Effects of Antiferromagnetic Coupling in the 5 K Electronic Spectra of Crystals of Vanadium Dichloride, Dibromide, and Di-iodide

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Single-crystal absorption spectra at 300, 80, and 5 K of the antiferromagnetic compounds VCl_2, VBr_2, and VI_2 are reported between 5000 and 30,000 cm^{-1}. The energy positions and intensities of the bands are similar to those for isolated V^{2+} but spin-forbidden levels are more intense.

This intensity effect and some sharp, fine structure are explained in terms of magnetic exchange effects. A combination band due to two spin-allowed single-centre transitions is detected.

IN an investigation of the spectra of V^{2+} ions in halide crystals,[1] doped samples gave spectra that could be explained in terms of crystal-field theory for a d^3 system but the spectra of pure VCl_2 and $KVCl_3$ were anomalous, probably due to the effects of antiferromagnetic ordering of spins in the crystals. The compounds VCl_2, VBr_2, and VI_2 form an isostructural series of the cadmium iodide type [2,3] having Neél points of 700, 400, and 100 K respectively.[4] This paper is an investigation at 300, 80, and 5 K of the spectra of the three materials, with specific reference to those parts where properties reflect most clearly the effect of interaction between the vanadium centres.

The crystal structure consists of layers of hexagonally packed halide ions with vanadium ions filling all the sites in every second layer of octahedral holes between them. The probable mechanism of exchange is an interaction of the metal wave function through the wave functions of the halides bridging them. Anderson,[5] who first proposed this type of interaction, has written a general explanation of the mechanism.

There is no complete theory of optical spectra in magnetically ordered crystals but Tanabe and Sugano [6] describe a simple theory which fits the presently available data. They start with the effect of the averaged molecular field (*i.e.* an electric or ligand field component and a magnetic component) on one paramagnetic centre and consider the effect of coupling with a second centre in condition where the molecular field is perturbed by an exchange field.

The energy of magnetic interaction is small compared to that required for electronic transitions so that the overall energy positions of bands should not be much affected by the exchange process. Further, the parity and symmetry rules applicable to the single ion will not

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[1] W. E. Smith, *J. Chem. Soc.* (*A*), 1969, 2677.

[2] P. Ehrlich and H. J. Seifert, *Z. anorg. Chem.*, 1959, **301**, 282.

[3] W. Klemm and L. Grimm, *Z. anorg. Chem.*, 1941, **249**, 198.

[4] W. Klemm and L. Grimm, *Z. anorg. Chem.*, 1941, **249**, 209.

[5] P. W. Anderson in 'Magnetism,' Academic Press, London, 1963, p. 25.

[6] Y. Tanabe and S. Sugano, in 'Magnetism,' Academic Press, London, 1963, p. 243.

be affected, so that the overall band intensities will not be much different.

The exchange field does, however, provide a mechanism to break down the spin selection rule. At temperatures below the Neél point, where there is long-range ordering of spin projection on the paramagnetic centres, extra satellite lines, or magnon sidebands, are expected on the high-energy side of formally one centre transitions. A comparison of $KNiF_3$ and $KMgF_3:Ni^{2+}$ by Knox *et al.*[7] demonstrates this clearly. In a thorough analysis of the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition in MnF_2, Sell *et al.*[8] give a discussion of the mechanism for these bands and the literature is reviewed by Sell.[9] Basically, the mechanism is that the one centre spin-forbidden transition is made spin allowed by a spin deviation on a neighbouring paramagnetic centre. (This spin deviation is best considered as a spin wave, or magnon, in the crystal and its energy is about a few hundred cm^{-1}. Excitation of these spin waves has been measured in the far-i.r. region.[10]) Since these transitions are essentially spin allowed, they are much more intense than the one centre spin-forbidden ones. Lohr and McClure [11] point out that the effects of ion interaction on the spectra of magnetic materials does not depend on long-range ordering as a magnon type of absorption process can be proposed equally well for a few ions interacting in the crystal. They measured the spectra of divalent manganese salts and showed that in those where manganese–manganese interactions were expected, higher intensities were found and that the effect persisted to well above the Neél point. The spin-allowed transitions in the vanadium halides will not gain intensity from these mechanisms but the spin-forbidden ones will, so that anomalously high spin-forbidden intensities compared to the spin-allowed ones would be expected and are found. Sharp detail on spin-forbidden systems can also be related to the magnetic effect.

Ferguson,[12] in investigating the spectra of $KMnF_3$ and $RbMnF_3$, assigns some of the high-energy bands in these systems to two electron transitions in which simultaneous absorption occurs at two coupled optical centres (combination bands). In antiferromagnetic manganese systems, the overall spin parity of the two centre transitions will be preserved in spite of the fact that the transition on each centre is itself spin forbidden, so that the intensity of the levels is quite high.

In the vanadium systems, combination bands arising from both spin-allowed and spin-forbidden single-centre levels can occur. Since they are two electron transitions they should be weak compared to the spin-allowed levels but may be strong compared to spin-forbidden ones. In the main, they occur at high energies where the spectra are most difficult to interpret but one level, due to a combination of two low-energy spin-allowed bands, can be assigned definitely in all three samples.

The intensities of the combination bands increase as the temperature decreases and a similar effect is normally observed for the one-centre transitions in manganese. Lohr and McClure also observed some cases in which the one-centre transitions decreased in intensity and point out that there will be hot bands at the higher temperature that may well be sufficiently intense to override the increase in intensity of the cold band.

The major advantage of the vanadium halide crystals is that they grow easily as thin plates with parallel faces so that good baselines are obtained and thicknesses can be measured reasonably accurately. Extinction coefficients can then be calculated. The spectra taken through the plate faces are axial and so no polarisation experiments are possible. Stout [13] * has already reported the spectra, including extinction coefficients, of VCl_2 at 22 K and his results are in good agreement, both with regard to energy positions and intensities, with those reported here.

EXPERIMENTAL

Preparation.—Vanadium metal was sealed in one end of a quartz tube containing a sintered frit at the centre and VCl_3, bromine, or iodine was added at the other end. The tubes were flushed with nitrogen and sealed under full vacuum. In the case of VBr_2, the bromine was solidified by immersing the tube in liquid nitrogen before sealing. The metal was heated to 800—900 °C and the VCl_3, bromine, or iodine temperature varied to give a good vapour pressure over the metal. When the reaction was complete, the product was sublimed through the sinter and the temperature of the tube adjusted to give a slow growth of platelet crystals from the gas phase. After some days the tubes were cooled, broken open in the dry box, and the material stored in stoppered bottles under nitrogen.

Crystal Structure and Morphology.—The crystals were thin, hexagonal plates, up to 1 cm across and up to 1 mm thick.

The site symmetry of the V^{2+} ion is trigonal, but very close to octahedral. The c/a ratio of the sides of the unit cell would be 1·63 for perfect hexagonal close packing and therefore an exactly octahedral V^{2+} site. For VCl_2 c/a is 1·62,[2] for VBr_2 it is 1·64,[3] and for VI_2, 1·67.[3] The iodide is appreciably more distorted and this may be expected to affect the spectrum.

Spectra.—The spectrometer used was a Cary 14. The major axis of the crystals was, in each case, perpendicular to the crystal plate faces and all spectra were taken along this axis. Attempts to cut good optical faces parallel to the major axis were unsuccessful and so polarisation studies were not possible.

The Applied Physics Cryostat was a cold finger device and spectra were measured at room temperature, liquid-nitrogen temperature and liquid-helium temperature.

With this spectrometer, the light passed through the sample compartment in the visible region (above 14,000 cm^{-1})

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* I am grateful to Professor Stout for a helpful communication on this point.

[7] K. Knox, R. G. Shurbman, and S. Sugano, *Phys. Rev.*, 1963, **130**, 512.

[8] D. D. Sell, R. L. Greene, and R. M. White, *Phys. Rev.*, 1967, **158**, 489.

[9] D. D. Sell, *J. Appl. Phys.*, 1968, **39**, 1030.

[10] P. L. Richards, *J. Appl. Phys. Suppl.*, 1963, **34**, 1237.

[11] L. Lohr and D. S. McClure, *J. Chem. Phys.*, 1968, **49**, 3516.

[12] J. Ferguson, *Austral. J. Chem.*, 1968, **21**, 307.

[13] S. S. Kim, S. A. Reed, and J. W. Stout, *Inorg. Chem.*, 1970, **9**, 1584.

is monochromatic, but the full polychromatic beam is passed in the i.r. region. In consequence, the temperature of the sample in the i.r. region may be appreciably raised, particularly at helium temperature.

Extinction Coefficients.—The plate-like crystals were well finished with sharp edges and smooth faces. The sample thickness was measured by using a comparator microscope focussed on the edges and from a knowledge of density data [14] the extinction coefficients were calculated.

To investigate the reliability of this method, the peak intensity for the spin-forbidden $^4A_{2g}\rightarrow{}^2T_{2g}$ level at *ca.* 15,000 cm^{-1} of VI_2 at 77 K was plotted against measured thickness for samples from 0·1 to 1·0 mm and the result was a straight line with deviations of less than 5%, so that the molar absorptivities are known to *ca.* ±5%. The units of molar absorptivity are l mol^{-1} cm^{-1}.

A listing of the energy levels and assignments is given in Table 2.

TABLE 1

Calculated ligand-field parameters

Compd.	*Dq* (cm^{-1})	*B* (cm^{-1})	*C* (cm^{-1})
VCl_2	920	615	2410
VBr_2	860	530	2550
VI_2	790	510	2450

TABLE 2

Energy positions (cm^{-1}) and assignments

	VCl_2	VBr_2	VI_2
$^4T_{2g}$	9200	8600	7870
$^2T_{1g}{}^2E_g$	11,450	11 700	
	11 560	11 430	
	11 660	12 050	
	11 860	12 270	
	12 150		
	11 180		
	12 380		
$^4T_{1g}$	14 270	13 330	12 270
$^2T_{2g}$	15 950	15 550	14 800
		15 810sh	14 850
		15 690sh	14 930
		16 010	14 950
			15 060
			15 240
$^4T_{2g}$ + $^4T_{2g}$	18 520	17 180	15 820
	20 790		
$^4T_{1g}$	22 220	20 330	18 920
	22 460	22 990	19 490
	22 940	23 420	22 470
	23 150	23 610	23 650
	23 750	24 210	
	25 190	25 130	
	27 620		
	28 190		
	30 490		

DISCUSSION

Although all three crystals belong to a trigonal space group, the distortion from cubic symmetry is very small in both the chloride and the bromide and no feature of the spectra of either can be assigned as due to a low symmetry field. The analysis is therefore carried out on the basis of an octahedral field of halide ion surrounding the metal ion. The spectrum of VI_2 is treated similarly but the appreciable trigonal distortion in this compound may be responsible for some differences in the spectra. The most obvious is a broad shoulder on the $^4A_{1g}\rightarrow{}^4T_{1g}(F)$ transition which appears in the spectra of V^{2+} in $CdCl_2$ where the site symmetry of the V^{2+} is also appreciably trigonally distorted.

Band Energies and Intensities below 20,000 *cm*$^{-1}$.—To assign the bands, a ligand-field calculation using a computer program, incorporating the matrices of Eisenstein [15] and a diagonalisation routine, was carried out. The program was checked against the results of Liehr [16] for Cr^{3+} with good agreement. Spin orbit coupling is small and fixed at $\xi = 140$ cm^{-1} throughout. Only three parameters were used (*Dq*, *B*, and *C*) and the accuracy of the fit and band assignments are shown in Figure 1. The values of the parameters are in reasonable agreement with results on other halide systems (Table 1).

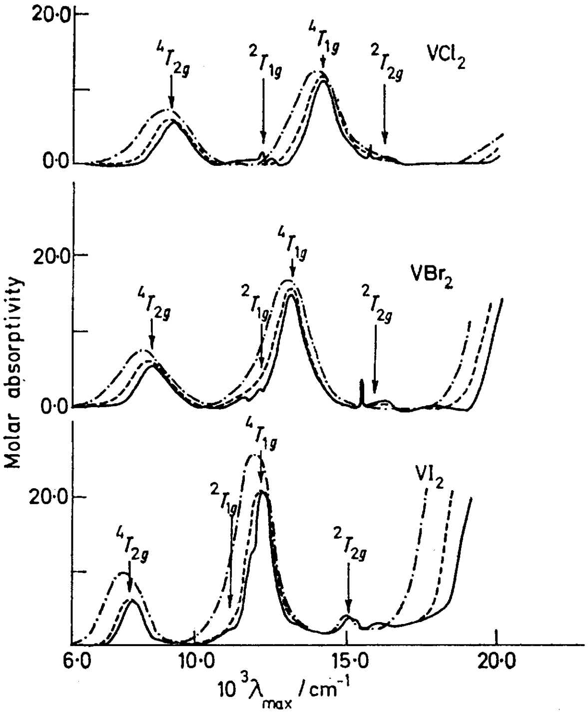

FIGURE 1 Electronic spectra up to 20,000 cm^{-1}: Room temperature — · — · —, 80 K — — —, and 50 K ——

The values of *C* do not follow a regular trend and the difference is too large to be due to errors in assignment of the bands. Inaccuracies in the calculation, such as the neglect of a Trees correction and the low-symmetry field, are probably responsible. Ligand-field calculations do not fit spin-forbidden levels at high energies very accurately and in the high-energy spectra of the present samples, two centre excitations may also appear. Apart from the spin-allowed $^4A_{1g}\rightarrow{}^4T_{1g}(P)$ transition, no attempt at an accurate assignment is made above 20,000 cm^{-1}.

The extinction coefficients of all the peaks are less than 20, showing that the parity and symmetry selection

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[14] R. J. H. Clark, 'Chemistry of Titanium and Vanadium,' Elsevier, Amsterdam, 1968, p. 55.

[15] J. C. Eisenstein, *J. Chem. Phys.*, 1961, **34**, 1968.

[16] A. D. Liehr, Symposium on Molecular Structure, Columbus, Ohio, June 1961.

rule does still apply but there are some interesting differences in the temperature dependence of the levels. The oscillator strength of the $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow T_{1g}(F)$ bands drops markedly between 300 and 5 K and the peak position shifts to higher energies. This behaviour is of the usual form for a centrosymmetric situation where the main intensity mechanism is vibronic. The baselines of the spectra are sufficiently good to allow some assessment of the oscillator strengths of spin-forbidden bands as well. In some cases (*e.g.* the $^4A_{2g}\rightarrow{}^2E_g,{}^2T_{1g}$ bands in VCl_2 at 12,000 cm^{-1}) there is no doubt that the oscillator strength of the band increases from 300 to 5 K. The most likely mechanism for the increase is the exchange effect and some fine structure attributable to this cause might be expected.

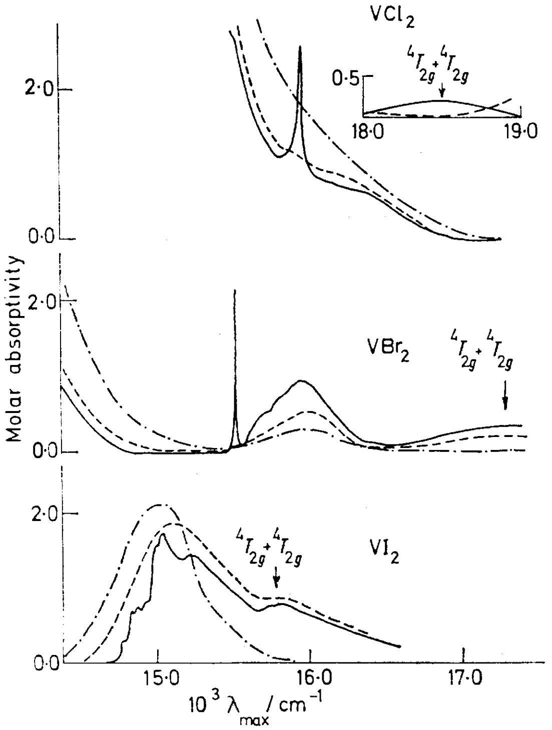

FIGURE 2 Formally spin-forbidden $^4A_{2g}\rightarrow{}^2T_{2g}$ transitions. Room temperature —·—·—, 80 K — — —, and 5 K ——

The $^4A_{2g}\rightarrow{}^2T_{2g}$ transition in VCl_2 and VBr_2 at 5 K shows a sharp line in the spectra (Figure 2). In VBr_2 it is clearly on the low-energy side of the main band and in VCl_2, although the band origin is obscured, it appears towards the low-energy side. The sharpness of the line is limited by the instrument but the half band width is less than 5 cm^{-1}, too sharp to be a vibrationally perturbed level.

Sell *et al.*[8] investigated the very sharp lines in the $^6A_{1g}\rightarrow{}^4T_{1g}$ transition of MnF_2. From polarised data, they were able to assign these pure electronic (zero phonon) levels to both electric dipole and magnetic dipole transitions. Since there is no spin orbit coupling between the $^4A_{2g}\rightarrow{}^2T_{2g}$ transition and the magnetic dipole-allowed quartet level ($^4T_{2g}$) in V^{2+}, magnetic dipole transitions are unlikely. It is probable that the sharp line is a zero phonon electric dipole level, normally strictly forbidden, but which can be made allowed in magnetic solids.[8]

In the case of the bromide, three shoulders appear on the broad band which follows this line and are separated from the no phonon line and from each other by 160 cm^{-1}. In a separate study,[17] some sharp vibrational lines spaced at 155 cm^{-1} are observed on a high-energy peak of VBr_2. The shoulders are probably phonon assisted, magnon allowed, electric dipole levels.

The spectra of the $^4A_{2g}\rightarrow{}^2E_g,{}^2T_{1g}$ bands in VCl_2 and VBr_2 (Figure 3) are again very similar, although the bromide spectrum is partially obscured by the spin-allowed band. The calculation gives two levels with the $^4A_{2g}\rightarrow{}^2E_g$ transition *ca.* 400 cm^{-1} lower in energy than the $^4A_{2g}\rightarrow{}^2T_{1g}$. The lower energy broad band is thus assigned to the ^2E_g level. The structure is too complex to explain in detail but the most noticeable features are the intense bands at 12,145 and 12,020 cm^{-1} respectively which appear only at 5 K. They are not as sharp as the pure electronic lines discussed previously and are probably phonon assisted magnon sidebands.

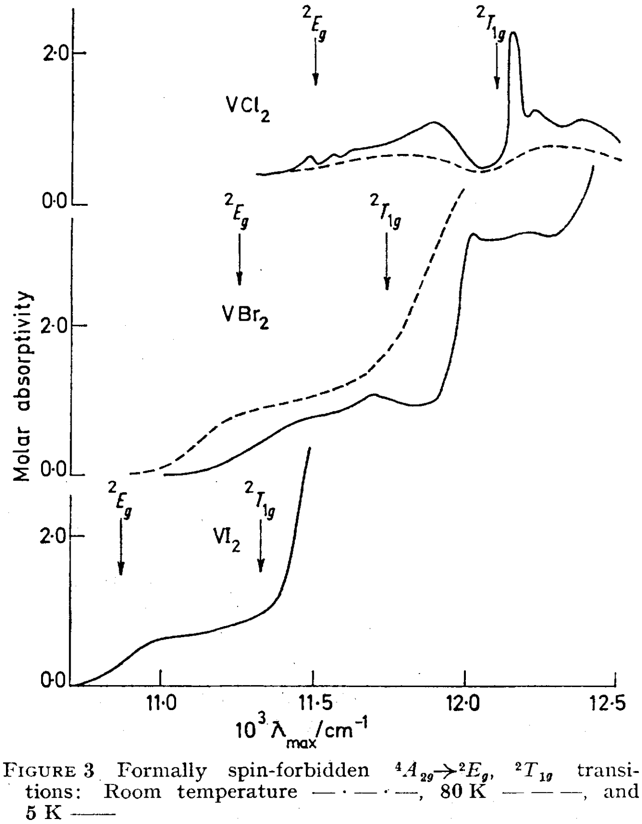

FIGURE 3 Formally spin-forbidden $^4A_{2g}\rightarrow{}^2E_g$, $^2T_{1g}$ transitions: Room temperature —·—·—, 80 K — — —, and 5 K ——

The spectra of these spin-forbidden transitions in the iodide are markedly different, probably due to the greater trigonal distortion. Although the $^4A_{1g}\rightarrow{}^2E_g$ shoulder can be detected at 5 K, most of the $^4A_{2g}\rightarrow{}^2E_g{}^2T_{1g}$ structure is obscured by the spin-allowed

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[17] W. E. Smith, unpublished results.

band and so the analysis is restricted to the $^4A_{2g} \rightarrow {}^2T_{2g}$ transition. In contrast to the chloride and bromide, the oscillator strength of this band drops with decreasing temperature but, as Lohr and McClure [11] point out, intensities due to an exchange type of mechanism can either increase or decrease, depending on the intensities of the hot bands. The large trigonal distortion could well have the necessary effect on the intensities and the slight increase in energy with decreasing temperature would support a vibronic mechanism. The fine structure is too complex to be analysed successfully, although it is possible to discern a rough vibrational progression based on two bands at 14,790 and 14,850 cm^{-1} with an interval of 140 cm^{-1}, about the expected value in VI$_2$.

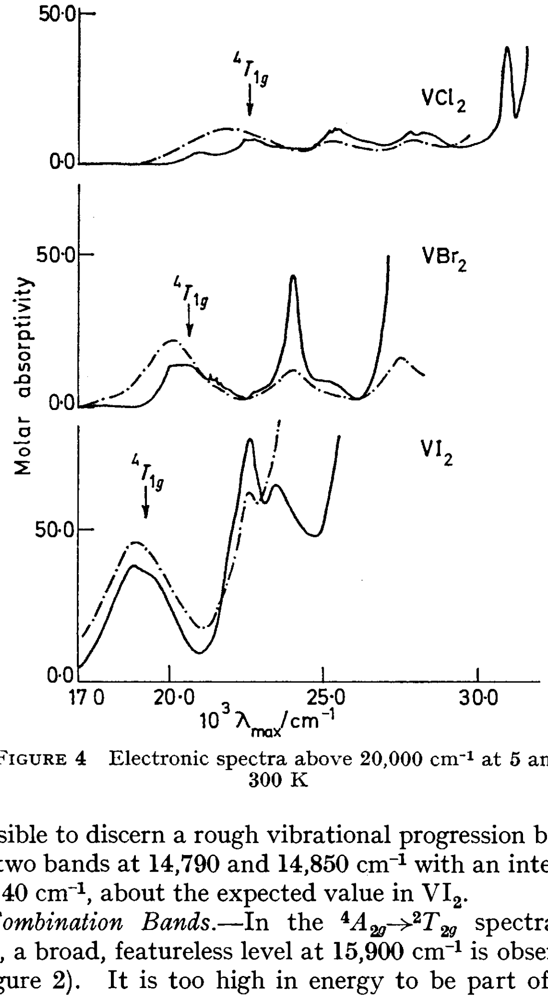

FIGURE 4 Electronic spectra above 20,000 cm^{-1} at 5 and 300 K

Combination Bands.—In the $^4A_{2g} \rightarrow {}^2T_{2g}$ spectra of VI$_2$, a broad, featureless level at 15,900 cm^{-1} is observed (Figure 2). It is too high in energy to be part of the spin-forbidden system and has the reverse temperature dependence. The peak position is exactly twice that of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition and weaker broad bands can also be identified in both bromide and chloride at exactly twice this transition frequency. In no case is a single-centre spin-forbidden band predicted close to these frequencies. The increase in intensity as temperature drops is expected for a combination band and the frequency agreement in all three samples makes its assignment to a $^4A_{2g} \rightarrow {}^4T_{2g} + {}^4T_{2g}$ band reasonably certain. Since it involves a two-electron jump and since each component is already spin-allowed, a low intensity compared to the spin-allowed peaks was to be expected.

Spectra above 20,000 *cm*$^{-1}$.—Only one spin-allowed band [$^4A_{2g} \rightarrow {}^4T_{1g}(P)$] is expected in this energy region and, if it has the same intensity mechanism as the other spin-allowed levels, should have a vibronic intensity mechanism. In each compound, only one region of the spectra shows a decrease in intensity with temperature but, even so, it is not always possible to discern the position of the low-temperature peak due to overlapping bands. It should be on the high-energy side of the high-temperature peaks and the calculated positions for this level at 5 K are in agreement with this.

The remaining peaks are due either to spin-forbidden levels of anomalously high intensity or to combination bands. Six one-centre spin-forbidden peaks arising from the $^4F \rightarrow {}^2P, {}^2D$ transitions are expected in this energy region but the calculation will not fit them accurately. A previous attempt to fit the spectra of crystals doped with V^{2+} ions and of VCl$_2$ was unsatisfactory, so that no assignment of individual bands is given here.[1] In the doped samples, the spin-forbidden levels in this energy region are 10—100 times as intense as those at lower energies. If the same relative intensities hold in the concentrated samples, then the bands observed here have about the expected intensities for formally one-centre spin-forbidden transitions. It is possible that some of the peaks are due to combination bands but the major peak positions do not relate in any simple way to combinations of single-centre energy levels.

CONCLUSIONS

The ligand-field calculation fits the spectra, within the limitations of the calculation, quite well and the parameters Dq, B and C, have values which are about those expected for the respective halide ligands.

Although spin-allowed band intensities are reasonable for V^{2+} in octahedral co-ordination, spin-forbidden levels are anomalously intense and this is explained in terms of the exchange effect.

Extremely sharp lines in the $^4A_{2g} \rightarrow {}^2T_{2g}$ transition in VCl$_2$ and VBr$_2$ are probably no phonon electric dipole lines made allowed by an odd parity magnon.

At least one combination band ($^4A_{2g} \rightarrow {}^4T_{2g} + {}^4T_{2g}$) is established.

The temperature dependence of intensities in the spin allowed levels is vibronic but bands which depend on the exchange mechanism for intensity, generally become stronger at 5 K. The only exception to this is the $^4A_{2g} \rightarrow {}^2T_{2g}$ level of VI$_2$ at 15,500 cm^{-1}.

The spectra on which this paper is based were taken at University College London and I acknowledge helpful discussion with the late Professor Sir Ronald Nyholm.

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