ESTIMATION OF THE BONDING CHARACTER OF PARAMAGNETIC ION COMPLEXES

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Stevens' model of covalent bonding has been used for the determination of bonding character as well as for the interpretation of g-factors of the complexes with a paramagnetic ion V^{4+} in the form of single crystals. Theoretical formulas were given for the g-factors of V^{4+} ions in the crystalline field of cubic nature with components of tetragonal symmetry. An account was taken of the presence of covalent binding between the d-electron of the V^{4+} ion and p-electrons of the surrounding environment. Computations show that one of the covalent binding factors should be less than 0.100 in order to fit the experimental g-values.

1. Introduction

Electron spin resonance studies of V^{4+} ions in different crystals have been reported earlier [1–7] in order to study the structure as well as the effect of temperature on the structure of vanadium complex in different crystals. Tetravalent vanadium exists as a stable vanadyl, VO^{2+}, ion and hence a large number of the paramagnetic resonance absorption studies as well as optical and magnetic studies have been performed for the complexes with a VO^{2+} ion. It has been confirmed from different studies [1, 3, 5, 7] of vanadyl complexes, viz. crystallographic, optical and magnetic, that a VO^{2+} ion occurs coordinated to other groups in the complex whether it is in the solid state or in solution form. As the vanadyl, the VO^{2+} ion, exhibts paramagnetic resonance due to the single unpaired $3d^1$ electron present in the molecule, energy levels of the VO^{2+} ion can be taken as that of the V^{4+} ion. It is interesting to consider whether it is possible to explain the experimental data obtained from the ESR spectra of the VO^{2+} ion doped in different single crystals as well as to determine the bonding character of vanadium complexes on the basis of theoretical analysis of the behaviour of a single $3d^1$ electron.

It was suggested earlier [8] that the expressions for g-factors determined by Bleaney et al. [9] can not explain the experimental g-values because of the presence of a lower symmetry crystalline field and the factors not taken into account by Bleaney et al. In the

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present paper we try to find out whether the experimental g-values as well as bonding character of vanadium ion complexes can be explained using Stevens' model of covalent binding [10]. It is evident from the results that in order to fit the experimental g-factors one of the covalent binding factors $K_\perp$ should be taken as less than 0.100.

2. Theory

In this section we give theoretical expressions for g-factors in the presence of a tetragonal crystalline field and covalent binding for the present case. Stevens gave expressions for $g_\parallel$ and $g_\perp$ for $(d\mathscr{E})^5$ in the presence of a strong cubic field with a small tetragonal component assuming $(d\mathscr{E})^5$ as a positive hole in the $d\mathscr{E}$ shell. These expressions can be used for the present case with some modification.

In a number of cases the crystalline field has predominantly cubic symmetry, with small distortions in the sense that the splitting of the orbital states due to the cubic field is larger than that due to the terms of lower symmetry. The matrix of the cubic field splitting is diagonalized first and then the effect of the terms of tetragonal symmetry is taken into account on the assumption that these can be treated by the first order perturbation theory. The crystal field calculation can be carried out simply using the "spin-operator technique" [11, 12]. We use this technique for the determination of energy of the lower states.

In a cubic field with a tetragonal distortion the equivalent operator Hamiltonian is

$$\mathscr{H} = B_4(0_4^0 + 50_4^4) + B_2^0 0_2^0 + B_4^0 0_4^0, \tag{1}$$

where the magnitude of the cubic field is denoted by B_4 and the other two terms represent the tetragonal distortion of the second and fourth degree in the potential, respectively. The energy levels and wave functions of lower states are given below (states are given in terms of $|L_z\rangle$ and $|\tilde{l}_z\rangle$, where $\tilde{l}$ is the fictitious orbital momentum)

State		
Doublet	$\|2^a\rangle \equiv \|\tilde{0}\rangle$	
Singlet	$\pm\|\mp 1\rangle \equiv \|\pm\tilde{1}\rangle$	(2a)

Energy	
$-3B_2^0 - 48B_4^0$	
$6B_2^0 + 12B_4^0$.	(2b)

Stevens has shown that because of π-binding between d-electrons and the surrounding p-electrons of the environment, states $|1\rangle$ and $|-1\rangle$ etc. do not exhibit a purely d-nature. The two lower states are obtained due to a combined effect of the tetragonal field (with negative Δ) and the spin-orbit interaction. The expressions are as follows:

$$\psi_1 = \cos\delta|-1\rangle|-1/2\rangle - \sin\delta|0\rangle|1/2\rangle$$

$$\psi_2 = \cos\delta|\ \ 1\rangle|1/2\rangle \ \ + \sin\delta|0\rangle|-1/2\rangle \tag{3}$$

TABLE I

Values of the covalent binding factors $K_\perp$ and $K_\parallel$ and the parametric angle δ for vanadium ions in different crystals

S. No.	Crystal lattices	$K_\perp$	$K_\parallel$	δ
1.	V^{4+} in Tridimite [13]	0.050	1.216	94°2.5′
		0.054	0.759	94°22′
		0.058	0.394	94°41.5′
		0.060	0.238	94°51′
		0.062	0.097	95°0.5′
2.	$MoO_3:V^{4+}$ [13]	0.030	1.152	98°21′
		0.040	0.819	98°50′
		0.050	0.526	99°20′
		0.060	0.283	99°51.5′
		0.070	0.041	100°24′
3.	$VOCl_2:VO^{2+}$ [13]	0.076	1.065	96°8.5′
		0.080	0.769	96°27′
		0.082	0.637	96°37′
		0.086	0.401	96°56′
		0.090	0.195	97°15′
4.	V^{4+} in Garnet $(Ca_2NaMg_2V_3O_{12})$ [14]	0.060	1.090	98°47′
		0.066	0.868	99°7′
		0.070	0.732	99°20.5′
		0.080	0.423	99°55.5′
		0.086	0.259	100°17′
		0.090	0.158	100°31′
5.	$NaCl:VO^{2+}$ [15]	0.066	1.064	96°22′
		0.068	0.926	96°30′
		0.070	0.805	96°38.5′
		0.076	0.481	97°4′
		0.080	0.294	97°21′
		0.082	0.208	97°29′
6.	$KCl:VO^{2+}$ [15]	0.030	1.307	95°49′
		0.036	0.981	96°8′
		0.040	0.784	96°20.5′
		0.046	0.516	96°40.5′
		0.050	0.355	96°54′
		0.060	0.005	97°29′
7.	$CsNO_3:VO^{2+}$ [16]	0.030	1.173	96°29′
		0.036	0.897	96°47.5′
		0.040	0.729	96°59.5′
		0.050	0.356	97°32′
		0.056	0.161	97°52′
		0.060	0.042	98°6′
8.	$Ba(NO_3)_2:VO^{2+}$ [16]	0.030	1.173	96°29′
		0.036	0.897	96°47.5′
		0.040	0.729	96°59.5′

TABLE I (continued)

S. No.	Crystal lattices	$K_{\perp}$	$K_{\parallel}$	δ
		0.050	0.356	97°32′
		0.056	0.161	97°52′
		0.060	0.042	98°6′
9.	RbAl: VO^{2+} [17]			
	(Rubidium aluminium alum)	0.004	0.586	96°35′
		0.006	0.523	96°40′
		0.008	0.460	96°45′
		0.010	0.399	96°50.5′
		0.020	0.118	97°18′
10.	CsAl: VO^{2+} [17]	0.001	0.916	96°11.5′
		0.004	0.806	96°19′
		0.008	0.662	96°29.5′
		0.010	0.594	96°34.5′
		0.020	0.277	97°1′
		0.030	0.002	97°29′
11.	KAl: VO^{2+} [17]	0.001	0.745	96°11.5′
		0.002	0.709	96°14.5′
		0.004	0.640	96°19′
		0.008	0.505	96°29.5′
		0.010	0.441	96°34.5′
		0.020	0.143	97°1′
12.	NH_4Al: VO^{2+} [17]	0.001	0.689	96°4′
		0.004	0.585	96°11′
		0.008	0.449	96°21′
		0.010	0.385	96°26.5′
		0.020	0.088	96°53′
13.	MAG: VO^{2+} [17]	0.002	0.477	96°22′
	(Methyl ammonium gallium	0.004	0.414	96°27′
	alum)	0.006	0.353	96°32′
		0.008	0.294	96°37.5′
		0.010	0.236	96°42.5′
14.	$UO_2(NO_3)_2.6H_2O$: VO^{2+}	0.010	1.189	96°1′
	[18]	0.020	0.764	96°27.5′
		0.026	0.538	96°44.5′
		0.030	0.399	96°56′
		0.036	0.207	97°14′
15.	$(NH_4)_2.Zn(SO_4)_2.$	0.010	1.048	96°1′
	$6H_2O$: VO^{2+} [18]	0.016	0.797	96°17′
		0.020	0.642	96°27.5′
		0.026	0.426	96°44.5′
		0.030	0.293	96°56′
		0.036	0.109	97°14′
16.	Glycine: VO^{2+} [19]	0.010	1.471	95°13.5′
		0.020	0.938	95°40.5′
		0.026	0.662	95°58′
		0.030	0.494	96°10′
		0.036	0.264	96°28′

TABLE I (continued)

S. No.	Crystal lattices	$K_\perp$	$K_\parallel$	δ
17.	Alanine: VO^{2+} [19]	0.060	1.147	94°51′
		0.062	0.949	95°0.5′
		0.066	0.605	95°20′
		0.070	0.318	95°39′
		0.074	0.077	95°58.5′
18.	Dimethylalanine: VO^{2+} [19]	0.060	1.028	96°23.5′
	(*A*)	0.066	0.689	96°47′
		0.070	0.491	97°3′
		0.076	0.229	97°27′
		0.080	0.075	97°45′
19.	Dimethylalanine: VO^{2+} [19]	0.030	1.629	95°15′
	(*B*)	0.040	0.982	95°47.5′
		0.046	0.660	96°8′
		0.050	0.469	96°22′
		0.056	0.214	96°43′
		0.060	0.062	96°58′

where

$$\tan 2\delta = \frac{\sqrt{2}\,\lambda_1}{(\lambda_1/2)+\Delta} \tag{4}$$

and λ_1 is the reduced value of the spin-orbit interaction with Δ as the energy spacing between the states Γ_5 and Γ_3. The expressions for the g-factors are obtained as

$$g_\parallel = 2|\sin^2\delta-(1+K)\cos^2\delta|, \quad g_\perp = 2|\sqrt{2}\,K\sin\delta\cos\delta+\sin^2\delta|, \tag{5}$$

where K is defined as $K = \langle 1|L_z|1\rangle$ and it is assumed that covalent binding is the same in all directions, that is, isotropic. If covalent binding is anisotropic, we have

$$g_\parallel = 2|\sin^2\delta-(1+K_\parallel)\cos^2\delta|, \quad g_\perp = 2|\sqrt{2}\,K_\perp\sin\delta\cos\delta+\sin^2\delta|, \tag{6}$$

where $K_\parallel = \langle 1|L_z|1\rangle$ and $K_\perp = \sqrt{2}\,\langle 1|L_x|0\rangle$.

3. Results and discussion

The covalent binding factors $K_\parallel$ and $K_\perp$ were determined with the help of expression (6). The values of these factors with the parametric angle δ which satisfy the experimental g-values, are given in Table I. In the presence of the tetragonal crystalline field the covalent binding factors are less than one, as there is no shifting of the doublet in $^2T_2$ and higher doublet E. Results show that $K_\perp$ should be less than 0.100 in order to have a better fit to the experimental g-factors. Small values of the covalent binding factors can be explained on the basis of the assumption that an electron migrates to neighbouring atoms. However, covalency is inversely proportional to the ESR parameters $g_\parallel$ and $g_\perp$. Also $g_\parallel$ depends

on the factor $K_{\|}$ (one of the covalent binding factors) and is inversely proportional to it, that is, covalency will decrease if $K_{\|}$ decreases meaning thereby that the character of the complex will be more ionic. While $g_{\perp}$ depends on the factor $K_{\perp}$ (next covalent binding factor) it is directly proportional to it. Hence its value will increase if $K_{\perp}$ increases giving thereby the same nature to the complex as above, as far as binding is concerned. In this way migration of electrons to neighbouring atoms will have to take place. These considerations suggest that some modification is needed in the crystal field theory of ionic complexes taking into account a certain amount of charge transfer.

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