Electron paramagnetic resonance of Cu^{2+} in descloizite mineral: an unusual electronic configuration

Electron paramagnetic resonance of Cu²⁺ in descloizite mineral: an unusual electronic configuration

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Abstract. The electron paramagnetic resonance (EPR) spectrum of descloizite (Pb(Zn, Cu)(VO$_4$)(OH)) has been studied at room temperature using conventional methods. The powder and single-crystal spectra revealed hyperfine structure of Cu²⁺ in axial site symmetry. The measured values $g_\parallel = 2.023$, $g_\perp = 2.222$, $A_\parallel = 110 \times 10^{-4}\,\mathrm{cm}^{-1}$ and $A_\perp = -56.2 \times 10^{-4}\,\mathrm{cm}^{-1}$ indicate that the Cu²⁺ ion is sited in a compressed octahedron (D$_{4h}$) so that $^2A_{1g}$ is the ground state. The experimental data were used to determine the constants P and K.

1. Introduction

Divalent copper has the electronic configuration 3d⁹ ²D. In an octahedral crystalline field this state splits into two degenerate e_g levels ($|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$) which are lowest in energy and three degenerate t_{2g} levels ($|yz\rangle$, $|xz\rangle$ and $|xy\rangle$) at energies E_x, E_y and E_z above the ground level. The ^2E_g state should be highly susceptible to a Jahn–Teller configurational instability [1]; so it is expected that no regular octahedral coordination should exist.

It is possible to distinguish two kinds of distortion which lift the orbital degeneracy in terms of regular octahedral stereochemistry in accordance with the Jahn–Teller effect; axial lengthening or shortening and simultaneous planar shortening or lengthening describe one of the simplest normal modes for the regular octahedron (figure 1). When there is a permanent distortion clearly described by one of these configurations, there is the case of the static Jahn–Teller effect. Sometimes both configurations are of lower energy than that of the undistorted octahedron and the potential barrier for interconversion between them is small. Then the molecule can convert easily from one form to the other and this is the case of the dynamic Jahn–Teller effect. In this case the structure cannot be considered rigid.

Stereochemically non-rigid but chemically equivalent configurations are called fluxional. Coordination polyhedra are usually thought of in essentially static terms, i.e. as if there are no intramolecular interchanges in ligands. Although in many cases this is valid, there is growing evidence that non-rigidity and particularly fluxionality is not uncommon [2].

Orbital degeneracy may be lifted also by other effects such as spin–orbit coupling or by the inequivalence of ligand atoms or an environment-forced ligand displacement.
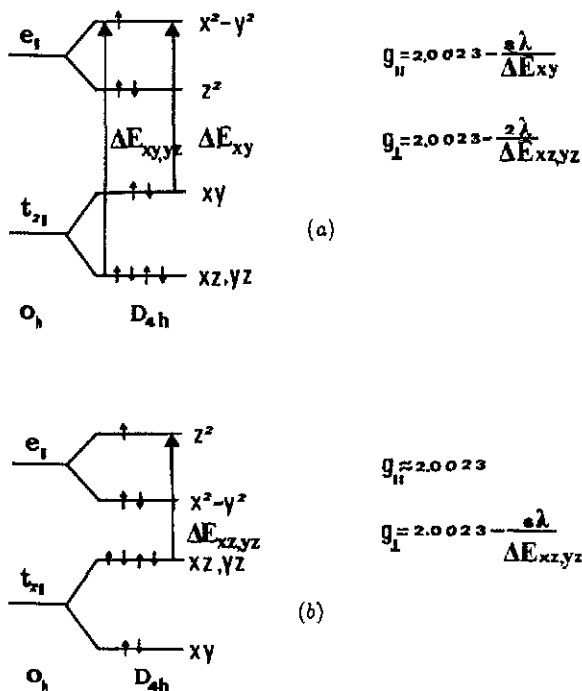
Figure 1. Energy level of diagrams for tetragonally distorted octahedra due to the Jahn–Teller effect: (a) elongated octahedron; (b) compressed octahedron.

A study of the ionic nature and the symmetry of Cu^{2+} in descloizite has been carried out in the present work.

2. Crystallography

Descloizite $(Pb(Zn, Cu)(VO_4)(OH))$ crystallizes in the *Pnma* (or *Pn2a*) space group as reported earlier [3–6]. The single site for the (Zn, Cu) cation is situated at the centre of a distorted tetragonal bipyramid for which the equatorial plane consists of alternating O and OH as concluded from the isostructural conichalcite $CaCu(AsO_4)(OH)$ where copper replaces zinc [7]. In a more recent crystal structure refinement [8], much emphasis has been placed on VO_4 tetrahedra. From the reported interatomic distances the location of the OH is not clear. So two different combinations of the ligands can be made:

(i) alternating O, OH sites on the equatorial plane: $\langle ZnO \rangle$ on plane, 2.077 Å; $\langle ZnO \rangle$ out of plane, 2.204 Å;

(ii) OH situated at the apices: $\langle ZnO \rangle$ on plane, 2.193 Å; $\langle ZnO \rangle$ out of plane, 1.973 Å.

The tetragonalities are low in both cases, 0.94 and 1.11, respectively.

3. Experimental details

Powder and single crystals of descloizites from Otavibergland, Namibia, were investigated by EPR. The measurements were carried out at room temperature on an X-band spectrometer model ER-414. Precise field values were determined using an NMR
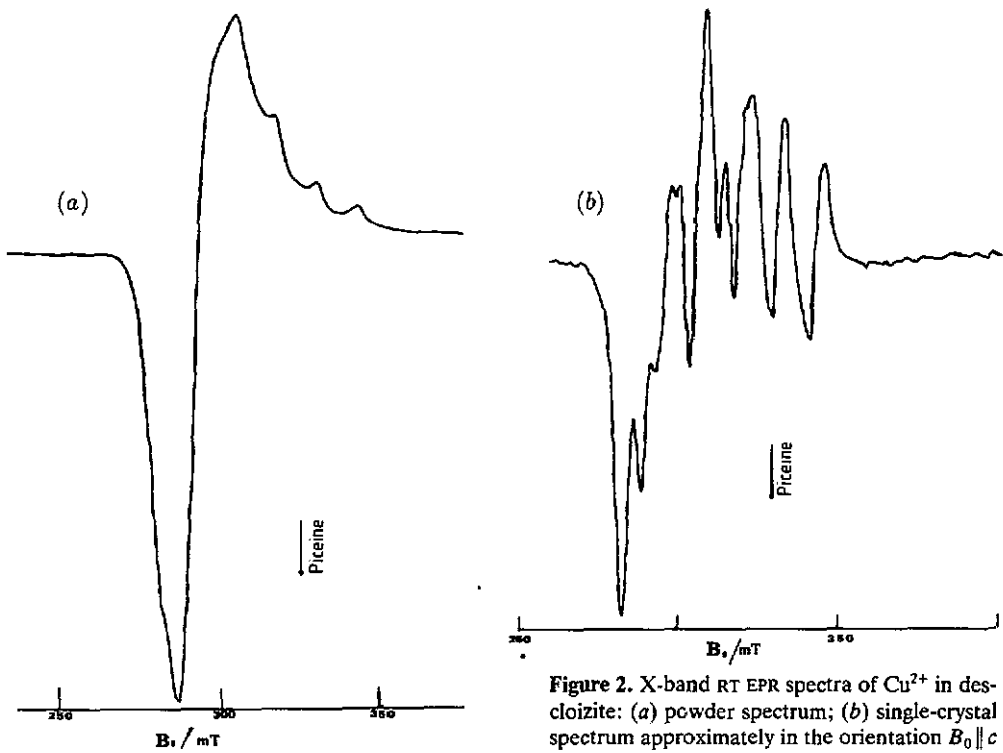
Figure 2. X-band RT EPR spectra of Cu^{2+} in descloizite: (a) powder spectrum; (b) single-crystal spectrum approximately in the orientation $B_0 \| c$ axis.

gaussmeter while the microwave frequency was measured using piceine as a standard [9].

The crystals had a conchoidal fracture and no cleavage; so rotations around three arbitrary mutually perpendicular axes were performed.

4. Results and analysis

The EPR spectrum of descloizite in single-crystal and powder form is shown in figure 2. It is typical of a transition-metal ion with $S = \frac{1}{2}$, $I = \frac{3}{2}$ in axial symmetry and Cu^{2+} is an indisputable candidate. For this ion the pronounced Jahn–Teller effect leads to sufficiently long spin–lattice relaxation times at room temperature; so the quartets should be easily observed in the first approximation.

Single-crystal spectra exhibited an axial symmetry as seen from the angular variation in the line positions with the orientation in the magnetic field (figure 3). The splittings of about 2 mT in certain orientations can be attributed to interfering quartets of ^{63}Cu and ^{65}Cu isotopes as reported also in the case of anatase [10] or to some site splitting due to the arbitrary orthogonal rotations. This latter reason is also supported by the fact that the g calculated from the single-crystal data is lower than the corresponding value from the powder spectrum. The concentration of the impurities must not be very high because the observed linewidths are much lower than estimated from the dipole–dipole formula for a cubic lattice [11].
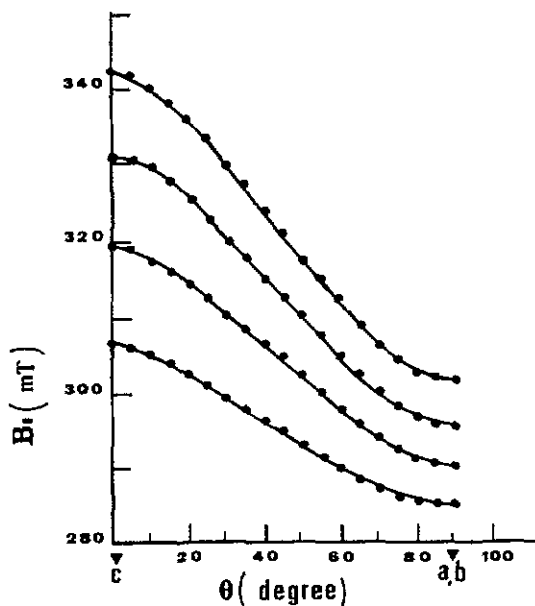
Figure 3. The angular dependence of the EPR spectrum of Cu^{2+} in descloizite.

A weak signal at $g = 4.24$ indicates the presence of Fe^{3+} but no more information could be extracted.

The spectra were analysed using the following spin Hamiltonian:

$$\mathcal{H} = g\beta HS + SAI \tag{1}$$

where the first term is the Zeeman term and the second is the hyperfine interaction term. The results are listed in table 1 with some data collected from the literature.

The unpaired electron can be described by first-order perturbation with the wavefunction:

$$|\pm\rangle = |0\rangle - \lambda \sum_n \frac{\langle n|LS|0\rangle}{(E_n - E_0)} |n\rangle$$

where $|0\rangle$ is the unperturbed ground state of the free ion and $|n\rangle$ are excited states, $E_n - E_0$ is the energy splitting of the levels due to the crystal field and λ is the spin–orbit coupling operator over the radial wavefunction of the manifold. Cu^{2+} has the configuration $t_{2g}^6 e_g^3$; so it can be considered as having one positive hole in the e_g orbital.

In a purely octahedral field the degeneracy of e_g orbitals is not removed even with allowance for spin–orbit coupling because the states $|0\rangle$ ($\equiv d_{z^2}$) and $(1/\sqrt{2})(|2\rangle + |-2\rangle)$ ($\equiv d_{x^2-y^2}$) are not coupled; so the electronic wavefunction for the ground state can be written

$$\psi = \sin^{1/2}\varphi\, d_{x^2-y^2} - \cos^{1/2}\varphi\, d_{z^2}.$$

According to the Jahn–Teller theorem for such a non-linear system with residual orbital degeneracy, the system will be strongly coupled to those lattice vibrations which remove the degeneracy and lower the ground state [23].

Neglecting π bonding, in octahedral symmetry the t_{2g} electrons are non-bonding, whereas the e_g electrons are highly antibonding. So a violent Jahn–Teller distortion would be expected to occur for E_g states; either a tetragonal or a rhombic distortion will

Table 1. EPR parameters for Cu^{2+} in various systems.

Mineral	g_{zz}	g_{yy}	g_{xx}	A_{zz} (10^{-4} cm^{-1})	A_{yy} (10^{-4} cm^{-1})	A_{xx} (10^{-4} cm^{-1})	Reference
Adamite	2.338	2.080	2.080	117	6.8	6.8	[12]
Anatase	2.253	2.019	2.343	82	71	21	[12]
Anatase	2.2080	2.0420	2.0420	172.9	18.6	18.6	[10]
	2.4340	2.0880	2.0880	84.8	21.0	21.0	[10]
	2.3930	2.0130	2.1970	65.7	67.1	23.5	[10]
Chabazite	2.324	2.068	2.068	159	18	18	[13]
Turquoise	2.339	2.035	2.108	—	—	—	[14]
Krohnkite	2.340	2.084	2.086	—	—	—	[15]
Tarbuttite	2.4352	2.0593	2.1337	−97.3	36.0	−4.6	[16]
Shattuckite	2.402	2.038	2.038	112	49.5	49.5	[17]
Quartz	2.420	2.130	2.021	26	75	108	[18]
Cudien$_2$Br$_2$, H$_2$O	2.2130	2.0968	2.0449	—	—	—	[19]
CuH$_2$,EDTA(H$_2$O)	2.2905	2.1142	2.0689	—	—	—	[19]
C$_{10}$H$_{16}$N$_2$O$_{10}$S$_2$Zn	2.0554	2.2212	2.2839	77	42	63	[20]
Zinc 3-pyridine sulphonate	2.030	2.263	2.202	74.05	53.3	56	[21]
Triglycine sulphate	2.259	2.027	2.092	165.4	84.8	24.2	[22]
Descloizite	2.023	2.222	2.222	119	−56.2	−56.2	This work

serve to remove the degeneracy. Depending on the sign of the distortion, compression or elongation of the octahedron, the state corresponding to $|0\rangle$ or to $(1/\sqrt{2})\,(|2\rangle + |-2\rangle)$, respectively, lies lower.

The signs of the hyperfine interaction constants cannot be determined by standard spectroscopic methods; so some assumptions have to be made before attempting an interpretation.

(1) A negative sign for the Fermi contact interaction term K is expected for dominant exchange polarization as is the case for transition series ions.

(2) The expectation value of the angular part of the dipole–dipole interaction tensor for the case of a tetragonally compressed octahedron over the ground state is

$$T_{\parallel}:\langle 3z^2 - 1|\,3\cos^2\theta - 1\,|3z^2 - 1\rangle = \tfrac{4}{7}$$

$$T_{\perp}:\langle 3z^2 - 1|\,3\sin^2\theta - 1\,|3z^2 - 1\rangle = -\tfrac{2}{7}.$$

$A_{\perp}$ should be negative since $A_{\perp} = K - (\tfrac{2}{7})\Omega\langle r^{-3}\rangle$ where $\Omega\langle r^{-3}\rangle = g_e\mu_B(g_N\mu_N/h)\langle r^{-3}\rangle = 1194$ MHz [20]. The sign of $A_{\parallel}$ could, however, be negative or positive according to whether K is or is not the dominant contribution. So it is usually to be decided from the evaluation of the results in each case.

The g- and A-values can be related to P and K according to the relations

$$A_{\parallel} = K\alpha^2 + P(-\tfrac{4}{7}\alpha^2 + \Delta g_{\parallel} + \tfrac{3}{7}\Delta g_{\perp}) \tag{2}$$

$$A_{\perp} = K\alpha^2 + P(\tfrac{2}{7}\alpha^2 + \tfrac{11}{14}\,\Delta g_{\perp}) \tag{3}$$

where α is a measure of electron localization ($\alpha = 1$ is the purely ionic limit). Inserting our results in (2) and (3) for the cupric ion in descloizite and assuming that $\alpha = 0.7$, we obtained $P = 0.0169 \times 10^{-4}\,\text{cm}^{-1}$ and $K = -0.3037 \times 10^{-4}\,\text{cm}^{-1}$.

5. Discussion

It has been shown [23] that measurements of the g-factors can decide which ground state the ion has. For a tetragonal compression in octahedral field,

$$\begin{aligned} g_{\parallel} &= g_e \\ g_{\perp} &= g_e - 6\lambda/\Delta_{\perp} \end{aligned} \tag{4}$$

while, for an elongation,

$$g_{\parallel} = g_e - 8\lambda/\Delta_{\parallel} \qquad g_{\perp} = g_e - 2\lambda/\Delta_{\perp}. \tag{5}$$

The observed values in descloizite agree with the case of a compressed octahedron.

Spin-Hamiltonian parameters of Cu^{2+} are affected significantly by the environment [24]. By inspection of table 1 it is clear that the results of the present work are unusual compared with the main body of previously reported data. Most of the experiments confirm that the stable configuration of copper complexes is an elongated octahedron.

If we assume an ionic bonding scheme, the compressed octahedron is expected to be stable, which is in contradiction to almost all experimental findings. Only three examples of a Cu^{2+} in a compressed rhombic octahedral environment are so far known, namely K_2CuF_4 [25], zinc(II) bis(pyridine-3-sulphonate) tetrahydrate (I) [21] and zinc 3-pyridine sulphonate [21] although the last two cases are questionable and can be interpreted

Table 2. List of parameters p, α^2 and K calculated from EPR data for Cu^{2+}. The references are as in table 1.

System	P ($10^{-4}\,cm^{-1}$)	α^2	K ($10^{-4}\,cm^{-1}$)
Anatase	0.0232 (RT)	—	0.377
	0.0232 (77 K)	—	0.397
	0.0234 (77 K)	—	0.260
	0.0246 (77 K)	—	0.232
Tarbuttite	0.0251 (RT)	—	0.268
	0.0264 (77 K)	—	0.287
Shattuckite	0.014 (120 K)	—	0.0112
Triglycine sulphate	0.0361 (77 K)	0.7166	−0.009
	0.0756 (77 K)	0.4418	0.0154
Zinc 3-pyridine sulphonate	—	0.703	0.0072
Descloizite	0.0169 (RT)	0.7	−0.3037

by a fluxional behaviour of chromophores. K_2CuF_4 would be likely indeed to possess a high degree of ionic bonding; so a large g_1-value is expected [26]. When covalency is taken into account, the electron is no longer localized in the central ion and molecular orbitals have to be introduced to describe its possible states. It should be pointed out in conclusion that the electronic configuration of Cu^{2+} in the present case presents special interest.

Low-temperature measurements that could provide a deeper insight to the problem are not available at the moment but the low tetragonality of Zn octahedra could suggest a structure of low stereochemical rigidity.

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