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Optical absorption and EPR studies on enargite

S. LAKSHMI REDDY ¹, N.C. GANGI REDDY ², G. SIVA REDDY ², B. JAGANNADHA REDDY ³ AND RAY L. FROST ^{3*}

1. Dept. of Physics, S.V.D. College, Kadapa 516 003, India
2. Dept. of Chemistry, S.V.U.P.G. Centre, Kadapa 516 003, India
3. Inorganic Materials Research Program, Queensland University of Technology, 2 George Street, Brisbane, GPO Box 2434, Queensland 4001, Australia

The behaviour of transition metal ions in enargite have been studied by electron paramagnetic resonance and absorption spectroscopy in the UV-Vis and NIR regions.

The ground state of Cu(II) ion in enargite is confirmed as ${}^2B_{1g}$ since $g_{||} > g_{\perp}$ ($2.54 > 2.11$).

Three characteristic bands observed in the optical absorption spectra at 8275, 13105 and 18420 cm^{-1} are assigned to the transitions, ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_2$ and ${}^2B_{1g} \rightarrow {}^2E_g$ of Cu(II) ion in tetragonal field. The presence of Fe(II) bands is an evidence for iron impurity in the mineral.

Keywords: Enargite; Electron paramagnetic resonance; Near-infrared spectroscopy; Optical absorption

1. Introduction

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P: +61 7 3864 2407 F: +61 7 3864 1804

Copper group minerals are interesting because that have gained the attention of many researchers due to their growing technological importance and desirable applications in several branches of science and technology. Copper exhibit interesting spectroscopic properties. Electronic and magnetic properties of these minerals depend on the oxidation state and its environment in the compound. These minerals can be studied using electron paramagnetic resonance (EPR) and optical absorption spectroscopy.

Optical absorption studies of these minerals give rise to ligand field absorption energies, which sensitively reflect the distortion of cubic, octahedral and tetrahedral co-ordinations.

The Cu(II) [(Ar)d⁹] is a transition metal ion that readily forms stable complexes.

It is equivalent to single positive charge in the 3d shell. Hence basic ideas of crystal field theory will be checked in naturally occurring minerals. Enargite is an important ore of copper. It occurs in association with pyrite, sphalerite, galena, bornite, tetrahedrite-tennantite, chalcocite, covellite, quartz and barite. [1]. Enargite, Cu₃[AsS₄] is orthorhombic and belongs to the space group Pmn2₁. The unit cell parameters a = 0.7407, b= 0.6436 and c = 0.6154 nm. The mineral contains impurities of Sb, Se and Fe.

Enargite is related to the rare mineral, wurtzite and structure is derived from the structure of wurtzite [2]. Semiconducting properties of natural samples of enargite were studied [3]. The chemical analyses of the sample from different localities indicate no marked variation in copper content which is about 48 % and iron content is up to 1.2 %.[1, 2]. In this study the authors made an attempt to determine the valency state of copper and iron and the site symmetry using EPR and optical absorption spectroscopic features of enargite.

2. Experimental

Grayish black to iron black colored enargite sample originated from Sierra de Famatina, lo Riajo, Argentina is used in the present investigations. EPR spectra of the powdered sample are recorded at room temperature (RT) on JEOL JES-TE100 ESR spectrometer operating at X-band frequencies ($\nu = 9.41233$ GHz), having a 100 KHz field modulation to obtain a first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g factor calculations. Optical absorption spectrum of the compound is recorded at RT on Carey 5E UV Vis-NIR spectrophotometer in mull form in the range 200-2000 nm.

3. Theory

The electronic configuration of Cu(II) is $[\text{Ar}] 3d^9$. 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 [4].

The wave numbers of the three different transitions are given by the following equations in the tetragonal field are [5]

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

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

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

In the above formulae Dq is crystal field and Ds, Dt are tetragonal field parameters.

These are defined as
$$Dq = \left(\frac{1}{6}\right)Ze^2 \left(\frac{r^{-4}}{a^5}\right) \quad (4)$$

$$Dt = \left(\frac{2}{21}\right)Ze^2 r^{-4} \left(\frac{1}{a^5} - \frac{1}{b^5}\right) \quad (5)$$

$$Ds = \left(\frac{2}{7}\right)Ze^2 r^{-2} \left(\frac{1}{a^3} - \frac{1}{b^3}\right) \quad (6)$$

Where r^{-2} and r^{-4} are interpreted as mean square and mean fourth power radii of the metal orbitals. The a and b are represented in terms of bond length differences for axial and equatorial bonds [6].

The ground state configuration of Fe(II) ion is $3d^6$. The configuration can be expressed as $t_{2g}^4 e_g^2$ for high spin octahedral field. Hence, the energy states are ${}^5T_{2g}$, 3E_g , ${}^3T_{2g}$ and some more triplets and singlets of which ${}^5T_{2g}$ forms the ground state. The other excited configurations, such as $t_{2g}^3 e_g^3$ gives rise to a several triplet and singlet states and one quintet state designated as 5E_g . Thus the spin allowed transition ${}^5T_{2g} \rightarrow {}^5E_g$ is expected to be strong and all other spin forbidden transitions are very weak [7,8]. Thus, the ${}^5T_{2g} \rightarrow {}^5E_g$ transition gives an intense, but broad absorption band. Often this band splits into two in an octahedral environment. The splitting of this band may be explained in terms of one or more of the following: (i) spin orbit coupling, (ii) static distortion of the

octahedron and (iii) dynamic Jahn-Teller effect [9]. If the splitting is due to spin orbit coupling, the splitting value is about 100 cm^{-1} . On the other hand, if the splitting is of the order of 2000 cm^{-1} , then it is due to static distortion of octahedron [9-11]. An intermediate value between 100 and 2000 cm^{-1} indicates a dynamic Jahn-Teller effect in the excited 5E_g state [12, 13]. In the latter case, the energy level split symmetrically to the centre of gravity and the average of these levels are to be taken as $10Dq$ value.

4. Results and discussion

4.1 UV-Vis and NIR spectroscopy

The Near-IR spectral regions are divided into two regions (a) high wavenumber region $>8000\text{ cm}^{-1}$ where bands appear due to electronic transitions and (b) low wavenumber region $7900\text{-}5000\text{ cm}^{-1}$ bands are of vibrational origin. The bands in the Near-IR spectrum are shown in the figure 1 and the optical absorption spectrum of the sample is shown in figure 2. Four bands in the high energy region of NIR spectrum are due to electronic transitions. Ferrous ion complexes derive strong bands in NIR. Here the appearance of two broad bands with weak intensity at 9200 and 10900 cm^{-1} indicates low concentration of iron in the mineral. The average of these bands is a known as $10 Dq$ band for Fe(II) ion and is assigned to ${}^5T_{2g} \rightarrow {}^5E_g(D)$ [8]. Tanabe-Sugano diagram of d^6 configuration is used to assign the transitions of other bands [14]. Relatively one sharp band at 11855 cm^{-1} and two other bands in the UV-Vis spectrum (figure 2) at 15500 and 22730 cm^{-1} are assigned to ${}^5T_{2g} \rightarrow {}^3T_{1g}(H)$, ${}^5T_{2g} \rightarrow {}^3T_{2g}(H)$ and ${}^5T_{2g} \rightarrow {}^3E_g(G)$

respectively. The energy matrices of d^6 configuration are solved for different values of Racah parameters Dq , B and C . The parameters that give good fit to the experimental data is $Dq = 1005$, $B = 890$ and $C = 3925 \text{ cm}^{-1}$. The band headed data and their assignments along with the calculated values are also presented in table 1. Three characteristic bands of Cu(II) ion observed at 8275 , 13105 and 18420 cm^{-1} are attributed to the transitions from ${}^2B_{1g}$ to 2E_g , ${}^2B_{2g}$ and ${}^2A_{1g}$ respectively. Based on these assignments the octahedral field (Dq) and tetragonal field (Dt and Ds) parameters are evaluated to be $Dq = 1311$, $Ds = 1941$ and $Dt = 102 \text{ cm}^{-1}$ using the formulae given in theory. The same sign of Dq and Dt indicates an axial elongation in the tetragonal field and also confirms the ground state [15, 16]. These values are in good agreement with the earlier reported data [17-20]. These parameters are compared with different copper bearing minerals that are given in table 2. Using the formulae given in the theory the radius of the metal orbital (r) is estimated to be 0.78 \AA which is agreeing with the theoretical value of Cu(II) ionic radius 0.72 \AA [21].

Vibrational spectrum in the low wavenumber region $7900\text{-}5000 \text{ cm}^{-1}$ (Figure 1) contains many significant absorption features. Three strong bands with components located at ~ 6700 , 5800 and 5200 cm^{-1} are due to molecular water. Water in fluid inclusions in the enargite probably causes these bands [22].

4.2 EPR Spectra

The EPR spectrum of powdered sample of enargite is shown in figure 3. The over all

spectrum is normally symmetric with two components of g . From the spectrum the g values obtained are $g_{11} = 2.54$ and $g_{\perp} = 2.11$. As the mineral contains a very high percentage of copper the hyperfine lines due to Cu(II) could not be resolved. However the g values are in agreement with previously reported data. [23, 24]. 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 ${}^2A_{1g}$. Further tetragonal cupric complexes with D_{4h} generally have g_{11} (corresponding to the magnetic field along the Z axis of the complexes) $> g_{\perp} > 2.04$ have the ground state $d_{x^2-y^2}$ [25-27]. In the present case $g_{11} > g_{\perp} > 2.00$ ($2.289 > 2.044 > 2.00$) and hence the ground state is ${}^2B_{1g}$ ($d_{x^2-y^2}$).

The EPR results can be correlated with optical data to obtain orbital reduction parameters using the formulae [24] $g_{11} = 2.0023 - \left(\frac{8K_{11}^2\lambda}{\Delta E_1} \right)$ and

$$g_{\perp} = 2.0023 - \left(\frac{2K_{\perp}^2\lambda}{\Delta E_2} \right). \quad (7)$$

Here $\lambda = -830 \text{ cm}^{-1}$ spin orbit coupling constant for free Cu(II) ion. ΔE_1 and ΔE_2 are the energies corresponding to the transitions $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{yz}$. Thus the orbital reduction parameters are evaluated as $K_{11} = 1.03 \text{ cm}^{-1}$ and $K_{\perp} = 1.93 \text{ cm}^{-1}$. Using the above data a new parameter [28] G is defined as

$$G = (g_{11} - g_e) / (g_{\perp} - g_e) = \left(\frac{4K_{11}^2\Delta E_2}{K_{\perp}^2\Delta E_1} \right) = 5.0. \quad (8)$$

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. [29-32]. In the present case $G = 5.0$ indicate that the unit cell contains magnetically equivalent ions.

The orbital reduction parameters r_{11} and r_{\perp} predict the covalency for Cu(II) ion of ligand bands [32]. For Cu(II) ion with $d_{x^2-y^2}$ ground state and having axial symmetry we

have

$$g_{11} = g_e - \left(\frac{8K_{11}^2 \lambda R_{11}}{\Delta E_1} \right) = g_e - \left(\frac{8r_{11}^2 \lambda}{\Delta E_1} \right) \quad (9)$$

$$g_{\perp} = g_e - \left(\frac{2K_{\perp}^2 \lambda R_{\perp}}{\Delta E_2} \right) = g_e - \left(\frac{2r_{\perp}^2 \lambda}{\Delta E_2} \right) \quad (10)$$

The reduction parameters are related to R_{11} and R_{\perp} as

$$r_{11} = (R_{11})^{\frac{1}{2}} K_{11} \quad \text{and} \quad r_{\perp} = (R_{\perp})^{\frac{1}{2}} K_{\perp}$$

The values obtained are $r_{11} = 1.03 \text{ cm}^{-1}$ and $r_{\perp} = 1.093 \text{ cm}^{-1}$ respectively.

5. Conclusions

The optical absorption spectrum of mineral enargite is due to copper and iron. The two metal ions are in distorted octahedron environment. The EPR results confirm the presence of copper in +2 state with tetragonally distorted environment in the mineral. It is also confirmed from chemical analysis that copper being a major constituent of the mineral with Fe as impurity.

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Figure 2. Optical absorption spectrum of enargite in the UV-Vis region.

Figure 3. Room temperature EPR spectrum of enargite ($\nu = 9.41233$ GHz).

Table1. Observed and calculated energies of the bands with their assignments in enargite.

Assignment	Band positions		
	Observed		Calculated
	Wavelength (nm)	Wavenumber (cm ⁻¹)	Wavenumber (cm ⁻¹)
a) Fe(II) transitions:-			
⁵ T _{2g} → ⁵ E _g (D)	1087	9200*	10050
	917	10900*	
⁵ T _{2g} → ³ T _{1g} (H)	843	11855	11818
⁵ T _{2g} → ³ T _{2g} (H)	645	15500	15534
⁵ T _{2g} → ³ E _g (G)	440	22730	23295
b) Cu(II) transitions:-			
² B _{1g} → ² A _{1g}	1209	8275	8275
² B _{1g} → ² B _{2g}	763	13105	13105
² B _{1g} → ² E _g	543	18420	18418

* average of these two bands: 10050 cm⁻¹

Table 2. Comparison of octahedral and tetragonal field parameters (cm^{-1}) for Cu(II) in different compounds.

Compound	Dq	Ds	Dt	Reference
Cornetite	1257	1434	380	[17]
Aurichalcite	1250	1600	520	[18]
NH_4Cl	1360	2000	140	[19]
$\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$	1333	1565	380	[20]
Enargite	1311	1941	102	Present work