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CRYSTALLINE FIELD EFFECT ON ESR PARAMETERS OF Cu^{2+} ION

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ABSTRACT

The ground state wave function of Cu^{2+} ion doped in different crystal lattices is estimated with the help of EPR parameters. The Fermi contact term K and hyperfine interaction parameter P_{hf} in different host lattices are calculated with the help of (A_i - f_i) diagram. Further, based on this method correct signs and directions of the spin Hamiltonian parameters g and A are assigned.

Keywords: Ground state wave function; Electron paramagnetic resonance; Fermi contact term; Hyperfine interaction parameter.

INTRODUCTION

Electron paramagnetic resonance (EPR) yields a great deal of information about the magnetic properties of paramagnetic ion in different single crystals and it also provides a detailed description of the ground state wave function of paramagnetic ions. EPR study can provide valuable information on the effective ligand field symmetry and orbital geometry as well as on the bonding of transition metal ions. It is used in the study of the biochemistry of metalloproteinase and inorganic metal complexes having at least one unpaired electron on the metal ion [1-2]. Presently, EPR is used as a tool for the characterization of transition metal ions and rare earth impurities in nonlinear optical and laser crystals [3-5].

Transaction metal complexes of $3d^9$ configuration represents a simple one magnetic hole system due to which it is easy to obtain information about the electron wave function in the crystalline field of lower symmetry. Different workers have estimated the values of g and A tensors of Cu^{2+} ion doped in various lattices but they have not provided the correct signs and directions to spin Hamiltonian constants which is very important in the evaluation of ground state wave function [6]. The Authors have therefore determined the ground state wave function of Cu^{2+} ion doped in different lattices to decide the signs and directions of spin Hamiltonian constants and to know how the changes in these constants reflect on the ground state wave function [7]. These calculations are very important for the study of various physical phenomena associated with Cu^{2+} ion.

Theoretical Aspect

The orbital wave function of the ground state in the presence of rhombic symmetry is given by

$$\left(\frac{1}{2}\right)\sqrt{5}\,f(r)\left(ax^2+by^2+cz^2\right) \quad (1)$$

with the condition

$a + b + c = 0$ and $a^2 + b^2 + c^2 = 6$

The wave function of the orbital triplet may be represented as

$$\sqrt{15}\,f(r)\,yz,\ \sqrt{15}\,f(r)\,zx,\ \sqrt{15}\,f(r)\,xy \quad (2)$$

their energies above the ground state will be denoted by E_x, E_y, E_z. For copper ion λ/E_x, λ/E_y, λ/E_z

is positive and denoted by u, v, w, respectively. One can have correct to the first order in λ,

$$P = u(b - c)$$
$$Q = v(c - a) \quad (3)$$
$$R = w(a - b)$$

The expressions for g values in terms of P, Q, R are

$$g_x = 2 + \frac{2}{3} P(b-c)$$
$$g_y = 2 + \frac{2}{3} Q(c-a) \quad (4)$$
$$g_z = 2 + \frac{2}{3} R(a-b)$$

The magnetic hyperfine structure can be expressed simultaneously in terms of hyperfine interaction parameter and the Fermi contact term K, which represents the admixture of configurations with unpaired s-electron, in the form.

$$A_x/P_{hf} = -K + \frac{2}{3} P(b-c) + \frac{1}{7}(2a^2 - 4 + Rc - Qb) = -K + f_x$$

$$A_y/P_{hf} = -K + \frac{2}{3} Q(c-a) + \frac{1}{7}(2b^2 - 4 + Pa - Rc) = -K + f_y \quad (5)$$

$$A_z/P_{hf} = -K + \frac{2}{3} R(a-b) + \frac{1}{7}(2c^2 - 4 + Qb - Pa) = -K + f_z$$

The expressions for g values contain unknown parameters u, v, w, and a, b, c. The parameters a, b, c are related by Eq.(1) and can be expressed in terms of single parametric angle ϕ as,

$$a = \cos\phi + \sqrt{3}\sin\phi$$
$$b = \cos\phi - \sqrt{3}\sin\phi \quad (6)$$
$$c = -2\cos\phi$$

These three parameters a, b, c will be evaluated with the help of EPR data. The |xz> and |yz> levels may be treated as close since the uniaxial symmetry leading to rhombic part of the crystals is usually small. Therefore we can take easily u = v and from this approximation we can find the value of other parameters using expressions (3), (4) and (6).

$$\sin 2\phi = (g_y - g_x) / 4\sqrt{3}u \quad (7)$$
$$\cos 2\phi = ((g_y + g_x - 4) / 4u) - 2$$

From these two equations, a quadratic equation in terms of u is obtained and u can be easily determined. Putting the value of u in Eq.(7) we can evaluate the value of sin2ϕ and cos2ϕ. With the help of Eqs. (4), (5) and (6) we can evaluate parameters a, b, c, P, Q, R and f_x, f_y, f_z. When a graph is plotted between the f_i (i = x, y, z) and hyperfine structure constant A_i (i = x, y, z) with proper signs and directions, the points must lie on straight line [7]. The intersection of the line on f_i axis gives the value of Fermi contact term K and the slope of the line gives the value of hyperfine interaction parameter P_{hf}.

Table 1 E PR parameter for Cu^{2+} ion in selected crystals lattices.

S. N.	Crystal Lattices	EPR Parameters						
		g_x	g_y	g_z	A_x	A_y	A_z	[Ref.]
1.	Zinc glutamate dihydrate (ZGD)							[8]
	Site I	2.0170	2.0768	2.2334	74	-99	-134	
	Site II	2.0180	2.0550	2.1633	100	-100	-115	
2.	Cadmium acetate Dihydrate (CAD)	2.0382	2.1644	2.4139	50.1	-25.1	-101.6	[9]
3.	Strontium tartrate trihydrate (STT)							[10]
	Site I	2.0380	2.1317	2.3918	26.3	-56.3	-110.8	
	Site II	2.0497	2.1297	2.3706	19.2	- 61.4	-107.2	
4.	Bisglycine strontium ChlorideTrihydrate (BST)	2.0120	2.1861	2.2132	31	-44	-183	[11]
5.	Sodium zinc sulfate Tetrahydrate(SZT)	2.2356	2.0267	2.3472	27	-54	-88	[12]

Results and Discussions

Various combinations have been tried giving different directions to g_i and A_i values and assigning positive and negative signs to A_i in order to have a straight line on the A_i-f_i diagram. The A_i-f_i diagram thus obtained is shown in Fig. 1.

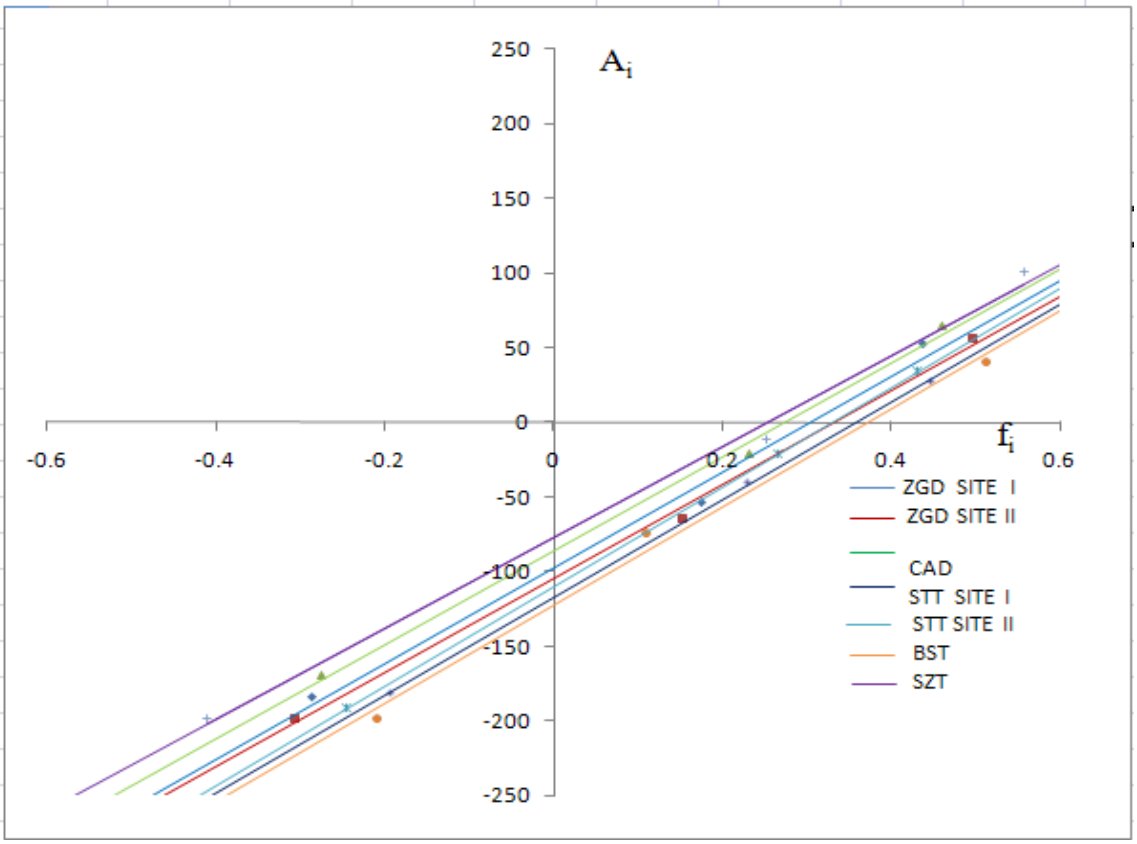

Fig. 1. (A_i-f_i) diagram of Cu^{2+} ion doped in different single crystals.

With the help of proper signs and directions of the spin Hamiltonian parameters given in Table 1, the hyperfine interaction parameter, Fermi contact term and parameters u, v, w, f_x, f_y, f_z and ground state wave function for the selected host lattices are obtained. These are given in Tables 2, 3 and 4, respectively.

Table 2 Fermi contact term, hyperfine interaction parameter, the percent ratio of hyperfine interaction parameter (P_{hf}) to the value for free ion (P_{fi}).

S.N. Crystal Lattices	Fermi contact term K	hyperfine interaction Parameter P_{hf}	(P_{hf}/P_{fi})%
1.Zinc glutamate dihydrate (ZGD)			
Site I	0.341	454	126
Site II	0.351	347	96
2. Cadmium acetate Dihydrate (CAD)	0.312	272	75
3. Strontium tartrate trihydrate (STT)			
Site I	0.371	175	48

Site II	0.361	199	54
4. Bisglycine strontium Chloride Trihydrate (BST)	0.401	261	72
5. Sodium zinc sulfate Tetrahydrate(SZT)	0.368	211	58

Table3 Theoretically investigated EPR parameters.

S.N. Crystal Lattices	|U|	|W|	f_x	f_y	f_z
1.Zinc glutamate dihydrate (ZGD)					
Site I	0.0181	0.0301	0.4382	0.1753	-0.2864
Site II	0.0192	0.0211	0.4959	0.1533	-0.3074
2. Cadmium acetate Dihydrate (CAD)	0.0469	0.0538	0.4601	0.2322	-0.0757
3. Strontium tartrate trihydrate (STT)					
Site I	0.0400	0.0504	0.4461	0.2293	-0.1137
Site II	0.0432	0.0470	0.4309	0.2650	-0.1449
4. Bisglycine strontium Chloride Trihydrate (BST)	0.0410	0.0297	0.5125	0.1089	-0.2102
5. Sodium zinc sulfate Tetrahydrate(SZT)	0.2571	0.0447	0.5567	0.2515	-0.4107

Table 4 Ground state wave function for Cu^{2+} ion in selected host lattices.

S.N. Crystal Lattices	Ground state wave function
1.Zinc glutamate dihydrate (ZGD)	
Site I	$1.871x^2-1.429y^2-0.355z^2$
Site II	$1.812x^2-1.486y^2-0.362z^2$
2. Cadmium acetate Dihydrate (CAD)	$1.895x^2-1.001y^2-0.395z^2$
3. Strontium tartrate trihydrate (STT)	
Site I	$1.877x^2-1.535y^2-0.3425z^2$
Site II	$1.851x^2-1.582y^2-0.269z^2$
4. Bisglycine strontium Chloride Trihydrate (BST)	$1.963x^2-1.313y^2-0.649z^2$
5. Sodium zinc sulfate Tetrahydrate(SZT)	$1.879x^2-1.532y^2-0.347z^2$

The various points on the A_i - f_i diagram lie on straight line in maximum cases but due to some inaccuracy in the experimental data a considerable scatter of the points from straight line are obtained. The ground state wave function of selected host lattices is predominately $|x^2-y^2>$ and the value of hyperfine interaction parameter in all the cases is lower then the value of the free ion [13]. This indicates that the value of r^{-3} in crystals is less as compared with the free ion [14]. The value of P_{hf}/P_{fi} is minimum in case of STT site I indicating that the covalency is maximum because of the fact that the covalency is inversely proportional to the values of P_{hf}/P_{fi} i.e. the covalency decreases as P_{hf}/P_{fi} increases and vice-versa. With the help of these the order of decrease of covalency may be written as, STT site I, STT site II, SZT, BST, CAD, ZGD site I, ZGD site II. From Table 4, it can be seen that the ground state wave function comes out to be $|x^2-y^2>$ type in all the selected host lattices. However, the parameters K and P_{hf} obtained theoretically in this investigation are well comparable with the experimental values given by earlier workers. This shows that the interpretation of ground state wave function in these systems to be of $|x^2-y^2>$ type seems appropriate.

Conclusion

Ground state wave function of Cu^{2+} ion doped in different single crystals is evaluated and the results show that the ground state is of $|x^2-y^2>$ type. The parameters u, v, w, a, b, c and f_x, f_y, f_z are also determined. The hyperfine interaction parameter P_{hf} and Fermi contact term K are calculated with the help of A_i-f_i diagram. Using the value of hyperfine interaction parameter in different host lattices and the value for free ion the order of covalency is determined. Further, from this method the correct signs and directions are assigned to the spin Hamiltonian parameters.

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