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EPR and optical absorption studies of Cu^{2+} ions doped magnesium citrate decahydrate single crystals

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ABSTRACT

X-band electron paramagnetic resonance (EPR) studies of Cu^{2+} ions in magnesium citrate decahydrate single crystals are done at room temperature. Detailed EPR analysis indicates the presence of only one Cu^{2+} site. Cu^{2+} is found to take up substitutional position at Mg site. The angular variation of the EPR spectra in three planes a^*b, bc and ca^* are used to determine principal g and A tensors. The spin Hamiltonian parameters are: $g_x = 2.0346$, $g_y = 2.1400$, $g_z = 2.3874$, $A_x = 57$, $A_y = 76$, $A_z = 99$ ($\times 10^{-4}$) cm^{-1}. The optical absorption study is also carried out at room temperature and absorption bands are assigned to various transitions. The theoretical band positions are estimated using energy expressions and a good agreement is obtained with the experimental values. By correlating EPR and optical data, different molecular orbital coefficients are evaluated and the nature of bonding in the complex is discussed.

1. Introduction

EPR study enables to understand the symmetry of the electric field produced by the ligands around the metal ion [1–7]. It also provides a detailed description of the ground state of paramagnetic ion. The optical absorption study gives energy level structure of the metal ion. Thus, EPR and optical absorption yield crystal field symmetry around the metal ion and the nature of bonding between the metal ion and its various ligands. Citrates have many biological and medical applications [8,9] and thus any information obtained about their growth and characterizations are very useful. In the systematic study on the growth and characterization of several citrates, use has been made of EPR as one of the tools. Magnesium citrate is used to treat constipation. It is a hyperosmotic saline laxative. It pulls water from the tissues into the small intestines. The movement of water stimulates the normal forward movement of the intestines. It can cause certain medicines to not work as well like blood thinners, etc. [10]. If one is taking opioid, he will need to take laxatives regularly to counter their action on the bowel. Magnesium citrate helps relax muscles and aids in fighting depression. It is essential for the maintenance of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). It promotes cardiovascular health, works with vitamin B6 in alleviating premenstrual syndrome (PMS) and aids in tissue respiration [11]. It is also used to treat asthma and emphysema, attention deficit/hyperactivity disorder, type 2 diabetes, fibromyalgia, high blood pressure, human immunodeficiency virus (HIV), infertility and miscarriage, menopause, migraine headache, osteoporosis, etc. [12]. Urinary calcium excretion is reduced significantly by magnesium citrate in animals fed on high-calcium diets [9]. Significant advances have been made recently in the field of non-linear optics in the area of optoelectronic device technologies. Organic materials are quite relevant in this context because the delocalized electronic structure of π-bonded organic compound provides a number of opportunities in applications as non-linear optical materials [13]. Numerous uses of magnesium citrate mentioned above indicate that the synthesis and characterization of such a compound will be of immense importance. EPR studies of Cu^{2+} ion in sodium citrate [6], vanadyl ion in trisodium citrate [14] as well as triammonium citrate [15] were reported earlier. The present study deals with the results of EPR and optical absorption of Cu^{2+} ions doped in magnesium citrate decahydrate (MCD) single crystal at room temperature. The purpose of the study is to find the spin Hamiltonian parameters, crystal field symmetry and energy level structure of the metal ion and nature of bonding of the metal ion with different ligands that provides information about its technical application.

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2. Crystal structure

The crystal structure of MCD was studied by Johnson [16]. The crystals are monoclinic and belong to space group $P2_1/n$. The unit cell dimensions are $a = 20.222$ Å, $b = 6.686$ Å and $c = 9.135$ Å and $\beta = 96.86^\circ$. The unit cell contains two $[Mg(H_2O)_6]^{2+}$ ions and four units of $[MgC_6H_5O_7(H_2O)]_2^- \cdot 2H_2O$. Each magnesium ion is coordinated to six oxygen atoms and there are no shared edges or corners between the two coordination octahedra. The magnesium at the center of symmetry, Mg (1), is a completely hydrated cation $[Mg(H_2O)_6]^{2+}$ and does not coordinate with the citrate oxygen atoms. The citrate ion is chelated to Mg (2) in a tridentate manner with the hydroxyl oxygen atom O (7) and two carboxyl oxygen atoms, one [O (4)] from an end carboxyl and one [O (5)] from the central carboxyl, forming the three points of attachment. The remaining three oxygen atoms of the second octahedron are a water oxygen atom [O (8)] and two carboxyl oxygen atoms [O (2′) and O (1″)] of two other citrate ions. These are related to the first by a b-lattice translation and by a two-fold screw operation, respectively. Only one water molecule [O (12)] is not coordinated to a magnesium.

3. Experimental

Single crystals of MCD, $[Mg(H_2O)_6][MgC_6H_5O_7\ (H_2O)]_2 \cdot 2H_2O$ were grown by slow evaporation of the saturated aqueous solution. The Cu^{2+} impurity was added by mixing 0.01 mole% of cupric chloride to the solution. After a few days, good single crystals of Cu^{2+} doped magnesium citrate decahydrate with well-developed faces were obtained. EPR spectra were recorded on X-band Varian E-4 spectrometer with 100 kHz field modulation at room temperature. A Varian flux meter with proton probe having 0.2 cm^3 of 0.25 M solution of $GdCl_3$ in H_2O was used for magnetic field measurement along with a Hewlett-Packard frequency counter . The measurement of EPR spectra are carried out by rotating the crystal about the three mutually perpendicular axes a^*, b and c in steps of 10°. The optical absorption spectra were recorded on a Unicam 5625-UV/vis spectrophotometer at room temperature in the wavelength range 195–325 and 325–1100 nm.

4. Results and discussion

The EPR spectra of Cu^{2+} doped MCD consist of four hyperfine lines as shown in Fig. 1. As given in the crystal structure, the unit cell contains two molecules per unit cell and hence two sets of four hyperfine lines should be observed. The observation of only one set

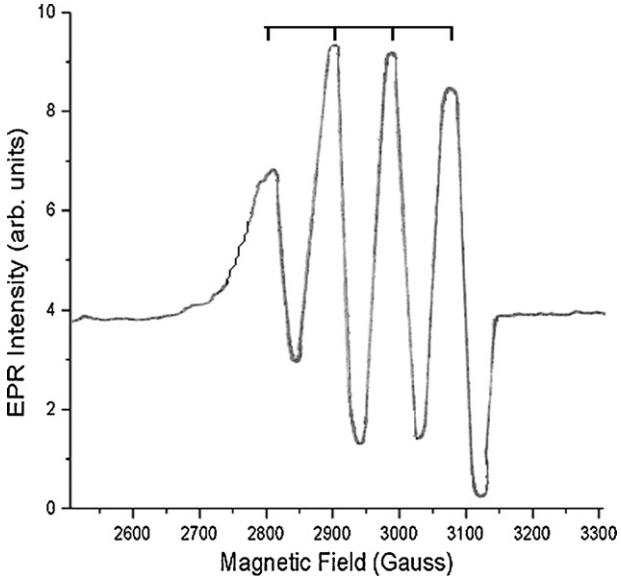

Fig. 1. EPR spectra of Cu^{2+} doped in magnesium citrate decahydrate when magnetic field is along a^* axis.

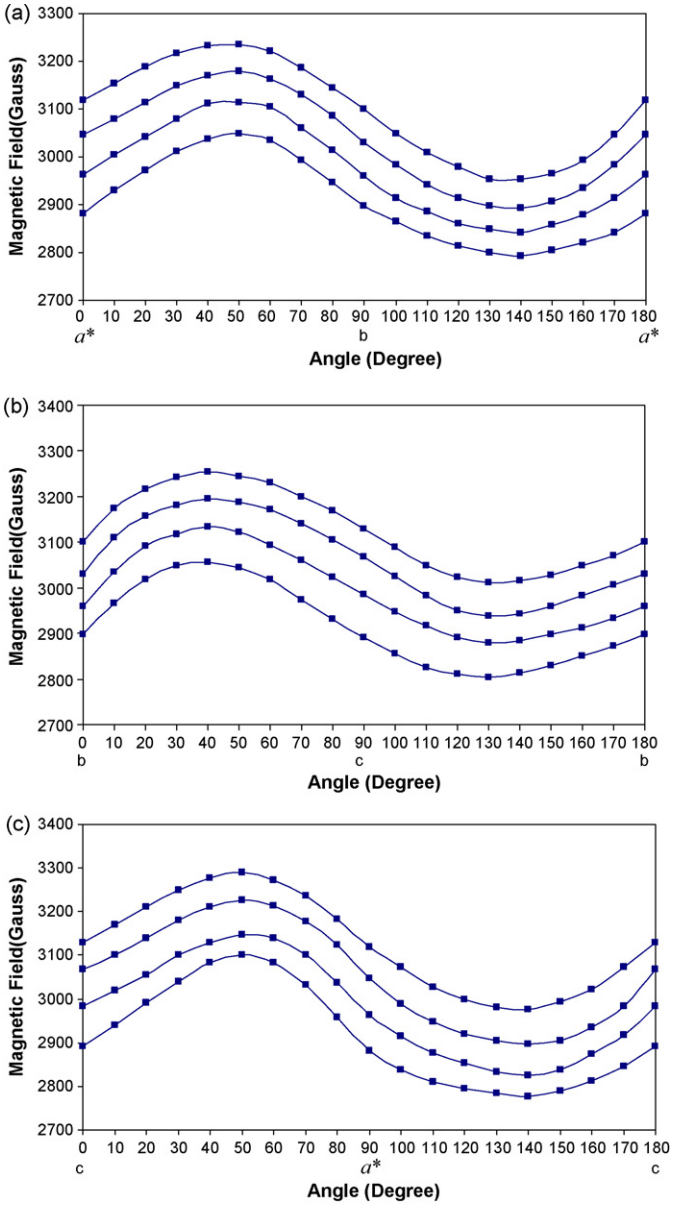

Fig. 2. (a) Angular variation of EPR spectra of Cu^{2+} ion in magnesium citrate decahydrate crystal for rotation in a^*b plane. (b) Angular variation of EPR spectra of Cu^{2+} ion in magnesium citrate decahydrate crystal for rotation in bc plane. (c) Angular Variation of EPR spectra of Cu^{2+} ion in magnesium citrate decahydrate crystal for rotation in ca^* plane.

of four hyperfine lines, thus indicates the presence of single Cu^{2+} ($S = 1/2$, $I = 3/2$) site in the lattice. Fig. 2(a–c) shows the variation of hyperfine lines in the three planes a^*b, bc and ca^*, respectively. The angular variation plots of g^2 (Fig. 3) indicate a rhombic local electric field symmetry for Cu^{2+} in MCD lattice. From the angular variation of the hyperfine pattern upon rotation about the a^*, b and c axis the principal values of g and A tensors for Cu^{2+} in MCD were evaluated by Schonland procedure [17] with the spin Hamiltonian:

$$H = \mu_B B_g S + S.A.I \quad (1)$$

The evaluated spin Hamiltonian parameters are given in Table 1. The values of these parameters of Cu^{2+} are similar to the results of earlier workers [18,19].

The Cu^{2+} ion can enter the lattice as a substitutional impurity in place of Mg. Therefore, the coordinating oxygens must determine the local electric field symmetry around the guest ion. A closer