# AN ELECTRON SPIN RESONANCE AND OPTICAL STUDY OF TURQUOISE[1]

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## Abstract

A study was made of the $Cu^{2+}$ ions in turquoise. The electron spin resonance spectrum was a powder pattern which provided the g-factors $g_1 = 2.043$, $g_2 = 2.135$, and $g_3 = 2.373$. The optical spectrum was a poorly resolved triplet with lines centered near 11, 13.5 and $15 \times 10^3$ cm$^{-1}$. A fourth line was found in the infrared region at $6.1 \times 10^3$ cm$^{-1}$. The ESR and optical spectra were found to be consistent with crystal field theory considerations.

## Introduction

Turquoise is a hydrated copper aluminum phosphate mineral with copper in the divalent state. Some samples contain small amounts of $Fe^{2+}$ substituted for $Cu^{2+}$, and $Fe^{3+}$ substituted for $Al^{3+}$. The paramagnetism of this mineral arises mainly from the divalent copper. In this investigation an optical and electron spin resonance (ESR) study was made of the $Cu^{2+}$ ions, and the results were interpreted in terms of the crystallographic structure.

## Experimental

The turquoise sample under study originated in Nevada, USA. The triclinic crystal structure corresponds (Cid-Dresdner, 1965) to the space group $C_1^1$, $P1$. The ion $Cu_2^+$ is in a special position with inversion symmetry, while all of the other atoms are in general positions which completely lack symmetry operations. The site symmetry of the copper atoms is important in determining the shape of the ESR spectrum.

The ESR measurements were carried out with an Alpha AL-X10 electron spin resonance spectrometer operating at X-band (9.2 GHz). All of the spectra were recorded at room temperature. The solid free radical $\alpha,\alpha'$-diphenyl-$\beta$-picryl hydrazyl (DPPH) was employed as a g-factor standard, and its signal appeared at 3286 gauss on the spectrum. The optical reflection spectra were obtained with a Cary 14 spectrophotometer equipped with a reflection accessory.

## Electron Spin Resonance Results

The electron spin resonance obtained from turquoise is shown in Figure 1. The line shape is a powder pattern resulting from a completely asymmetric g-factor (Kneubuhl, 1960). The positions of the principal g values are located on the spectrum at 2774, 3084, and 3222 gauss, and these field positions give

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$$g_1 = 2.043$$
$$g_2 = 2.135 \qquad (1)$$
$$g_3 = 2.373$$

since the DPPH signal at 3286 gauss corresponds to $g = 2.0036$. Kneubuhl's $g$-factor correction factors (Kneubuhl, 1960) were small and within the experimental error. The maximum spread in $g$-factor $g_3 - g_1 = 0.33$ is about 15 percent of the average $g$-factor

$$g_0 = \tfrac{1}{3}(g_1 + g_2 + g_3)$$
$$= 2.184 \qquad (2)$$

These values of $(g_3 - g_1)$ and $g_0$ found for turquoise are typical of those obtained in cupric compounds (Al'tshuler and Kozyrev, 1964; König,
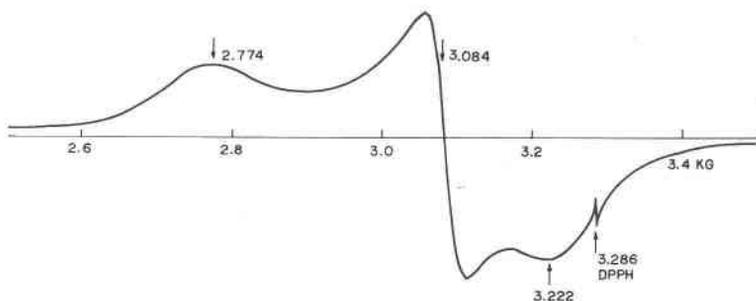


Fig. 1. Electron spin resonance spectrum of turquoise showing the location in kilogauss of the principal $g$-values $g_1$, $g_2$, $g_3$, and that of the free radical marker DPPH.

1966; Low and Offenbacher, 1965). The peak-to-peak linewidth of the middle component centered at $g_2$ is 60 gauss, while the linewidth fitted in the wings is about 75 gauss, and is closer to Gaussian than to Lorentzian. The linewidth estimated from the dipole-dipole formula for a simple cubic lattice is (Anderson and Weiss, 1953)

$$\Delta H_{pp} = 2.3(g_0\beta\rho)\sqrt{S(S+1)} \qquad (3)$$

where $\beta$ is the Bohr magneton, the spin $S = 1/2$ and $\rho$ is the density in spins/cm$^3$. For turquoise with a density of 3.22 g/cm$^3$ and a molecular weight of 814 the calculated linewidth is

$$\Delta H_{pp} = 86 \text{ gauss} \qquad (4)$$

which agrees quite closely with the observed linewidth. Hence the principal line-broadening mechanism is dipole-dipole broadening. The cupric spins are too far apart for exchange narrowing to be appreciable.

Pronounced exchange narrowing would have averaged out the anisotropy, and such averaging is not noticeable on Figure 1.

As was mentioned above, the only symmetry element present at the $Cu^{2+}$ site is inversion. The low symmetry of the site is evident from the crystal structure. Therefore, a completely anisotropic $g$-factor is expected.

To a first approximation the deviation of the $g$-factor from the free-spin value $g = 2.0023$ is proportional to the spin orbit coupling constant and inversely proportional to the main crystal field splitting (Ballhausen, 1962) $E_{T_{2g}} - E_{E_g}$. For axial symmetry one has a dependence of $g_i$ on the ratios $\lambda/(E_{E_{g'}} - E_{B_{1g}})$ and $\lambda/(E_{B_{2g}} - E_{B_{1g}})$, with a generalization to three ratios for lower symmetry (Ballhausen, 1962). For $Cu^{2+}$ with $\lambda \approx 830$ cm and an average $\Delta E = 1.8 \times 10^3$ cm$^{-1}$ as reported in the next section one may write the explicit expression

$$g_3 - g_1 = \frac{8\lambda}{\Delta E} = 0.37$$

which is in fair agreement with the measured value $g_3 - g_1 = 0.33$.

## OPTICAL RESULTS

The optical reflection spectrum obtained for turquoise is shown in Figure 2, and Figure 3 gives the same spectrum converted to relative
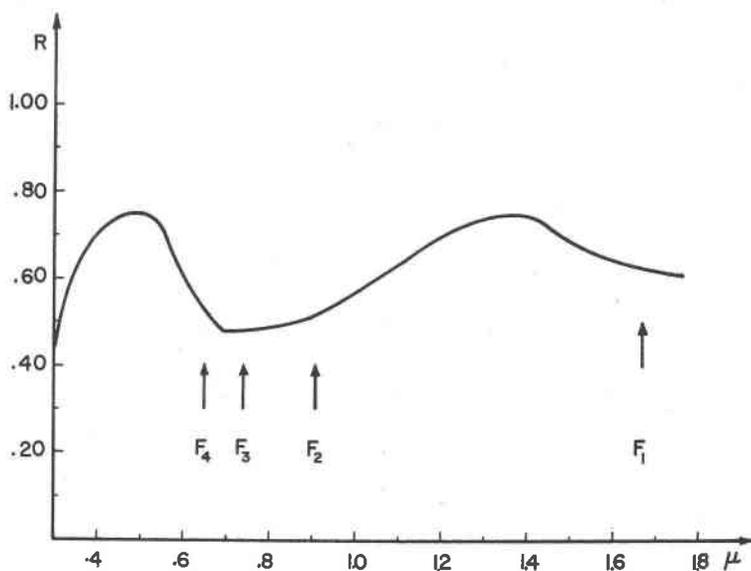


FIG. 2. Optical reflection spectrum of turquoise showing the reflectivity $R$ as a function of the wavelength in microns.
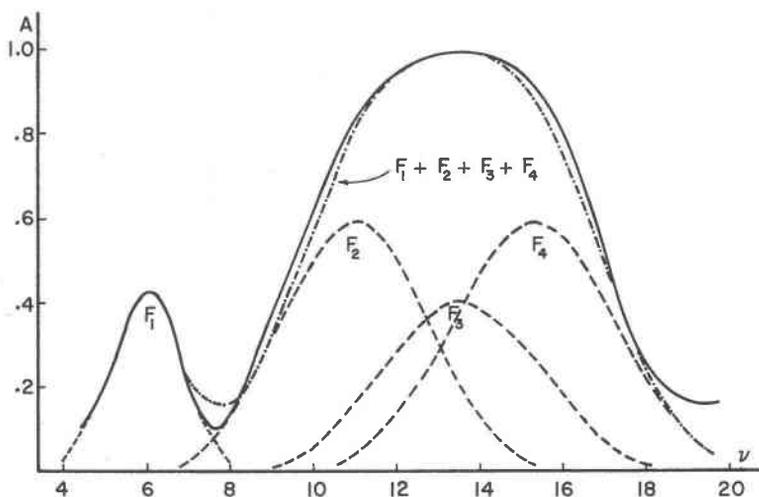
Fɪɢ. 3. The equivalent transmission spectrum of turquoise after converting from the experimental reflection spectrum. The abscissa is given in the units $10^3$ cm$^{-1}$.

extinction coefficient reciprocal centimeter units (Melamed, 1953; Poole and Itzel, 1963). It is possible to fit the spectrum to four gaussian absorption curves (Belford, Calvin, and Belford, 1957), as shown in Figure 3. The formulae for these curves normalized to an amplitude of one for the composite spectrum are

$$F_1 = 0.43e^{-[(\nu-6.0)/0.8]^2/2}$$
$$F_2 = 0.60e^{-[(\nu-11.0)/1.7]^2/2}$$
$$F_3 = 0.41e^{-[(\nu-13.5)/1.8]^2/2}$$
$$F_4 = 0.60e^{-[(\nu-15.3)/1.9]^2/2}$$

(5)

The respective linewidths contained in the denominator of the exponential are 0.8, 1.7, 1.8, and $1.9 \times 10^3$cm$^{-1}$, and are typical for Cu$^{2+}$ ions.

Cupric complexes tend to be coordinated in tetragonally distorted octahedra due to the Jahn-Teller effect (McClure, 1959). For this case one expects three optical transitions, two in the visible and one in the infrared region of the spectrum. In turquoise the distortion is lower than tetragonal, and hence there is an additional splitting of the doublet $E$ upper level as indicated on Figure 4. All of the other four levels are orbital singlets, and so cannot split further. The raising of the $E$ level degeneracy gives four expected optical transitions, as observed.
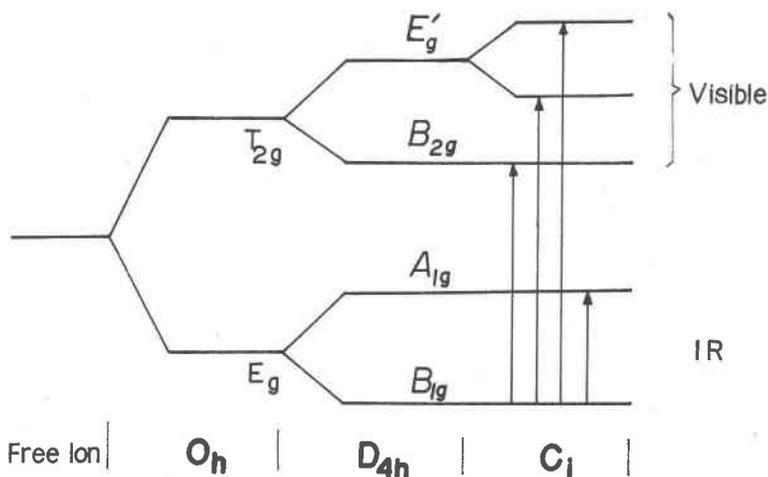
## CRYSTAL FIELD ENERGY LEVELS



FIG. 4. Energy level splitting of the $Cu^{2+}$ $3d^9$, $^2D$ electron configuration in an octahedral ($O_h$), tetragonal ($D_{4h}$), and lower symmetry ($C_i$) crystal field. Observed transitions are shown.

### THE CRYSTALLINE ELECTRIC FIELD

It will be instructive to compare the magnitude of the observed splitting to that predicted by crystal field theory. The electrostatic potential for a perfect octahedron is

$$V_{\text{oct}} = A_0 + B_0 Z_{40} + C_0 Z_{44}^{\text{c}} \tag{6}$$

where the constants $A_0$, $B_0$ and $C_0$ are functions of the ligand distances and the average value $\langle r^4 \rangle$, and $Z_{lm}$ and $Z_{lm}^{\text{c}}$ are the real spherical harmonics defined by Griffith (1961) in terms of the usual spherical harmonics $Y_{lm}$.

$$Z_{10}^{\text{c}} = Z_{10} = Y_{10}$$

$$Z_{lm}^{\text{c}} = \frac{1}{\sqrt{2}} \left( Y_l^{-m} - Y_l^{-m*} \right)$$

These real spherical harmonics $Z_{lm}$ have orthonormality properties similar to those of their counterparts $Y_{lm}$. The potential does not contain $l > 4$ since we are concerned only with $d$ electrons.

If the octahedron undergoes a small generalized distortion which pre-

serves the inversion symmetry of the $Cu^{2+}$ site, then the crystal field potential will be of the form

$$V = A_0 + B_0 Z_{40} + C_0 Z_{44}{}^c + \sum_{l=0}^{4} \sum_{m=0}^{1} D_{lm} Z_{lm}{}^c$$

$$= V_{oct} + V_{dist}$$

The generalized distortion may be represented by the configuration in Figure 5. The undistorted octahedron has atoms at $x = \pm R$, $y = \pm R$, $z = \pm R$. In spherical coordinates this corresponds to

$$A: x = R, \qquad \theta = \frac{\pi}{2}, \qquad \phi = 0$$

$$B: y = R, \qquad \theta = \frac{\pi}{2}, \qquad \phi = \frac{\pi}{2} \qquad (9)$$

$$C: z = R, \qquad \theta = 0$$

After distortion the A-A', B-B', C-C' pairs have the coordinates

$$A: r = (R + \Delta R_A), \qquad \theta = \frac{\pi}{2} + \Delta\theta_A, \qquad \phi = \Delta\phi_A$$

$$B: r = (R + \Delta R_B), \qquad \theta = \frac{\pi}{2} + \Delta\theta_B, \qquad \phi = \frac{\pi}{2} + \Delta\phi_B \qquad (10)$$

$$C: r = (R + \Delta R_C), \qquad \theta = \Delta\theta_C, \qquad \phi = \Delta\phi_C$$

where all changes except $\Delta\phi_c$ are considered small, and all may be positive or negative. For such small distortions the various coefficients $D_{lm}$ in Equation (8) may be shown to be proportional to one or more quantities such as $\Delta R_i / R$, $\sin \Delta\theta_i$, $\sin 2\Delta\theta_i$, $\cos \Delta\theta_i$, $\cos 2\Delta\theta_i$, $\sin^2 \Delta\theta_i$, etc. where $i = A$, B, C. An exact determination of the energy level shifts due to the crystal field distortion is not appropriate since the equations are so complex, and the resulting energy levels are not resolved experimentally. Nevertheless, the proportionality of the distorted hamiltonian to terms such as $\sin \Delta\theta_i$ will permit us to estimate the extent to which the $V_{dist}$ term splits or broadens the observed spectral lines.

For the Cu octahedron of turquoise the three O-Cu ligand distances are

$$R_A = 2.109 \text{ Å}$$
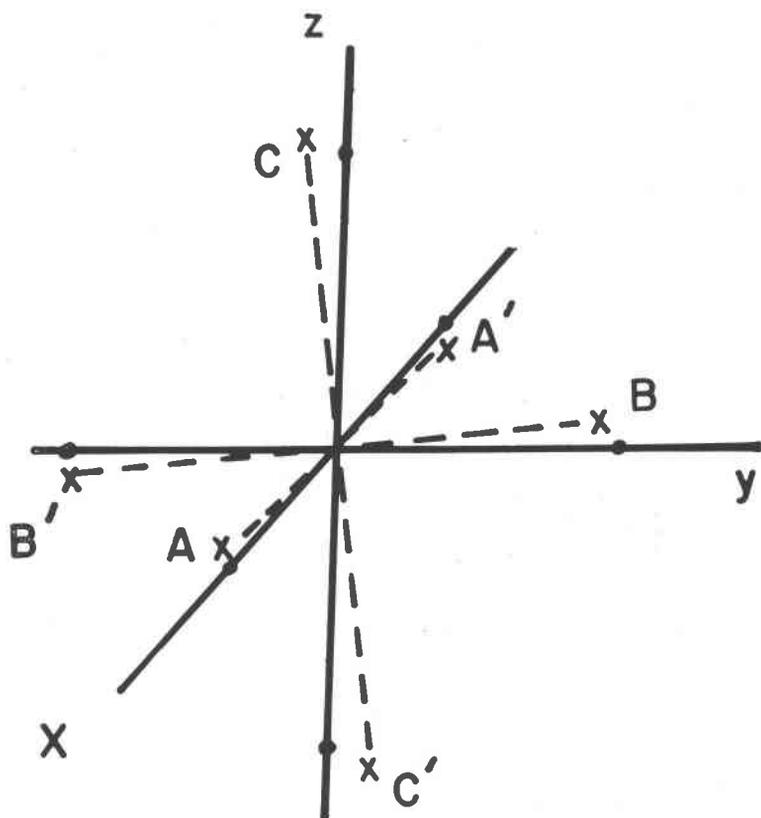$$R_B = 1.915 \qquad (11)$$
$$R_C = 2.422$$

If we define

FIG. 5. Six atoms arranged in a slightly distorted octahedron with inversion symmetry.

$$R_0 = \tfrac{1}{3}(R_A + R_B + R_C) = 2.149 \tag{12}$$

the deviation of each from the average is

$$\Delta R_i = R_i - R_0 \tag{13}$$

with the explicit values

$$\begin{aligned}
\Delta R_A/R_0 &= -0.02 \\
\Delta R_B/R_0 &= -0.11 \\
\Delta R_C/R_0 &= +0.13
\end{aligned} \tag{14}$$

The various O-Cu-O bond angles 77.4°, 83.3°, 83.3°, and their supplementary angle counterparts may be subtracted from 90° to give a first approximation to the angles $\Delta\theta_i$ and $\Delta\phi_i$. A more accurate approach con-

sists in setting up an orthogonal coordinate system which minimizes the angle between each axis and its adjacent Cu-O bond direction. Such a procedure gives values of $\Delta\theta_i \sim 8°$ or less and

$$\sin \Delta\theta_i \sim 0.14 \tag{15}$$

As a result the potential $V_{\text{dist}}$ is about 1/8 of the octahedral potential for each such lower symmetry term. Since $V_{\text{dist}}$ contributes to the splitting (or linewidth) $\Delta E$ of the octahedral spectral line $E_g \to T_{2g}$ we expect

$$\begin{aligned} \Delta E &\approx (E_{\text{T}2g} - E_{\text{E}g})/8 \\ &\approx 1.7 \times 10^3 \text{ cm}^{-1} \end{aligned} \tag{16}$$

The combined distortions from each $\Delta R_i$, $\Delta\theta_i$, and $\Delta\phi_i$ will to a great extent cancel, but their overall effect should be at least twice that of an individual term estimated by Equation (16), and so the observed splitting of 4,000 cm$^{-1}$ for the $F_4$-$F_2$ lines is a general accordance with expectations.

More sophisticated types of ligand field theory are based on the admixture of the wavefunctions of the central ion and ligands. As a result the $E_g$ and $T_{2g}$ levels may be said to intermingle. A calculation of this type will provide more precise energy levels for comparison with the observed spectra. In this paper we have limited ourselves to an estimate of the energy shifts by the use of a perturbation treatment. This procedure is valid for the predominately ionic chemical bonding of the cupric ions to their surrounding oxygens.

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