxide bonds in glass. The same trend has also been observed in the case of octahedral nickel(II) complexes in glass (see Table II).

Comparing absorption spectra of nickel(II) in halide containing glasses with those of crystalline pure $NiCl_2$ and $NiBr_2$ it is evident that while pure $NiCl_2$ and $NiBr_2$ are distorted octahedra [6], the nickel(II) complex in the halide containing glasses occur with a mixture of oxide and halide ligands and is in tetrahedral symmetry. It may be seen from Fig. 5 the tetrahedral nickel(II) absorption bands in glasses containing bromide are shifted to lower energies in comparison to oxide and oxide-chloride complexes. This is consistent with the spectrochemical series where oxide>chloride>bromide.

Unlike B_2O_3-rich glasses no striking change in the nickel (II) absorption spectra occurred in

TABLE III Optical transitions and ligand field parameters of some tetrahedral nickel(II) complexes

Complex	Optical transitions (cm^{-1})			Δ_{tet} (cm^{-1})	B (cm^{-1})
	$^3T_1 \rightarrow {}^3T_2$	$^3T_1 \rightarrow {}^3A_2$	$^3T_1 \rightarrow {}^3T_1(P)$		
$Ni(Ph_3AsO)_2Br_2$	(3435)*	7500	15 000	4065	813
Nickel(II) in $16Na_2O, 84B_2O_3$ glass containing chloride	(3615)*	7900	15 800	4285	857
Nickel(II) in $8Na_2O,92B_2O_3$ glass containing bromide	(3250)*	7100	14 200	3850	770
Nickel(II) in $16Na_2O,84B_2O_3$ glass containing bromide	(3740)*	7700	14 600	3960	792

*Calculated values

$25Na_2O,75B_2O_3$ glasses even with much larger amounts of bromide. This may arise due to two reasons: (a) nickel(II) in this glass is four co-ordinated and covalently bonded [1], and thus bromide substitution is not favourable. It is known with other transition metal ions like copper(II) [10], vanadium(IV) [11] in Na_2O–B_2O_3 glasses that the metal-oxygen covalency increases sharply above 20 mol % Na_2O in the glass; (b) the activity coefficient of bromide in this glass may be too small to produce noticeable substitution with the limited amount of bromide added in these glasses (2d). Although no activity measurement of NaBr in Na_2O–B_2O_3 melt has yet been reported, the solubility of NaCl in Na_2O–B_2O_3 melts is known to increase sharply with Na_2O content of the melt [12].

5. Absorption due to square planar nickel(II)

Nickel(II) having d^8 electronic configuration is prone to square planar complex formation with simple ligands [7]. The five degenerate d-orbitals of the uncomplexed metal ion split into four different levels in a square planar complex. The general molecular orbital energy levels for square planar complexes in which the ligands have no π-orbital system (chloride, bromide, oxide, etc.) is shown in Fig. 8. Almost all square planar complexes of nickel(II) with simple ligands are diamagnetic and the ground state is $^1A_{1g}$ Three spin-allowed d—d type transitions, corresponding to $b_{2g}(\pi^*) \rightarrow b_{1g}(\delta^*)$ ($^1A_{1g} \rightarrow {}^1A_{2g}$), $a_{1g}(\delta^*) \rightarrow b_{1g}(\delta^*)$ ($^1A_{1g} \rightarrow {}^1B_{1g}$) and $e_g(\pi^*) \rightarrow b_{1g}(\delta^*)$ ($^1A_{1g} \rightarrow 1E_g$) are expected. All these are parity forbidden as electric dipole transitions. In addition two allowed charge transfer transitions may be anticipated corresponding to:

$$b_{2u}(\pi) \rightarrow b_{1g}(\delta^*)\ ({}^1A_{1g} \rightarrow {}^1A_{2u})$$
$$\text{and } e_u(\pi^b) \rightarrow {}^b 1g(\delta^*)\ ({}^1A_{1g} \rightarrow {}^1E_u).$$

These are transitions from molecular orbitals essentially localized on the ligands to molecular orbitals essentially localized on the metal atom.

All these transitions in square planar nickel(II) complexes have been observed [8]. One distinctive feature of the square planar nickel(II) complex when compared to the octahedral complex is the development of a strong shoulder around 20 000 cm^{-1} [1, 9]. It is clear from Figs. 2 and 3 that with smaller amounts of halides in $8Na_2O,92B_2O_3$ and $16Na_2O,84B_2O_3$ glasses, prior to tetrahedral nickel(II) formation, the shoulder around 20 000 cm^{-1} gets stronger with halide content indicating square planar nickel(II) formation in these glasses.

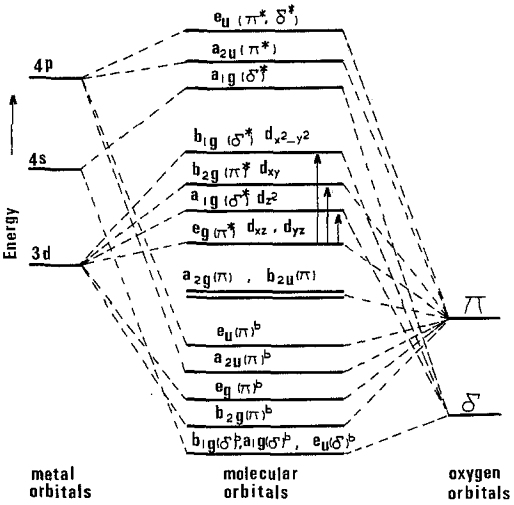

Figure 8 Qualitative molecular orbital energy level scheme for square planar d^8 metal complexes with no intra-ligand π-orbital system (after Gray and Ballhausen).

Appendix

The symbols used in this paper are all standard spectroscopic symbols. For those not conversant in this field the following brief explanations are given:

A, B and C: Racah parameters
10Dq: ligand field strength

Energy of any "state" of an ion in an electrostatic field of strength 10Dq, can be expressed in terms of A, B, C and 10Dq (as written in the equations on page 1060) by solving the appropriate Tanabe-Sugano matrices.

λ: Spin-orbit coupling; this originates from coupling of spin angular momentum of electron with orbital angular momentum.

δ and π: These indicate bonding molecular orbitals formed by combination of suitable atomic orbitals.

δ* and π*: These are antibonding orbitals. δ and π indicate particular type of overlap of electronic wavefunctions. Antibonding orbitals of any kind are at higher energy (unstable) than the corresponding bonding orbitals.

References

1. A. PAUL and R. W. DOUGLAS, *Phys. Chem. Glasses* **8** (1967) 233.

2. (a) A. PAUL and R. W. DOUGLAS, *ibid* **10** (1969) 133, 138; **11** (1970) 46; **13** (1972) 144.
   (b) A. PAUL, S. C. SEN and D. S. SRIVASTAVA, *J. Mat. Sci.* **8** (1973) 1110.
   (c) A. PAUL and A. N. TIWARI, *Phys. Chem. Glasses*, in press (August, 1974).
3. J. S. GRIFFITHS, in "Theory of transition metal ions" (Cambridge University Press, London, 1964).
4. C. K. JORGENSEN, *Acta Chem. Scand.* **9** (1955) 1362.
5. A. D. LIEHR and C. J. BALLHAUSEN, *Ann. Phys. (NY)* **6** (1959) 134.
6. J. ACKERMAN, C. FOUASSIER, E. M. HOLT and S. L. HOLT, *Inorg. Chem.* **11** (1972) 3118.
7. H. B. GRAY and C. J. BALLHAUSEN, *J. Amer. Chem. Soc.* **85** (1963) 260.
8. *Idem*, in "Coordination Chemistry", Vol 1 (ACS monograph 168) (Van Nostrand Reinhold, New York) p. 22.
9. (a) L. M. VENANZI, *J. Chem. Soc.* (1961) 4816; (1967) 693.
   (b) R. G. HAYTER and F. S. HUMICE, *Inorg. Chem.* **4** (1965) 1701.
   (c) B. T. KILBOURN, H. M. POWELL and J. A. C. DARBYSHIRE, *Proc. Chem. Soc.* (1963) 207.
   (d) L. SACCONI, *Inorg. Chem.* **4** (1965) 918.
   (e) A. CHAKROVORTY, *ibid* **4** (1965) 26.
   (f) S. M. NELSON and J. M. SHEPHERD, *J. Chem. Soc.* (1965) 3284.
   (g) F. BASOLO and W. R. MATOUSH, *J. Amer. Chem. Soc.* **75** (1953) 5663.
   (h) H. C. CLARK and A. L. ODELL, *J. Chem. Soc.* (1955) 3431, 3435.
   (i) D. R. EATON, W. D. PHILLIPS and D. J. CALDWELL, *J. Amer. Chem. Soc.* **15** (1963) 397.
   (j) R. H. HOLM and K. SWAMINATHAN, *Inorg. Chem.* **2** (1963) 181; **1** (1962) 599.
   (k) L. SACCONI, P. PAOLETTI and M. CIAMPOLINI, *J. Amer. Chem. Soc.* **85** (1963) 411.
   (l) F. A. COTTON and J. P. FACKLER JUN, *ibid* **83** (1961) 2818, 3775.
10. H. IMAGAWA, *Phys. Stat. Sol.* **30** (1968) 469.
11. H. TOYUKI and S. AKAGI, *Phys. Chem. Glasses* **13** (1972) 15.
12. M. H. ROWELL, *Inorg. Chem.* **4** (1965) 1804.

Received 26 September and accepted 11 December 1973