The spectroscopy of copper-oxide – Minerals

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Abstract:

The structure of copper minerals is explained on the basis of EPR and optical absorption spectral studies. The minerals contain not only copper but also manganese and iron as impurities. The environments of these ions in the crystal were explained based on crystal field theory. The ground state is confirmed with EPR studies. Optical absorption spectral results show that Cu(II) is present in tetragonal elongation in minerals and whereas in synthetic compound in compression. The mineral studied are beaverite, chalcocite, voglite and atacamite.

Key words: Beaverite, chalcocite, voglite, atacamite, EPR, optical absorption studies

Introduction

Among the noble metals (Au, Ag, Cu) copper is a cheap and more abundant in nature than the silver and gold. Its atomic number is 29 with electronic configuration of $[\text{Ar}]3d^{10}4s^1$. Copper gives two ionic states as Cu(I) and Cu(II). Among them Cu(II) is more stable and paramagnetic in nature.

Most of the naturally occurring solid compounds are inorganic nature. These are minerals, herbs, plants and trees etc., and are widely used in industry, medicine and agriculture and also in daily life. They exhibit different colors, which are due to the presence of copper and other transition metal ions. A detailed explanation of structural features of a few copper minerals has been studied using EPR and Optical absorption studies.

Copper oxide is formed when copper is exposed to oxygen and oxidizes. There are two types of copper oxides: i) cuprous oxide [Cu(I)] and cupric oxide [Cu(II)]. Both are used as pigments and can be used as semiconductors. Cupric oxide (CuO), is a black material that melts above 1200°C. This copper oxide is used as a pigment in clay glazes. Several colors, including red, blue, and green, can be derived from it. It is also used to produce rayon.

Role of minerals in health

The minerals that are relevant to human nutrition include water, sodium, potassium, chloride, calcium, phosphate, sulfate, fluoride, magnesium, iron, copper, zinc, manganese, iodine, selenium, and molybdenum and cobalt.

Copper is required for blood and nerve fiber development. It is found in liver, nuts, and seafood. The minimum copper requirement is between 0.4 and 0.8 mg/day. Copper is critical for the function of several

enzymes, especially blood. Iron is essential for the formation of hemoglobin, the chemical in the blood that carries oxygen to the cells. Low levels of iron cause anemia.

Color of a mineral

Several theories have been proposed to explain the spectral properties of the mineral [1]. They are 1) **Crystal field theory** (cause of color: transitional metal compounds, transition metal impurity and color centers), 2) **Molecular orbital theory** (cause of color: charge transfer, organic material), 3) **Band theory** (Conductors, semiconductors and doped semiconductors) and 4) **Physical optics** (dispersion, scattering, interference and diffraction). We will apply crystal field theory (CFT) in the present investigations.

The complex behavior of minerals, fossils and herbs can be understood by employing different techniques such as optical absorption, electron paramagnetic resonance (EPR), Mossbuer, IR and Raman spectroscopy studies. At present we will focus our attention on Optical absorption and EPR spectral techniques.

Electronic spectra of transition metal ions in these compounds can be studied both by optical and EPR spectra. But in optical spectroscopy, transitions proceed between orbital levels, whereas in EPR spectroscopy they take place between spin sub levels emerging in the external magnetic field following splitting of the ground state of the atom. Thus EPR spectroscopy is a natural sequel to optical spectroscopy. In EPR, detailed nature of the ground state comes under consideration since only the spin degeneracy of the lower orbital state is more sensitive in these studies. Optical spectroscopy supports the EPR analysis and also gives information of the higher energy states. Thus optical absorption not only supplements but also complements the EPR results [2].

Free transition metal ions have unfilled d-shells and d-d transitions are forbidden. However, when the transition metal ions are embedded in crystal lattice, the degeneracy of the d-levels is removed and they split into various energies. The study of the nature of splitting and position of the absorptions in EPR and optical spectra of the transition metal ions in solid state reveal the site symmetry of the transition metal ion and the nature of the surrounding ligands. Further, it gives an evidence on the oxidation state of transition metal ion [3].

Copper systems

EPR spectra: Copper(II) complexes in an octahedral ligand field environment produce a 2E_g ground state which is unstable due to Jahn-Teller distortion. The distortion results in lowering of symmetry and energy of the compound. The Jahn-Teller distortion normally observed is a tetragonal elongation along the Z axis or contraction in the equatorial x, y plane ultimately resulting in a square planar ligand environment as in D_{4h} shown in Fig. 1.

Fig. 1 . Distorted octahedral (tetragonal) environment

The d orbital splitting experimentally observed for D_{4h} from optical spectroscopy is given in Fig. 2.[4].where the highest-energy of the half occupied orbital is $d_{x^2-y^2}$ as it has the largest repulsive interaction with the ligands in the equatorial plane.

Fig. 2 Energy level diagram of d-orbitals in different environments

The unpaired electron in this produces the EPR spectrum as shown in Fig. 3

Fig. 3. EPR signals of Cu(II) in tetragonal distortion

Here g_{11} (corresponding to the magnetic field oriented along the z axis of the complexes) $> g_{\perp} > 2.00$ is a characteristics of the $d_{x^2-y^2}$ ground state. Additionally copper has a nuclear spin of $3/2$ which couples the electron spin to produce a four line hyperfine splitting of the EPR spectrum. Tetragonal cupric complexes generally have large A_{11} value than that of D_{4h} . If $g_{11} > g_{\perp}$, the ground state is ${}^2B_{1g}$, where as if $g_{\perp} > g_{11}$ or $g_{11} = 2.00$, the ground state is ${}^2A_{1g}$. Using the above data a new parameter [5] G is defined as $G = (g_{11} - g_e) / (g_{\perp} - g_e)$. If G value falls in between 3 and 5 the

unit cell contains magnetically equivalent ions. If G value is less than 3 the exchange coupling among the magnetically non-equivalent Cu(II) ions in the unit cell are not very strong. If G is greater than 5, a strong exchange coupling take place among the magnetically non-equivalent Cu(II) ions in the unit cell [6-9]. Truly compressed structures are relatively rare when compared with elongated structures. In general $g_{\perp} > g_{11}$ which is an unusual observation, implies two possibilities. 1) The concentration of copper in the complex is very high, which produces interaction between Cu(II) $\leftrightarrow$ Cu(II) ions; 2) The Cu(II) ion is in a compressed octahedron. If the complex contains low copper content, we assume that Cu(II) ion is in a compressed octahedron. Hence the ground state is ${}^2A_{1g}(d_{z^2})$ [5].

Fig. 4. EPR spectrum of Cu(II) in rhombic field.

If the EPR spectrum reveals three sets of resolved four lines in low, mid and high fields shown in Fig.4 corresponding of which give rise to g_1 , g_2 and g_3 respectively. The corresponding hyperfine structure constants (A values) are to be noted as A_1 , A_2 and A_3 . The calculated g values provide valuable information on the electronic ground state of the ion. If $g_1 > g_2 > g_3$, the quantity $R = (g_2 - g_3)/(g_1 - g_2)$ is greater than unity; the ground state is ${}^2A_{2g}(d_z^2)$ and if it is less than unity it is ${}^2A_{1g}(d_{x^2-y^2})$ [10].

Optical spectra: The electronic configuration of divalent copper is $[Ar] 3d^9$. In an octahedral crystal field, the corresponding ground state electronic configuration is $t_{2g}^6 e_g^3$ which yields 2E_g term. The excited electronic configuration, $t_{2g}^5 e_g^4$ corresponds to ${}^2T_{2g}$ term. Thus only one single electron transition ${}^2E_g \rightarrow {}^2T_{2g}$ is expected in an octahedral crystal field. Normally, the ground 2E_g state is split due to Jahn-Teller effect and hence lowering of symmetry is expected for Cu(II) ion and this state splits into ${}^2B_{1g}(d_{x^2-y^2})$ and ${}^2A_{1g}(d_{z^2})$ states in tetragonal symmetry and the excited term ${}^2T_{2g}$ also splits into ${}^2B_{2g}(d_{xy})$ and ${}^2E_g(d_{xz}, d_{yz})$ levels. In rhombic field, 2E_g ground state splits into ${}^2A_{1g}(d_{x^2-y^2})$ and ${}^2A_{2g}(d_z^2)$ whereas ${}^2T_{2g}$ splits into ${}^2B_{1g}(d_{xy})$, ${}^2B_{2g}(d_{xz})$ and ${}^2B_{3g}(d_{yz})$ states. Thus, **three bands** are expected for **tetragonal (C_{4v})** symmetry and **four bands** are expected for **rhombic (D_{2h})** symmetry [11].

The wave numbers of the three transitions in the tetragonal field are given by the following equations [12]

$${}^2B_{1g} \rightarrow {}^2A_{1g} : 4Ds + 5Dt$$

$${}^2B_{1g} \rightarrow {}^2B_{2g} : 10Dq$$

$${}^2B_{1g} \rightarrow {}^2E_g : 10Dq + 3Ds - 5Dt$$

In the above formulae, Dq is crystal field and Ds , Dt are tetragonal field parameters. The same sign of Dq and Dt indicates an axial elongation and opposite sign indicates an axial compression [13, 14]

In particular tetragonal symmetry, EPR studies can be correlated with optical data to obtain the orbital reduction parameter [15].

$$g_{11} = 2.0023 \quad (1)$$

$$g_{\perp} = 2.0023 - \frac{6\lambda K_{\perp}^2}{E[{}^2E_g(xz, yz)]} \quad (2)$$

Here $\lambda = -830 \text{ cm}^{-1}$ is the spin orbit coupling constant for free Cu(II) ion. Thus the orbital reduction parameter ($K_{\perp}$) could be evaluated.

Results and Discussion

Beaverite mineral

1) The chemical analyses of the **beaverite** mineral from USA indicate that $\text{Fe}_2\text{O}_3 = 19.13$ and $\text{CuO} = 10.74$ wt%. The EPR spectra of powdered sample of **beaverite** $[\text{Pb}(\text{Fe}^{3+}, \text{Cu}, \text{Al})_3(\text{SO}_4)_2(\text{OH})_6]$ at room temperature at X-band frequency ($\nu = 9.41097, 9.40968 \text{ GHz}$) is shown in Fig. 5. From the spectra the g values ($g_{11} = 2.42$ and $g_{\perp} = 2.097$) are obtained for Cu(II). The g value obtained at $g = 2.017$ is due to Fe(III) in the compound. It indicates that the mineral contains a very high percentage of copper than iron. As the mineral contains high percentage of copper, the hyperfine lines due to Cu(II) could not be resolved. As mentioned earlier, the observed g values are, $g_{11} > g_{\perp} > 2.00$ ($2.32 > 2.076 > 2.0023$) and hence the ground state is ${}^2B_{1g}(d_{x^2-y^2})$ [5]. Using the above data G is calculated as

$G = (g_{11} - g_e)/(g_{\perp} - g_e) = 4.4$. The G value falls in between 3 and 5 and hence the unit cell contains magnetically equivalent ions.

Fig. 5 Powder EPR spectrum of beaverite at room temperature (a) ($\nu = 9.41097$ GHz) (b) ($\nu = 9.40968$ GHz)

The optical absorption spectrum shows energies at 8350, 10480, 11550, 13125, 14535, 16255, 18848 and 21050 cm^{-1} . The optical absorption spectrum is analyzed based on chemical analysis of the compound.

Three characteristic bands of Cu(II) ion observed at 8275, 10270 and 13020 cm^{-1} in the first set and 11550, 13125 and 16255 cm^{-1} and in the second set are attributed to the same transitions from ${}^2B_{1g}$ to 2E_g , ${}^2B_{2g}$ and ${}^2A_{1g}$ respectively. Based on these assignments the octahedral field (Dq 1048, 1313 cm^{-1}) and tetragonal field (Dt 413, 632 cm^{-1} and Ds 1571, 2097 cm^{-1}) parameters are evaluated. The same sign of Dq and Dt indicates an axial elongation in the tetragonal field and also confirms the ground state.

The bands observed at 14535, 18840 cm^{-1} in the third set are assigned to the transition ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, ${}^4T_{2g}(G)$. The third at 21050 cm^{-1} is assigned to ${}^4E(G)$ transition. These bands are characteristic of Fe(III) ion occupying in octahedral symmetry in the mineral. The evaluated Racah parameters which gave good fit are $B = 700$, $C = 2800$, $Dq = 975$ cm^{-1} . By assuming $\lambda = -620$ cm^{-1} spin orbit coupling constant (for free Cu(II) is $\lambda = -830$ cm^{-1}) and using the EPR results the transitions $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{yz}$ are calculated as 11874 and 13093 cm^{-1} . These values are agreeing with the observed values (second set of energies 11550 and 13125 cm^{-1}) [16].

Chalcocite Mineral

2) The **chalcocite** [Cu_2S] mineral is black gray in color. It contains Cu = 79.8%. The EPR spectrum is shown in Fig. 6. The spectrum consists of a broad line with a small sextet and a shoulder at low field. The g value for the shoulder is calculated as 2.18 which is due to Cu(II) in the sample. The hyperfine line from either ${}^{63}\text{Cu}$ or ${}^{65}\text{Cu}$ could not be resolved since the copper content in the mineral is very high. The broad line under the sextet is due to Fe(III) impurity with a g value close to 2.0. The six hyperfine lines are having uniform intensity indicating the presence of Mn(II) impurity in the mineral. The observed g and A values are 1.997 and 7.5 mT. After the third hyperfine line, one sharp resonance line is noticed having g value of 1.998 which can be ascribed to sulphate radical. Hence the EPR analysis of the sample indicates that the paramagnetic impurities present in the mineral are Mn(II), Fe(III), Cu(II).

Fig. 6 Room temperature EPR spectrum of chalcocite ($\nu = 9.40657$ GHz)

For easy analysis of the optical absorption spectrum of covellite mineral, the bands are divided into two sets as 8275, 10270, 13070, 17335 cm^{-1} as first set, and 11855, 15200, 23310 cm^{-1} as the second set. The spectral features are similar to Cu(II) and Fe(III). The first set of bands at 8275, 10270, 13070, 17335 cm^{-1} in the UV-Vis region are assigned to Cu(II) in rhombic symmetry. The optical absorption bands observed for Cu(II) in chalcocite at 17335, 13070, 10270, 8275 cm^{-1} are attributed to the transitions from ${}^2A_{1g}(d_{x^2-y^2})$ to ${}^2A_{2g}(d_z^2)$, ${}^2B_{1g}(d_{xy})$, ${}^2B_{2g}(d_{xz})$, ${}^2B_{3g}(d_{yz})$ respectively. The bands accordingly are ascribed to Cu(II) in octahedral coordination with rhombic distortion (D_{2h}) symmetry. [17]

Vogelite mineral

3) Generally, whenever a mineral is formed under the earth's crust, the nearby impurities will enter the mineral in various locations such as interstitial, substitutional or both. The mineral **vogelite** contains CaO = 14.72, $\text{UO}_2 = 35.44$, CuO = 10.44 Wt%. EPR spectrum of the **vogelite mineral** $\{\text{Ca}_2\text{Cu}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{CO}_3)6\text{H}_2\text{O}\}$ recorded at room temperature is given in Fig. 7. It is well known that the EPR studies of transition metal ion, Mn(II), is easily observed at room temperature, even if present in minute levels, compared to other ions. The spectra clearly indicate the presence of Mn(II) in the sample.

Fig. 7 contains a strong sextet at the centre of the spectrum corresponding to the electron spin transition $+1/2 \rightarrow +3/2$. Generally, in most of the cases, the powder spectrum is characterized by a sextet, corresponding to this transition. The other four transitions, corresponding to $|\pm 5/2\rangle \leftrightarrow |\pm 3/2\rangle$ and $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ are not seen due to their high anisotropy in D . If $E \neq 0$, the EPR spectrum will not be symmetrical about the central sextet. From the powder spectrum of the mineral, the following parameters have been calculated: $g = 1.997$, $A = 9.6$ mT and $D = 31.6$ mT. The large value of D indicates a considerable amount of distortion around the central metal ion. The approximate value of hyperfine constant (A) is calculated by using covalency (C) equations as 91×10^{-4} cm^{-1} . This calculated value agrees well with the observed hyperfine constant for the sample indicating

ionic character for Mn-O bond in the mineral under study. The number of ligands around Mn(II) ion is estimated using the covalency equation for C [18]

$$C = \frac{1}{n} [1 - 0.16(X_p - X_q) - 0.035(X_p - X_q)^2]$$

Here X_p and X_q represent electronegativities of metal and ligand. Assuming $X_p = X_{Mn} = 1.4$ and $X_q = X_O = 3.5$, the number of ligands (n) obtained are 30. This suggests that Mn(II) may be surrounded by six CO_3^{2-} .

EPR spectrum of mineral reveals that in between third and fourth manganese hyperfine resonance lines a very sharp peak at (33.5 mT) having a g value 2.001 and a peak at (32.6 mT) having a g value 2.063, are observed. These can be ascribed to a radical such as CO_3^{2-} , because the mineral contains CO_3 as a constituent. The absence of any super hyperfine structure in the radical suggests that the radical may be CO_3^{2-} .

To know the ions which are responsible for low field resonances in the spectrum, amplitude is changed from 10 to 100 without change in magnetic field scale and the same is recorded as above (Fig.7) on left side. The overall spectrum is normally symmetric with two components of g . From the spectrum the g values obtained are $g_{11} = 2.27$ and $g_{\perp} = 2.20$. As the mineral contains a very high percentage of copper the hyperfine lines due to Cu(II) could not be resolved. Here $g_{11} > g_{\perp} > 2.00$ ($2.27 > 2.20 > 2.00$) and hence the ground state is $^2B_{1g}(d_{x^2-y^2})$. A weak resonance centered at $g = 2.39$ in the EPR spectrum is attributed to the presence of isolated Fe(III) ion incorporated as an impurity in the mineral.

Fig. 7. EPR spectrum of voglite mineral recorded at (RT) temperature ($\nu = 9.38253$ GHz)

Synthetic organic compound

4) We report the synthesis and characterization of rare **compressed Copper complex of organic ligand** derived from 2, 5-Dimercapto1,3,4-thiadiazole pthlimide complex of Cu(II) by spectroscopic techniques. It may find the application in the field of anti-microbial activities. The mixture of 2,5-Dimercapto1,3,4-thiadiazole (0.60096g (4 mmol), Aldrich), pthlimide

(0.5884g (4mmol), SD fine) and $CuCl_2$ (2mmol) was stirred for 1 min and then irradiated with microwaves (used a domestic LG microwave oven Grill model Mc 8083 MLR) at 200W for 10-12 min. After completion of the reaction the brown colour solid obtained. It was washed thoroughly with ethanol and dried *in vacuo*.

Room temperature powdered EPR spectrum of the organic complex is shown in Fig. 8.

Fig.8. Room temperature EPR spectrum of organic sample

The overall spectrum of the complex is normally symmetric with two components of g values. From the spectrum the g values obtained are $g_{\perp} = 2.16$ and $g_{11} = 2.026$ with $A_{11} = 9.3$ mT. Truly compressed structures are relatively rare when compared with elongated structures. In the present case $g_{\perp} > g_{11}$ which is an unusual observation, implies two possibilities. 1) The concentration of copper in the complex is very high, which produces interaction between $Cu(I)$ and $Cu(II)$ ions; 2) The $Cu(II)$ ion is in a compressed octahedron. Since the complex contains high [Cu = 9.14 wt%] copper content, we assume that $Cu(II)$ ion is in a compressed octahedron. Hence the ground state is $^2A_{1g}(d_{z^2})$. The sharp low intensity peak at 33.5 mT, having a g value of 1.99 can be ascribed to a radical formed with carbon or nitrogen. The absence of any super hyperfine structure in the radical suggests that the radical may be CO_3^- .

Atacamite mineral

5) The compositional analysis of *atacamite* [$\text{Cu}_2(\text{OH})_3\text{Cl}$] indicates that Cu = 15.05 and CuO = 55.43 Wt%. The EPR spectrum of *atacamite* is shown in Fig. 9. It reveals three sets of resolved four lines in low, mid and high fields corresponding to g_1 , g_2 and g_3 respectively. From the peak positions and their separations the g values evaluated as $g_1 = 2.191$, $g_2 = 2.010$ and $g_3 = 1.92$. The hyperfine structure constants (A values) are determined as $A_1 = 11.0$ mT, $A_2 = 3.0$ mT and $A_3 = 5.0$ mT. The calculated g values provide valuable information on the electronic ground state of the ion. If for g values $g_1 > g_2 > g_3$ the quantity $R = (g_2 - g_3)/(g_1 - g_2)$ is greater than unity, the ground state is $^2A_{2g}(d_z^2)$ and if it is less than unity it is $^2A_{1g}(d_{x^2-y^2})$. In the present study the value of $R = 0.50$ which is less than unity and thus $^2A_{1g}(d_{x^2-y^2})$ is the ground state for Cu(II) ion in *atacamite*. From the spin-Hamiltonian parameters, the dipolar term (P) and the Fermi contact term (k) are calculated as $k = 0.3$. The value of P obtained is 0.38 cm^{-1} . The value of α^2 was found to be 0.28. The bonding parameter α^2 would be close to unity for ionic bonding between the central metal ion and the ligands and decreases with increasing covalency. In the present case the value is far less than unity indicating reasonably high percentage of covalent bonding [19, 20].

Fig.9 Powder EPR spectrum of *atacamite* at room temperature

Conclusions

Crystal field theory is applied to minerals for explaining their structural properties. EPR spectra of minerals show numerous signals due to the presence of more than one metal ion in the compound.

The chemical analysis of the *beaverite* sample indicate that iron and copper ($\text{Fe}_2\text{O}_3 = 19.13$ and $\text{CuO} = 10.74$ wt %) being a major constituent of the mineral with copper as minor constituent. The optical absorption spectrum of mineral is due to copper and iron. Copper is present in two sites. The two metal ions are in distorted octahedron environment. Near infrared spectra is due to water fundamentals and supports the formula of the mineral. The EPR results confirm the presence of copper in +2 state with tetragonally distorted environment in the mineral and iron is in +3 state in distorted octahedron. Further divalent copper in the unit cell contains magnetically equivalent ions. The EPR results and optical absorption

spectral results are in agreement. Due to high concentration of copper, two sites noticed in optical spectrum are not resolved in EPR spectrum.

Chalcocite [Cu_2S], is a mono sulphide of copper which contains 79.8 % of copper. The EPR studies confirm the presence of Fe(III), Mn(II), Cu(II) and a free radical sulphate. Optical absorption spectrum is due to Cu(II) which is in rhombic symmetry and whereas Fe(III) is in octahedral environment. Mid-infrared spectral studies are indicative of combination over tones and combination tones of water fundamentals and sulphate ligands.

The optical absorption spectrum of mineral *voglite* is due to copper only which is in a distorted octahedron environment. The EPR results confirm the presence of copper as its constituent and manganese and iron as impurities in the mineral. Further it is evident from the chemical analysis that copper is present in higher concentration. EPR results are suggesting Mn(II) impurity might have entered the lattice in place of Ca(II). The optical absorption spectrum is due to only Cu(II) and charge transfer bands are explained basing on electro negativities and are supporting that spectrum is due to Cu(II) only but not either manganese or iron impurity. NIR results confirm the presence of water fundamentals, which also supports the formula of the mineral.

The optical absorption spectrum of the **synthetic organic compound** is due to copper only which is in a distorted octahedron environment. The EPR results confirm the presence of copper in the compound. EPR results are suggesting Cu(II) impurity might have entered the ring and have compressed by surrounded ligands. The optical absorption spectrum is due to only Cu(II) and charge transfer bands are explained based on electro negativities. NIR results confirm the presence of water fundamentals.

The EPR results confirm the presence of copper in +2 state with distorted rhombic environment in *atacamite* mineral. The EPR results and optical absorption spectral results agree well with the earlier reported data. In the *atacamite* mineral the experimental results suggest that predominant covalent bond exists between metal ion and ligand.

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