Studies on the Spin Hamiltonian Parameters for the Cu$^{2+}$-\(V_c\) Centers in NH$_4$I at Room Temperature

Jin-Song Yao, Shao-Yi Wu, Guang-Duo Lu and Hua-Ming Zhang
Department of Applied Physics,
University of Electronic Science and Technology of China,
Chengdu 610054, People’s Republic of China
International Centre for Materials Physics, Chinese Academy of Sciences,
Shenyang 110016, People’s Republic of China

Abstract: The spin Hamiltonian parameters \(g_0\), \(g_\parallel\), \(A_0\), and \(A_\parallel\) for the two Cu$^{2+}$-\(V_c\) centers \(I_1\) and \(II_1\) in NH$_4$I at room temperature are theoretically studied by means of diagonalization procedure of complete \(10 \times 10\) 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 \(I_1\), and \(II_1\), respectively.

Key words: Electron paramagnetic resonance, crystal-fields and spin hamiltonian, Cu$^{2+}$; NH$_4$I

INTRODUCTION

Ammonium iodide (NH$_4$I) 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$_4$I and the spin Hamiltonian parameters \(g\) factors \(g_0\), \(g_\parallel\) and the hyperfine structure constants \(A_0\) and \(A_\parallel\) for the two tetragonal Cu$^{2+}$ centers \(I_1\) and \(II_1\) 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$_4$I: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 \(I_1\) and \(II_1\) in NH$_4$I: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.

Corresponding Author: Shao-Yi Wu, Department of Applied Physics,
University of Electronic Science and Technology of China, Chengdu 610054,
People’s Republic of China

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CALCULATIONS

NH₄⁺ belongs to NaCl structure at room temperature (Wyckoff, 1968). When a Cu⁺⁺ ion is doped into the lattice of NH₄I, it can occupy the octahedral NH₄⁺ site due to their similar charge. Since the impurity has extra charge, one second or fourth neighbour cation vacancy V₃ may occur along the C₄ axis as charge compensation, forming centers I₃ or II₄ with tetragonal (C₄v) symmetry (Chand and Upreti, 1982). Due to the negative effective charge of V₃, the nearest ligand 1⁻ intervening in the impurity Cu⁺⁺ and the second (or fourth) neighbour V₃ are expected to shift towards the impurity along the C₄ axis by an amount ΔZ. Thus, the local structure of both centers can be described as the ligand octahedron compressed along the C₄ axis due to the axial displacement ΔZ.

The complete (10·10) energy matrix for a 3d⁰ (Cu⁺⁺) ion in octahedra can be established from the basis functions (ξ₁, η₁, ξ², η², θ, and e), corresponding to |yz⁺1/2>, |xz⁺1/2>, |xy⁺1/2>, |z²⁺1/2>, and |x²−y²⁺1/2>, respectively) and the crystal-field theory (Huang et al., 2003). For the 3d¹ ion in tetragonally compressed octahedra, the θ irreducible representation is the lowest. The matrix elements are expressed in terms of the crystal-field parameters B₂, B₄, B₆, and the spin-orbit coupling coefficients ξ (or ξ²). The crystal-field parameters can be determined from the superposition model (Newman and Ng, 1989) and the local geometrical relationship of the studied Cu⁺⁺-V₃ centers:

\[
\begin{align*}
B₂ &= 2\bar{A}_₃ \{1-[R_μ/(R_μ−ΔZ)²]\}, \\
B₄ &= -4 \bar{A}_₃ \{(3+4[R_μ/(R_μ−ΔZ)²]\}, \\
B₆ &= 2/70 \bar{A}_₃.
\end{align*}
\]

(1)

Here τ₁ = 3 and τ₂ = 5 are the power-law exponents (Newman and Ng, 1989). \bar{A}_₃ and \bar{A}_₄ are the intrinsic parameters with the reference bonding (or cation-anion distance) R₀. The relationships \bar{A}_₃ = (3/4) D₀₂ and \bar{A}_₄ = (3/5) D₀₄ are proved to be valid in many crystals (Newman and Ng, 1989; Edgar, 1976) and reasonably applied here.

By means of DPCEM for a 3d¹ ion in tetragonal symmetry, the wave functions of the ground state can be obtained and written as

\[
|\xi_±\frac{1}{2}\rangle = \sum_{i=1}^n \Psi_i \xi_±\frac{1}{2} \Psi_i^* \]

(2)

where Ψ and Ψ* stand for the basis functions of the \(\Gamma\) and \(\Gamma'\) representations of the \(C₄v\) double group and \(C₄\) (and \(C₄'\)) are the corresponding coefficients. By applying the orbital angular momentum operator

\[J = k L + g_s S\]

(3)

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

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

(4)

the expressions of the spin Hamiltonian parameters for the 3d¹ 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 3d¹ ion and \(\kappa\) is the core polarization constant (Abragam and Bleaney, 1970). Thus we have:

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In the above formulas, the spin-orbit coupling coefficients \( \zeta \) (and \( \zeta' \)) and the orbital reduction factors \( k \) (and \( k' \)) for the 3d\(^{10}\) ion in octahedral clusters contain the contributions from 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)

\[
\zeta = N_\zeta (\xi_\alpha^2 + \lambda_\alpha^2 \xi_\beta^2/2), \quad \zeta' = (N_\zeta N_\beta)^{1/2} (\xi_\alpha^2 - \lambda_\alpha \lambda_\beta \xi_\beta^2/2), \\
k = N_\zeta (1 + \lambda_\alpha^2/2), \quad k' = (N_\zeta N_\beta)^{1/2} [1 - \lambda_\alpha (\lambda_\alpha + \lambda_\beta) A]/2
\]

Here the subscripts \( \alpha \) and \( \beta \) denote the irreducible representations of the \( O_h \) group. \( \xi_\alpha \) and \( \xi_\beta \) are the spin-orbit coupling coefficients of the 3d\(^{10}\) and the ligand ions in free states, respectively. \( A \) denotes the integral \( R_{\text{in}} \sum |\phi(\bar{\alpha})|/|\phi(\bar{\beta})| \).

\[
N_\zeta (\lambda_\alpha S_{\text{ip}} + \lambda_\beta) = 1, \\
N_\zeta (1-2\lambda_\alpha S_{\text{ip}} - 2\lambda_\beta S_{\text{ip}} + \lambda_\beta^2 + \lambda_\alpha^2) = 1,
\]

and the approximation relationships

\[
N^2 = N_\zeta^2 \left[ 1 + \lambda_\alpha^2 S_{\text{ip}}^2 - 2 \lambda_\alpha S_{\text{ip}} \right], \\
N^2 = N_\zeta^2 \left[ 1 + \lambda_\alpha^2 S_{\text{ip}}^2 + \lambda_\beta^2 S_{\text{ip}}^2 - 2 \lambda_\beta S_{\text{ip}} - 2 \lambda_\alpha \lambda_\beta \right]
\]

Here \( S_{\text{ip}} \) (and \( S_{\text{ip}} \)) 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., \( \lambda_\alpha S_{\text{ip}} = \lambda_\beta S_{\text{ip}} \) within the same irreducible representation \( \epsilon_\zeta \).

For the studied systems, the cubic field parameter \( D_{\text{q}} = 590 \text{ cm}^{-1} \) can be estimated from the octahedral \( \text{Cu}^{2+} \) clusters in halides (Chakravarty, 1980). The cation-anion distance \( R_{\text{in}} = 3.63 \text{ Å} \) (Wyckoff, 1968).

From the Slater-type SCF functions (Clementi and Raimondi, 1963) and the distance \( R_{\text{in}} \) the integrals \( S_{\text{ip}} = 0.00044, S_{\text{ip}} = 0.0023, S_{\text{ip}} = 0.0007 \) and \( A = 2.6938 \) are calculated. Thus, only the average covalency factor \( N \) and the displacement \( \Delta Z \) 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

\[
N \approx 0.980 \text{ and } 0.984, \quad \Delta Z = 0.15 \text{ Å and } 0.14 \text{ Å}
\]
Table 1: The spin Hamiltonian parameters for the tetragonal Cu⁺⁺ centers I₁ and II₁ in NH₄I

<table>
<thead>
<tr>
<th>Centers</th>
<th>( g )</th>
<th>( A ) (×10⁻⁴ cm⁻¹)</th>
<th>( A ) (×10⁻⁴ cm⁻¹)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₁</td>
<td>Cal.</td>
<td>1.999</td>
<td>1.789</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>2.012</td>
<td>2.216</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>2.011 (1)</td>
<td>2.216 (1)</td>
</tr>
<tr>
<td></td>
<td>Cal.</td>
<td>1.998</td>
<td>1.790</td>
</tr>
<tr>
<td>II₁</td>
<td>Cal.</td>
<td>2.019</td>
<td>2.222</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>2.019 (1)</td>
<td>2.222 (1)</td>
</tr>
</tbody>
</table>

*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., \( \zeta = \zeta' = N \), \( k = k' = N \)). ^Calculated based on both the ligand displacements in Eq. 9 and the ligand orbital and spin-orbit coupling contributions, Chand and Upadhyay (1982). ^The signs of the experimental and theoretical (Cal.) spin Hamiltonian parameters are positive.

\[
\kappa = 0.439 \text{ and } 0.453
\] (10)

for centers I₁ and II₁, 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., \( \zeta = \zeta' = N \), \( k = k' = N \)) are also collected in Table 1.

**DISCUSSION**

From Table 1, one can find that the theoretical spin Hamiltonian parameters (Cal. ^) for the tetragonal Cu⁺⁺ centers I₁ and II₁ in NH₄I based on the displacements \( \Delta Z \) 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 \( \Delta Z \) obtained in this work are in agreement with the expectation based on the electrostatic interaction between the charge compensator \( V \) 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 II₁ than that (≈ 0.15 Å) in I₁ is also consistent with the farther distance of the ligand from the (fourth neighbour) \( V \), 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⁺⁺ and the ligands is very small. The tiny covalency for the studied [Cu₂⁺⁺]⁺ clusters may originate from the very slight electronic cloud overlap between the ligand \( I^- \) and the impurity Cu⁺⁺ due to their large distance \( \approx 3.63 \text{ Å} \) (Wyckoff, 1968). This point is somewhat different from the cases for Cu⁺⁺ 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.) 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 \( (g_x-g_y) \) are even positive. Meanwhile, the above disagreement cannot be removed by adjusting the values of \( N \) and \( \Delta Z \) 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 ~ 0.4 (Murav’ev, 2005) and 0.3 (Abragum and Pryce, 1951) for Cu⁺⁺ in halides and tutton salts and can be regarded as reasonable. Further, the slight difference between the fitted values of \( N \) and \( \kappa \) for centers I₁ and II₁ may account for their distinct hyperfine structure constants. According to the present studies, center I₁ has less covalency and slightly larger \( N \), corresponding to the larger magnitudes of the A factors. The tiny deviation of \( N \), \( \kappa \) and the resultant
A factors for the two centers may be physically ascribed to the small structure difference around the impurity CuIII due to the different positions of the V5 and the displacements ΔZ. In addition, the calculated A, for Π5 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 Π6 to Π5 in accordance with the order of ionicity. Meanwhile, the experimental A, for Π6 is even 80% larger than that for Π5, 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 V5 to these ions are much larger than the distance R, (= R, -ΔZ) between V5 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 \(\bar{A}_z\) and \(\bar{A}_x\). 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 CuIII 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) \([CuX_4]^+\) 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 \([CuX_4]^+\) clusters in this work may be dissimilar to those for the tetragonally elongated \([CuX_4]^+\) 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 NH4:CuIII seem not as important as those in the \([CuX_4]^+\) clusters probably due to the tiny covalency (i.e., N - 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 CuIII-V, centers in NH4I at room temperature, there is also another interstitial \([Cu_4(H_2O)_4]^+\) cluster at lower (4.2K) temperature (Chand et al., 1985). This center may be attributed to the impurity CuIII occupying the interstitial site associated with two adjacent water molecules along the C4 axis in acidic environments, since NH4I 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 H2O 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.

REFERENCES


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