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Electron-Spin Resonance Study of Cu(II) Doped into Zn(II) Phosphate Dihydrate and Tetrahydrate

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Introduction

As part of a study to evaluate the effect of "inner sphere" phosphate coordination on the electron-spin resonance (ESR) parameters of Cu^{2+}, magnetic dilution was attempted by coprecipitating Cu^{2+} into a series of diamagnetic, phosphate host lattices. Whereas poorly defined ESR spectra were obtained for Cu doped into the highly hydrated, noncrystalline hydroxyphosphates obtained with Mg, Ca, and Al, Cu-doped zinc phosphate formed a crystalline product with well-defined magnetic parameters. This paper reports the results of an investigation into the spectroscopic (ESR and ir) properties of Cu-doped zinc phosphate in its di- and tetrahydrate form.

Experimental Section

Hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) was prepared by reacting 500 ml of 2×10^{-2} *M* $Zn(CH_3COO)_2 \cdot 2H_2O$ – 10^{-4} *M* $Cu(NO_3)_2$ solution (0.5 mole% Cu) with a stoichiometric amount of H_3PO_4 at 353°K. The pH of the suspension was raised gradually from <2 to 4 by addition of small aliquots of 2 *M* NaOH and the precipitate aged at the same temperature for a further 2 hr (*1*). Following isolation by filtration, the product was washed twice with 300 ml of distilled water before being air-dried.

The crystalline material consisted of thin subhedral platelets containing prominent stepped etch pits (*2*), and identified as hopeite by X-ray powder diffraction. Samples heated for 16 hr at temperatures between 295 and 623°K were examined spectroscopically by standard techniques using a Varian E-104 (x-band) ESR spectrometer equipped with a E-257 Variable Temperature Accessory, and a Perkin–Elmer 281 ir spectrometer.

Results

ESR spectroscopy. Prior to thermal dehydration, powder spectra obtained at 295°K (Fig. 1) reveal that Cu doped in hopeite is able to undergo dynamic Jahn–Teller distortion (g_0 = 2.207), and that as

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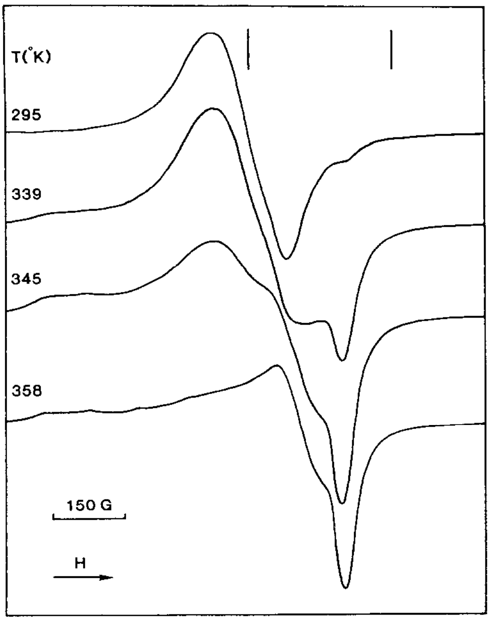

FIG. 1. Effect of increasing temperature of dehydration on the ESR powder spectrum of Cu-doped $Zn_3(PO_4)_2 \cdot 4H_2O$ obtained at 295°K. The vertical lines at low and high field represent $g_0 = 2.207$, and a strong pitch signal at $g = 2.0023$, respectively.

the sample is heated, there is a gradual transition to an anisotropic spectrum which is complete by 358°K. Corresponding spectra obtained at 153°K (Fig. 2) enable the hyperfine splitting to be resolved with the subsequent determination of magnetic parameters.

Between 295 and approximately 340°K, Cu is located in two distinct environments (Fig. 2), the more prominent characterized by parameters $g_\parallel = 2.452$, $A_\parallel = 0.0105\ \text{cm}^{-1}$ with a much diminished contribution arising from a second site ($g_\parallel = 2.457$, $A_\parallel = 0.0086\ \text{cm}^{-1}$). Deconvolution and determination of the spectral parameters for the perpendicular resonances was not possible using computer-simulation techniques. The ligand environment about copper gradually alters on further heating (340–360°K), then stabilizes in the range 360–550°K as evidenced by the appearance and persistence of a single set of spectral parameters at higher temperature with the values: $g_\parallel = 2.539$, $A_\parallel = 0.0053\ \text{cm}^{-1}$, $g_\perp = 2.107$, and $A_\perp = 0.0027\ \text{cm}^{-1}$. Temperatures higher than 550°K caused the decomposition of this second product.

Infrared spectroscopy. The ir spectrum at 295°K of the tetrahydrate (Fig. 3) has features common to other inorganic hydrated phosphate compounds (*3–5*). The broad absorption bands centered at 3300 and 1640 cm^{-1} correspond to the OH stretch and deformation modes of structural water. Their positions are consistent with the presence of a hydrogen-bonding network within the crystal lattice (*6*); however, the sharp band at 3540 cm^{-1} indicates that some OH groups do not participate in hydrogen bonding.

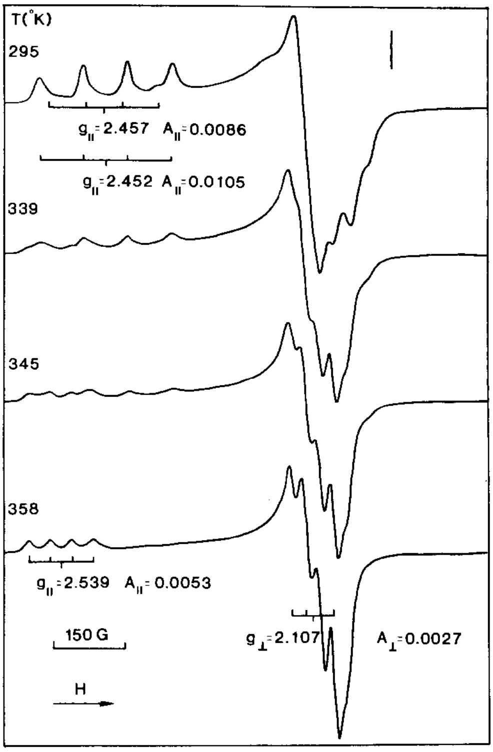

FIG. 2. Effect of increasing temperature of dehydration on the ESR powder spectrum obtained at 153°K of Cu-doped $Zn_3(PO_4)_2 \cdot 4H_2O$. The vertical line represents the free-electron resonance at $g = 2.0023$. Units for hyperfine splittings are in cm^{-1}.

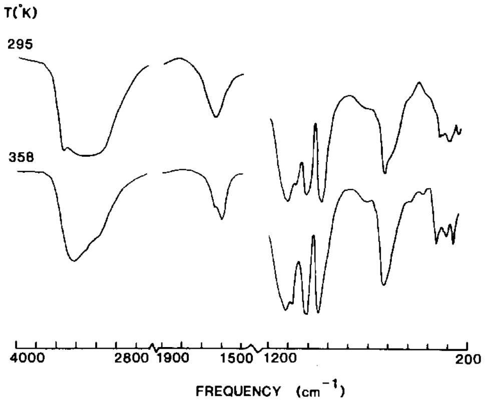

FIG. 3. Infrared absorbance spectrum of $Zn_3(PO_4)_2$ $4H_2O$ in the frequency region 200–4000 cm^{-1} at 295°K, and after heating at 358°K.

As the temperature is raised to near 360°K, the stretch and deformation modes move to higher (3440 cm^{-1}) and lower (1600 cm^{-1}) frequencies, respectively (Fig. 3). Features in the spectrum attributable to PO_4 vibrational modes are only slightly affected by heating; ν_3 shifting from 1068 to 1080 cm^{-1} and ν_1 from 939 to 949 cm^{-1}. The direction of shift in the PO_4 and OH vibrational frequencies indicates that a reduction in hydrogen bonding occurs at the higher temperature.

Discussion

Changes in the ESR and ir spectra near 360°K result from the loss of two water molecules (determined by mass difference) from the tetrahydrate structure. This conclusion is confirmed by the X-ray diffraction pattern of the zinc phosphate after dehydration at 373°K, which is in good agreement with the published pattern for $Zn_3(PO_4)_2 \cdot 2H_2O$ (*2, 7*). The loss of water molecules from zinc phosphate at temperatures <373°K has not previously been observed; however, disparity among the thermal response characteristics obtained by other workers for synthetic hopeite preparations is not uncommon (*1, 4, 8*). It has been suggested that the discrepancies may be related to the formation of distinct phases governed by the pH of the precipitating medium, with differing hydrogen atom bonding schemes, since X-ray powder diffraction data are indistinguishable for various preparations (*4*).

Single-crystal ESR studies of anhydrous KH_2PO_4 and $Ca_3(PO_4)_2$ doped with traces of Cu suggest that the crystal field effect of phosphate is not significantly different from that of other oxygen-containing ligands when bound to Cu; hence, the atypical magnetic parameters (large $g_\parallel$, $g_\perp$, and $A_\perp$; small $A_\parallel$) observed for Cu in zinc phosphate is attributable to a unique crystal geometry within the crystalline lattice (*9, 10*). Some indication of the geometry of possible environments responsible for such parameters can be obtained by reviewing hopeite structural studies. Zinc occupies two distinct crystallographic sites in hopeite, four- and six-coordinated (*4, 11, 12*). Oxygen atoms from four phosphate groups surround Zn in a distorted tetrahedral geometry. In addition, two phosphate oxygens in *cis* arrangement in combination with four oxygens from water molecules form a distorted octahedral site.

The ESR data demonstrate that the majority of the Cu^{2+} ions are located at only one of these sites in the tetrahydrate, and the magnitude of the g factors can be best accounted for if flattened tetrahedral or tetrahedrally distorted square-planar geometry is assumed. Comparison of the g values with a recent compilation of data for pseudotetrahedral complexes shows $g_\parallel$ for the dihydrate to be quite unusual, equalling the largest value yet recorded: 2.538 for a methylene bis(diphenylphosphine oxide) complex with $CuCl_2$ (*13, 14*). Similarly the increase in $g_\parallel$ from 2.452 to 2.539, and decrease in $|A_\parallel|$ from 0.0086 to 0.0053 cm^{-1} upon dehydration of the tetrahydrate to the dihydrate may be attributable to a decrease of approximately 8° in the angular distortion parameter if a distorted D_{2d} symmetry is assumed and the Cu^{2+} electronic interaction parameters remain unaltered on deformation (*15*). In effect, perturbation of the ligand environment following dehydration appears to shift Cu from a flattened tetrahedral to a less-distorted tetrahedral symmetry with a deformation angle near 60° (the deformation angle for undistorted tetrahedral symmetry is 54.7°). Crystal field theory predicts that Cu^{2+} should favor octahedral to tetrahedral coordination, suggesting that the $g_{\parallel} = 2.45$ spectrum of hopeite can be attributed to Cu^{2+} in severely flattened tetrahedral (i.e., distorted square-planar or octahedral) sites. Since natural hopeite appears to have a deficiency of Zn^{2+} in the octahedral site (*4*), Cu^{2+} may be able to occupy a fraction of these sites in the synthetic mineral.

Upon the dehydration of hopeite, Cu^{2+} appears to be forced into more nearly tetrahedral coordination ($g_{\parallel} = 2.54$) of the dihydrate. While the crystal structure of the dihydrate is not known, the loss of water from hopeite presumably results in an elimination of the distorted octahedral sites.

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