75. *Diffuse-reflectance Spectra of Some Anhydrous Transition-Metal Halides.*

By R. J. H. CLARK.

The diffuse-reflectance spectra of a number of anhydrous transition-metal halides have been recorded from *ca.* 9000 cm.$^{-1}$ to the onset of high-intensity charge-transfer bands at about 25,000 cm.$^{-1}$. The ligand-field spectra have been interpreted, where possible, in terms of the essentially octahedral field of halide ions around the metal, within the lattice. Values of Dq for chloride ion, and in some cases for bromide and fluoride ions, are obtained and estimates for the nephelauxetic ratio, β, are given. The effect of liquid-nitrogen temperatures on the spectra is indicated.

THE value of the ligand-field parameter, Dq, for halide ions is not known for all the transition elements in each valence state, particularly for those at the beginning of each transition series. This is mainly because many ions, such as the hexachlorotitanium(III) ion, have not yet been reported to be stabilized by a suitable cation, but their existence has only been implied from the spectra of melts.[1] It seemed of interest to record the diffuse-reflectance spectra of some anhydrous transition-metal halides, *e.g.*, of the types MX_2, MX_3 (d^0—d^6), and to see whether the spectra could be interpreted as d–d transitions located essentially on the metal atom.

In many of these halides, crystal-structure analyses[2] have shown that the metal atom is situated in an octahedral hole between close-packed halide ions, *e.g.*, the trichlorides of scandium, titanium, vanadium, and iron have the bismuth tri-iodide structure, which consists of hexagonal close packing of halide ions with the metal atoms occupying two-thirds of the octahedral holes between alternate close-packed layers. The arrangement is similar in chromium trichloride, except that the halide ions are cubic close-packed. Certain halides of the type MX_2 (*e.g.*, $TiCl_2$, VCl_2, $FeBr_2$) have the cadmium iodide structure, which consists of hexagonal close packing of halide ions with the metal atoms occupying alternate close-packed layers. The cadmium chloride structure, which is similar except that the halide ions are cubic close-packed, is found for ferrous chloride. Hence, to a first approximation, the metal atom in these halides may be regarded as being subjected to an octahedral ligand field of six halide ions.

A number of points of interest arise in a study of this type. These may be summarized as follows: (i) a comparison of the ligand-field strengths of terminal and bridging halide ions;[3] (ii) a comparison of the values of Dq for the first and second members of a group of the periodic table; (iii) the variation of Dq and of the nephelauxetic (covalency) parameter, β, with the valence of the metal; and (iv) the effect of liquid-nitrogen temperatures on the spectra.

[1] Gruen and McBeth, Plenary Lecture, 7th Internat. Conf. on Co-ordination Chemistry, Butterworths, London, 1963, p. 23.

[2] Wells, "Structural Inorganic Chemistry," Oxford, 1962, Ch. 8; Klemm and Krose, *Z. anorg. Chem.*, 1947, **253**, 218.

[3] Hatfield, Fay, Pfluger, and Piper, *J. Amer. Chem. Soc.*, 1963, **85**, 265.

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RESULTS AND DISCUSSION

The following halides have been investigated:

Electronic configuration	d^0	d^1	d^2	d^3	d^4	d^5	d^6
Valence							
2			$TiCl_2$	VCl_2	$CrCl_2$ CrF_2 $MoCl_2$	$MnCl_2$	$FeCl_2$ FeF_2 $FeBr_2$
3	$ScCl_3$	$TiCl_3$	VCl_3 VF_3 K_3VF_6 VBr_3	$CrCl_3$ CrF_3	MnF_3	$FeCl_3$ FeF_3	
	YCl_3	$ZrCl_3$ $ZrBr_3$	$NbCl_3$	$MoCl_3$ $MoBr_3$			
4	$ZrCl_4$	$NbCl_4$					

The spectra are most conveniently discussed according to the d electronic configuration.

d^0 *Halides.*—The d^0 halides are white and show no absorption in the 9000—25,000 cm.$^{-1}$ region.

d^1 *Halides.*—The spectrum of the violet (α) form of titanium trichloride is shown in Fig. 1. The broad, strong band at *ca.* 18,300 cm.$^{-1}$ appears to be a charge-transfer band,
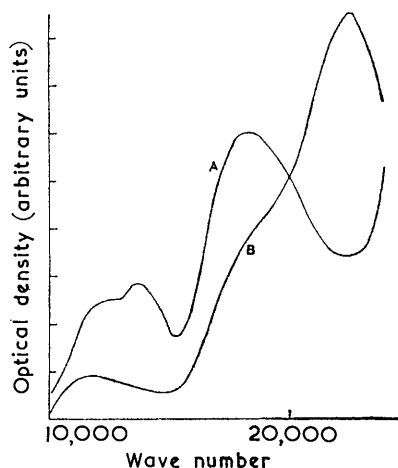
Diffuse-reflectance spectra. FIG. 1. Violet (A) and brown (B) forms of titanium trichloride.

but it is not present in the spectrum of isomorphous scandium trichloride. The weaker band at 13,800 cm.$^{-1}$ is in the region expected for the $^2E_g \longleftarrow {}^2T_{2g}$ transition of titanium(III) octahedrally co-ordinated to chloride ions. This band also shows a shoulder at *ca.* 12,000 cm.$^{-1}$ which could result from a splitting of the ^2E_g term by lower-symmetry components to the ligand field in the lattice or to a Jahn–Teller mechanism. (The point symmetry of the metal, is not higher than D_{3d} and may be lower.) [2] The $^2E_g \longleftarrow {}^2T_{2g}$ transitions of d^1 complexes characteristically show a splitting of *ca.* 2000 cm.$^{-1}$.[4] If this interpretation is correct, the cubic-field splitting parameter, Dq, is about 1300 cm.$^{-1}$ less an amount dependent on the concomitant splitting of the $^2T_{2g}$ term. As this quantity is not known, it is thought preferable to follow the usual practice for d^1 and d^4 systems [5] and make no correction for lower-symmetry components to the octahedral ligand field in either the upper or the ground states, *i.e.*, to take $Dq \sim 1380$ cm.$^{-1}$. The spectrum is sharpened very slightly at liquid-nitrogen temperatures, but not otherwise changed.

The brown (β) form of titanium trichloride (spectrum in Fig. 1) has a chain rather than

[4] Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379; Clark, *ibid.*, p. 1377.
[5] Holmes and McClure, *J. Chem. Phys.*, 1957, **26**, 1686.

a layer structure,[6] with short titanium–titanium distances (2·91 Å compared with 3·54 Å in the layer structure). This latter fact undoubtedly accounts for the very low para-magnetism observed for this form of the halide (α-form, $\mu = 1\cdot31$ B.M.; β-form, $\mu <$ 0·7 B.M., at 300°K).[7] The charge-transfer band of the β-form has moved towards the ultraviolet region compared with that of the α-form. The weakness of the ill-defined band at *ca.* 12,000 cm.$^{-1}$, in the region expected for the $^{2}E_{g} \longleftarrow {}^{2}T_{2g}$ transition, may also be a reflection of the metal–metal bonding in this chloride. The apparently lower ligand field for the β-form would not be suggested by the titanium–chlorine bond lengths for the two forms, for these are identical [6] within experimental error (2·45 Å).

The spectrum [1] of titanium(III) in a lithium chloride–potassium chloride eutectic at 400° is also characterized by an absorption band at 13,000 cm.$^{-1}$ with a shoulder at 10,000 cm.$^{-1}$, and has been interpreted similarly on the assumption that $TiCl_6$ octahedra exist in the melt.

The spectra of zirconium trichloride and tribromide are shown in Fig. 2, and consist of bands at 17,300 (shoulder at 21,000) and 16,200 cm.$^{-1}$, respectively. As the crystal structures of these halides are not yet known, and also because extinction coefficients
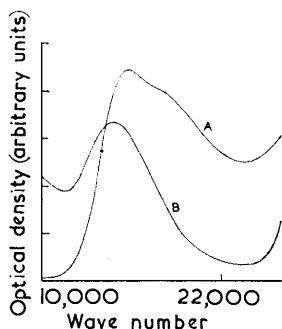
FIG. 2.   FIG. 3.

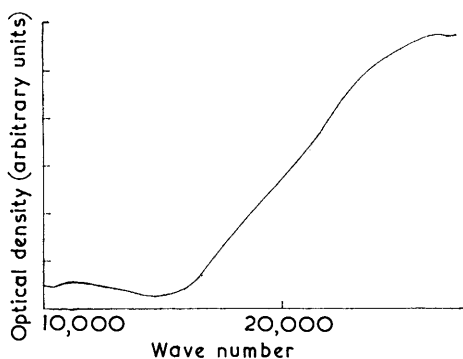Diffuse-reflectance spectra.   FIG. 2. (A) Zirconium trichloride and (B) zirconium tribromide.   FIG. 3. Niobium tetrachloride.

cannot be obtained from diffuse-reflectance measurements, it is not certain that these are ligand-field bands and, if so, whether they refer to transitions brought about by an essentially octahedral ligand field. However, if the above assumptions are correct, and if the bands arise from $^{2}E_{g} \longleftarrow {}^{2}T_{2g}$ transitions on the zirconium atoms, then the ratio of Dq for chloride to that for bromide, and of Dq for the second-row transition metal to that for the corresponding first-row metal, are consistent with previous findings.[8]

Niobium tetrachloride consists of $NbCl_6$ octahedra linked together by opposite edges. The spectrum (Fig. 3) is complex, and it is clear that charge-transfer transitions have occurred at sufficiently low energies to overlie the ligand-field transitions.

d^2 *Halides.*—The spectra of vanadium and niobium trichlorides are drawn in Fig. 4. The former shows a relatively sharp band at 12,500 cm.$^{-1}$, assigned to the $^{3}T_{2g} \longleftarrow {}^{3}T_{1g}(F)$ transition, and a more intense band system with the main peak at 17,300 cm.$^{-1}$ and a shoulder at 19,600 cm.$^{-1}$. It seems likely that the 17,300 cm.$^{-1}$ band is a charge-transfer band analogous to that found at 18,300 cm.$^{-1}$ for titanium trichloride, while the shoulder represents the $^{3}T_{1g}(P) \longleftarrow {}^{3}T_{1g}(F)$ transition. With these assignments, and allowing for configurational interaction between the two $^{3}T_{1g}$ terms,[9] one obtains $Dq = 1390$ cm.$^{-1}$ and

[6] Natta, Corradini, and Allegra, *J. Polymer Sci.*, 1961, **51**, 399.
[7] Lewis, Machin, Newnham, and Nyholm, *J.*, 1962, 2036.
[8] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon, London, 1962.
[9] Ballhausen, " Ligand Field Theory," McGraw-Hill, New York, 1962.

the ^3P ◄— ^3F inter-term separation $= 8450$ cm.$^{-1}$ (this quantity $= 15B = 12,925$ cm.$^{-1}$ in the free ion).[10] Hence the nephelauxetic ratio, β, $= B'/B = 0.65$.

The spectrum of the very dark niobium trichloride shows ill-defined peaks in the region of 15,000 and 22,000 cm.$^{-1}$, which could be the $^3T_{2g}$ ◄— $^3T_{1g}(F)$ and $^3T_{1g}(P)$ ◄— $^3T_{1g}(F)$ transitions superimposed on the side of a charge-transfer band.

In Fig. 5 are drawn the spectra of K_3VF_6 and vanadium trifluoride. Both show the transitions expected above: at 14,800 and 23,250 cm.$^{-1}$, for the former, and at 14,700 cm.$^{-1}$ (shoulder at *ca.* 12,300 cm.$^{-1}$) and *ca.* 22,500 cm.$^{-1}$, for the latter. These data yield $Dq = 1610$ cm.$^{-1}$, $B = 648$ cm.$^{-1}$, and $\beta = 0.75$ for the former, and $Dq \sim 1460$ cm.$^{-1}$, $B \sim 510$ cm.$^{-1}$,
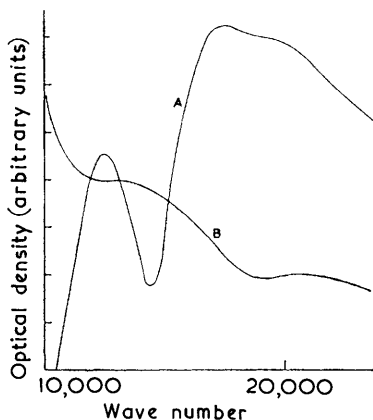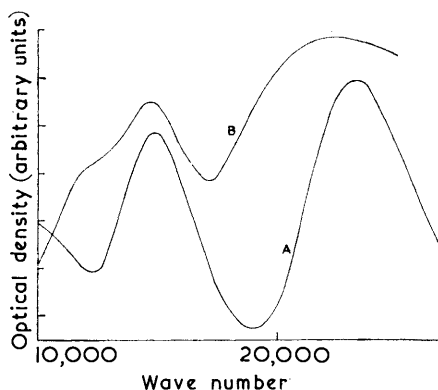

FIG. 4.   FIG. 5.

Diffuse-reflectance spectra. FIG. 4. (A) Vanadium trichloride and (B) niobium trichloride. FIG. 5. (A) K_3VF_6 and (B) vanadium trifluoride.

and $\beta \sim 0.60$ for the latter [for the $V(H_2O)_6^{3+}$ ion, the comparable quantities are 1850 cm.$^{-1}$, 602 cm.$^{-1}$, and 0.70, respectively]. The band maxima for the compound K_3VF_6 are raised by *ca.* 150 and *ca.* 300 cm.$^{-1}$, respectively, at liquid-nitrogen temperatures, but for vanadium trifluoride the only effect of such treatment is a reduction of *ca.* 300 cm.$^{-1}$ in the splitting of the $^3T_{2g}$ ◄— $^3T_{1g}(F)$ band. The splitting of this band indicates that the point symmetry of the metal atom is lower in vanadium trifluoride (D_3 in fact) than in the VF_6^{3-} ion. The transition $^3A_{2g}$ ◄— $^3T_{1g}$ (F) would be expected to lie at about 31,000 cm.$^{-1}$, *i.e.*, out of the sensitive range of the instrument.

The spectra of vanadium tribromide and titanium dichloride (both black compounds) show continuous absorption through the whole spectral region studied.

d^3 *halides.*—It is the d^3 halides which appear to be the least subject to charge-transfer bands in the visible region, and hence complexes with this configuration are most amenable to ligand-field analysis. The spectra of chromium trichloride (which has been recorded previously [8]), chromium trifluoride, vanadium dichloride, and molybdenum trichloride and tribromide are shown in Figs. 6—8. The band positions and assignments are given in Table 1, together with comparable data for the hexa-aquo-ions of chromium(III) and vanadium(II) [8] and other related data.

Using a first-order perturbation treatment [9] to allow for interaction between the two $^4T_{1g}$ terms arising from a d^3 configuration, it is possible to calculate the ^4P ◄— ^4F term separation in a complex (equal to $15B$ in the Racah nomenclature) and the position of the $^4T_{1g}(P)$ term, from the position of the first two bands, assigned as $^4T_{2g}$ ◄— $^4A_{2g}(= 10\ Dq)$ and $^4T_{1g}(F)$ ◄— $^4A_{2g}$. In those cases where the $^4T_{1g}(P)$ ◄— $^4A_{2g}$ transition can also be observed, it is possible to compare prediction with experiment (Table 1). The

[10] " Atomic Energy Levels," ed. Charlotte E. Moore, U.S. Bur. Stand., Circ. no. 467.

TABLE 1.

Spectra of d^3 halides (ground term $^4A_{2g}$) (cm.$^{-1}$).

Transitions to:	$^4T_{2g}$	$^4T_{1g}(F)$	$^4T_{1g}(P)$ found	$^4T_{1g}(P)$ calc.	Dq	B	β
CrF$_3$	16,100	22,900	—	—	1610	693	0·76
CrF$_6$$^{3-}$ [a]	14,900	22,700	34,400	35,400	1490	895	0·97
CrCl$_3$	13,500	18,900	—	—	1350	540	0·59
CrCl$_6$$^{3-}$ [b]	13,180	18,700	—	—	1320	561	0·61
Cr(III)LiCl,KCl) [c]	12,500	18,500	—	—	1250	—	—
Cr(H$_2$O)$_6$$^{3+}$ [a]	17,400	24,500	37,800	38,200	1740	698	0·76
VCl$_2$	9000	14,000	21,500	22,100	900	606	0·80
V(II)(LiCl,KCl) [c]	7200	12,020	19,050	—	720	—	—
V(H$_2$O)$_6$$^{2+}$ [a]	12,350	18,500	27,900	28,800	1235	681	0·90
MoCl$_3$	19,300	—	—	—	1930	—	—
MoCl$_6$$^{3-}$ [a]	19,150	23,900	—	—	1915	431	0·71

[a] Ref. 8. [b] Ref. 3. [c] Ref. 1.

differences between the calculated and observed positions of this band are very small and are in the same sense in each case.

It seems that for d^3 halides the ligand-field strength of a terminal halide ion is slightly lower than that of a lattice halide ion, and that the ratio of the Racah parameter (B') in the complex to that in the free ion (B) is slightly higher. This ratio, the so-called nephelauxetic ratio, β, is regarded as a measure of the covalency of a complex, and values

FIG. 6.   FIG. 7.   FIG. 8.
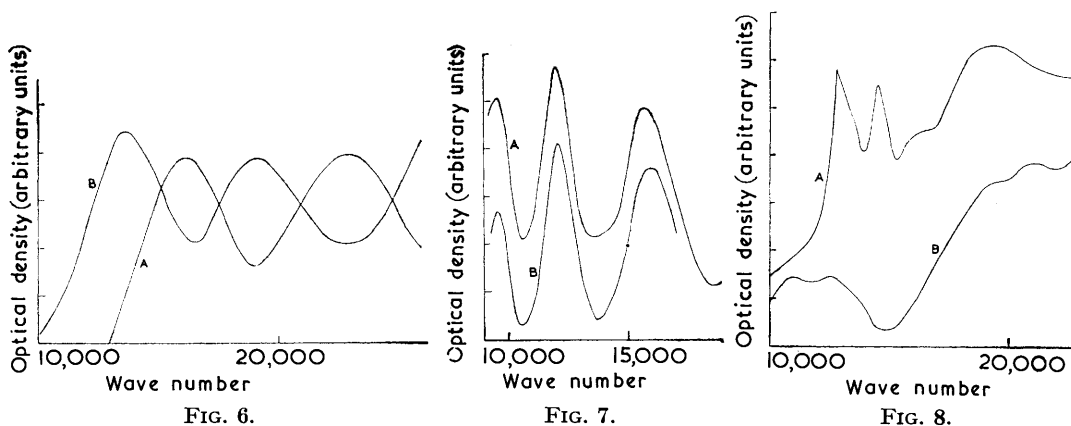
Diffuse-reflectance spectra. FIG. 6. (A) Chromium trifluoride and (B) chromium trichloride. FIG. 7. Vanadium dichloride (A) at room temperature and (B) at liquid-nitrogen temperatures. FIG. 8. (A) Molybdenum trichloride and (B) molybdenum tribromide.

obtained here indicate that β decreases (*i.e.*, the degree of covalency increases) in the order F$^-$ > H$_2$O > Cl$^-$ and M(II) > M(III) and M (second row) > M (first row), in agreement with previous conclusions [8] (M = transition metal).

The spectra of vanadium(II) and chromium(III) in a lithium chloride–potassium chloride eutectic at 400°c are completely analogous with those of vanadium dichloride and chromium trichloride, respectively, except that in each case the ligand-field strength is lower in the melt. If the metal atom strictly maintained six-co-ordination in the melt, then these data, on a $1/r^5$ dependence of Dq, would indicate that the metal–chlorine bonds are 0·04—0·10 Å longer in the melt than in the corresponding chloride lattice.

The chromium spectra show shifts of *ca.* 100 cm.$^{-1}$, and those of vanadium dichloride shifts of *ca.* 200 cm.$^{-1}$, towards higher frequencies on cooling to liquid-nitrogen temperatures. These facts are consistent with the assignments.[8,9]

The spectrum of molybdenum tribromide has bands in the 19,000 cm.$^{-1}$ region, indicative of the $^4T_{2g} \longleftarrow {}^4A_{2g}$ transition, but it is obviously complex, with charge-transfer bands in the same region. The molybdenum spectra are a little different from those implied by the band positions given previously. The most notable features of the spectra of molybdenum trichloride and tribromide are the appearance of relatively sharp bands at 12,750 (shoulder at 13,500) and 14,500 cm.$^{-1}$, for the former, and at 10,900 and 12,500 cm.$^{-1}$, for the latter. The positions of these bands are unaffected by cooling to liquid-nitrogen temperatures, and hence they are clearly quartet–doublet transitions, *i.e.*, occurring within the t_{2g} subshell. While their positions are not close to those found [8] for the $MoCl_6{}^{3-}$ ion (^2E_g, $^2T_{1g} \longleftarrow {}^4A_{2g}$, 9650 cm.$^{-1}$; $^2T_{2g} \longleftarrow {}^4A_{2g}$, 14,800 cm.$^{-1}$), they are close to bands reported [11] for the $Mo_2Cl_9{}^{3-}$ ion [13,100, 13,700 (shoulder), and 15,000 cm.$^{-1}$]. This ion, which also has its $^4T_{2g} \longleftarrow {}^4A_{2g}$ transition at 19,000 cm.$^{-1}$, dimerizes by sharing the faces of two $MoCl_6$ octahedra. Molybdenum trichloride may polymerize in the same manner (as is known to be true for molybdenum tribromide and molybdenum tri-iodide) [12] and if so, then the similarity between its spectrum and that of the $Mo_2Cl_9{}^{3-}$ ion is understandable in terms of the similar distortion of the ligand field from octahedral.

d^4 *Halides.*—The spectra of chromium dichloride and difluoride are shown in Fig. 9. The band at 11,300 cm.$^{-1}$ in the dichloride moves *ca.* 100 cm.$^{-1}$ to higher frequencies at liquid-nitrogen temperatures and is assigned to the $^5T_{2g} \longleftarrow {}^5E_g$ transition. Thus Dq is 1130 cm.$^{-1}$, a value which is anomalously high due to the presence of low-symmetry components to the ligand field, which would result in a large splitting of the ^5E_g ground term. Distortion of d^4 complexes from octahedral symmetry is well substantiated crystallographically, and is regarded as a consequence of the Jahn–Teller theorem. [13]

The spectrum of the difluoride has two bands in the region expected for the $^5T_{2g} \longleftarrow {}^5E_g$ transition. The first, at 11,400 cm.$^{-1}$, is unaffected by cooling to liquid-nitrogen temperatures, while the second, at 14,700 cm.$^{-1}$, is raised *ca.* 100 cm.$^{-1}$ thereby. The bands probably arise from a splitting of the upper $^5T_{2g}$ term. This splitting is not surprising, for it is known that in the solid there is a 0·43 Å tetragonal distortion of the fluoride octahedron. [13] A further band at 23,000 cm.$^{-1}$ is raised *ca.* 50 cm.$^{-1}$ at liquid-nitrogen temperatures.

The spectrum of molybdenum dichloride (Fig. 10) has a weak band at 12,100 cm.$^{-1}$ which is raised *ca.* 200 cm.$^{-1}$ on cooling to liquid-nitrogen temperatures. The ligand field to which the metal atom is subjected is not octahedral, [2] and no interpretation of the spectrum can be advanced at this stage.

An interesting spectrum is that of manganese trifluoride (Fig. 11) for which only one spin-allowed transition is possible, $^5T_{2g} \longleftarrow {}^5E_g$. It is located [9] at 21,700 cm.$^{-1}$ in the ion $MnF_6{}^{3-}$, and thus in manganese trifluoride the broad strong band at *ca.* 19,000 cm.$^{-1}$ might reasonably be assigned to this transition. Superimposed on the $^5T_{2g} \longleftarrow {}^5E_g$ transition, however, are two sharp bands at 19,100 and 23,200 cm.$^{-1}$ which may be assigned to quintet–triplet transitions. The Tanabe–Sugano diagram for the d^4 configurations [14] indicates that there are several triplet terms whose energies are almost independent of ligand-field strength and hence transitions to them would be expected to be sharp, *e.g.*, possible assignments for the sharp bands are $^3E_g(H)$, and $^3T_{2g}(H) \longleftarrow {}^5E_g$. Consistent with their sharpness, their positions are unaffected by cooling to liquid-nitrogen temperatures. A further weak, broad band at 12,000 cm.$^{-1}$ is lowered *ca.* 50 cm.$^{-1}$ on cooling to liquid-nitrogen temperatures, and thus could reasonably be assigned to the $^3T_{1g}(H) \longleftarrow {}^5E_g$ transition. This band is dependent on Dq in a negative sense and, in fact, the $^3T_{1g}(H)$ term becomes the ground term for a d^4 configuration on spin-pairing.

[11] P. W. Smith, Ph.D. Thesis, London, 1962.
[12] Lewis, Machin, Nyholm, Pauling, and Smith, *Chem. and Ind.*, 1960, 259.
[13] Ham, *Spectrochim. Acta*, 1962, **18**, 775.
[14] Dunn, in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 282.

Thus, as also observed for the molybdenum trihalides, spin-forbidden bands may be more intense when the metal atom is in a lattice than when it is part of a discrete ion.

d^5 *halides.*—The spectra of ferric fluoride and ferric chloride are shown in Fig. 12. Both show weak bands in the near-infrared region, the former at 11,800 cm.$^{-1}$ and the latter at 11,400 cm.$^{-1}$, which lie *ca.* 50—100 cm.$^{-1}$ to lower frequencies at liquid-nitrogen temperatures. These data would be consistent with the assignment $^4T_{1g}(G) \longleftarrow {}^6A_{1g}(S)$.
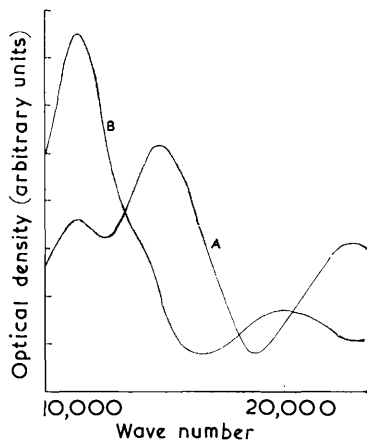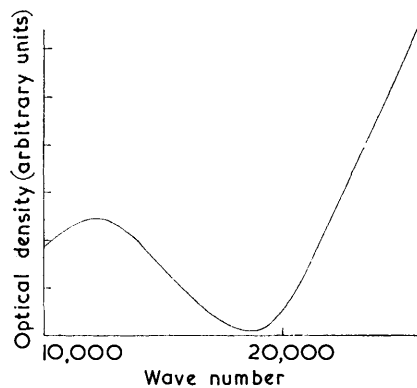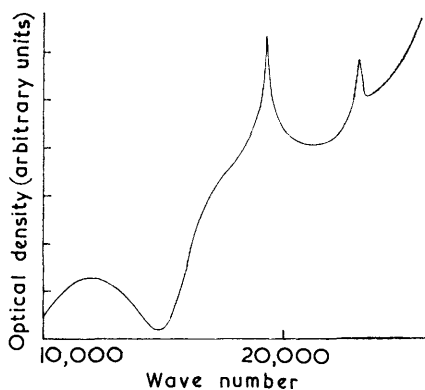

FIG. 9.

FIG. 10.

FIG 11.

Diffuse-reflectance spectra. FIG. 9. (A) Chromium difluoride and (B) chromium dichloride. FIG. 10. Molybdenum dichloride. FIG. 11. Manganese trifluoride.

The spectra of these halides in the visible region are considerably different from that [8] of the discrete ion FeF_6^{3-} whose spectrum is completely analogous with the spectra of manganous halides.[15] In particular, poorly resolved bands at 17,300 and 24,900 cm.$^{-1}$, in the chloride, and upwards of 19,000 cm.$^{-1}$, in the fluoride (essentially unchanged at low temperatures), are probably of the charge-transfer type and analogous to the 18,300 cm.$^{-1}$ band of titanium trichloride (isomorphous with ferric chloride).[2]

In the case of manganous chloride, the diffuse-reflectance spectrum has been recorded (Fig. 13) for direct comparison with the crystal spectrum obtained by Pappalardo.[15] The positions of the bands and the assignments [15] are as shown (Table 2) (ground term $^6A_{1g}$). There are small differences between the relative intensities of the various transitions obtained by the two methods, but the positions of the bands are almost identical. This fact establishes the general validity of the diffuse-reflectance technique.

d^6 *halides.*—The spectra of ferrous fluoride, chloride, and bromide, which are spin free halides, should show the $^5E_g \longleftarrow {}^5T_{2g}$ transition at somewhat lower energies than the

[15] Stout, *J. Chem. Phys.*, 1959, **31**, 709; 1960, **33**, 303; Pappalardo, *J. Chem. Phys.*, 1959, **31**, 1050.

TABLE 2.

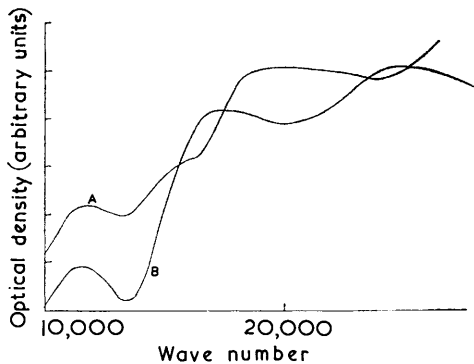| Transitions to	Diffuse-reflectance spectrum (cm.$^{-1}$)	Crystal spectrum [15] (cm.$^{-1}$)	Transitions to	Diffuse-reflectance spectrum (cm.$^{-1}$)	Crystal spectrum [15] (cm.$^{-1}$)
$^4T_{1g}(G)$	18,650	18,500	$^4E_g(G)$	23,900	23,825
$^4T_{2g}(G)$	22,100	22,000	$^4T_{2g}(D)$	27,040	26,750
$^4A_{1g}(G)$	23,700	23,590	$^4E_g(D)$	28,080	28,065

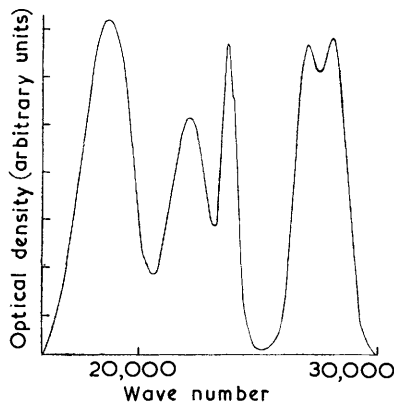Diffuse-reflectance spectra.   FIG. 12. (A) Ferric fluoride and (B) ferric chloride.
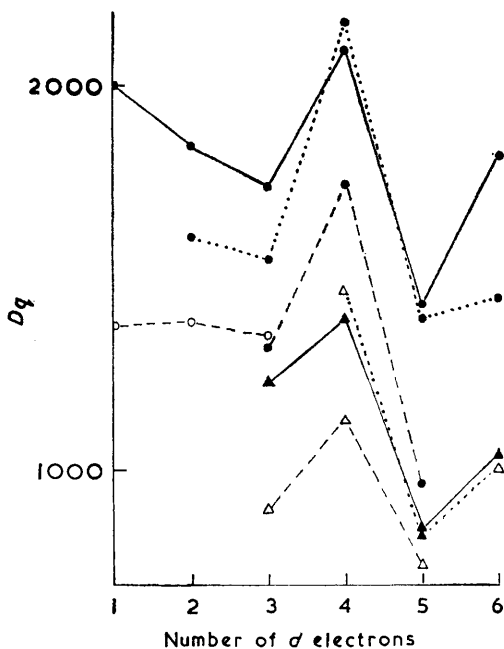FIG. 13. Manganous chloride.

FIG. 14. Values for the parameter Dq, uncorrected for the effects of low symmetry fields. Circles, metal(III); triangles, metal(II); full line, water; dotted line, fluoride ion; dashed line, chloride ion; open symbol, bridging ligand; closed symbol, terminal ligand.

corresponding band of the hexa-aquo iron(II) ion (10,400 cm.$^{-1}$).[8]   The band at 10,000 cm.$^{-1}$ in the fluoride, which is raised *ca.* 200 cm.$^{-1}$ at liquid-nitrogen temperatures, is assigned accordingly, but the corresponding bands of the other halides occur at frequencies which are too low to be located in this work.   High-intensity bands also occur for these halides in the 20,000 cm.$^{-1}$ region.

General Discussion.—In Fig. 14 are plotted the values of Dq (uncorrected for the effects

of low-symmetry fields) for $M(H_2O)_6^{3+}$, MF_3, MF_6^{3-}, MCl_3, and MCl_6^{3-} and for $M(H_2O)_6^{2+}$, MF_2, and MCl_2, where these are known (M = transition metal). In general, the ligand-field strength decreases in the order $H_2O > F^- > Cl^- > Br^-$ in agreement with previous conclusions, and trends in the value of Dq for water [5] with different metals are followed closely for these other ligands. In particular, d^4 halides show exceptionally large apparent values for Dq, because the tetragonal component to the field, known from X-ray studies to be present, has not been allowed for. The intensities of comparable ligand-field bands fall off in the order $Br^- > Cl^- > F^-$, and the increase in Dq in passing from M(II) to M(III) and from M(III) (first row) to M(III) (second row) with the same ligand field is, in each case, about 45%.

It may be concluded that there is very little difference between the ligand-field strength of terminal and bridging halide ions. It is also of interest to note that, although many of the halides of the transition metals are known to be antiferromagnetic and many others suspected of such behaviour, the ligand-field transitions are not greatly affected by this kind of magnetic ordering in the lattice. But it is possible that the lowest energy "charge-transfer" transition may be associated with the overlap of $3d$ wave functions in the lattice to form an energy band. The radical wave function of titanium, being greater than that of chromium, would favour collective rather than localised d electrons, consistent with the appearance of an extra intense band in the spectrum of titanium trichloride but not of chromium trichloride. Metal oxide spectra show similar behaviour.[16]

Liquid-nitrogen temperatures have the effect of slightly increasing the value of Dq, for a given metal and ligand field, over the room-temperature value, and of slightly sharpening the band envelope, as discussed by Dunn.[14]

Further work is in progress in an attempt to elucidate the nature of the charge-transfer transitions.

Experimental

The diffuse-reflectance spectra were recorded by using the standard attachment to the Unicam S.P. 500 spectrophotometer. Most of the halides investigated are unstable to oxygen and all are unstable to water. Samples were therefore ground up in a nitrogen-filled dry-box and placed between glass plates, the edges of which were greased to prevent access of air. Resolution improves with decreasing particle size, and the apparent optical density for a charge-transfer band is much closer to that for a ligand-field band by this technique than would be expected from the ratio of their extinction coefficients.

Spectra at liquid-nitrogen temperatures were recorded by use of a second diffuse-reflectance attachment, modified so that the sample lay on a brass block attached to a liquid-nitrogen feed. The attachment was enclosed, in order to prevent frosting of the glass plates, and equilibrium was reached in about 15 min. It is unlikely that the samples actually reached 77°K, but, as the only information required was the qualitative effect of such temperatures on the spectra, no attempt has been made to determine the temperature of the samples exactly. However, the increase in resolution of the 19,000 cm.$^{-1}$ band system of potassium permanganate-potassium perchlorate mixed crystals, on passing from room temperature to liquid-nitrogen temperatures, was identical with that reported previously.[17]

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[16] Morin, in "Semiconductors," ed. Hannay, Reinhold Publ. Corp., New York, 1959.
[17] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.