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THEORETICAL RESEARCH ON OPTICAL,THERMAL AND MAGNETIC PROPERTIES OF DICHLOROTETRAPYRAZOLENICKEL(TYPE II)COMPLEX*

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In this paper, we have calculated and analyzed theoretically and consistently the absorption spectra, the ZFS and EPR parameters of the ground state, the Schottky low-temperature heat capacity, and the paramagnetic susceptibility of $Ni(pz)_4Cl_2$ (Dichlorotetrapyrazolenickel) complex by using $d^8[(1-C_2)D^*_{4h}+C_2D^*_{2h}]$ complete configuration mixing unified crystal field theory. The theoretical results agree with the experimental observation very well. We can give a complete and reasonable theoretical interpretation of the optical, thermal and magnetic properties of $Ni(pz)_4Cl_2$.

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I. INTRODUCTION

There have been a lot of reports[1−3] on the experimental results of the optical absorption spectra , the paramagnetic resonance spectra , the paramagnetic susceptibility and the Schottky heat capacity of the Ni^{2+} ions in $Ni(pz)_4Cl_2$ complex (pz=pyrazole). Reimann[1] has measured the absorption spectra of $Ni(pz)_4Cl_2$, Klaaijsen *et al.*[2] have measured the total heat capacity, the paramagnetic susceptibility of Ni $(pz)_4Cl_2$ and fitted the experimental values of the heat capacity using the ZFS (zero field splitting) parameters D and E, thus obtained the parameter E=0.0 (1). In using the ZFS and electron paramagnetic resonance (EPR) parameters to fit the experimental values of the paramagnetic susceptibility, they have made an a priori supposition that E=0 and $g_x=g_y=g_\perp$. Structure data[1,4] showed that the molecular structure of $Ni(pz)_4Cl_2$ is not axially symmetrical, therefore $E\neq 0, g_x\neq g_y$. Vermaas *et al.*[3] have used the energy matrix of D_{4h} point group symmetry to calculate the absorption spectra, the ZFS and EPR parameters of $Ni(pz)_4Cl_2$ and the complex of its similar structure. In order that the theoretical results agree with the experimental data,

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they have used ten fitting parameters and regarded the ZFS and EPR parameters as the parameters with which they fit the experimental curves of the heat capacity and susceptibility in their calculation. And because they have used two groups of different fitting parameters to calculate the spectra, heat capacity and susceptibility , they cannot give a complete and uniform interpretation of the optical, thermal and magnetic properties of $Ni(pz)_4Cl_2$. Zhou and Yan *et al.*[5−7] have made use of D_{4h} point group symmetry and the unified crystal field theory to explain the optical and magnetic properties of $Ni(pz)_4X_2$(X=Cl,Br etc.), with only one group of parameters being used. In all the above works, D_{4h} point group symmetry model has been used, thus $E = 0, g_x = g_y = g_\perp$,which is the result expected from D_{4h} symmetry. But the parameter E obtained from the fitting of the experimental data of the heat capacity is not zero, and the structure data also show that the Cl—Ni bond deviates by 0.3° and 0.36°(the angles between the Cl—Ni—Cl bond and the two N—Ni—N bonds equal 90.3° and 89.64° respectively) from the C_4 axis, and the four nitrogen atoms (belonging to the four pyrazole radicals) close to the central Ni^{2+} ion form a quadrilateral, the lengths of the four sides of the quadrilateral are not equal to each other and their relative deviation is 0.017; and so are the lengths of diagonals of the quadrilateral, their relative deviation is 0.005. The interior angles have a relative deviation of 0.003 from 90°. These facts show that the symmetry of molecular structure of $Ni(pz)_4Cl_2$ deviates slightly from D_{4h}, strictly speaking, it belongs to C_i point group symmetry. Thus one should take $E \neq 0$ and $g_x \neq g_y$.

In this paper, we use a linear superposition $(1 - C_2)D_{4h} + C_2D_{2h}$, [$C_2$ being taken to be 0.005 (the relative deviation of the lengths of the diagonals)]of two kinds of low symmetry groups as the symmetric crystal field of $Ni(pz)_4Cl_2$, and by the aid of complete configuration mixing unified crystal field theory we calculate and fit, theoretically and consistently, the spectra , the ZFS and EPR parameters, the Schottky heat capacity, and the paramagnetic susceptibility of $Ni(pz)_4Cl_2$, with only seven spectrum parameters being used. Thus we have overcome the shortcomings that Vermaas *et al.*[3] did in their calculations: the spectra and the ZFS and EPR parameters they used were treated separately, more fitting parameters had to be used and conflict between these parameters appeared, hence they could not consistently explain the optical, thermal and magnetic properties of Ni $(pz)_4Cl_2$. We have obtained results that are much more realistic than others did.[3,5−7]

II. THEORETICAL CALCULATIONS

The perturbation Hamiltonian of the $d^8[(1-C_2)D^*_{4h}+C_2D^*_{2h}, C_2 = 0.005]$ ion is expressed as

$$\widehat{H}' = \widehat{H}_{\mathrm{e,e}}(B,C) + \widehat{H}_{\mathrm{so}}(\varepsilon) + \widehat{H}_{O_h}(Dq) + (1-C_2)\widehat{H}_{D_{4h}}(a,b)$$

$$+C_2\widehat{H}_{D_{2h}}(a,b) + 2\alpha\sum_{i>j=1}^{8}\widehat{L}_i\cdot\widehat{L}_j + \beta(\widehat{L} + 2.0023\widehat{S})H, \qquad (1)$$

where $H_{\mathrm{e,e}}$ is the Coulomb interaction energy between the valence electrons, H_{so} the spin-orbit interaction energy, $H_{O_h}(Dq)$ the component of O_h symmetry of the potential of crystal field, $H_{D_{4h}}$ and $H_{D_{2h}}$ are the components of the low symmetry groups D_{4h} and D_{2h} of the crystal-field potential, respectively. The second term counted backwards is the Trees correction , and the last one the Zeeman energy.

In the O_h point group representation, the base functions of the corresponding energy levels of D_{4h} and D_{2h} are the same,so are the reduced matrix elements $a = \langle E \parallel V(E) \parallel E\rangle$, $b = \langle T_2 \parallel V(E) \parallel T_2\rangle$ of the potential of the crystal field, and their reduced relationships are $A_1' = A_1 + B_1, B_1' = A_2 + B_2, B_2' = E_y, B_3' = E_x$,where A_1', B_1', B_2', B_3' and $A_1, A_2, B_1, B_2, E_y, E_x$ belong to irreducible representations of D_{2h} and D_{4h} group respectively. When external magnetic field $H = 0$, the four irreducible complete energy matrices for d^8 are $A_1'(15), B_1'(10), B_2'(10)$ and $B_3'(10)$, where the numbers in parentheses are dimensions of the corresponding matrices. The matrix elements are the linear combination of the Racah parameters B and C, the coefficients of spin-orbit coupling, the cubic crystal field parameter D_q, the D_{4h} distorted low symmetric crystal field parameters a and b, and the Trees coefficients of correction. We can determine the spectra from the difference between the eigenvalues of energy levels of the excited states and of the ground state of the matrices $A_1'(15), B_1'(10), B_2'(10)$ and $B_3'(10)$ (see Table 1).

In the crystal field of $[(1-C_2)D_{4h}+C_2D_{2h}]$ symmetry, the effective spin Hamiltonian of d^8 electron system in the coordinate system with z axis parallel to C_2 axis can be expressed as

$$\widehat{H}_{s'} = D[\widehat{S}_z'^2 - (1/3)\widehat{S}'(\widehat{S}'+1)] + E(\widehat{S}_x'^2 - \widehat{S}_y'^2) + \sum_{\alpha}\beta g_\alpha \widehat{S}_\alpha' H_\alpha, \quad \alpha = x, y, z \qquad (2)$$

where the effective spin S' is equal to the real spin $S(\widehat{S}' = S = 1)$.

When external magnetic field $H = 0, \widehat{H}'$ has a group of eigenvectors $\mid B_1'(5)\rangle, \mid B_2'(5)\rangle$, $\mid B_3'(5)\rangle$ of the ground state corresponding to the ZFS energy levels of the ground state $(t_2^6 e^{2\,3}A_2)$ and according to the requirement of the same symmetry we can form a group of corresponding irreducible representation base functions $\mid \Gamma_i'(5S')\rangle$,i.e.

$$\mid B_1'(5s')\rangle = -\mathrm{i}X_{10}f(A_2), \mid B_2'(5s')\rangle = (1/\sqrt{2})(X_{11} + X_{1-1})f(A_2)$$

and

$$\mid B_3'(5s')\rangle = (\mathrm{i}/\sqrt{2})(X_{11} - X_{1-1})f(A_2),$$

in equivalent spin space,where $f(A_2)$is the normalized orbital wave function factor of $A_2([(1-C_2)D_{4h} + C_2D_{2h}])$ symmetry.

Because the Zeeman term $\beta\sum_{\alpha} g_\alpha \widehat{S}_\alpha' H_\alpha$ in the effective spin Hamiltonian is equivalent to the Zeeman term $\beta(\widehat{L} + 2.0023\widehat{S})\cdot H$ in $\widehat{H}'$, the matrix elements $\langle \Gamma'_i(5) \mid \widehat{M}_\alpha \mid \Gamma'_j(5)\rangle$ of the operator $\widehat{M}_\alpha = (\widehat{L}_\alpha + 2.0023\widehat{S}_\alpha)$ between the eigenvectors of the splitting states of the

Table 1. Observed and calculated absorption spectra for Ni(pz) $_4Cl_2$ at room temperature (295K).

Assignment			Band/cm^{-1}	
D_{4h}	D^*_{4h}	$(1-C_2)D^*_{4h}+C_2D^*_{2h}$ $C_2=0.005$	Calc.	Obs.[1,3]
$^3B_{1g}$	B_2	$B'_1(t_2^6e^2\ \ ^3A_{2g})\rightarrow$	0	
	E	$B'_2(t_2^6e^2\ \ ^3A_{2g})$	7.14844	
	E	$B'_3(t_2^6e^2\ \ ^3A_{2g})$	7.12109	
^3E_g	A_1	$A'_1(t_2^5e^3\ \ ^3T_{2g})$	7420	
	A_2	$B'_1(t_2^5e^3\ \ ^3T_{2g})$	7488	
	B_2	$B'_1(t_2^5e^3\ \ ^3T_{2g})$	7329	
	E	$B'_2(t_2^5e^3\ \ ^3T_{2g})$	7745	
	E	$B'_3(t_2^5e^3\ \ ^3T_{2g})$	7735	
	B_1	$A'_1(t_2^5e^3\ \ ^3T_{2g})$	7935	8000
$^3B_{2g}$	B_1	$A'_1(t_2^5e^3\ \ ^3T_{2g})$	11028	10950
	E	$B'_2(t_2^5e^3\ \ ^3T_{2g})$	11120	
	E	$B'_3(t_2^5e^3\ \ ^3T_{2g})$	11120	
$^3A_{2g}$	E	$B'_2(t_2^5e^3\ \ ^3T_{1g})$	13015	
	E	$B'_3(t_2^5e^3\ \ ^3T_{1g})$	13016	
	A_1	$A'_1(t_2^5e^3\ \ ^3T_{1g})$	13170	13100
$^1B_{1g}$	B_1	$A'_1(t_2^6e^3\ \ ^1E_g)$	13421	13500
^3E_g	A_2	$B'_1(t_2^4e^4\ \ ^3T_{1g})$	15943	
	A_1	$A'_1(t_2^5e^3\ \ ^3T_{1g})$	16020	
	E	$B'_2(t_2^5e^3\ \ ^3T_{1g})$	16102	
	E	$B'_3(t_2^5e^3\ \ ^3T_{1g})$	16106	
	B_1	$A'_1(t_2^4e^4\ \ ^3T_{1g})$	16396	16400
	B_2	$B'_1(t_2^4e^4\ \ ^3T_{1g})$	16583	
^1E_g	E	$B'_2(t_2^5e^3\ \ ^1T_{2g})$	20498	21000*
$^1B_{2g}$	B_2	$B'_1(t_2^5e^3\ \ ^1T_{2g})$	24121	23200*
^3E_g,$^3A_{2g}$	A_1	$A'_1(t_2^4e^4\ \ ^3T_{1g})$	26635	
	A_1	$A'_1(t_2^4e^4\ \ ^3T_{1g})$	24939	
	B_1	$A'_1(t_2^5e^3\ \ ^3T_{1g})$	26405	26500
	A_2	$B'_1(t_2^5e^3\ \ ^3T_{1g})$	26589	
	B_2	$B'_1(t_2^5e^3\ \ ^3T_{1g})$	26728	
	E	$B'_2(t_2^4e^4\ \ ^3T_{1g})$	26453	
	E	$B'_3(t_2^4e^4\ \ ^3T_{1g})$	26463	
	E	$B'_2(t_2^4e^4\ \ ^3T_{1g})$	24894	
	E	$B'_3(t_2^4e^4\ \ ^3T_{1g})$	24893	

Spectrum parameters[5]/cm^{-1}: $B=790, C=3600, \xi=420, D_q=915, a=5450, b=1350, \alpha=-125$.
*: at 77K.

ground state are equivalent to the corresponding matrix elements $\langle \Gamma'_i(5s') \mid g_\alpha \widehat{S}'_\alpha \mid \Gamma'_j(5s')\rangle$ of the operator $(\widehat{S}'_\alpha g_\alpha)$ in equivalent spin space $\mid \Gamma'_i(5s')\rangle$. From this, the formula used to calculate the paramagnetic resonance g factor is derived as follows:

$$g_x = -\mathrm{i}\langle B'_1(5) \mid \widehat{M}_x \mid B'_2(5)\rangle\,,$$

$$g_y = \mathrm{i}\langle B_1'(5) \mid \widehat{M}_y \mid B_3'(5)\rangle\,, \tag{3}$$
$$g_z = -\mathrm{i}\langle B_2'(5) \mid \widehat{M}_z \mid B_3'(5)\rangle\,.$$

According to formula (3), we can calculate $g_\alpha(\alpha = x, y, z)$ (see Table 2) by using each component of the eigenvector of the ground state, and the results are in agreement with the g value ($g_x \approx g_y = 2.21$) that Klaaijsen[2] calculated based on the observation value of the paramagnetic susceptibility.

Table 2. The ZFS parameters and the EPR parameters of $Ni(pz)_4Cl_2$(in cm^{-1}).

Parameters	Calc. value	Obs. value[2]	
		From heat capacity	From susceptibility
D	7.1348	7.2(1)	7.2(2)
E	0.0137	0.0(1)	
g_x	2.2103		2.21(3)
g_y	2.2104		2.21(3)
g_z	2.1469		2.14(3)

We form the matrix of $\widehat{H}_s'$

$$H_{s'} = \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{ccc} B_3'(5s') & B_1'(5s') & B_2'(5s') \end{array} \\ \begin{bmatrix} D-E & \mathrm{i}\beta g_y H_y & -\mathrm{i}\beta g_z H_z \\ -\mathrm{i}\beta g_y H_y & 0 & \mathrm{i}\beta g_x H_x \\ \mathrm{i}\beta g_z H_z & -\mathrm{i}\beta g_x H_x & D+E \end{bmatrix} \end{array}$$

in the equivalent spin space $\mid \Gamma'\mathrm{i}(5s')\rangle$, corresponding to each splitting state $\mid \Gamma_i(5)\rangle$ of the ground state $t_2^6 e^{2\,3}A_2$.

When external magnetic field $H = 0$, the effective spin Hamiltonian $\widehat{H}_{s'}$ is equivalent to the real Hamiltonian. So the eigenvalues of matrix just given above is equivalent to that of the corresponding splitting states of the ground state in matrices $A_1'(15), B_1'(10), B_2'(10)$and $B_3'(10)$, i.e.

$$\varepsilon[B_3'(5)] - \varepsilon[B_1'(5)] = D - E\,, \tag{4}$$
$$\varepsilon[B_2'(5)] - \varepsilon[B_1'(5)] = D + E\,.$$

By using the eigenvalues of the three splitting states of the ground state in matrices $A_1'(15), B_1'(10), B_2'(10)andB_3'(10)$ (H=0) and the expression (4), we can evaluate the ZFS

parameters D and E (see Table 2), which agree very well with the D and E values that Klaaijsen *et al.*[2] calculated using the experimental values of heat capacity.

Klaaijsen *et al.*[2] have measured total heat vcapacity of the $Ni(pz)_4Cl_2$ at low temperatures, and by subtracting the crystal lattice heat capacity (Debye temperature is 64.2K) from the total heat capacity, we can obtain the C-T curves of the Schottky heat capacity. Therefore, the Schottky heat capacity is the contribution of Ni^{2+} ions to the total heat capacity. At low temperatures, the Ni^{2+} ions lie basically on the energy level corresponding to the ground state, and when $H = 0$, the average energy of the Ni^{2+} is

$$\begin{aligned}\overline{\varepsilon} &= \sum_i \varepsilon_i \exp(-\varepsilon_i/kT) / \sum_i \exp(-\varepsilon_i/kT) \\ &= \{(D-E)\exp[-(D-E)/kT] + (D+E)\exp[-(D+E)/kT]\} \\ &\quad \div \{1 + \exp[-(D-E)/kT] + \exp[-(D+E)/kT]\}.\end{aligned}$$

The Schottky heat capacity reads

$$\begin{aligned}C_p \approx C_v &= N_0 \partial\overline{\varepsilon}/\partial T \\ &= (N_0/kT^2)\{(D-E)^2\exp[-(D-E)/kT] + (D+E)^2\exp[-(D+E)/kT] \\ &\quad + 4E^2\exp(-2D/kT)\}/\{1 + \exp[-(D-E)/kT] + \exp[-(D+E)/kT]\}^2 , \qquad (5)\end{aligned}$$

where N_0 is Avogadro's constant, k Boltzmann constant, T absolute temperature. Putting N_0, k, and the calculated values of D and E listed in Table 2 into Eq.(5), we can obtain the results that agree with the C-T curves of the Schottky heat capacity in Ref.[2].

We have used the approximation $C_p \approx C_v$ in formula (5), and this is reasonable within the limit of experimental errors for the solid $Ni(pz)_4Cl_2$ complex.

The basic formula used to calculate the susceptibility is

$$\chi = -\left[\sum_i (N_0/H)(\partial\varepsilon_i/\partial H)\exp(-\varepsilon_i/kT)\right] / \sum_i \exp(-\varepsilon_i/kT) , \qquad (6)$$

where ε_i is the eigenvalue of matrix $H_{s'}$.

When the external magnetic field H is parallel to the x axis, we have $H_z = H_y = 0$, $H_x = H$, and putting them into matrix $H_{s'}$, we obtain the eigenvalues

$$\begin{aligned}\varepsilon_1 &= \{(D+E) + [(D+E)^2 + 4\beta^2 g_x^2 H^2]^{1/2}\}/2 , \\ \varepsilon_2 &= \{(D+E) - [(D+E)^2 + 4\beta^2 g_x^2 H^2]^{1/2}\}/2 , \\ \varepsilon_3 &= D - E .\end{aligned}$$

Putting these eigenvalues into Eq. (6) yields the following expression:

$$\chi_x = -2N_0\beta^2 g_x^2[(D+E)^2+4\beta^2 g_x^2 H^2]^{-1/2}[\exp(-\varepsilon_1/kT)-\exp(-\varepsilon_2/kT)]$$
$$\div[\exp(-\varepsilon_1/kT)+\exp(-\varepsilon_2/kT)+\exp(-\varepsilon_3/kT)]\,.$$

We can get χ_y and χ_z in a similar manner.

Using the formula[5−7] which is used to evaluate the average susceptibility of solid powdery $Ni(pz)_4Cl_2$, we have

$$\begin{aligned}\chi &= (1/3)(\chi_x+\chi_y+\chi_z)\\ &= \{(-2N_0\beta^2/3)g_x^2W_1^{-1}[\exp(-\varepsilon_1/kT)-\exp(-\varepsilon_2/kT)]/[\exp(-\varepsilon_1/kT)\\ &\quad+\exp(-\varepsilon_2/kT)+\exp(-\varepsilon_3/kT)]\}+\{(-2N_0\beta^2/3)g_y^2W_2^{-1}[\exp(-\varepsilon_4/kT)\\ &\quad-\exp(-\varepsilon_5/kT)]/[\exp(-\varepsilon_4/kT)+\exp(-\varepsilon_5/kT)+\exp(-\varepsilon_6/kT)]\}\\ &\quad+\{(-N_0\beta^2/3)g_z^2W_3^{-1}[\exp(-\varepsilon_7/kT)-\exp(-\varepsilon_8/kT)]/[\exp(-\varepsilon_7/kT)\\ &\quad+\exp(-\varepsilon_8/kT)+1]\}\,, \qquad (7)\end{aligned}$$

where $W_1 = [(D+E)^2+4\beta^2g_x^2H^2]^{1/2}, W_2 = [(D-E)^2+4\beta^2g_y^2H^2]^{1/2}$, $W_3 = [E^2+\beta^2\,g_z^2\,H^2]^{1/2}$, $\varepsilon_4 = (D-E+W_2)/2$, $\varepsilon_5 = (D-E-W_2)/2$, $\varepsilon_6 = D+E$, $\varepsilon_7 = D+W_3$, $\varepsilon_8 = D-W_3, \varepsilon_9 = 0$.

We can obtain the theoretical curve that agrees with the experimental curve of susceptibility in Ref.[2], if we put the values of D, g_x, g_y, and g_z listed in Table 2, the constants N_0, k, β(Bohr magneton) and H (about 4×10^5A/m) into Eq. (7).

III. CONCLUSION

The experimental values of the absorption spectra, the heat capacity, and the paramagnetic susceptibility of $Ni(pz)_4Cl_2$ complex can be fitted with one group of spectrum parameters, which shows that the optical, thermal, and magnetic properties of the complex may be closely related to each other.

Because the strong magnetic field[3] needed for the paramagnetic resonance spectra could not be achieved in laboratory, Klaaijsen *et al.*[2] fitted the observed values of heat capacity to obtain the ZFS parameters D and E. As E was very small, by assuming the molecular structure of $Ni(pz)_4Cl_2$ to be axially symmetrical, they fitted the observed values of the susceptibilities to obtain the values of ZFS and EPR parameters. In our numerical calculation, we found that the magnitude of E reflects the degree of deviation from axial symmetry for the structure. The E value obtained from the experimental heat capacity is very small, which means that the molecular structure of $Ni(pz)_4Cl_2$ deviates slightly from

D_{4h} symmetry. Structure data[1,4] also show that the structure of $Ni(pz)_4Cl_2$ exhibits non-axial symmetry. We have used the linear superposition of a distorted crystal field D_{4h} with an axial symmetry and a weak distorted crystal field d_{2h} with a nonaxial symmetry as the distorted crystal field of the complex. The method of using superposition of a distorted crystal field to deal with the structure problem can give theoretical results which agree well with the experimental data. Thus we can conclude that this method is a very good approximation.

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