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Investigation on the electronic paramagnetic resonance parameters of vanadyl in di-ammonium D-tartrate single crystal

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ABSTRACT

In this work, the electronic paramagnetic resonance (EPR) parameters $g_{//}$ *and* $g_{\perp}$ *and the hyperfine structure constants* $A_{//}$ *and* $A_{\perp}$ *of vanadyl* (VO^{2+}) *center in di-ammonium D-tartrate* $[(NH_4)_2C_4H_4O_6]$ *single crystal are theoretically studied from the high order perturbation formulas of these parameters for a* $3d^1$ *ion in tetragonally compressed octahedron. In these formulas, the energy denominators are correlated with the local structure around the impurity center and the contributions to the spin Hamiltonian parameters from the s- and p-orbitals as well as the spin-orbit coupling coefficient of the ligands are taken into account. The calculated EPR parameters are in good agreement with the experimental data.*

Key words: Electron paramagnetic resonance(EPR), Di-ammonium D-tartrate, $(NH_4)_2C_4H_4O_6$, VO^{2+}

INTRODUCTION

The vanadyl ion is probably the most stable biatomic ion which is frequently used as an impurity probe to study local structures and properties in doped crystals by means of electronic paramagnetic resonance technique.[1-8] Due to the short V-O bond, the unpaired electron is always in a nondegenerate state, leading to resolved EPR spectra over a wide range of temperatures. The hyperfine interaction is highly anisotropic and is therefore sensitive to orientation, conformation, and rotational relaxation. These features are responsible for extensive EPR studies of vanadyl in a variety of environments[2]. For example, R.Tapramaz etal had studied the EPR spectra of VO^{2+} in di-ammonium D-tatrate $[(NH_4)_2C_4H_4O_6]$(DADT) single crystal and got the spin Hamiltonian parameters ($g_{//}$, $g_{\perp}$, $A_{//}$, $A_{\perp}$)[5] . Based on the EPR spectral analyses, they found that when VO^{2+} doped into DADT crystal, the distorted $[VO(H_2O)_5]^{2+}$ octahedron was formed and had nearly axial symmetry for the distortion along the V=O direction[5]. But until now, the above experimental results have not been satisfactorily interpreted. In this work, the anisotropic g factors and hyperfine structure constants-A of the VO^{2+} in $[VO(H_2O)_5]^{2+}$ were investigated by the perturbation formulas of a $3d^1$ ion in tetragonally compressed octahedra. In these formulas, the energy separations are correlated with the local structure and the contributions from the s- and p- orbitals and the spin-orbit coupling coefficients of the ligands are taken into account based on the cluster approach.

CALCULATIONS

For a $3d^1$ ion in tetrognally compressed octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2A_{1g}$ ($|z^2>$),and $^2B_{1g}$ ($|x^2-y^2>$) wherea the original lower orbital triplet $^2T_{2g}$ would be separated into a singlet $^2B_{2g}$ ($|xy>$) and a doublet ^2Eg ($|xz>$ and $|yz>$), with the former lying lowest[9]. From crystal- and ligand-field theory, the LCAO molecular-orbitals can be taken as the one-electron basic functions[10][11]:

$$\psi_t = N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt})$$

$$\psi_e = N_e^{1/2} (\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s) \qquad (1)$$

Where φ_γ (the subscript $\gamma=e$ or t represents the irreducible representation of O_h group) is the d-orbital of the $3d^n$ ion . $\chi_{p\gamma}$. and χ_s are the p- orbital and s- orbital of ligand. N_γ (the normalization coefficient)and λ_γ (or λ_s)(the orbital mixing coefficients.) are the molecular orbital coefficients. The normalization relation can be given as[12]:

$$N_t (1- 2\lambda_t S_{dpt} + \lambda_t^2) = 1$$

$$N_e (1- 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1 \qquad (2)$$

And the approximate relation can be expressed as[12]:

$$N^2 = N_t^2 [1 + \lambda_t^2 S_{dpt}^2 - 2 \lambda_t S_{dpt}]$$

$$N^2 = N_e^2 [1+ \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2 \lambda_e S_{dpe} - 2 \lambda_s S_{ds}] \qquad (3)$$

Here N is the average covalency factor, characteristic of the covalency effect of (or reduction of the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter) for the central ion in crystals. $S_{dp\gamma}$ (and S_{ds}) denote the group overlap integrals. In general, the mixing coefficients increase with increasing the group overlap integrals, and one can approximately adopt proportional relationship between the mixing coefficients and the related group overlap integrals, i.e., $\lambda_e / S_{dpe} \approx \lambda_s / S_s$ within the same irreducible representation e_g.

By using the similar perturbation procedure in refs. [13,14], the high-order perturbation formulas of the g-factors and the hyperfine structure constants for the $3d^1$ ion in tetragonally compressed octahedra can be derived on the basis of the cluster approach [15]:

$$g_{//}=g_s-8 k'\zeta'/E_1-2k\zeta^2/E_2^2+2 k'\zeta'^2/E_1^2$$
$$g_\perp=g_s-2k\zeta/E_2+2 k'\zeta'\zeta[1/E_1 E_2-1/E_1^2]$$
$$A_{//}=P[-\kappa-4 N^2/7 +(g_{//}-g_s) +6(g_\perp-g_s)/14]$$

$$A_\perp= P'[-\kappa+2 N^2/7 +11(g_\perp-g_s)/14] \qquad (4)$$

where g_s (≈2.0023) is the spin-only value. κ is the isotropic core polarization constant. Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k', and the dipolar hyperfine structure parameters P and P' in equation (4) may be expressed as:

$$\zeta = N_t (\zeta^0_d + \lambda_t^2 \zeta^0_p /2) \qquad \zeta' = (N_t N_e)^{1/2} (\zeta^0_d - \lambda_t\lambda_e\zeta^0_p /2)$$
$$k = N_t (1 + \lambda_t^2/2) \qquad k' = (N_t N_e)^{1/2} [1- \lambda_t (\lambda_e+\lambda_s A)/2]$$

$$P= N_t P_0 \qquad P'= (N_t N_e)^{1/2} P_0 \qquad (5)$$

where ζ^0_d and ζ^0_p are the spin-orbit coupling coefficients of the $3d^n$ and ligand ions in free states, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^1$ ion. A denotes the integral $R\left\langle ns \left| \frac{\partial}{\partial y} \right| np_y \right\rangle$, where R is the impurity-ligand distance of the present system. The energy denominators E_1 and E_2 stand for the energy separations between the excited $^2B_1$, ^2E and the ground $^2B_2$ states. They can be obtained from the strong cubic field approach as follows:

$$E_1 =E(^2B_2)-E(^2B_1)=10 D_q$$

$$E_2=E(^2B_2) -E(^2E_2)=-3D_s+5D_t \qquad (6)$$

Here D_q is the cubic field parameter and D_s, D_t tetragonal ones. From the superposition model and the geometrical relationship of the studied $[VO(H_2O)_5]^{2+}$ cluster, they can be determined as follow:

$$D_s=(4/7) \bar{A}_2 (R_0)[(R_0/R_\perp)^{t2}-(R_0/R_{//})^{t2}] \qquad (7)$$
$$D_t= (16/21) \bar{A}_4 (R_0) [(R_0/R_\perp)^{t4}-(R_0/R_{//})^{t4}]$$

Where the t_2 (≈3)and t_4(≈5) are the power-law exponents, $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference bonding length R_0, here R_0≈0.197nm were taken for the VO^{2+} in cubic field[16]. From the reference bonding length R_0 and slater-type SCF functions[17][18], the integrals $S_{dpt}\approx0.0477$, $S_{dpe}\approx0.1239$, $S_{ds}\approx0.0986$, and $A\approx1.0206$ are obtained. For $3d^n$ octahedral clusters, the ratio $\bar{A}_2(R_0)\approx10.8\bar{A}_4(R_0)$ and $\bar{A}_4(R_0)\approx\frac{3}{4}D_q$ have been proved to be valid in many crystals[15][19], and can be reasonably adopted here. for $[VO(H_2O)_5]^{2+}$, to our knowledge, no optical spectra data were reported. However, the value $Dq\approx2012cm^{-1}$ was obtained for the $(VF_6)^{2-}$[20], according to the chemical series $Dq(F^-)<Dq(O^{2-})<Dq(H_2O)$, one can approximately estimate the $Dq\approx2040$ cm^{-1} for present octahedral $[VO(H_2O)_5]^{2+}$ cluster here. The crystal structure data $R_\perp$ and $R_{//}$ denote the metal-ligand distances parallel and perpendicular to the tetragonal axis, respectively. Here we take the $R_\perp\approx R_0\approx0.197nm$[16] and $R_{//}$ as the adjustable parameter. Thus, by fitting the calculated results to the experimental data, one can have

$$N\approx0.95,\qquad R_{//}\approx0.158\text{nm},\qquad \kappa\approx0.735\,.$$

The values $N_t\approx0.9625$, $N_e\approx0.9999$, $\lambda_t\approx0.2547$, $\lambda_e\approx0.2502$ and $\lambda_s\approx0.2019$ are calculated from equations (2) and (3). The parameters $\zeta\approx243.4\ cm^{-1}$, $\zeta'\approx239.0\ cm^{-1}$, $k\approx0.993$, $k'\approx0.926$, $P\approx130.1\times10^{-4}\ cm^{-1}$ and $P'\approx133.6\times10^{-4}\ cm^{-1}$ can be determined from equation (4) and the free-ion values $\zeta^0_d\approx248\ cm^{-1}$ and $P_0\approx136\times10^{-4}\ cm^{-1}$ for V^{4+} [21] and $\zeta^0_p\approx151\ cm^{-1}$ for O^{2-} [22].

The corresponding calculated values are shown in Table 1.

Table 1. The EPR parameters for paramagnetic vanadyl in DADT single crystal

	$g_{//}$	$g_\perp$	$A_{//}/10^{-4}\cdot cm$	$A_\perp/10^{-4}\cdot cm$
Ca	1.91	1.99	-181.96	-58.87
Ca	1.91	1.98	-183.07	-61.42
Ex	1.91	1.98	-183.08	-61.05

[a] calculations by using the high-order perturbation formulas in equation(4) but ignoring the ligand orbital contributions(i.e., taking $\zeta'=\zeta=N\zeta^0_d$ and $k=k'=N$).

[b] Calculations by using equation(4) and considering the ligand orbital contributions in this work.

c The signs of the experimental hyperfine structure constants were not given in Ref[5]. Based on the theoretical calculations in this work and various observed results for V^{4+} (or VO^{2+}) in oxides [25], these signs should be negative.

DISCUSSION

From Table 1, one can find that the calculated results of VO^{2+} in DADT crystal by using higher perturbation formulas are in good agreement with the observed values, This suggests that the formulas and the related parameters adopted in this work can be regarded as suitable. From table 1, one can also find that the calculated results including the contributions from the SO coupling coefficient and the orbitals of the ligands are slightly better than those neglecting above contributions. In view of the high valence state of V^{4+}, the covalency and hence moderate admixture of the metal and ligand orbitals can be expected. This point may be illustrated by small covalency factor N (≈0.95‹1) in equation (3) and the mixing coefficients ($\lambda_t\approx0.2547$, $\lambda_e\approx0.2502$ and $\lambda_s\approx0.2019$) obtained in present work. Therefore, the formulas of the EPR parameters containing the ligand orbital and spin-orbit coupling contributions seem to be more applicable than the simple ones in the absence of these contributions for the investigations on the EPR parameters of impurity ions in covalent systems.

By fiting the calculated values to the experimental results, one can have the $R_{//}\approx0.158nm$, this means that the $[VO(H_2O)_5]^{2+}$ octahedron around V^{4+} ion is significantly compressed ($\Delta R=R_0-R_{//}\approx0.039nm$) along the C_4 axis. Similar local distortions were also found in other VO^{2+} ions doped crystals. For example, $\Delta R\approx0.047nm$ was found for VO^{2+} in $KZnClSO_4\cdot3H_2O$[2][16]). Therefore, the local distortion obtained in this study can be regard as reasonable.

Many studies show that the core polarization κ in various V^{4+}(or VO^{2+}) clusters in crystals is in the range 0.6-1.0[23][24]. The value $\kappa\approx0.735$ obtained in this work is within the range and can be regarded as rational.

CONCLUSION

In this paper, the EPR parameters for $[VO(H_2O)_5]^{2+}$ cluster in DADT crystal are theoretically studied from the high order perturbation formulas of these parameters including the ligand contributions. Based on the EPR analyses, the octahedron around V^{4+} ion is significantly compressed(about 0.039nm) along the C_4 axis. The calculated EPR parameters are in good agreement with the observed values.

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