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## Electron paramagnetic resonance response of $\text{Cu}^{3+}$ in $\text{D}_{4h}$ coordination symmetry

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**Abstract.** Theoretical calculations of the wavefunctions and energy level structure of the  $^3\text{F}$  ion with a  $3d^8$  electronic configuration in a  $\text{D}_{4h}$  distorted  $\text{O}_h$  weak crystal field, including the spin-orbit interaction, indicate the possible paramagnetic features of strongly distorted octahedrally coordinated  $\text{Cu}^{3+}$  ions, up to the square-planar coordination. The Zeeman matrices are evaluated over all the states of the ion in order to calculate the generalized Van Vleck susceptibility and the EPR transition probabilities. It is shown that no paramagnetic resonance should be expected for sufficiently large distortions, even when the system possesses a non-null magnetic moment. These results may contribute to the interpretation of several EPR experimental data on copper oxides whose meaning has been in many cases misunderstood.

### 1. Introduction

Trivalent copper ( $3d^8$  ion) exhibits two different spin states: high spin (HS) with  $S = 1$  and low spin (LS) with  $S = 0$ . The free ion is characterized by the HS configuration as a result of the Hund rules in filling the degenerate  $3d$  orbitals. In solids it prefers the HS configuration when the degeneration of the  $3d$  multiplet is only partially removed by the crystal field (CF), a doublet or triplet of states being at the highest energy. This happens in octahedral coordination ( $\text{O}_h$  sites) with very small distortions, as in  $\text{Al}_2\text{O}_3$  with  $\text{Cu}^{3+}$  substitutional impurities [1] or in copper exafluorides [2]. On the contrary the LS configuration seems to occur only in ligand geometries which strongly deviate from the octahedral symmetry, including some compounds with the copper ion in square-planar (SP) coordinations ( $\text{D}_{4h}$  sites) [3–7].

The spin state of  $\text{Cu}^{3+}$  in  $\text{D}_{4h}$  distorted  $\text{O}_h$  sites is a subject of research [8–10] nowadays, mainly in the framework of the perovskite cuprate chemistry, where new synthesized oxides with different coordination parameters and covalency degrees [3, 4, 11–13] have been systematically analysed. Recently, it has also been proposed that the equilibrium between the  $\text{Cu}^{3+}$  spin states plays a role in the mechanisms responsible for the superconductivity of the high-temperature superconductors [3], where the trivalent copper ions are assumed to be in square-planar coordinated sites surrounded by four oxygen atoms. In any case, all these studies demonstrate that the covalency of the Cu–O bond may strongly affect the spin state of the  $\text{Cu}^{3+}$  by increasing the CF splitting without symmetry changes; this effect modifies the ratio of the energy splitting of electronic levels (which favours the coupling of electronic spin in the LS state) to the competitive intra-atomic exchange energy (the Racah parameter  $B$ ) responsible in free ions for the largest spin value consistent with the exclusion principle; the resulting strong effective CF (large  $Dq$ -value) favours LS states. Nevertheless,

some workers suggest that, in copper oxides, the covalency may also contribute to inducing the HS state, the relevant parameter being the reduced energy difference  $\epsilon$  between Cu 3d and O 2p levels [3]; as a consequence, the energy spacing between the highest antibonding molecular orbitals may not be large enough to predominate over the intra-atomic exchange energy.

So, the LS state in these Cu<sup>3+</sup> compounds is usually ascribed to the presence of a strong effective CF, whose value is directly inferred from optical absorption data [1] and comprises both the CF and the covalency contributions to the total energy splitting. Clearly, the LS state of Cu<sup>3+</sup> has no magnetic response.

As regards the HS states, small CF values together with covalency-reduced energies  $\epsilon$  are required; in this case, the system should give a paramagnetic response, detectable by susceptibility measurements. By contrast, it is not clear what EPR signal is to be expected in the specific cases, because the EPR response may drastically change from the known features analysed in regular octahedral coordinations to the unknown response in nearly planar geometries for which no detailed analysis is available. Owing to this difficulty, some experimental data on cuprates have been misunderstood [14, 15] and both the lack and the presence of paramagnetic Cu<sup>3+</sup> ions have been supported on the basis of questionable speculations [16–20], taking EPR measurements as the relevant tool for monitoring the presence of Cu<sup>3+</sup> in HS states.

In order to clarify these aspects, we have analysed the paramagnetic features of HS Cu<sup>3+</sup> ions by reproducing the coordination effects in a weak-CF approach. The calculation of the energy level structure and wavefunctions in D<sub>4h</sub> distorted octahedral sites shows that, for sufficiently large distortions, up to the SP coordination, the ion possesses a non-null magnetic moment, but an intrinsically EPR-inactive ground state.

## 2. Crystal-field approach

In order to determine the level structure of a Cu<sup>3+</sup> ion in the CF with strong deviations from O<sub>h</sub>, the standard perturbative calculation of contributions from low-symmetry components has been avoided. Low-symmetry terms have been accounted for, in each coordination geometry, by starting *ab initio* from the positions of the surrounding ions. We calculated the electrostatic potential  $V(\mathbf{r})$  due to the charges  $q_j$  at the position  $\mathbf{R}_j$  of the surrounding ions according to the expression  $V(\mathbf{r}) = \sum_j q_j / 4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{r}|$ , where the sum may be limited, to a good approximation, to the next-nearest-neighbour ions coordinated with the cation. We use the following form of the potential:

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_n \sum_m \sum_j \frac{4\pi}{2n+1} q_j \frac{r^n}{R^{n+1}} Z_{nm}^{c/s}(\mathbf{R}_j) Z_{nm}^{c/s}(\mathbf{r}_j) \quad (1)$$

where the expansion in  $n$  terms with the tesseral harmonics  $Z_{nm}^{c/s}$  (where  $s$  indicates sin and  $c$  cos type) is based on the expansion of  $1/|\mathbf{R} - \mathbf{r}|$  using the Legendre polynomials. The terms

$$c_{nm}^{c/s} = \sum_j \frac{4\pi}{2n+1} \frac{q_j}{R^{n+1}} Z_{nm}^{c/s}(\mathbf{R}_j) \quad (2)$$

have been calculated as a function of the anionic coordinates to obtain the expression of the Hamiltonian  $\mathcal{H}_{CF}$  with the Stevens equivalent operator  $\mathcal{O}_{nm}^{c/s}$ :

$$\mathcal{H}_{CF} = \sum_{nm} F_{nm}^{c/s} \mathcal{O}_{nm}^{c/s} \quad \text{with} \quad F_{nm}^{c/s} = -|e| \langle r^n \rangle a_{nm}^{c/s} c_{nm}^{c/s} \vartheta_n \quad (3)$$

where  $a_{nm}^{c/s}$  are the numerical factors which multiply the Cartesian functions  $f_{nm}^{c/s}$  in the expression  $Z_{nm}^{c/s} = a_{nm}^{c/s} f_{nm}^{c/s}(x, y, z)/r^n$ ,  $\vartheta_n$  are the Stevens multiplicative factors and  $\langle r^n \rangle$  is the expectation value of  $r^n$  for the 3d orbitals of the  $\text{Cu}^{3+}$  ion. The eigenstates and the eigenvalues of the  $\text{Cu}^{3+}$  ion have been calculated diagonalizing the  $21 \times 21$  matrix obtained from the Hamiltonian  $\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{SO}} = -|e|V(r) + \lambda \mathbf{L} \cdot \mathbf{S}$  operating on the basis  $|\mathbf{L}, \mathbf{M}_L, \mathbf{S}, \mathbf{M}_S\rangle$  of the  ${}^3F d^8 \text{Cu}^{3+}$  ion, assuming for the spin-orbit coupling constant  $\lambda$  the free-ion value of  $-438 \text{ cm}^{-1}$  [21] or the experimentally evaluated value of  $-214 \text{ cm}^{-1}$  [1]. Then, in order to obtain the  $\mathbf{g}$ -tensor and, more generally, the EPR response of the system, the Zeeman Hamiltonian  $\mathcal{H}_Z = \mu_B(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}$  is applied on the low-lying energy levels which are significantly populated; the  $g$ -values are obtained from the resonance condition  $h\nu = g\mu_B B$ , where the incident energy  $h\nu$  equals the energy difference  $\langle \psi_a | \mathcal{H}_Z | \psi_a \rangle - \langle \psi_b | \mathcal{H}_Z | \psi_b \rangle$  between the states  $\psi_a$  and  $\psi_b$  which diagonalize  $\mathcal{H}_Z$ .

The magnetic moment of the ion is related to the static magnetic susceptibility whose value is given by the generalized Van Vleck expression [22]

$$\chi_{\alpha\beta} = \left[ \mu_0 \frac{N}{V} \sum_i \left( \sum_j \frac{\langle i | \mu_\alpha | j \rangle \langle j | \mu_\beta | i \rangle}{kT} - \sum_k \frac{\langle i | \mu_\alpha | k \rangle \langle k | \mu_\beta | i \rangle + \langle i | \mu_\beta | k \rangle \langle k | \mu_\alpha | i \rangle}{E_i - E_k} \right) \times \exp\left(-\frac{E_i}{kT}\right) \right] / \sum_i \exp\left(-\frac{E_i}{kT}\right) \quad (4)$$

where  $i$  is summed over all the energy levels,  $\sum_j$  is a sum over all  $j$  levels degenerate with  $i$ ,  $i$  included, while  $\sum_k$  is restricted to the  $k$  levels not degenerate with  $i$ . The indexes  $\alpha$  and  $\beta$  refer to the  $x$ ,  $y$  and  $z$  projections of the magnetic moment operator  $\mu = \mu_B(\mathbf{L} + 2\mathbf{S})$ , and the energies  $E_n$  are those of the unperturbed system.

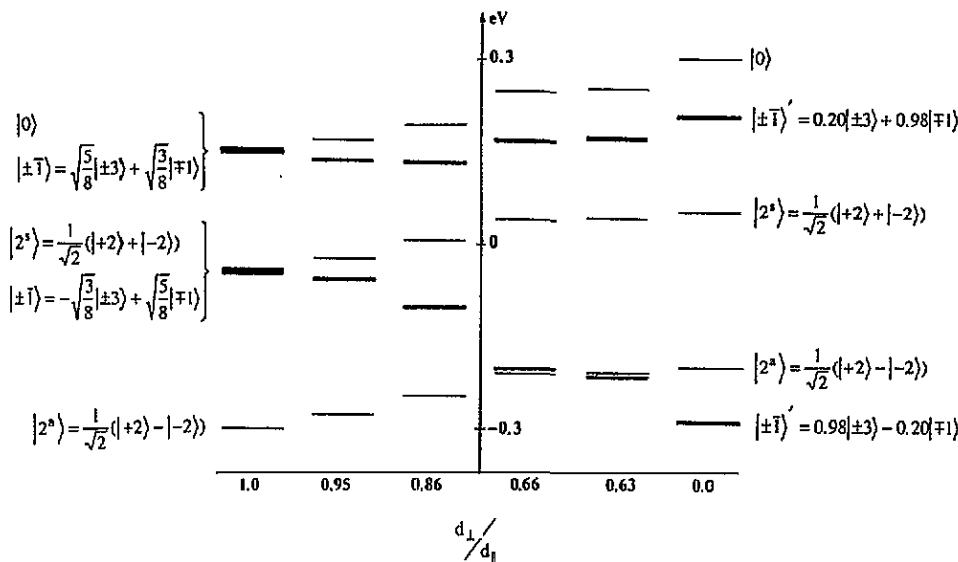


Figure 1. Energy levels and wavefunctions of the  $\text{Cu}^{3+}$  ion in an octahedral crystal field (left) with an increasing  $D_{4h}$  distortion  $d_{\perp}/d_{\parallel}$  (see text), up to the square-planar symmetry (right).

### 3. Energy level structure

In order to reproduce realistic CF effects, the lattice parameters of typical copper oxides are used in a simplified ionic picture; the ligands are assumed to be divalent anions  $O^{2-}$  placed at the edges of a regular or distorted octahedron; four anions are in the  $xy$  plane 0.19 nm from the central cation, as in the case of the  $YBa_2Cu_3O_7$ -based HTSC, whilst two anions are progressively displaced, on the  $z$  axis, from the regular octahedral position ( $z = \mp 0.19$  nm) to infinity (SP coordination). The values  $\langle r^2 \rangle$  and  $\langle r^4 \rangle$  are 0.8763 au ( $2.5 \times 10^{-3}$  nm<sup>2</sup>) and 1.662 au ( $1.3 \times 10^{-5}$  nm<sup>4</sup>), respectively, according to [21]. Figure 1 shows how the sevenfold degenerate  $^3F$  manifold of the free  $d^8$  ion splits owing to the distortion of the environment; from the octahedral to the SP coordination, the  $d_{\perp}/d_{\parallel}$ -values represent the ratio of the in-plane to out-of-plane cation–anion distances. The energy levels calculated in octahedral CF reproduce the expected configuration, in agreement with standard CF results [21], with an orbital singlet in the ground state (GS) and two triplets at higher energies. The separation between the GS and the first excited triplet is the CF parameter  $10Dq$  [1, 21]; its low value (about 250 meV) is consistent with other theoretical calculations [23], but it is an order of magnitude lower than the value estimated on comparison of EPR and optical data [1], supporting the already-proposed existence of a large contribution of covalency to the effective level splitting. The wavefunctions are listed on the left of figure 1; the GS is a  $|2^a\rangle$  state, the lowest triplet is composed of a  $|2^s\rangle$  state and a  $|\pm \bar{1}\rangle$  doublet, while the highest triplet consists of the  $|\pm \bar{1}\rangle$  doublet and the  $|0\rangle$  state. The progressive  $D_{4h}$  distortion partially removes the degeneracy, splitting the triplets into doublets and singlets. The  $|\pm \bar{1}\rangle$  doublet arising from the lowest triplet is progressively lowered and, for  $d_{\perp}/d_{\parallel}$  smaller than about 0.65, is pushed below the  $|2^a\rangle$  singlet. In these cases and in the SP coordination, the GS is the  $|\pm \bar{1}\rangle$  doublet, as shown on the right of figure 1.

The effect of SO coupling has been evaluated by recalculating the eigenfunctions and eigenvalues of the Hamiltonian  $\mathcal{H} = \mathcal{H}_{CF} + \mathcal{H}_{SO}$ . The degeneracy of the levels is further removed, and 16 different eigenvalues are found (see table 1 for SP coordination). The two lowest levels are not degenerate and in table 2 the associated wavefunctions for  $\lambda = -214$  cm<sup>-1</sup> are reported; their orbital part shows that they arise from a mixing of the  $|\pm \bar{1}\rangle$  and  $|\pm \bar{1}\rangle$  doublets in figure 1. The energy difference between the lowest levels depends on the  $\lambda/Dq$ -ratio and in fact, by increasing the strength of the CF, we verified that the two levels converge to a doubly degenerate state.

### 4. Paramagnetic properties

Table 2 shows that the two lowest states of  $Cu^{3+}$  in SP coordination are well separated from the upper level and their energies differ very little compared with  $kT$ , at least at temperatures higher than a few kelvins. They show similar features for distortion in the range  $0 < d_{\perp}/d_{\parallel} < 0.65$  and constitute the thermally populated GS levels which determine most of the magnetic properties of the ion, especially its EPR features. The Zeeman matrices for the two levels along the reference directions have been calculated for different  $D_{4h}$  distortions above the value that pushes them at the GS (in table 3 the results obtained in SP symmetry are reported). For all these coordination geometries, independently of the direction of the quantization axis, two facts are to be noted.

(i) All the diagonal terms are zero.

(ii) In the directions orthogonal to the fourfold symmetry axis (the  $z$  axis in table 3) all the matrix elements are zero.

**Table 1.** Eigenvalues and degeneration of the 3d manifold of  $\text{Cu}^{3+}$  in sp coordination.

Eigenvalues			
$\lambda = -214 \text{ cm}^{-1}$	$(-26.5 \text{ meV})$	$\lambda = -438 \text{ cm}^{-1}$	$(-54.3 \text{ meV})$
366.4 meV		469.5 meV	
339.1	(2)	412.4	(2)
233.4		270.2	
217.9		258.6	
195.9	(2)	193.8	(2)
194.7		190.9	
171.6		94.4	
43.3	(2)	4.4	(2)
25.1		-32.5	
-150.7		-48.3	
-193.3	(2)	-155.3	
-216.2		-170.9	(2)
-268.9		-312.1	
-308.3	(2)	-362.9	(2)
-363.2		-443.9	
-363.5		-444.9	

**Table 2.** Wavefunctions of the two lowest energy levels in sp coordination ( $\lambda = -214 \text{ cm}^{-1}$ ).

Energy (meV)	Wavefunction
-363.2	$0.6973 +3, +1\rangle - 0.1172 -1, +1\rangle - 0.6973 -3, -1\rangle + 0.1172 +1, -1\rangle$
-363.5	$-0.6967 +3, +1\rangle + 0.1196 -1, +1\rangle - 0.6967 -3, -1\rangle + 0.1196 +1, -1\rangle + 0.0233 0, 0\rangle$

**Table 3.** Zeeman matrix elements  $\langle i|\mu|j\rangle$  (in Bohr magnetons) between the lowest states calculated with  $\lambda = -214 \text{ cm}^{-1}$  (see table 2). The state  $|i\rangle$  corresponds to the eigenvalue  $-363.5 \text{ meV}$ , and the state  $|j\rangle$  to  $-363.2 \text{ meV}$ .

$\mu_{xx}$	$ i\rangle$	$ j\rangle$	$\mu_{yy}$	$ i\rangle$	$ j\rangle$	$\mu_{zz}$	$ i\rangle$	$ j\rangle$
	0	0		0	0		0	-4.9
	0	0		0	0		-4.9	0

The non-null off-diagonal terms suggest possible magnetic dipole transitions, and not an EPR transition, induced by radiation with magnetic component parallel to the  $z$  axis of the system. Now we discuss the probability of EPR transitions for these levels. Static magnetic fields can mix the states and change their energies. In the case of strong static magnetic fields the two levels appear as nearly degenerate. When the Zeeman matrix in the field direction is not zero, it may be diagonalized in order to calculate directly the Zeeman energies. In any case, the Zeeman matrices in the orthogonal directions, computed with the states diagonalizing the matrix along the static magnetic field, turn out to be zero or show null off-diagonal elements; an oscillating magnetic field orthogonal to the static field does not induce EPR transitions. Therefore, none of the EPR signals observed up to now in copper compounds can be associated with any detectable EPR response of  $\text{Cu}^{3+}$  ions in a weak CF of SP symmetry or  $D_{4h}$  symmetry with sufficiently small  $d_{\perp}/d_{\parallel}$ .

Now, we show that, in spite of its intrinsic 'EPR silence', the  $\text{Cu}^{3+}$  ion in  $D_{4h}$  sites should be properly detected by means of the static magnetic susceptibility  $\chi$ . By assuming a typical value of ion density ( $n = 10^{22} \text{ cm}^{-3}$ ) we calculated the adimensional  $\chi$ -tensor which turns out to be diagonal in the chosen reference frame. The Zeeman matrix elements

which are needed for the calculation are elevated for all the 21 states arising from the complete Hamiltonian  $\mathcal{H}$  with  $\lambda = -214 \text{ cm}^{-1}$ . In figure 2 we report the temperature dependence of the magnetic susceptibility  $\chi$  and that of  $\chi^{-1}$ , calculated by using the Van Vleck expression (4), parallel to the  $z$  axis and orthogonal to it.

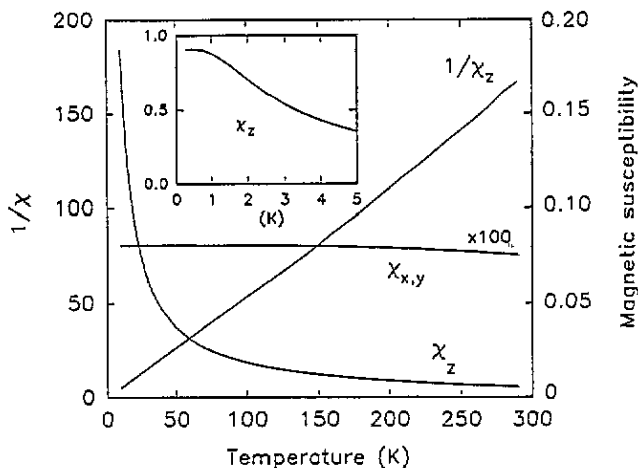


Figure 2. Temperature dependence of the principal values of the adimensional  $\chi$ -tensor (right-hand scale) and of  $\chi_z^{-1}$  (left-hand scale) of square-planar coordinated  $\text{Cu}^{3+}$ , with an ion density  $n = 10^{22} \text{ cm}^{-3}$  and spin-orbit coupling constant  $\lambda = -214 \text{ cm}^{-1}$ . In the inset, the low-temperature behaviour of  $\chi_z$  is shown.

The nearly linear behaviour of  $\chi_z^{-1}(T)$  and the relatively high value of  $\chi_z$  at a fixed temperature ( $5.7 \times 10^{-3}$  at 300 K) are typical paramagnetic features. In this regard, it is worthwhile to remark that the main contribution to  $\chi_z$  does not derive from the diagonal Zeeman elements, the so-called Curie terms, in spite of the resulting Curie-like behaviour; in fact, as just evidenced, the terms  $\langle i|\mu|i\rangle$  are zero for the lowest levels, the only levels significantly populated at room temperature. By contrast, the strong paramagnetism arises from the Van Vleck terms with a large Boltzmann factor  $\exp(-E_i/kT)$  and small denominator  $E_i - E_k$ , containing the crossed matrix elements  $\langle i|\mu|k\rangle$  between the lowest levels. In fact, deviations from the usual paramagnetic behaviour are indeed expected at low temperatures (see inset in figure 2), where the parallel susceptibility approaches a constant asymptotic value which is inversely proportional to  $E_2 - E_1$ , the energy difference between the lowest states. The analysis of the  $\chi$ -tensor also evidences strong anisotropy with the principal values in the  $xy$ -plane ( $\chi_x = \chi_y = 8 \times 10^{-4}$ ) independent of the temperature and arising from Van Vleck paramagnetism due to the highly excited levels.

The results of the calculation of  $\chi$  for SP-coordinated  $\text{Cu}^{3+}$  may now be compared with the typical paramagnetic features in real cuprates, where  $\text{Cu}^{3+}$  seems to exist in nearly planar fourfold coordination. Possible experimental evidence of paramagnetic contribution from  $\text{Cu}^{3+}$  ions (but deviating from SP-coordination) has recently been reported for  $\text{NaSrCuO}_3$  [3]. In many other copper compounds, particularly in the HTSCs and their precursors (where a fraction of planar Cu sites should be occupied by trivalent copper), the  $\chi$ -value is often relatively low and less than that expected from our calculations. Therefore one should deduce that the lack of relevant paramagnetic contribution from  $\text{Cu}^{3+}$  ions may be caused

firstly by too low a concentration, secondly by magnetic interactions, as in the case of  $\text{Cu}^{2+}$  ions in these compounds, or thirdly and more likely by the LS configuration.

In summary, our results rule out any experimental detectability of paramagnetic resonance from sixfold-coordinated  $\text{Cu}^{3+}$  with  $d_{\perp}/d_{\parallel}$  smaller than about 0.7 (with the extreme case of SP coordination), not only when the ion is in the LS state but also when it is in the HS state (weak CF). Moreover we predict the paramagnetic behaviour of the static magnetic susceptibility deriving from isolated  $\text{Cu}^{3+}$  SP-coordinated ions.

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