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Studies on the Spin Hamiltonian Parameters for the Cu^{2+}-V_c Centers in NH_4I at Room Temperature

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Abstract: The spin Hamiltonian parameters $g_{//}$, $g_\perp$, $A_{//}$ and $A_\perp$ for the two Cu^{2+}-V_c centers I_2 and II_4 in NH_4I at room temperature are theoretically studied by means of diagonalization procedure of complete (10×10) energy matrix (DPCEM) for a $3d^9$ ion in tetragonal symmetry. Based on the calculations, the nearest ligand I-intervening in the impurity Cu^{2+} and the second (or fourth) neighbour cation vacancy V_c are found to be displaced towards the impurity by about 0.15Å (or 0.14Å) for centers I_2 and II_4, respectively.

Key words: Electron paramagnetic resonance, crystal-fields and spin hamiltonian, Cu^{2+}; NH_4I

INTRODUCTION

Ammonium iodide (NH_4I) has received attentions of researchers due to interesting properties of structure, Raman spectrum and phonon density of states (Raghurama and Narayan, 1983; Heyns *et al.*, 1980; Sanyal and Sharma, 1982). Particularly, this crystal doped with some transition-metal ions (such as Cu^{2+}, Mn^{2+}, Co^{2+}) may exhibit unique optical and magnetic properties as well as charge compensation mechanisms at different temperatures, which can be observed by means of optical absorption and Electron Paramagnetic Resonance (EPR) techniques (Chand and Upreti, 1984; Chand and Upreti, 1985a,b; Chand *et al.*, 1985). For instance, EPR experiments were carried out on Cu^{2+}-doped NH_4I and the spin Hamiltonian parameters g factors $g_{//}$, $g_\perp$ and the hyperfine structure constants $A_{//}$ and $A_\perp$ for the two tetragonal Cu^{2+} centers I_2 and II_4 were also measured at room temperature (Chand and Upreti, 1982). As for the theoretical studies, systematic investigations have been made on some square planar CuX_4 (here X denotes halide ligand Cl and Br) clusters by including the charge-transfer and vibronic coupling contributions to the spin Hamiltonian parameters (Murav'ev, 2005). Up to now, however, the above EPR experimental data of NH_4I:Cu^{2+} have not been quantitatively explained, although the two centers were attributed to the substitutional impurity Cu^{2+} associated with a second and fourth neighbour cation vacancy V_c along one of the (100) (or C_4) axis, respectively (Chand and Upreti, 1982).

In order to make further investigations on the spin Hamiltonian parameters and to verify the defect structure for centers I_2 and II_4 in NH_4I:Cu^{2+}, in this work, these parameters are theoretically interpreted by means of Diagonalization Procedure of Complete Energy Matrix (DPCEM) for a $3d^9$ ion in tetragonal symmetry. The crystal-field parameters in the energy matrix are determined from the superposition model based on the defect structure of the impurity centers.

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CALCULATIONS

NH_4I belongs to NaCl structure at room temperature (Wyckoff, 1968). When a Cu^{2+} is doped into the lattice of NH_4I, it can occupy the octahedral NH_4^+ site due to their similar charge. Since the impurity has extra charge, one second or fourth neighbour cation vacancy V_c may occur along the C_4 axis as charge compensation, forming centers I_2 or II_4 with tetragonal (C_{4v}) symmetry (Chand and Upreti, 1982). Due to the negative effective charge of V_c, the nearest ligand I^- intervening in the impurity Cu^{2+} and the second (or fourth) neighbour V_c are expected to shift towards the impurity along the C_4 axis by an amount ΔZ. Thus, the local structure of both centers can be described as the ligand octahedron compressed along the C_4 axis due to the axial displacement ΔZ.

The complete (10×10) energy matrix for a $3d^9$ (Cu^{2+}) ion in octahedra can be established from the basis functions ($\xi^\pm$, $\eta^\pm$, $\zeta^\pm$, $\theta^\pm$ and $\varepsilon^\pm$, corresponding to $|yz,\pm1/2>$, $|xz,\pm1/2>$, $|xy,\pm1/2>$, $|z^2,\pm1/2>$ and $|x^2-y^2,\pm1/2>$, respectively) and the crystal-field theory (Huang *et al.*, 2003). For the $3d^9$ ion in tetragonally compressed octahedra, the θ irreducible representation is the lowest. The matrix elements are expressed in terms of the crystal-field parameters B_{20}, B_{40}, B_{44} and the spin-orbit coupling coefficients ζ (or ζ'). The crystal-field parameters can be determined from the superposition model (Newman and Ng, 1989) and the local geometrical relationship of the studied $Cu^{2+}-V_c$ centers:

$$B_{20} = 2\overline{A}_2 \ \{1-[R_0/(R_0-\Delta Z)^{t_2}]\},$$
$$B_{40} = -4\ \overline{A}_4 \ \{3+4\ [R_0/(R_0-\Delta Z)^{t_4}]\}, \tag{1}$$
$$B_{44} = 2\sqrt{70}\ \overline{A}_4 \ .$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents (Newman and Ng, 1989). $\overline{A}_2$ and $\overline{A}_4$ are the intrinsic parameters, with the reference bonding (or cation-anion distance) R_0. The relationships $\overline{A}_4 \approx (3/4)$ Dq (here Dq is the cubic field parameter) and $\overline{A}_4 \approx 10.8\ \overline{A}_4$ are proved to be valid in many crystals (Newman and Ng; 1989; Edgar, 1976) and reasonably applied here.

By means of DPCEM for a $3d^9$ ion in tetragonal symmetry, the wave functions of the ground state can be obtained and written as

$$\left| z^2,\pm\frac{1}{2}\right> = \sum_{i=1} C_i^{(\Gamma)} \Psi_i^{(\Gamma)} \tag{2}$$

where Ψ_i and Ψ_i' stand for the basis functions of the Γ (and Γ') representations of the C_{4v} double group and C_i (and C_i') are the corresponding coefficients. By applying the orbital angular momentum operator

$$J = k\,L + g_s\,S \tag{3}$$

and the hyperfine structure interaction operator (Abragam and Bleaney, 1970).

$$H_{hf} = P\,[L\bullet I + \xi\,\{L\,(L+1) - \kappa\}\,(S\bullet I)\,-(3/2)\,\xi\,\{(L\bullet S)(L\bullet I)+(L\bullet I)(L\bullet S)\}], \tag{4}$$

the expressions of the spin Hamiltonian parameters for the $3d^9$ ion in compressed octahedra can be obtained from the method similar to that in Huang *et al.* (2003). Here $g_s = 2.0023$ is the spin-only value. k (and k') are the orbital reduction factors, related to the average covalence factor N. P is the dipole hyperfine structure parameter of the $3d^9$ ion and κ is the core polarization constant (Abragam and Bleaney, 1970). Thus we have:

$$g_{//} = 2<z^2 \; \tfrac{1}{2} \mid kL_z + g_s S_z \mid z^2 \; 1/2>,$$
$$g_{\perp} = 2<z^2 \; \tfrac{1}{2} \mid kL_x + g_s S_x \mid z^2\text{-}1/2>, \tag{5}$$
$$A_{//} = P\,[\text{-}\kappa\text{-}(4/7)\,(g_{//}\text{-}g_s) + (3/7)\,(g_{\perp}\text{-}g_s) + 4\,N/7\,]$$
$$A_{\perp} = P\,[\text{-}\kappa + (15/14)\,(g_{\perp}\text{-}g_s) + 2\,N/7]$$

In the above formulas, the spin-orbit coupling coefficients ζ (and ζ') and the orbital reduction factors k (and k') for the $3d^9$ ion in octahedral clusters contain the contributions from the p-and s-orbitals as well as the spin-orbit coupling coefficient of ligands. They are determined from the cluster approach (Dong and Chen, 2006)

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2),\; \zeta' = (N_t N_e)^{1/2}(\zeta_d^0 \text{-} \lambda_t \lambda_e \zeta_p^0/2),$$
$$k = N_t(1 + \lambda_t^2/2\,),\; k' = (N_t N_e)^{1/2}[1\text{-}\lambda_t(\lambda_e + \lambda_s A)/2] \tag{6}$$

Here the subscripts e and t denote the irreducible representations of the O_h group. ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the $3d^9$ and the ligand ions in free states, respectively. A denotes the integral $R_0 \langle ns \mid \partial/\partial y \mid np_y\rangle$. $N_\gamma(\gamma = e \text{ and } t)$ and λ_γ (and λ_s) are, respectively, the normalization factors and the orbital mixing coefficients. They satisfy the normalization conditions

$$N_t(\;1\text{-}2\lambda_t S_{dpt} + \lambda_t^2) = 1\;,$$
$$N_e(\;1\text{-}2\lambda_e S_{dpe}\text{-}2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1, \tag{7}$$

and the approximation relationships

$$N^2 = N_t^2\,[\;1 + \lambda_t^2 S_{dpt}^2\text{-}2\,\lambda_t\,S_{dpt}\,]\;,$$
$$N^2 = N_e^2\,[\;1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2\text{-}2\,\lambda_e\,S_{dpe}\text{-}2\,\lambda_s\,S_{ds}] \tag{8}$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the mixing coefficients increase with the increase of the group overlap integrals and one can approximately adopt the 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.

For the studied systems, the cubic field parameter $Dq \approx 590$ cm^{-1} can be estimated from the octahedral Cu^{2+} clusters in halides (Chakravarty, 1980). The cation-anion distance $R_0 \approx 3.63$Å (Wyckoff, 1968). From the Slater-type SCF functions (Clementi and Raimondi, 1963) and the distance R_0, the integrals $S_{dpt} \approx 0.0004$, $S_{dpe} \approx 0.0023$, $S_{ds} \approx 0.0007$ and $A \approx 2.6938$ are calculated. Thus, only the average covalency factor N and the displacement ΔZ are unknown in the formulas of the g factors. Substituting these values into Eq. 5 and fitting the calculated g factors to the experimental data, we have

$$N \approx 0.990 \text{ and } 0.984,\; \Delta Z \approx 0.15 \text{ Å and } 0.14 \text{ Å} \tag{9}$$

for centers I_2 and II_4, respectively. Note that the displacement direction towards the impurity Cu^{2+} is defined as positive here. Thus the molecular orbital coefficients $N_t \approx N_e \approx 0.990$, $\lambda_t \approx 0.103$, $\lambda_e \approx 0.099$, $\lambda_s \approx 0.030$ for I_2 and $N_t \approx N_e \approx 0.984$, $\lambda_t \approx 0.128$, $\lambda_e \approx 0.123$, $\lambda_s \approx 0.037$ for II_4 can be calculated from Eq. 7 and 8. By using the free-ion values $\zeta_d^0 \approx 829$ cm^{-1} for Cu^{2+} (Griffith, 1964) and $\zeta_p^0 \approx 5060$ cm^{-1} for I^- (McPerson *et al.*, 1974), the parameters $\zeta \approx 847$ cm^{-1}, $\zeta' \approx 795$ cm^{-1}, $k \approx 0.995$ and $k' \approx 0.981$ for I_2 and $\zeta \approx 856$ cm^{-1}, $\zeta' \approx 776$ cm^{-1}, $k \approx 0.992$ and $k' \approx 0.970$ for II_4 are obtained from Eq. 6. The corresponding g factors are shown in Table 1.

Substituting the dipolar hyperfine structure parameter $P \approx 388 \times 10^{-4}$ cm^{-1} (McGarvey *et al.*, 1967) for Cu^{2+} into the formulas of the hyperfine structure constants and fitting the calculated results to experiment, one can acquire the core polarization constants:

Table 1: The spin Hamiltonian parameters for the tetragonal Cu^{2+} centers I_2 and II_4 in NH_4I

Centers		$g_{//}{}^d$	$g_\perp{}^d$	$A_{//} (10^{-4} cm^{-1})^d$	$A_\perp (10^{-4} cm^{-1})^d$
	Cal. [a]	1.999	1.789	15	-149
I_2	Cal. [b]	2.012	2.216	83	28
	Expt. [c]	2.011 (1)	2.216 (1)	84 (1)	28 (1)
	Cal. [a]	1.998	1.790	8	-155
II_4	Cal. [b]	2.019	2.222	75	25
	Expt. [c]	2.019 (1)	2.222 (1)	75 (1)	52 (1)

[a]Calculations based on the displacements of the intervening ligand in Eq. 9 but neglecting of the ligand orbital and spin-orbit coupling contributions (i.e., $\zeta = \zeta' = N \zeta_d^0$, $k = k' = N$), [b]Calculations based on both the ligand displacements in Eq. 9 and the ligand orbital and spin-orbit coupling contributions, [c]Chand and Upreti (1982), [d]The signs of the experimental and theoretical (Cal.[b]) spin Hamiltonian parameters are positive

$$\kappa \approx 0.439 \text{ and } 0.453 \qquad (10)$$

for centers I_2 and II_4, respectively. The corresponding theoretical results are also shown in Table 1. For comparison, the calculation values based on Eq. 1-5 but neglecting of the ligand orbital and spin-orbit coupling contributions (i.e., $\zeta = \zeta' = N \zeta_d^0$, $k = k' = N$) are also collected in Table 1.

DISCUSSION

From Table 1, one can find that the theoretical spin Hamiltonian parameters (Cal. [b]) for the tetragonal Cu^{2+} centers I_2 and II_4 in NH_4I based on the displacements ΔZ of the intervening ligand in Eq. 9 and the ligand orbital and spin-orbit coupling contributions show good agreement with the observed values.

The positive displacements ΔZ obtained in this work are in agreement with the expectation based on the electrostatic interaction between the charge compensator V_c and the intervening ligand I^- and can be regarded as reasonable. Therefore, the local structure of both centers can be illustrated as tetragonally compressed octahedron due to the inward shift of the nearest intervening ligand. Interestingly, the slightly smaller displacement (≈ 0.14 Å) in II_4 than that (≈ 0.15 Å) in I_2 is also consistent with the farther distance of the ligand from the (fourth neighbour) V_c and its weaker electrostatic repulsion in the former.

The large average covalency factors (~ 1) and the small mixing coefficients (~ 0.1) obtained in this work reveal that the admixture (or covalency) between the orbitals of the Cu^{2+} and the ligands is very small. The tiny covalency for the studied $[CuI_6]^{4-}$ clusters may originate from the very slight electronic cloud overlap between the ligand I^- and the impurity Cu^{2+} due to their large distance [≈ 3.63Å (Wyckoff, 1968)]. This point is somewhat different from the cases for Cu^{2+} in several halides with considerable covalency, as pointed out in various instructing and interesting works (Aramburu and Moreno, 1985; Aramburu and Moreno, 2004). On the other hand, despite of the small covalency of the studied systems, the calculation results (Cal.[a]) based on neglecting of the ligand orbital and spin-orbit coupling contributions show disagreement with the experimental data, especially the g factors are smaller than the spin-only value 2.0023 and the anisotropies ($g_{//}$-$g_\perp$) are even positive. Meanwhile, the above disagreement cannot be removed by adjusting the values of N and ΔZ in Eq. 9. This means that due to the huge ligand spin-orbit coupling coefficient (≈ 5060 cm^{-1}) the ligand contributions to the g factors should be taken into account.

As for the hyperfine structure constants, the fitted core polarization constants (~ 0.4) for both centers are close to the values $0.3 \sim 0.4$ (Murav'ev, 2005) and 0.3 (Abragam and Pryce, 1951) for Cu^{2+} in halides and tutton salts and can be regarded as reasonable. Further, the slight difference between the fitted values of N and κ for centers I_2 and II_4 may account for their distinct hyperfine structure constants. According to the present studies, center I_2 has less covalency and slightly larger N, corresponding to the larger magnitudes of the A factors. The tiny deviation of N, κ and the resultant

A factors for the two centers may be physically ascribed to the small structure difference around the impurity Cu^{2+} due to the different positions of the V_c and the displacements ΔZ. In addition, the calculated $A_\perp$ for II_4 is only half of the experimental finding. However, the theoretical A factors obtained here are comparable for both centers as regards similarity in structure and show slight decrease from I_2 to II_4 in accordance with the order of ionicity. Meanwhile, the experimental $A_\perp$ for II_4 is even 86% larger than that for I_2, which seems somewhat abnormal. This point remains to be further checked with experimental investigations.

There are some errors in the calculations. First, approximation of the theoretical model and the formulas can lead to some errors. Second, the displacements of the impurity and the other five ligand ions are not considered in the computations. Fortunately, since the distances from the V_c to these ions are much larger than the distance R_1 ($= R_0-\Delta Z$) between V_c and the intervening ligand, the displacements of these ions can be regarded as negligible. Therefore, only the displacement ΔZ of the intervening ligand is taken into account here for the sake of simplicity and reduction in the number of the adjustable parameters. Third, some errors also arise from approximation of the intrinsic parameters $\bar{A}_2$ and $\bar{A}_4$. Based on the calculations, the errors of the theoretical spin Hamiltonian parameters and the fitted ligand displacement ΔZ are estimated to be no more than 5% as the intrinsic parameters change by 10%. In order to overcome the approximation of the empirical superposition model and to carry out further studies on the electronic states and local structures for the Cu^{2+} centers, more powerful Density Function Theory (DFT) should be applied. Fourth, the charge transfer and vibronic coupling contributions, which were found to be important for the planar square (tetragonally elongated) $[CuX_4]^{2-}$clusters ($X = Cl^-$ and Br^-) in the interesting and instructing works (Murav'ev, 2005; Aramburu and Moreno, 1985; Aramburu and Moreno, 2004), are not taken into account here. In fact, neglecting of the above contributions in this work leads to some errors. Since the ground state and its spin Hamiltonian parameters for the tetragonally compressed $[CuI_6]^{4-}$clusters in this work may be dissimilar to those for the tetragonally elongated $[CuX_4]^{2-}$clusters in the previous works (Murav'ev, 2005; Aramburu and Moreno, 1985), the difference in importance of charge transfer (and vibronic coupling) contributions for distinct clusters can be understood. Therefore, the charge transfer contributions in $NH_4I:Cu^{2+}$ seem not as important as those in the $[CuX_4]^{2-}$clusters probably due to the tiny covalency (i.e., $N \sim 1$) arising from the very large Cu-I distance in the former. Thus the antibonding orbitals are principally metal like, while the bonding orbitals are of dominant ligand nature, with only very slight admixture. In view of the above points and the agreement between theory and experiment, the calculations and the related parameters adopted in this study can be regarded as reasonable.

Apart from the substitutional Cu^{2+}-V_c centers in NH_4I at room temperature, there is also another interstitial $[CuI_4 (H_2O)_2]^{2-}$cluster at lower (4.2K) temperature (Chand *et al.*, 1985). This center may be attributed to the impurity Cu^{2+} occupying the interstitial site associated with two adjacent water molecules along the C_4 axis in acidic environments, since NH_4I belongs to CsCl structure at low temperature. The above cluster also exhibits local compression of ligand octahedron, due to the stronger crystal fields (arising from H_2O groups) in the axial direction than those (arising from I^- ligands) in the perpendicular direction. Thus, the structure properties and the similar spin Hamiltonian parameters of this interstitial center can be understood.

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