Crystal Growth of \( \text{Cu}_6(\text{Ge},\text{Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O} \) and Assignment of UV-VIS Spectra in Comparison to Dehydrated Dioptase and Selected Cu(II) Oxo-compounds Including Cuprates.

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Abstract: It is reported on growth of mm-sized single-crystals of the low-dimensional \( S = \frac{1}{2} \) spin compound \( \text{Cu}_6(\text{Ge},\text{Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O} \) by a diffusion technique in aqueous solution. A route to form Si-rich crystals down to possibly dioptase, the pure silicate, is discussed. Further, the assignment of \( dd \) excitations from UV-VIS spectra of the hexahydrate and the fully dehydrated compound is proposed in comparison to dioptase and selected Cu(II) oxo-compounds using bond strength considerations. Non-doped cuprates as layer compounds show higher excitation energies than the title compound. However, when the antiferromagnetic interaction energy as \( J_z \cdot \ln(2) \) is taken into account for cuprates, a single linear relationship between the \( D_q \) excitation energy and equatorial Cu(II)-O bond strength is confirmed for all compounds. A linear representation is also confirmed between \( 2A_{1g} \) energies and a function of axial and equatorial Cu-O bond distances, when auxiliary axial bonds are used for four-coordinated compounds. The quotient \( Du/Db \) of experimental orbital energies deviating from the general trend to smaller values indicates the existence of \( \text{H}_2\text{O} \) respectively \( \text{Cl}^{-} \) axial ligands in comparison to oxo-ligands, whereas larger \( Du/Dq \) values indicate missing axial bonds. The quotient of the excitation energy \( 2A_{1g} \) by \( 2\cdot 2E_{g} - 2B_{2g} \) allows to check for correctness of the assignment and to distinguish between axial oxo-ligands and others like \( \text{H}_2\text{O} \) or \( \text{Cl}^{-} \). Some assignments previously reported were corrected.

Keywords: dioptase, Ge-dioptase, copper(II) compounds, cuprates, crystal growth, UV-VIS spectroscopy, EPR, color, d-d excitations, bond strength, super-exchange interaction

1. Introduction

Low-dimensional quantum spin systems are of considerable theoretical and experimental interest together with some applications to which they may lead. In spite of the ability of the \( d^9 \) transition metal ion Cu\(^{2+} \) to form, apart from 3D networks, chains, ladders and small clusters, copper compounds are among the most interesting phases. With equal electronegativity compared to silicon, but in contrast to its tetrahedral networks, Cu(II) mainly forms oxo-compounds with chains and networks of connected ‘octahedra’.

For instance, copper polygermanate, CuGeO\(_3\), has a rather simple crystal structure of ‘einer’ single chains of GeO\(_4\) tetraedra alongside \( S = 1/2 \) spin single chains of edge-sharing CuO\(_{4+2}\) octahedra \([1] [2]\). It was the unique inorganic compound showing the Spin-Peierls-transition \([3,4]\). As a quasi-one-dimensional system it has been the subject of an intensive experimental and theoretical work for the past years. It was a great surprise, when Otto and Meibohm \([5]\) succeeded in the synthesis of pure
copper polysilicate, CuSiO$_3$, by thermal decomposition of the mineral dioptase, Cu$_6$Si$_6$O$_{18}$·6H$_2$O. CuSiO$_3$ represents the example of a fully stretched silicate chain structure. It is isotypic to CuGeO$_3$, but does not show the spin-Peierls transition, instead an antiferromagnetic ordering below $T_N = 7.9$ K [6,7].

The rhombohedral title compound Cu$_6$(Ge,Si)$_6$O$_{18}$·6H$_2$O represents a hexacyclo-germanate (silicate) that contains copper-oxygen spiral chains along the c-axis, which are connected (intra-chain) by edge-sharing dimers (Figure 1). This structure is interesting because it allows for a quantum phase transition between an anti-ferromagnetically ordered state and a quantum spin liquid [8]. Large quantum fluctuations in green dioptase have been described [9]. Recently, also the germanate analogue, Cu$_6$Ge$_6$O$_{18}$·6H$_2$O [10], has been the object of detailed magnetic and structural investigations [11,12].

![Figure 1. Crystal structure of dioptase projected down [001]. A framework of copper oxide octahedra (yellow) screws around the c-axis with non-bonding axial water ligands (red) pointing towards empty channels. Six-membered silicate single rings are depicted in green.](image)

If near the empty structural channels located water molecules are removed, a screwed framework of edge-sharing disphenoids rather than flat CuO$_4$ plaquettes remains in the dehydrated compound. As part of a systematic study of transition metal germanates, silicates and arsenates we have undertaken syntheses of rare copper minerals and new copper compounds in view of its power as low dimensional $S = 1/2$ spin compounds allowing for interesting physical and physico-chemical properties. First, the synthesis serves not to waste rare mineral specimens for research. There is also the possibility to study an improvement in the crystal growth by replacement of copper by other elements, apart from the chance of doping with electronically or magnetically interesting ones. For example, the replacement of copper by manganese was observed in natural samples of dioptase by EPR measurements [13,14].

2. Experimental

2.1 Crystal Growth

The method described below was used by the author many years earlier for the synthesis of rare minerals, for instance the synthesis of Pb$_5$Ge(OH)$_6$(SO$_4$)$_2$·3H$_2$O, the piezoelectric Tsumeb mineral fleischerite [15]. For the synthesis of the title compound freshly precipitated gels of GeO$_2$ and Cu(OH)$_2$ were separately filled in 200 ml beaker glasses and thoroughly filled up with distilled water. Then an U-shaped glass pipe of 6 mm inner diameter, well annealed before use to reduce crystal nucleation frequency, was filled free of air bubbles with distilled water. This pipe is then used to
connect the distinct solutions in the beakers. Finally, the water surface in the beakers is covered with a film of liquid paraffin to prevent water evaporation and entry of CO$_2$, respectively.

The desired slow diffusion of the distinct solutions into one another leads to the formation of Cu$_6$(Ge,Si)$_6$O$_{18}$·6H$_2$O seeds that grow up to 1 mm size of light blue crystals within 8 weeks. Interestingly, most individual crystals form double-crystals. The symmetry situation of this finding must be investigated further. The crystals of stocky prismatic, nearly spherical habit developed {110} and {021} forms (Figure 2).

![Figure 2](image)

**Figure 2.** Stocky prismatic habitus of the as-grown Cu$_6$(Ge,Si)$_6$O$_{18}$·6H$_2$O crystals, showing a combination of the {110} prism and the {021} rhombohedron.

One can extrapolate the time scale to get a crystal of about 2mm diameter and calculate about 1 year of growing time. Trying to exchange Ge by Si by this method seems to be less efficient, only a slightly greenish sheen shows that a small exchange occurred.

The other method of co-precipitation of GeO$_2$, SiO$_2$ and Cu(OH)$_2$ gel and longer time vigorous stirring resulted in a vivid green colored polycrystalline material of about 12 at-% Si determined from lattice parameter changes [13,16]. Also the substitution of some B$^{3+}$ for Ge$^{4+}$ is possible, leading to a beautiful green color [16]. Stirring a longer period and in addition changing the pH to more acidic milieu gives at least about 15 at-% Si ($a = 14.640$ Å, $c = 7.806$ Å, this work). The effect is based on the different solubility of the Ge-compound in comparison to dioptase. Cu$_6$Ge$_6$O$_{18}$·6H$_2$O is easily decomposed by dilute acetic acid, but dioptase does not dissolve. Recently we observed a deepening of color to dioptase green, when the Si-rich solution was exposed to ultrasonic waves, in this way superseding vigorous stirring. The energy that is released when voids implodes (super-cavitation) may be able to assemble more easily and faster the six-membered silicate rings within the cuprate framework of dioptase.

A proposed approach for a possible synthesis of pure polycrystalline dioptase results as follows. The first step will be the spontaneous formation of pure germanate and exchange of maximum Ge by Si through stirring or sonochemical treatment. Then pH as well as temperature is altered to increase the solubility of the still Ge-rich compound combined with a simultaneous offer of more Si to form a dioptase layer. A new core of silico-germanate can be grown epitaxially and subsequently transformed to dioptase. Repetition of this process may finally form pure dioptase in mm-sized crystals. An automated process would make sense. Nature has similar tools in the quiver such as rhythmic property changes (concentration, pH, temperature) of metal bearing ascending or descending solutions, apart from a lot of time.

2.2 UV-VIS Spectroscopic Investigation

First results of UV-VIS spectroscopy on Cu$_6$(Ge,Si)$_6$O$_{18}$·6H$_2$O are given in the doctoral theses of my coworkers Brandt [17] and Meibohm [13], respectively, whereas dioptase itself has been investigated earlier by different researchers [18-21].
Brandt [17] reported a color change from turquoise-green to blue on dehydration of dioptase-type copper germanate. In addition, the dehydrated compound showed thermochromic behavior on heating up to 500 °C with a reversible color change to vivid green similar to that of annealed CuGeO$_3$. The color persists when Cu$_6$Ge$_6$O$_{18}$ is rapidly cooled down to room temperature. A possible interpretation for this effect is according to [17] the low relaxation rate of the four oxygen ligands around copper. Remember that the equatorial coordination in dioptase is not planar but disphenoidic, and a change to a stiffer, more tetrahedral one may occur with raising temperature.

A reinvestigation of the fully hydrated and dehydrated compounds is primarily undertaken in order to deconvolute and understand the broad UV-VIS spectrum of the synthetic color pigment litidionite, KNaCuSi$_4$O$_{10}$ [22,23], which shows similarity to that of dioptase.

The room temperature UV-VIS spectra of the samples were taken with the double beam light scanning UV-2501PC CE spectrometer from Shimazu with selectable light sources (50W halogen lamp and D2 lamp). The powder sample was coated on a polished aluminium disk and measured in the reflection modus against a BaSO$_4$ standard in the wavelength range between 190 and 900 nm with a spectral bandwidth of 0.1 nm using a 50 nm/min scan and choosing 0.5 nm intervals. From the less structured absorbance profile, recalculated from the measured reflectance, the energy bands were fitted with Gaussian profile functions. The better resolved spectra of the dehydrated compounds were fitted first and then the results used as start parameters for the broad spectra of the hydrated compounds.

2.3 EPR Data

Electron paramagnetic resonance spectroscopy (EPR) provides information about the electronic structure of transition metal ion complexes. For $d^{1,9}$ systems such as Cu$^{2+}$ centered complexes with no fine structure the principal values of the $g$-tensor of the spin Hamiltonian $H = \beta \cdot B \cdot g \cdot S$, reflecting the symmetry of the ligand field, can be derived from the EPR spectrum, where $B$ is the external magnetic field, $S$ is the spin vector, and $\beta_e = g_e \cdot \mu_B$ (Landé $g$-factor for the free electron, $g_e = 2.0023$, Bohr magneton $\mu_B$). In this contribution $g$ values for dioptase, Cu$_6$Si$_6$O$_{18}$·6H$_2$O, determined by Reddy et al. [19], and data measured by Meibohm [13] for synthetic Cu$_6$Ge$_6$O$_{18}$·6H$_2$O were used as expressed in its principal axes system.

3. Results and Discussion

Results of a Gaussian deconvolution of the UV-VIS spectra for the hydrated and dehydrated compounds, respectively, are given in Table 1 and depicted in Figures 2a to 2d. $\lambda$(nm) and $\Gamma$(nm) represent wavelength and full width of the excitation peaks, and the wavenumber $E$(cm$^{-1}$) denotes the excitation energy. The remarkable oscillator strength $f$ (given in arbitrary units) is the consequence of non-zero $dd$ transition probabilities due to the absence of symmetry elements on the Cu position with $C_1$ site symmetry and the disphenoidic (stocky tetrahedral) oxygen environment with 4 distinct equatorial bond lengths indicating Cu$_3d^2$-O$_2p$ hybridization. The relative width $\Gamma/\lambda$ of the bands of the dehydrated compounds is about 18%, whereas that of the hydrated ones suffer additional broadening to about 23% caused by a vibronic contribution of the water molecule rings and due to assumed peak overlapping according to the below presented assignment.

The steep increase of absorption at the badly resolved high energy limit of the UV-VIS spectra has been simulated by a Gaussian curve, too, and may be interpreted as absorption edge, the large gap between valence and conduction band of isolator compounds. The gap is determined around 3.80 eV for dioptase and shifts to 3.76 eV for Ge-dioptase, respectively. It is slightly lower for the dehydrated compounds, giving 3.52 and 3.47 eV, respectively (Table 1). For comparison, Rudko [24] observed an absorption edge near 3.5 eV for the charge transfer insulator CuGeO$_3$. The absorption structures at
high energy just before the energy gap may be attributed to simultaneous ligand field transitions involving both metal centres of the dimer at twice the monomer transition energy (SPE), because their oscillator strengths are too weak for charge transfer (CT) transitions.

The color of Cu$^{2+}$ compounds with their Jahn-Teller distorted coordination polyhedra [25] is the conspicuously recognized property of this transition metal ion and is attributed to electronic excitations between its d-orbitals. The coordination polyhedron of copper in the d$^9$ state with the unpaired electron in the $x^2$-$y^2$ orbital is an elongated octahedron leading to splitting of formerly degenerated d-states. A recently found impressive example for a Jahn-Teller elongated octahedron is the new prototypic crystal structure of tetragonal CuO with a $c > a$ rock salt structure [26].

The transition energies $\Delta_n$ (cm$^{-1}$), derived from broad Gaussian-shaped absorption bands of UV-VIS spectra, are the energy differences between the $2B_{1g}(x^2-y^2)$ ground state and the $2B_{2g}(xy)$, $2A_{1g}(z^2)$ and $2E_g(xz,yz)$ excited states and can be connected with crystal field splitting parameters representing orbital energies. Bearing in mind the Cu$^{2+}$ site symmetry of $D_{4h}$ or lower, we are faced with an equatorial $D_{q_e}$ splitting parameter and two radial $D_s$ and $D_t$ ones (Gerloch and Slade, [27]). The crystal field theory (CFT) allows for the following relations:

$$\Delta_n = 2B_{2g}(xy) - 2B_{1g}(x^2-y^2) = 10D_{q_e} \quad (1)$$

[Figure 3. UV-VIS spectra of a) dioptase, b) dioptase dehydrated, c) Ge-dioptase, d) Ge-diptase dehydrated. Measured spectra red, calculated spectra blue.]
\[ \Delta_E = 2E_p(xz, yz) - 2B_{1g}(x^2 - y^2) = 3Ds + 10Dq_e - 5Dt. \]  
(2)

\[ \Delta_A = 2A_{1g}(z^2) - 2B_{1g}(x^2 - y^2) = 4Ds + 5Dt \]  
(3)

Conversely, the \( D \) parameters can be recalculated as

\[ Dq_e = \Delta_B/10 \]  
(4)

\[ Ds = (\Delta_A + \Delta_b - \Delta_b)/7 \]  
(5)

\[ Dt = (3\Delta_A + 4(\Delta_B - \Delta_e))/35 \]  
(6)

Whereas \( \Delta_E \) is always moderately larger than \( \Delta_B \), \( \Delta_A \) ranges from about 8500 cm\(^{-1}\) (< \( \Delta_B \)) for shortest axial bonds to at least 21500 cm\(^{-1}\) (> \( \Delta_B \)) for axially non-existent bonds (squared-planar coordination). A more quantitative description of ligand field parameters using effective charges and bond lengths results in the following relations [26]:

\[ Dq_e = \eta_eZ_e \cdot e^2<r^2>(6-R_e^2) \]
\[ Dq_a = \eta_eZ_a \cdot e^2<r^2>/(6-R_a^2) \]  
(7)a,b

\[ C_p = 2\eta_eZ_e \cdot e^2<r^2>/(7-R_e^2) \]
\[ C_p = 2\eta_eZ_a \cdot e^2<r^2>/(7-R_a^2) \]  
(8)a,b

\[ Ds = C_p - C_p \]  
(9)

\[ Dt = 4/7 \cdot \eta \cdot (Dq_e - \eta_Dq_a) \]  
(10)

where \( \eta \cdot Z_e \) represents an effective ligand charge, \( R_e \) and \( R_a \) are equatorial and axial bond lengths in Å, and \(< r^2 > = 0.214 \) Å is the mean value of the fourth power of a 3d orbital radial distance from the nucleus, respectively \( < r^2 > = 0.294 \) Å is the mean of the second power of the radial distance. For \(< r^2 > \) the values calculated by Haverkort within the Hartree-Fock approximation are used [28]. Because \(< r^2 > \) is a measure proportional to the Cu(II) effective nuclear charge, one should multiply this value by a factor of 4 to give a realistic value of about 0.85 for the Scott charge, which would represent 42.5% ionicity of the Cu-O bond.

**Table 1.** Results of the Gaussian profile deconvolution of the UV-VIS spectra of the dioptase family. 

| Cu₆Si₆O₁₈·6H₂O (dioptase) | Cu₆GeO₁₈·6H₂O (Ge-dioptase) |
|---------------------------|-------------------------------|
| \( f \) | \( \lambda \) (nm) | \( I \) (nm) | \( E \) (cm\(^{-1}\)) | Assignment | \( f \) | \( \lambda \) (nm) | \( I \) (nm) | \( E \) (cm\(^{-1}\)) | Assignment |
| 329 | 935 | 208 | 10700 | \( \Delta_A \) | 1000 | 842 | 198 | 11884 | \( \Delta_B + \Delta_A \) |
| 815 | 869 | 208 | 11507 | \( \Delta_B \) | 645 | 698 | 166 | 14321 | \( \Delta_E \) |
| 1000 | 695 | 194 | 14400 | \( \Delta_B \) | 185 | 616 | 129 | 16230 | \( \text{Cu}^{2+} \) |
| 256 | 600 | 109 | 16670 | \( \text{Cu}^{2+} \) | 271 | 462 | 147 | 21650 | \( \text{SPE} \) |
| 421 | 414 | 108 | 24160 | \( \text{SPE} \) | 871 | 353 | 97 | 28350 | \( E_g \) |
| (554) | 326 | 102 | 30660 | \( E_g \) |

| Cu₆Si₆O₁₈ (dioptase dehydrated) | Cu₆GeO₁₈ (Ge-dioptase dehydrated) |
|-----------------------------|-----------------------------------|
| \( f \) | \( \lambda \) (nm) | \( I \) (nm) | \( E \) (cm\(^{-1}\)) | Assignment | \( f \) | \( \lambda \) (nm) | \( I \) (nm) | \( E \) (cm\(^{-1}\)) | Assignment |
| 1000 | 811 | 158 | 12330 | \( \Delta_B \) | 1000 | 827 | 155 | 12100 | \( \Delta_B \) |
| 866 | 668 | 120 | 14960 | \( \Delta_B \) | 843 | 679 | 127 | 14723 | \( \Delta_B \) |
| 492 | 558 | 96 | 17930 | \( \Delta_B \) | 450 | 565 | 97 | 17700 | \( \Delta_B \) |
| 235 | 441 | 100 | 22680 | \( \text{SPE} \) | 355 | 437 | 108 | 22880 | \( \text{SPE} \) |
| (869) | 330 | 120 | 30300 | \( E_g \) | (630) | 357 | 102 | 28000 | \( E_g \) |
Quoting Gerloch and Slade [27] ones more, in the crystal-field theory with its point-charge formalism charges as well as bond lengths have to be considered as effective parameters that are not independent of each other. Therefore, cationic and ligand charges should be combined to common adaptable factors \( Q_e^2 = \eta_e Z_e \langle r^2 \rangle \) respectively \( Q_s^2 = \eta_s Z_s \langle r^2 \rangle \).

For comparison of calculated band energies with experimental ones given in cm\(^{-1}\) an energy conversion factor \( c_{E} = e^2/(4\pi \varepsilon_0 \cdot 1(\text{Å})) = 1.1608 \times 10^5 \) is applied.

Lebernegg et al. [29] found no general theoretical justification for \( R^{-5} \) dependence of ligand-field splitting. Nevertheless, one can use the inverse fifth power relationship \( \Delta q_e \propto R^{-5} \) in order to calculate a linear regression curve of \( \Delta q_e \) (or \( \Delta B \)) values against the mean of the four equatorial copper-oxygen distances \( R_e(\text{Å}) \) according to Equation 7a for selected compounds with a reduced connectedness with respect to equatorial sharing, at the beginning excluding sheet structures as exemplified by cuprates. The plot is depicted in Figure 3 and extrapolates well through the origin with \( Q_e^2 = 1.723 \), giving effective charge numbers of \( Q_e = \pm 1.313 \) assumed evenly distributed over Cu\(^{2+}\) and ligands. The calculated \( \Delta q_e \) values deviate less than 1.6\% from the experimental ones.

![Figure 4](image-url) Calculated \( \Delta q \) energies versus experimental ones for dioptase and related compounds.

In the right plot, an additional magnetic contribution of \( \Delta q_{\text{calc}} \) was considered for cuprates.

We chose compounds of the *Egyptian Blue* family (cuprorivaite, wesselite, effenbergite,) with isolated \( D_{4h} \) plaquettes, the dehydrated dioptase compounds with equatorially edge-shared dimers, further connected via water oxygen to corner-shared spiral chains in the fully hydrated compounds, litidionite as characterized by pyramid-edge-shared dimers (cis-arrangement), in contrast to lammerite with infinite chains of such units and with two distinct Cu sites, further azurite with ‘octahedral’ chains (two distinct sites), and finally conichalcite and CuGeO\(_3\) showing infinite single chains with equatorially edge-shared ‘octahedra’. One may learn more about the structural hierarchy of special copper oxy-salt minerals from Eby and Hawthorne [30].

Recently, the energy and symmetry of dd excitations of some undoped layered cuprates have been measured by CuL\(_3\) resonant X-ray scattering [31]. The well assigned \( dd \) excitations of these compounds with high connectedness were found to be higher than the energies of the compounds described before. Two further compounds can be added to this group with due allowance, the ‘green’ ino-cuprate phase \( Y_2\text{BaCuO}_5 \) and multiferroic CuO as limiting case. Applying Eq. 7a, a steeper slope with \( Q_e^2 = 1.82 \) results, representing higher excitation energies and effective charges \( Q_e = \pm 1.35 \) than for the dioptase group. Too low a bond strength of the ‘green’ phase \( Y_2\text{BaCuO}_5 \) is striking (Table 2) and a distinct \( Q_e^2 \) has been applied (Table 4).
The different connectedness of cuprates in comparison to the dioptase group is manifested in a larger contribution of the principal magnetic super-exchange interaction $J_z$ to the optical excitation energies. In Figure 5, this contribution is depicted versus the Cu–O–Cu bond angle $\Phi$, a representation first used by Rocquefelte et al. [32], and here applied in an extended form, illustrating both dioptase group compounds and cuprate ones. A data fit resulted in the relation

$$J_z(\Phi) = 0.091 \cdot (\Phi - 90)^{1.652} \text{(meV)} = 0.734 \cdot (\Phi - 90)^{1.652} \text{(cm}^{-1})$$

with an exponent near 5/3, explained by chemical pressure (Rocquefelte et al., 2012) [32][33]. Adding $J_z(\Phi) \cdot \ln(2)$ as bond angle dependent contribution to the bond length dependent one, a surprisingly good agreement is achieved between the two groups of compounds, now giving $Q_e = 1.722$, respectively $Q_e = 1.312$. It should be noticed that for the dioptase group an antiferromagnetic contribution is not included, because $T_N$ is lower than room temperature, at which the optical spectra are taken.

Table 2. Coordination numbers $CN$, bond length and bond valence sums $s$ for selected Cu(II) compounds $s_e$ equatorial sum, $s_a$ axial sum, $\Sigma_s$ overall sum (particularly striking values in red).

| Compound                           | CN | $d$(Cu-O) (Å) | Bond strength | Reference |
|-----------------------------------|----|--------------|---------------|-----------|
| $\text{Ca}_3\text{Sr}_5\text{CuO}_6$ | 4  | 1.945        | $s_e$ 1.913 $s_a$ - $\Sigma_s$ 1.913 | [39]      |
| $\text{CaCu}_2\text{O}_3$        |    | 1.928        |              |           |
| $\text{BaCuSi}_2\text{O}_6$      | 4  | 1.925        | $s_e$ 2.022 $s_a$ - $\Sigma_s$ 2.022 | [40]      |
| $\text{SrCuSi}_2\text{O}_6$      | 4  | 1.925        | $s_e$ 2.022 $s_a$ - $\Sigma_s$ 2.022 | [41]      |
| $\text{CuCuSi}_2\text{O}_6$      |    | 1.929        | $s_e$ 1.998 $s_a$ - $\Sigma_s$ 1.998 | [42]      |
| $\text{Cu}_6\text{Si}_6\text{O}_{18}$ | 6  | 1.9250 1.9294 1.9354 1.9466 3.3153 | $s_e$ 1.969 $s_a$ 0.023 $\Sigma_s$ 1.992 | [12]      |
| $\text{Cu}_6\text{Ge}_6\text{O}_{18}$ | 6  | 1.9043 1.9284 1.9380 1.9979 3.3841 | $s_e$ 1.954 $s_a$ - $\Sigma_s$ 1.954 | [16]      |
| $\text{Y}_2\text{BaCu}_2\text{O}_5$ | 2 + 2 + 1 | 1.985 1.988 2.206 | $s_e$ 1.692 $s_a$ 0.232 $\Sigma_s$ 1.923 | [43]      |
| $\text{CuGeO}_3$                 | 4 + 2 | 1.941 2.926 | $s_e$ 1.941 $s_a$ 0.093 $\Sigma_s$ 2.022 | [1][2][3] |
| $n\text{Cu}_2\text{Si}_6\text{O}_{10}$ | 6  | 1.952 1.952 1.959 1.983 2.502 2.648 | $s_e$ 1.818 $s_a$ 0.195 $\Sigma_s$ 2.014 | [44]      |
| $\text{Cu}_6\text{Ge}_6\text{O}_{18}$ ·6$\text{H}_2\text{O}$ | 6  | 1.9037 1.9486 1.9547 1.9884 2.6364 2.6696 | $s_e$ 1.894 $s_a$ 0.159 $\Sigma_s$ 2.053 | [10]      |
| $\text{Cu}_6\text{Si}_6\text{O}_{18}$ ·6$\text{H}_2\text{O}$ | 6  | 1.9387 1.9455 1.953 2.036 | $s_e$ 1.995 $s_a$ 0.083 $\Sigma_s$ 2.036 | [45]      |
| $\text{Cu}_6\text{Ge}_6\text{Si}_6\text{O}_{18}$ ·6$\text{H}_2\text{O}$ | 6  | 1.9385 1.9388 1.9675 1.9947 2.3608 2.7578 | $s_e$ 1.830 $s_a$ 0.223 $\Sigma_s$ 2.053 | [46]      |
| $\text{Cu}_4\text{(CO}_3)_2\text{(OH)}_2$ | 2 + 2 | 1.9387 1.9455 1.953 2.036 | $s_e$ 1.995 $s_a$ 0.083 $\Sigma_s$ 2.036 | [45]      |
| $\text{Cu}_4\text{As}_2\text{O}_{12}$ | 2 + 2 | 1.933 1.974 2.923 | $s_e$ 1.864 $s_a$ 0.093 $\Sigma_s$ 1.957 | [47]      |
| $\text{Cu}_3\text{As}_2\text{O}_{12}$ | 2 + 2 | 1.941 1.947 1.972 2.028 2.282 2.782 | $s_e$ 1.772 $s_a$ 0.254 $\Sigma_s$ 2.026 | [48][49]  |
| $\text{CaCu}_3\text{AsO}_4\text{OH}$ | 6  | 1.8850 1.8855 2.0666 2.0688 2.2976 2.3882 | $s_e$ 1.811 $s_a$ 0.332 $\Sigma_s$ 2.143 | [48][49]  |
| $\text{La}_2\text{Cu}_2\text{O}_4$ | 4 + 2 | 1.9043 2.4145 2.151 0.278 $\Sigma_s$ 2.439 | [49]      |
| $\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2$ | 4 + 2 | 1.9864 2.860 1.687 0.292 $\Sigma_s$ 1.979 | [50]      |
Table 3. Collection of some properties and data for selected Cu(II) oxo-compounds

\[ \Delta_B = 2 B_{2 g}(x^2-y^2), \quad \Delta_E = 2 E_g(xz,yz), \quad \Delta_A = 2 A_{1 g}(z^2) \]

energies in cm\(^{-1}\). Other transitions: CT charge transfer, SPE simultaneous pair excitation, \(E_g\) energy gap, Cu\(^{2+}\) fluorescence peak.

| Compound                  | Color        | Cu site symmetry | \(\Delta_B\) | \(\Delta_E\) | \(\Delta_A\) | Other Transition | Reference          |
|---------------------------|--------------|------------------|--------------|--------------|--------------|-----------------|--------------------|
| CaCuO                     |              | D\(_{4h}\)       | 12930        | 15730        | 21370        |                 | [31]              |
| Conichalcite synth.       |              | C\(_1\)          | 12170        | 12930        | 15530        | 16670 many      | [51] **            |
| Tenorite CuO              | brownish     | C\(_i\)          | 10575        | 12170        | 15530        | 15313 Cu\(^{2+}\) 31370 (\(E_g\)) | [52]              |
| Lammerite synth.          |              | C\(_i\)          | 11530        | 12400        | 14050        | 23260 CuO 31250 (\(E_g\)) | [22]; this work * |
| Y\(_2\)BaCuO\(_4\)        |              | D\(_{4h}\)       | 11700        | 12400        | 14050        | 15313 Cu\(^{2+}\) 31370 (\(E_g\)) | [53] **            |
| Azurite Cu\(_4\)(CO\(_3\))(OH)\(_2\) | blue       | C\(_1\)          | 11806        | 16484        | 16484        | 19793 17952     | [54] **            |
| Conichalcite synth.       |              | C\(_1\)          | 11407        | 13308        | 9699         | 15234 Cu\(^{2+}\) 15567 Cu\(^{2+}\) | [55]              |
| Lithionite synth. KNaCuSi\(_4\)O\(_10\) | light blue | C\(_1\)          | 11723        | 14700        | 13900        | 21400 SPE 31600 (\(E_g\)) | [22] [23]; this work |
| Cu\(_6\)Ge\(_5\)O\(_18\) |              | C\(_1\)          | 12100        | 14723        | 17700        | 22880 CT         | [16]; this work    |
| Cu\(_6\)Ge\(_5\)O\(_18\) 6H\(_2\)O | bluish-green | C\(_1\)          | 11880        | 14320        | 11880        | 16230 Cu\(^{2+}\) 21650 CT 30300 (\(E_g\)) | [16]; this work    |
| Cu\(_6\)Ge\(_5\)Si\(_4\)O\(_18\) 6H\(_2\)O | dark green  | C\(_1\)          | 13300        | 19400        | 23900 CT       |                 | [17]              |
| BaCuSi\(_4\)O\(_10\) synth. (Efﬁenbergite) |               | D\(_{2h}\)       | 12570        | 13970        | 12920        | 15733 Cu\(^{2+}\) 15800 CT | [24]; this work |
| SrCuSi\(_4\)O\(_10\) synth. (Wessellite) |               | D\(_{4h}\)       | 12200        | 15950        | 18520        |                 | [56]              |
| CaCuSi\(_4\)O\(_10\) synth. (Cuprorivaitte) |               | D\(_{4h}\)       | 12480        | 16050        | 18520        |                 | [56]              |
| Dioptase dehydrated       |              | C\(_1\)          | 12330        | 14960        | 17930        | 22680 CT         | This work; [19]    |
| Dioptase partly dehydrated|              | C\(_1\)          | 11500        | 14500        | 17000        |                 | [18] [19]         |

* synthetic lammerite with an amount of CuO

** for this work a different assignment as given in the reference was used
The $R^{-5}$ inverse power of Cu-O bond lengths is nearly a measure for the bond strength. Therefore, the reliability of the fit can be enhanced applying the empirical Cu-O bond strength relation $s = \Sigma(R/R_0)^{-N}$ [34] by choosing only the bond strength sum $s_e$ of the four equatorial bonds. New values $R_0 = 1.713(9)$ Å, $N = 5.76(16)$ were re-calculated for this work [35]. Results of a double-regression yielded for the cuprate group

$$\Delta_B \text{ (cm}^{-1}\text{)} = (6658 \pm 38) \cdot s_e \quad \text{and} \quad \Delta_B \text{ (cm}^{-1}\text{)} = (6269 \pm 21) \cdot (s_e + 1.38 \cdot 10^{-4} J_z)$$

for both the dioptase group and cuprates, the last mentioned corrected by a bond angle dependent (magnetic) contribution (Figure 6). It is recommended to extend the analytic bond strength – bond length expression by a magnetic (angle dependent) contribution. In contrast to this result, the quoted authors [31] fitted their cuprate data with a lower slope of $N = 4.2$. On the other hand, the selection of compounds for such fit is not convincing, because an influence of some equatorial $O^{1-}$ ions in $La_2CuO_4$ (high bond strength, see Table 2) on the excitation energies can be expected. In addition, the epitaxially grown infinite-layer structure of $Ca_{0.5}Sr_{0.5}CuO_2$ is obviously strained.

**Figure 5.** Principal superexchange interaction $J_z$ versus Cu–O–Cu bond angle $\Phi$ [32,33].

**Figure 6.** Linear relation between $Dq$ (cm$^{-1}$) and the equatorial bond strength $s_e$, in case of cuprates (red curve) corrected by a bond angle dependent (magnetic) contribution to show a single linear plot (green curve) with dioptase group compounds (yellow) besides cuprates (now green).

Turning now to the calculation of splitting parameters $Ds$ (Eq.9) and $Dt$ (Eq.10) involving axial ligands one has to distinguish between pure oxo-ligands and more ionic ones like $H_2O$ and $Cl^{1-}$ with increased cationic charge and assumed higher $Dq_a$ values. $H_2O$ (as equatorial ligands) are found in
chalcanite, and hydroxyl groups in azurite and conichalcite; the last compound has the most distorted ‘octahedron’ and should show a pronounced splitting of the $^2E_g$ term, which is not considered here. In the case of square-planar environment it is useful to limit the extent of the $d_{z^2}$ orbital with ‘long’ auxiliary axial bonds. Dehydrated dioptase and the germanate analogue already have some far distant oxygen ions (see Table 2) within the $d_{z^2}$ orbital sphere of influence. For the group of $M^{2+}CuO_2$ layered cuprates the limit is given by the layer separation down $c$ of about 3.3 Å. Again the results differ somewhat for the two groups of compounds with slightly different effective charges. From the fitted values for $D_s$ and $D_t$ the $\Delta E$ (Equation 2) and $\Delta A$ (Equation 3) energies have been calculated as well as $^2E_g$ and $^2A_{1g}$. Results are summarized in Table 4. 

In order to check the correct assignment one can use a relation between experimental $B_{2g}$, $E_g$ and $A_{1g}$ values of the form $f(A) = \Delta A/(2·\Delta E - \Delta B) = 2/3$, which results from equations 1 to 3. Obviously this relation holds only for shortest axial bonds and more octahedral ligand environment, such fulfilling the precondition for the underlying ionic model. For non-existent axial bonds the value for the quotient is close to unity. The values listed in Table 4 indicate clearly a bond length dependence. An empirical function $f(R) = a_1·(R_A/R_e)$ may serve as a correction giving quotients $f(A)/f(R)$ near unity when using $a_1 = 0.59$ for dioptase group compounds respectively 0.70 for cuprates. Compounds with axial water ligands or $Cl^-$ can clearly be identified by relatively small values. Another possibility here published the first time ever is to use the linear relation

$$\Delta A = \alpha \cdot \left(\frac{<R_A>}{<R_e>} - \varepsilon\right),\text{ where } \alpha = (17892 \pm 60) \text{ cm}^{-1},$$

with a $R_A/R_e$ ratio including well adapted auxiliary $R_A$ bonds for compounds of coordination number 4, but different $\varepsilon$ values for the dioptase group ($\varepsilon = 1/\sqrt{2}$) and cuprates ($\varepsilon = 1/2$) to guide the regression line well through the origin (Figure 7 and Table 5).

**Figure 7.** $\Delta A$ excitation energies (cm$^{-1}$) depicted versus a function of axial to equatorial bond distances. Again the cuprate group excitations (in red) must be corrected by a (magnetic) contribution to reliably represent all data in a single regression line. Auxiliary axial bonds (see yellow field) were introduced in case of compounds with really missing axial bonds (coordination number 4).

It should be stressed with respect to the use of mean bond distances in equation 13 that also in the equations 7 to 10 the mean of corresponding bond distances is taken first and then their inverse fifth power is calculated to yield the convincing results of Table 4.
Table 4. Comparison of experimental and calculated excitation energies and orbital ones in cm⁻¹.

\( \Delta_{b} \) is sorted from high values to low ones down the table; \( f(A) = \Delta_{b}/(2\cdot\Delta_{A} - \Delta_{b}) \), \( f(R) = a_{1}/(R_{L}/R_{A}) \). Experimental and calculated \( \Delta \) values are arranged one above the other.

| Isolated CuO plaquettes, clusters and chains: Calculation with \( Q_{c}^{2} = 1.733 \), \( Q_{c}^{2} = 0.761 \), \( \eta = 1.276 \), \( \eta = 1.738 \), \( \alpha = 0.59 \) | Ligands | \( \Delta_{b} \) | \( \Delta_{a} \) | \( \Delta_{A} \) | \( D_{S} \) | \( D_{q} \) | \( D_{t} \) | \( D_{U/Dq} \) | \( D_{U/Dr} \) | \( f(A) \) | \( f(A)/(R) \) | equat. | axial |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cuprorivaita | 1.2590 | 15760 | 18530 | 3100 | 1259 | 1226 | 0.974 | 0.395 | 0.979 | 0.956 | oxygen | no |
| CuGeO₃ | 1.2570 | 13970 | 14209 | 1319 | 1250 | 1026 | 0.825 | 0.472 | 0.909 | 1.081 | oxygen | oxygen |
| Effenbergeite | 1.2500 | 15950 | 18502 | 3100 | 1250 | 1123 | 0.955 | 0.380 | 0.955 | 0.930 | oxygen | no |
| Wesselite | 1.2480 | 16050 | 18502 | 3100 | 1250 | 1179 | 0.945 | 0.374 | 0.944 | 0.920 | oxygen | no |
| Diopside black | 1.2330 | 14960 | 17930 | 2937 | 1223 | 1236 | 1.003 | 0.419 | 1.020 | 1.013 | oxygen | no |
| Cu₂GeO₄ | 1.2100 | 14723 | 14845 | 1130 | 1130 | 750 | 0.623 | 0.362 | 0.709 | 0.866 | oxygen | H₂O |
| Ge-Diopside | 1.1884 | 14321 | 11188 | 2046 | 1132 | 740 | 0.718 | 0.464 | 0.808 | 1.067 | oxygen | H₂O |
| Azurite (1) | 1.1806 | 16484 | 16104 | 2444 | 1132 | 740 | 0.770 | 0.317 | 0.809 | 1.024 | OH⁻ / oxygen | oxygen |
| Azurite (2) | 1.1550 | 12770 | 11300 | 1789 | 1155 | 829 | 0.718 | 0.464 | 0.808 | 1.067 | oxygen | H₂O |
| Litidionite | 1.1723 | 14700 | 13900 | 2411 | 1172 | 851 | 0.726 | 0.353 | 0.786 | 0.915 | oxygen | oxygen |
| Lammerite (1) | 1.1780 | 13444 | 14356 | 2331 | 1178 | 1006 | 0.854 | 0.432 | 0.914 | 0.914 | oxygen | oxygen |
| Lammerite (2) | 1.1280 | 12400 | 12029 | 1617 | 1128 | 746 | 0.662 | 0.461 | 0.754 | 1.023 | oxygen | oxygen |
| Chalcantite (1) | 1.1407 | 12600 | 8900 | 1442 | 1141 | 627 | 0.549 | 0.435 | 0.645 | 0.906 | H₂O | oxygen |
| Chalcantite (2) | 1.1135 | 12302 | 8828 | 1428 | 1113 | 623 | 0.549 | 0.435 | 0.645 | 0.906 | H₂O | oxygen |
| Diopside green | 1.1508 | 14398 | 10700 | 1940 | 1151 | 588 | 0.511 | 0.303 | 0.619 | 0.801 | oxygen | H₂O |
| Conichalcite | 1.1400 | 12954 | 8585 | 1340 | 1140 | 654 | 0.566 | 0.481 | 0.661 | 0.940 | OH⁻ | oxygen |
| Y₂BaCuO₅ | 1.0700 | 12500 | 14700 | 2357 | 1070 | 966 | 0.985 | 0.447 | 1.028 | 1.018 | oxygen | oxygen |

| Cuprates (undoped): Calculation with \( Q_{c}^{2} = 1.755 \), \( Q_{c}^{2} = 0.936 \), \( \eta = 1.587 \), \( \eta = 2.18 \), \( \alpha = 0.70 \) | Ligands | \( \Delta_{b} \) | \( \Delta_{a} \) | \( \Delta_{A} \) | \( D_{S} \) | \( D_{q} \) | \( D_{t} \) | \( D_{U/Dq} \) | \( D_{U/Dr} \) | \( f(A) \) | \( f(A)/(R) \) | equat. | axial |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La₂CuO₄ | 1.4516 | 17097 | 13710 | 2327 | 1452 | 880 | 0.606 | 0.378 | 0.697 | 0.788 | oxygen | O²⁻ ? |
| Ca₂CuO₂ | 1.3226 | 15726 | 21370 | 3410 | 1323 | 1546 | 1.169 | 0.453 | 1.173 | 0.994 | oxygen | no |
| Sr₂Ca₂CuO₄ | 1.2581 | 15565 | 21452 | 3491 | 1258 | 1498 | 1.190 | 0.429 | 1.157 | 0.976 | oxygen | no |
| Nb₂Ba₃CuO₆ | 1.2258 | 14113 | 15968 | 2546 | 1226 | 1157 | 0.944 | 0.454 | 1.000 | 1.072 | oxygen | oxygen |
| CuO (tenorite) | 1.2170 | 14230 | 16670 | 2676 | 1217 | 1193 | 0.981 | 0.446 | 1.023 | 1.027 | oxygen | oxygen |
| Sr₂Cu₂O₃Cl | 1.2097 | 14839 | 15887 | 2661 | 1210 | 1048 | 0.867 | 0.394 | 0.904 | 0.897 | oxygen | Cl⁻ |

An additional scaling \( \eta \) between 1.7 and 2.0 (equation 10) is needed to fit the \( D_{t} \) values of compounds with H₂O respectively Cl⁻ as axial bonds. Also La₂CuO₄ needs such correction (\( \eta = 1.71 \)) possibly caused by some O²⁻ expected as axial ligands.
Table 5. Experimental $\Delta_A$ energies versus calculated ones using the relation:

$$\Delta_A = 17892 \cdot \frac{<R_a>}{<R_e>} - \epsilon \text{ (cm}^{-1}\text{)}, \quad \epsilon = \frac{1}{\sqrt{2}} \text{ for dioptase group and } \epsilon = \frac{1}{2} \text{ for cuprates.}
$$

Auxiliary bonds introduced in case of compounds with coordination number $CN = [4]$ are underlined.

| Phase            | $CN$  | $<R_e>$ (Å) | $<R_a>$ (Å) | $\Delta_A$ (exp.) | $\Delta_A$ (calc.) |
|------------------|-------|-------------|-------------|-------------------|-------------------|
| Cuprorivaitie    | [4]   | 1.9307      | 3.35        | 18530             | 18393             |
| CuGeO$_3$        | [4+2] | 1.9326      | 2.7549      | 12920             | 12854             |
| Effenbergite     | [4]   | 1.9265      | 3.35        | 18520             | 18460             |
| Wesselite        | [4]   | 1.9265      | 3.35        | 18520             | 18460             |
| Dioptase black   | [4]   | 1.9340      | 3.30        | 17930             | 17874             |
| Cu$_6$Ge$_6$O$_{18}$ | [4] | 1.9404      | 3.30        | 17700             | 17777             |
| Ge-Dioptase      | [4+2] | 1.9474      | 2.6622      | 11884             | 11808             |
| Azurite (1)      | [4+2] | 1.9434      | 2.9840      | 16488 (?)         | 14821             |
| Azurite (2)      | [4+1+1]| 1.9593     | 2.5143      | 11806             | 10309             |
| Litidionite      | [4+2] | 1.9525      | 2.8434      | 13900             | 13404             |
| Lammerite (1)    | [4+2] | 1.9529      | 2.9230      | 14350             | 14128             |
| Lammerite (2)    | [4+1+1]| 1.9703     | 2.4609      | 10200             | 9695              |
| Chalcantite (1)  | [4+2] | 1.9759      | 2.3858      | 8900              | 8952              |
| Chalcantite (2)  | [4+2] | 1.9569      | 2.4400      | 9735              | 9657              |
| Dioptase green   | [4+2] | 1.9613      | 2.5688      | 10700             | 10735             |
| Conichalcite     | [2+2+2]| 1.9640     | 2.3403      | 8585              | 8668              |
| Y$_2$BaCuO$_4$   | [4+1] | 1.9899      | 2.196+3.90  | 14700             | 14754             |
| La$_2$CuO$_4$    | [4+2] | 1.9043      | 2.4045      | 13710             | 13646             |
| CaCuO$_2$        | [4]   | 1.9281      | 3.26        | 21370             | 21306             |
| Sr$_{0.5}$Ca$_{0.5}$CuO$_2$ | [4] | 1.9440 | 3.30 | 21452 | 21426 |
| NdBa$_2$Cu$_3$O$_{7-\delta}$ | [4+1] | 1.9609 | 2.275+3.25 | 15968 | 16260 |
| CuO (tenorite)   | [4+2] | 1.9558      | 2.7842      | 16670             | 16524             |
| Sr$_2$CuO$_2$Cl$_2$ | [4+2] | 1.9864      | 2.8600      | 15887             | 16841             |

Indeed, the connectedness of copper-ligand units, representing the number of shared copper-oxygen polyhedral, should be important for the $dd$ excitation energy. Therefore, besides the equatorial ligand sum that are calculated as fit coordinate we used the bond valence sums to check for inconsistent structural details and signs for mixed valences. Copper polygermanate in the $Pbmm$ prototypic structure [1,2] shows too high a sum with $\Sigma s = 2.08$. There is evidence from EPR [36], X-ray diffraction [37] and NQR measurements [38] that copper is statistically out of center of the CuO$_2$ plaquette, in this way the copper bond strength is reduced towards net charge of 2+. Even large thermal displacement ellipsoids indicate structural features that require a careful evaluation. Bond lengths should be corrected for ‘thermal’ displacement, because not less than their inverse fifth power is used in calculations (see for instance [49]).

4. EPR Analysis

Finally, the assignment of the $dd$ excitations can be compared with results of EPR measurements. For $3d^9$ ions in (nearly) tetragonal ligand symmetry one can apply the following two formulae for the principal components $g_{||}$ and $g_\perp$ if the ground state is $^2B_1g$.

$$
\begin{align*}
    g_{||} &= g_e - \frac{8\lambda}{A_B} - \frac{\lambda_2^2}{A_e^2} - \frac{4\lambda_2^2}{A_B A_e}, \\
    g_\perp &= g_e - \frac{2\lambda}{A_e^2} - \frac{\lambda_2^2}{A_e^2}.
\end{align*}
$$
where \( g_e = 2.0023 \) is the \( g \)-value for the free electron, and \( \lambda \) is the spin-orbital coupling parameter, which yields for the free electron \( \lambda_0 = 829 \text{ cm}^{-1} \) \[58\].

The \( k \) values are the spin orbital reduction factors used to scale the coupling parameters to the free electron value, \( k = \lambda / \lambda_0 \). This parameter reduction is attributed to covalence effects. Table 5 compares the results for dioptase and Ge-dioptase, respectively. Not surprisingly, the found covalence reduction effect is markedly smaller for the copper germanate than for the copper silicate, in accordance with crystal-chemical experience, confirming higher ionicity of the germanate (Table 6). Unfortunately, EPR data for the dehydrated compounds were not available.

### Table 6. EPR analysis of dioptase related compounds

| Notation | Dioptase | Ge-Dioptase |
|----------|----------|-------------|
| \( \Delta_B \) | 11508 | 11884 |
| \( \Delta_B \) | 14395 | 14321 |
| \( \Delta_A \) | 10700 | 11884 |
| \( g_\parallel \) | 2.3601 | 2.3780 |
| \( g_\perp \) | 2.0511 | 2.0970 |
| \( \lambda_\parallel \) | -504.08 | -545.53 |
| \( \lambda_\perp \) | -346.91 | -662.63 |
| \( k_\parallel \) | 0.608 | 0.658 |
| \( k_\perp \) | 0.418 | 0.799 |

### 5. Conclusions

As shown, a comparative reappraisal of \( \text{Cu}^{2+} \) UV-VIS spectra benefits from a special consideration of crystal-chemically similar groups of compounds, comparing exemplarily the dioptase group, covering minerals as well as synthetic samples, with cuprates. The assignment of \( dd \) excitations and their representation each on a single curve is possible by attributing a magnetic (bond angle dependent) contribution to the cuprate group. It is recommended to extend the bond strength – bond length relation by a bond angle dependent (magnetic) contribution. Deviations of the linear representation of orbital excitation energies may be helpful to discriminate results of compounds with peculiar orbital features from those with normal behavior. Fortunately, the first done assignment of well resolved spectra of dehydrated dioptase \( \text{Cu}_6(\text{Ge, Si})_6\text{O}_{18} \) served as input data to deconvolute the badly resolved spectra of as-grown \( \text{Cu}_6(\text{Ge, Si})_6\text{O}_{18} \cdot \text{6H}_2\text{O} \) samples. At present, the deconvolution of superposed spectra resulting from different Cu sites of a structure is inadequate. However, a pre-calculation of the expected energy levels can serve as input for fitting the experimental spectra. This has been successfully applied to lammerite. It is recommended to take a series of UV-VIS spectra step by step over the entire temperature range from hydrated to fully dehydrated dioptase as a didactic tool to follow the energy levels and their correct assignment, thereby simultaneously controlling the crystal water content by IR spectroscopy with a device that offers both analytical possibilities.

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### Conflict of Interest:
The author declares no conflict of interest.
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**Supplemented material**

Table 7. Comparison of scaling factors used for Cuprates in comparison to dioptase group compounds.

| Scaling factor notation | Cuprates | Dioptase group | Ratio |
|-------------------------|----------|----------------|-------|
| $Q_e^2$                 | 1.755    | 1.733          | 1.013 |
| $Q_a^2$                 | 0.936    | 0.761          | 1.230 |
| $\eta_s$                | 1.587    | 1.276          | 1.244 |
| $\eta_{se}$             | 2.180    | 1.738          | 1.254 |