

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

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Abstract

Low-dimensional quantum spin systems with the Cu^{2+} central ion are still in the focus of experimental and theoretical research. Here is reported on growth of mm-sized single-crystals of the low-dimensional $S = 1/2$ spin compound $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ by a diffusion technique in aqueous solution. A route to form Si-rich crystals down to possible dioptase, the pure silicate, is discussed. Motivated by previously reported incorrect assignments of UV-VIS spectra, the assignment of dd excitations from such 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 $J_z \ln(2)$ is taken into account for cuprates, a single linear relationship between the D_{q_e} 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 if auxiliary axial bonds are used for four-coordinated compounds. The quotient D_t/D_s of experimental orbital energies deviating from the general trend to smaller values indicates the existence of H_2O respectively Cl^- axial ligands in comparison to oxo-ligands, whereas larger D_t/D_{q_e} values indicate missing axial bonds. The quotient of the excitation energy ${}^2A_{1g}$ by $2 \cdot {}^2E_g - {}^2B_{2g}$ allows checking for correctness of the assignment and to distinguish between axial oxo-ligands and others like H_2O or Cl^- .

Keywords

Dioptase, Ge-Dioptase, Copper(II) Compounds, Cuprates, Crystal Growth,

1. Introduction

Low-dimensional quantum spin systems are of considerable theoretical and experimental interests 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 tetrahedra 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] [6] succeeded in the synthesis of pure copper polysilicate, CuSiO_3 , by thermal decomposition of the mineral diopside, CaSiO_3 . 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 $T_N = 7.9 \text{ K}$ [7] [8].

The rhombohedral title compound $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ 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).

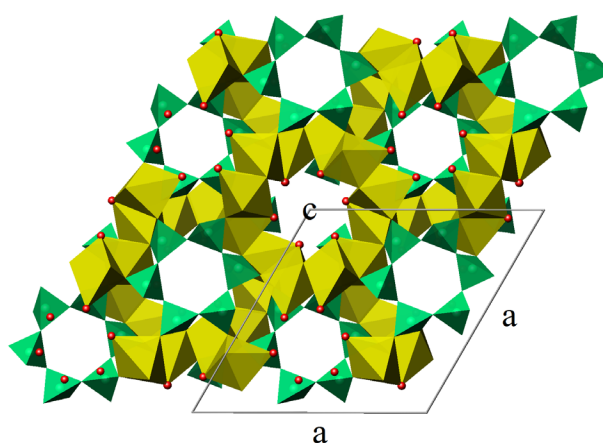


Figure 1. Crystal structure of diopside projected down [001]. A framework of copper oxide octahedra (yellow) screws around the c -axis with non-bonding axial water ligands (red) pointing towards empty channels. Six-membered silicate single rings are depicted in green.

This structure is interesting because it allows for a quantum phase transition between an anti-ferromagnetically ordered state and a quantum spin liquid [9]. Large quantum fluctuations in green diopside have been described [10]. Recently, also the germanate analogue, $\text{Cu}_6\text{Ge}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ [11], has been the object of detailed magnetic and structural investigations [12] [13].

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 physicochemical 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 diopside by *EPR* measurements [14] [15].

Because the assignment of the *dd* excitations derived from the *UV-VIS* spectra of copper-bearing compounds are often found to be incorrect, this work contributed some simple tools that could lead to the right assignment. It is not the intent of this paper to review *UV-VIS* spectroscopy of Cu^{2+} compounds in general.

2. Experimental

2.1. Crystal Growth and Dehydration of the Samples

The method described below was used by the author many years earlier for the synthesis of rare minerals, for instance, the synthesis of $\text{Pb}_3\text{Ge}(\text{OH})_6(\text{SO}_4)_2\cdot 3\text{H}_2\text{O}$, the piezoelectric *Tsumeb* mineral fleischerite [16]. For the synthesis of the title compound freshly precipitated gels of GeO_2 and $\text{Cu}(\text{OH})_2$ were separately filled in 200 ml beaker glasses and thoroughly filled up with distilled water. Then a 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 $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ 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).

One can extrapolate the time scale to get a crystal of about 2 mm diameter and calculate about 1 year of growing time. Trying to exchange Ge by Si by this method

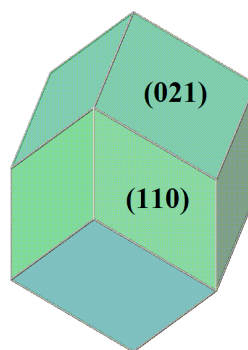


Figure 2. The stocky prismatic habit of the as-grown $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ crystals, showing a combination of the $\{110\}$ prism and the $\{021\}$ rhombohedron.

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 $\text{Cu}(\text{OH})_2$ gel and longer time vigorous stirring resulted in a vivid green colored polycrystalline material of about 12 at-% Si determined from lattice parameter changes [14] [17]. Also, the substitution of some B^{3+} for Ge^{4+} is possible, leading to a beautiful green color [17]. Stirring a longer period and in addition changing the pH to more acidic milieu gives at least about 15 at-% Si ($a = 14.640 \text{ \AA}$, $c = 7.806 \text{ \AA}$, this work). The effect is based on the different solubility of the Ge-compound in comparison to diopside. $\text{Cu}_6\text{Ge}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ is easily decomposed by a dilute acetic acid, but diopside does not dissolve. Recently we observed a deepening of color to diopside 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 diopside.

A proposed approach for a possible synthesis of pure polycrystalline diopside 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 diopside layer. A new core of silico-germanate can be grown epitaxially and subsequently transformed to diopside. Repetition of this process may finally form pure diopside 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.

A single-phase crystalline powder of synthetic Ge-diopside for the *UV-VIS* spectroscopic investigation is best obtained from an aqueous solution of pH 5.5 at room temperature, formed by mixing and stirring equal amounts of 0.02 M cupric acetate with freshly produced 0.02 M GeO_2 solution. The initially formed gel settles as fully crystalline precipitate after an induction period of two days

[10].

Complete dehydration of synthetic Ge-diopside was performed by annealing of the polycrystalline sample up to 920 K for 6 h, followed by cooling down to room temperature with a moderate cooling rate of 20 K/h. The chosen annealing temperature lies about 53 K below the temperature of decomposition to the orthorhombic spin-*Peierls* phase CuGeO_3 [10].

A natural diopside samples from the locality *Altyn Tyube*, Kazakhstan, was used as pure silicate sample. Its complete dehydration to “black” diopside occurs at 660 K and should be controlled by X-ray powder diffraction analysis because decomposition into CuO (tenorite) and SiO_2 (partly quartz and cristobalite) starts only a few degrees higher at 673 K.

2.2. UV-VIS Spectroscopic Investigation

First results of *UV-VIS* spectroscopy on $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ are given in the doctoral theses of my coworkers *Brandt* [17] and *Meibohm* [14], respectively, whereas diopside itself has been investigated earlier by different researchers [18] [19] [20] [21].

Brandt [17] reported a color change from turquoise-green to blue on dehydration of diopside-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 $\text{Cu}_6\text{Ge}_6\text{O}_{18}$ 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 diopside is not planar but disphenoidic, and a change to a stiffer, more tetrahedral one may occur with raising the 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, $\text{KNaCuSi}_4\text{O}_{10}$ [22] [23], which shows similarity to that of diopside.

The room temperature *UV-VIS* spectra of the samples were taken with the double-beam light scanning *UV-2501PC CE* spectrometer from *Shimadzu* with selectable light sources (50W halogen lamp and D2 lamp). The powder sample was coated on a polished aluminum disk and measured in the reflection mode 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 $H = \beta_e B \cdot g \cdot S$, 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 $\beta_e = g_e \mu_B$ (*Landé* g -factor for the free electron, $g_e = 2.0023$, *Bohr* magneton μ_B). In this contribution g values for dioptase, $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$, determined by *Reddy et al.* [19], and data measured by *Meibohm* [14] for synthetic $\text{Cu}_6\text{Ge}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ were used as expressed in its principal axes system.

3. Results and Discussion

The *Gaussian* peak analysis of the *UV-VIS* spectra was performed with the aid of own *Turbo-Basic* programs using recast software modules once developed for X-ray powder profile analysis, supplemented by a program to provide an illustration of single *Gaussian* peaks besides the cumulative curve. Fortunately, the spectra of the dehydrated compounds are well-resolved and their reliably fitted profile data could serve as input for the less-resolved spectra of the as-grown respectively hydrated natural compounds, thereby applying variable constraints to parameters (mainly the band width) during successive refinement cycles. 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 3(a)-(d)**. $\lambda(\text{nm})$ and $\Gamma(\text{nm})$ represent wavelength and the full width of the excitation peaks, and the wavenumber $E(\text{cm}^{-1})$ denotes the excitation energy. The

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

Cu ₆ Si ₆ O ₁₈ ·6H ₂ O (dioptase)					Cu ₆ Ge ₆ O ₁₈ ·6H ₂ O (Ge-dioptase)				
<i>P</i>	$\lambda(\text{nm})$	$\Gamma(\text{nm})$	$E(\text{cm}^{-1})$	Assignment	<i>P</i>	$\lambda(\text{nm})$	$\Gamma(\text{nm})$	$E(\text{cm}^{-1})$	Assignment
329	935 ± 37	208	10,700	Δ_A	1000	842 ± 30	198	11,884	$\Delta_B + \Delta_A$
815	869 ± 12	208	11,507	Δ_B					
1000	695 ± 7	194	14,400	Δ_E	645	698 ± 24	166	14,321	Δ_E
256	600	109	16,670	<i>ZRS?</i>	185	616	129	16,230	<i>ZRS?</i>
421	414	108	24,160	<i>SPE?</i>	271	462	147	21,650	<i>SPE?</i>
(554)	326	102	30,660	E_g	(531)	353	97	28,350	E_g
Cu ₆ Si ₆ O ₁₈ (dioptase dehydrated)					Cu ₆ Ge ₆ O ₁₈ (Ge-dioptase dehydrated)				
<i>P</i>	$\lambda(\text{nm})$	$\Gamma(\text{nm})$	$E(\text{cm}^{-1})$	Assignment	<i>P</i>	$\lambda(\text{nm})$	$\Gamma(\text{nm})$	$E(\text{cm}^{-1})$	Assignment
1000	811 ± 14	158	12,330	Δ_B	1000	827 ± 14	155	12,100	Δ_B
866	668 ± 12	120	14,960	Δ_E	843	679 ± 12	127	14,723	Δ_E
492	558 ± 11	96	17,930	Δ_A	450	565 ± 12	97	17,700	Δ_A
235	441	100	22,680	<i>SPE?</i>	355	437	108	22,880	<i>SPE?</i>
(869)	330	120	30,300	E_g	(630)	357	102	28,000	E_g

P integrated band intensity (arbitrary units), $\Gamma(\text{nm})$ full band width at half \int , $E(\text{cm}^{-1})$ band energy, *SPE* assumed simultaneous pair excitation, *ZRS* less intense band observed only in the hydrated compounds around 2 eV could correspond to a Zhang-Rice singlet excitation, E_g large energy gap.

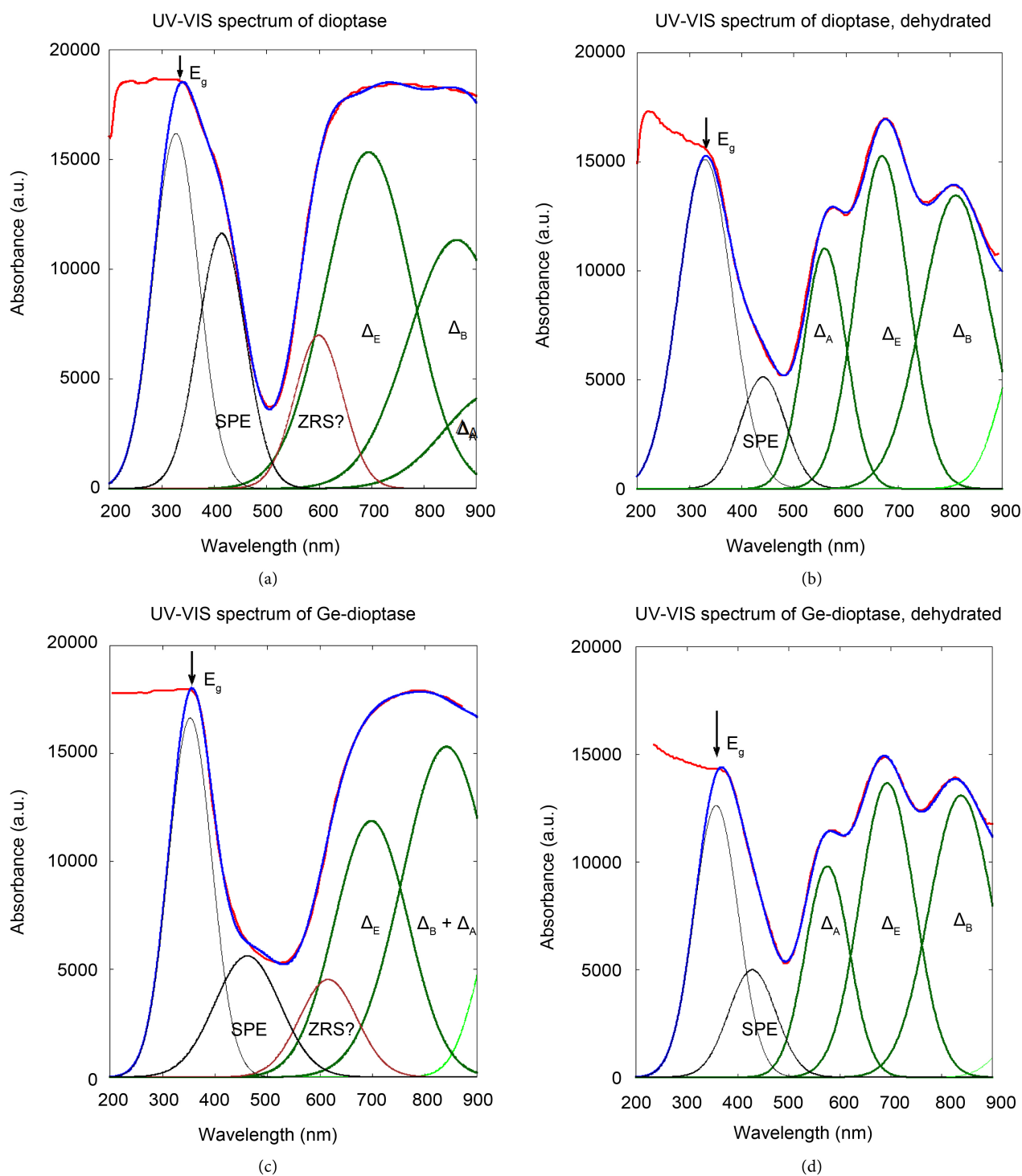


Figure 3. UV-VIS spectra of (a) diopside; (b) diopside dehydrated; (c) Ge-diopside; (d) Ge-diopside dehydrated. Measured spectra red, calculated spectra blue. A mineral sample of diopside from *Altyn Tyube*, Kazakhstan was used besides synthetic Ge-diopside.

remarkable integrated band intensity P (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 indi-

cating $\text{Cu}_{3d}\text{-O}_{2p}$ hybridization. The relative width Γ/λ 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 diopside and shifts to 3.76 eV for Ge-diopside, 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 centers of the dimer at twice the monomer transition energy (*SPE*), because their oscillator strengths are too weak for charge transfer (*CT*) transitions. The position of a less intense absorption band observed only for the hydrated compounds around 2 eV ($16,670\text{ cm}^{-1}$, $16,230\text{ cm}^{-1}$) would correspond to *Zhang-Rice* singlet excitations (*ZRS*), for instance, measured at this energy on CuO (tenorite) [25] and CuGeO_3 , respectively [26].

The color of Cu^{2+} compounds with their *Jahn-Teller* distorted coordination polyhedra [27] 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 [28].

The transition energies $\Delta_n\text{ (cm}^{-1}\text{)}$, 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 Dq_e splitting parameter and two radial Ds and Dt ones (*Gerloch and Slade*, [29]). The crystal field theory (*CFT*) allows for the following relations:

$$\Delta_B = B_{2g}(xy) - B_{1g}(x^2 - y^2) = 10Dq_e \quad (1)$$

$$\Delta_E = E_g(xz, yz) - B_{1g}(x^2 - y^2) = 3Ds + 10Dq_e - 5Dt \quad (2)$$

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

Conversely, the D parameters can be recalculated as

$$Dq_e = \Delta_B/10 \quad (4)$$

$$Ds = (\Delta_A + \Delta_E - \Delta_B)/7 \quad (5)$$

$$Dt = (3\Delta_A + 4(\Delta_B - \Delta_E))/35 \quad (6)$$

Whereas Δ_E is always moderately larger than Δ_B , Δ_A ranges from about 8500 cm^{-1} ($<\Delta_B$) for shortest axial bonds to at least 21,500 cm^{-1} ($>\Delta_E$) 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 [29]:

$$Dq_e = \eta_e \cdot Z_L \cdot e^2 \langle r^4 \rangle / (6 \cdot R_e^5), \quad Dq_a = \eta_a \cdot Z_L \cdot e^2 \langle r^4 \rangle / (6 \cdot R_a^5) \quad (7)$$

$$Cp_e = 2\eta_s \cdot Z_L \cdot e^2 \langle r^2 \rangle / (7 \cdot R_e^3), \quad Cp_a = 2\eta_s \cdot Z_L \cdot e^2 \langle r^2 \rangle / (7 \cdot R_a^3) \quad (8)$$

$$Ds = Cp_e - Cp_a \quad (9)$$

$$Dt = 4/7 \cdot \eta_i \cdot (Dq_e - \eta_i \cdot Dq_a) \quad (10)$$

where $\eta \cdot Z_L$ represents an effective ligand charge, R_e and R_a are equatorial and axial bond lengths in Å, and $\langle r^4 \rangle = 0.214 \text{ Å}^4$ is the mean value of the fourth power of a 3d orbital radial distance from the nucleus, respectively $\langle r^2 \rangle = 0.294 \text{ Å}^2$ the mean of the second power of the radial distance. For $\langle r^n \rangle$ the values calculated by *Haverkort* within the *Hartree-Fock* approximation are used [30]. Because $\langle r^4 \rangle$ 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.

Quoting *Gerloch and Slade* [29] 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

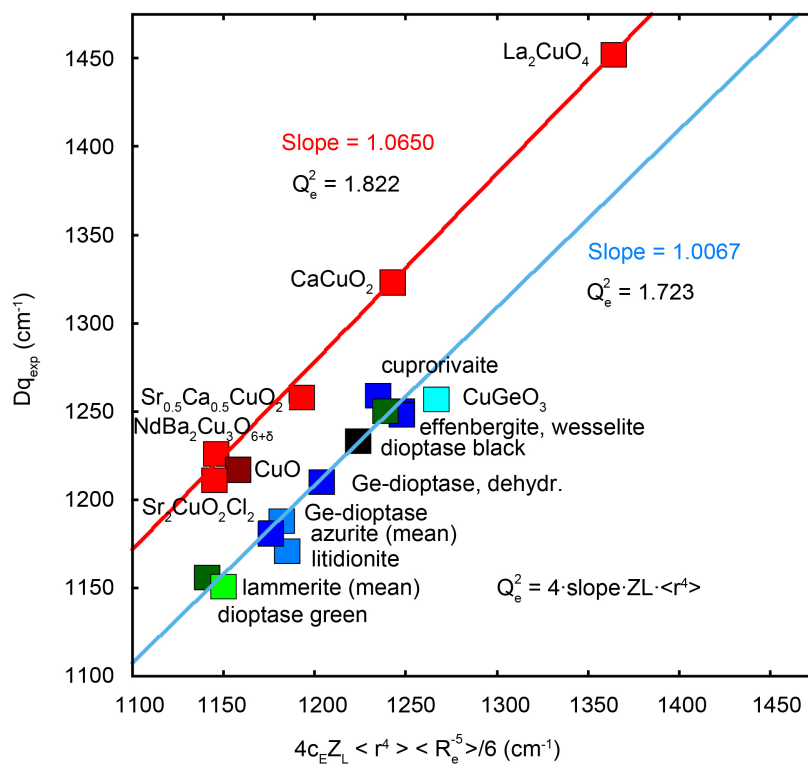
$$Q_e^2 = \eta_e \cdot Z_L \langle r^4 \rangle \quad \text{respectively} \quad Q_s^2 = \eta_s \cdot Z_L \langle r^2 \rangle.$$

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

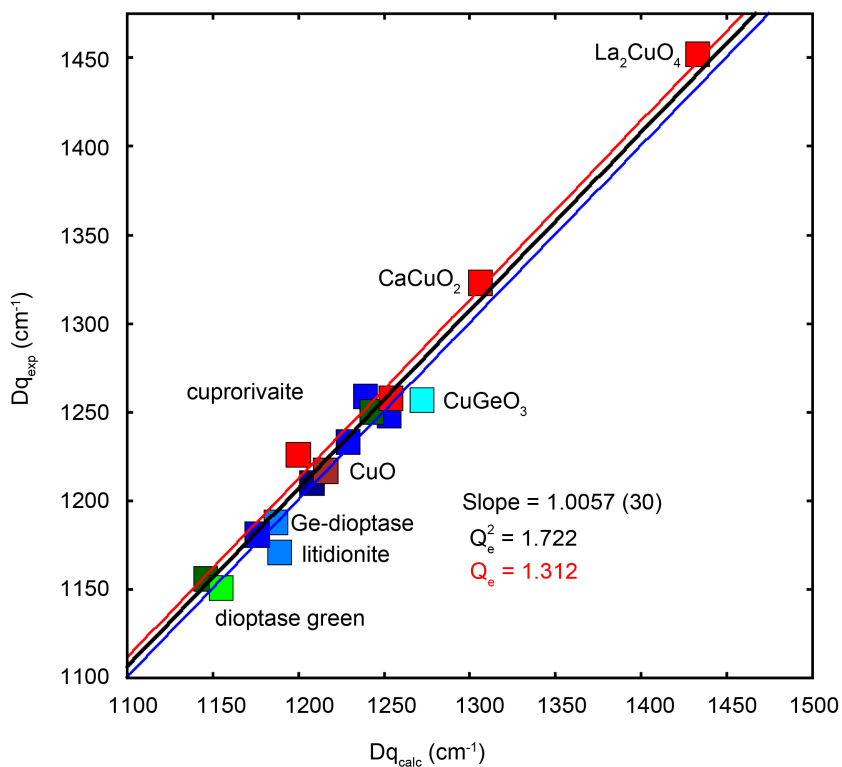
Lebernegg et al. [31] found no general theoretical justification for R^{-5} dependence of ligand-field splitting. Nevertheless, one can use the inverse fifth power relationship $Dq_e \propto R^{-5}$ in order to calculate a linear regression curve of Dq_e (or Δ_B) values against the mean of the four equatorial copper-oxygen distances $R_e(\text{Å})$ according to Equation (7) 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 4** and extrapolates well through the origin with $Q_e^2 = 1.723$, giving effective charge numbers of $Q_e = \pm 1.313$ assumed to be evenly distributed over Cu^{2+} and ligands. The calculated Dq_e values deviate less than 1.6% from the experimental ones.

We chose compounds of the *Egyptian Blue* family (cuprorivaite, wesselite, ef-ferbergite,) with isolated D_{4h} plaquettes, the dehydrated diopside compounds with equatorially edge-shared dimers, further connected via water oxygen to



(a)



(b)

Figure 4. Calculated Dq energies versus experimental ones for diopside and related compounds. In the right plot, an additional magnetic contribution of Dq_{calc} for cuprates was considered.

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 CuGeO₃ 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* [32]. Selected crystal data as well as *UV-VIS* data were summarized in the **Table 2** and **Table 3** with references.

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, *Σs* overall sum (particularly striking values in red).

Compound	<i>CN</i>	<i>d</i> (Cu-O) (Å)	Bond strength			Reference
			<i>s_e</i>	<i>s_a</i>	<i>Σs</i>	
Ca _{0.5} Sr _{0.5} CuO ₄		1.945	1.913	-	1.913	[41]
CaCuO ₂		1.928	2.004	-	2.004	[33]
BaCuSi ₄ O ₁₀ Effenbergite	4	1.925	2.022	-	2.022	[42]
SrCuSi ₄ O ₁₀ Wesselite		1.925	2.022	-	2.022	[43]
CaCuSi ₄ O ₁₀ Cuprorivaite		1.929	1.998	-	1.998	[44]
Cu ₆ Si ₆ O ₁₈	4 + (1)	1.9250 1.9294	1.969	0.023	1.992	[20]
		1.9354 1.9466 3.3153				
Cu ₆ Ge ₆ O ₁₈		1.9043 1.9284	1.954	-	1.954	[17]
		1.9380 1.9979 3.3841				
Y ₂ BaCuO ₅	2 + 2 + 1	1.985 1.988 2.206	1.692	0.232	1.923	[45]
CuGeO ₃	4 + 2	1.941 2.926	1.941	0.093	2.022	[1] [2] [3]
Cu ₆ Si ₆ O ₁₈ ·6H ₂ O	6	1.952 1.952 1.959	1.818	0.195	2.014	[46]
		1.983 2.502 2.648				
Cu ₆ Ge _{5.4} Si _{0.6} O ₁₈ ·6H ₂ O	6					[17]
Cu ₆ Ge ₆ O ₁₈ ·6H ₂ O	6	1.9037 1.9486 1.9547	1.894	0.159	2.053	[11]
		1.9884 2.6364 2.6696				
Cu ₃ (CO ₃) ₂ (OH) ₂ Azurite	2 + 2 + 2					
	Cu(1) site	1.9387 1.9455 2.9840	1.953	0.083	2.036	
	6 Cu(2) site	1.9385 1.9388 1.9675	1.830	0.223	2.053	[47]
		1.9947 2.3608 2.7578				
CuSO ₄ ·5H ₂ O Chalcantite	2+2+2 Cu(1) site	1.9748 1.9770 2.3858	1.769	0.250	2.019	
	2+2+2 Cu(2) site	1.9447 1.9696 2.4400	1.739	0.293	2.033	[48]
KNaCuSi ₄ O ₁₀ Litidionite	6	1.9220 1.9434	1.863	0.109	1.972	[22]; this work
		1.9683 1.9799				
		2.6238 3.4024				
Cu ₃ (AsO ₄) ₂ Lammerite	2 + 2 + 2					
	Cu(1) site	1.933 1.974 2.923	1.864	0.093	1.957	
	6	1.941 1.947 1.972	1.772	0.254	2.026	[49]
	Cu(2) site	2.028 2.282 2.782				
CaCuAsO ₄ OH Conichalcite	6	1.8850 1.8855	1.811	0.332	2.143	[50]; this work
		2.0666 2.0688				
		2.2976 2.3882				
La ₂ CuO ₄	4 + 2	1.9043 2.4145	2.151	0.278	2.439	[51]
Sr ₂ CuO ₂ Cl ₂	4 + 2	1.9864 2.860	1.687	0.292	1.979	[52]

Table 3. Collection of some properties and data for selected Cu(II) oxo-compounds. $\Delta_B = {}^2B_{2g}(xy) - {}^2B_{1g}(x^2 - y^2)$, $\Delta_E = {}^2E_g(xz, yz) - {}^2B_{1g}(x^2 - y^2)$, $\Delta_A = {}^2A_g(z^2) - {}^2B_{1g}(x^2 - y^2)$, energies in cm^{-1} . Other transitions: *CT* charge transfer, *SPE* simultaneous pair excitation, *ZRS?* Zhang Rice excitation, E_g energy gap.

Compound	Color	Cu site symmetry	Δ_B	Δ_E	Δ_A	Other Transition	Reference
CaCuO ₂ (infinite layer)	dark-grey	D _{4h}	13,230	15,730	21,370	-	[33]
Tenorite CuO	brownish	C _i	12,170	12,930 15,530	16,670	many	[53]**
Conichalcite synth. CaCuAsO ₄ OH	light green	C _i	10,575	12,500	8585	15,313 <i>ZRS?</i> 31,370 (E_g)	[54]
Lammerite synth. Cu ₃ (AsO ₄) ₂	dark green	C _i C _i	11,530	12,400 14,050	10,200 14,050	23,260 CuO 31,250 (E_g)	[22]; this work*
Y ₂ BaCuO ₅	vivid green	D _{4h}	12,500 10,700	13,200	14,700	25,970 CT	[55]**
Azurite Cu ₃ (CO ₃) ₂ (OH) ₂	blue	C _i C _i	11,806 11,806	16,484 11,806	16,484 11,806	19,793 17,952	[56]** $T = 80$ K
Chalcanthite CuSO ₄ ·5H ₂ O	deep blue	C _i C _i	11,407 11,860	13,308 13,488	9699 9735	15,234 <i>ZRS?</i> 15,567	[57]
Litidionite synth. KNaCuSi ₄ O ₁₀	light blue	C _i	11,723	14,700	13,900	21,400 <i>SPE</i> 31,600 (E_g)	[22] [23]; this work
Cu ₆ Ge ₆ O ₁₈	dirty blue	C _i	12,100	14,723	17,700	22,880 <i>SPE</i>	[17]; this work
Cu ₆ Ge ₆ O ₁₈ ·6H ₂ O	bluish-green	C _i	11,880	14,320	11,880	16,230 <i>ZRS?</i> 21,650 <i>CT</i> 30,300 (E_g)	[17]; this work
Cu ₆ Ge _{5.4} Si _{0.6} O ₁₈ ·6H ₂ O	dark green	C _i	13,300		19,400	23,900 <i>CT</i>	[17]
CuGeO ₃	turquoise	D _{2h}	12,570	13,970	12,920	15,733 <i>ZRS?</i> 15,800	[24]; this work
BaCuSi ₄ O ₁₀ synth. (Effenbergite)			12,200	15,950	18,520	-	[58]
SrCuSi ₄ O ₁₀ synth. (Wesselite)	deep blue	D _{4h}	12,480	16,050	18,520	-	[58]
CaCuSi ₄ O ₁₀ synth. (Cuprorivaite)			12,590 12,740	15760 16130	18,530 18,520	-	[44] [59]
Diopside dehydrated Diopside partly dehydrated	black dark blue	C _i	12,330 12,500	14,960 14,500	17,930 17,600	22,680 <i>SPE</i> -	This work; [19]
Diopside Cu ₆ Si ₆ O ₁₈ ·6H ₂ O	emerald green	C _i	11,500 12,495 11,507	14,500 15,010 14,400	17,000 10,200 10,700	16,670 <i>ZRS?</i> 24,160 <i>CT</i> 30,660 (E_g)	[18] [19] This work

*synthetic lammerite with an amount of CuO; **for this work a different assignment as given in the reference was used.

Recently, the energy and symmetry of *dd* excitations of some undoped layered cuprates have been measured by CuL₃ resonant *X*-ray scattering [33]. The well-

assigned dd excitations of these compounds with high connectedness were found to be higher than the energies of the compounds described before. Multi-ferroic CuO as limiting case can be added to this group with due allowance. Applying Equation (a), 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 diopside group.

The different connectedness of cuprates in comparison to the diopside 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 Φ , a representation first used by *Rocquefelte et al.* [34], and here applied in an extended form, illustrating both diopside group compounds and cuprate ones. A data fit resulted in the relation

$$J_z(\Phi) = 0.091 \cdot (\Phi - 90)^{1.652} \text{ (meV)} = 0.734 \cdot (\Phi - 90)^{1.652} \text{ cm}^{-1}. \quad (11)$$

with an exponent near 5/3, explained by chemical pressure (*Rocquefelte et al.*, 2012) [34] [35]. 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 $Q_e^2 = 1.722$, respectively $Q_e = 1.312$. It should be noticed that for the diopside group an antiferromagnetic contribution is not included because T_N is lower than room temperature, at which the optical spectra are taken.

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 $s = \Sigma(R/R_0)^{-N}$ [36] by choosing only the

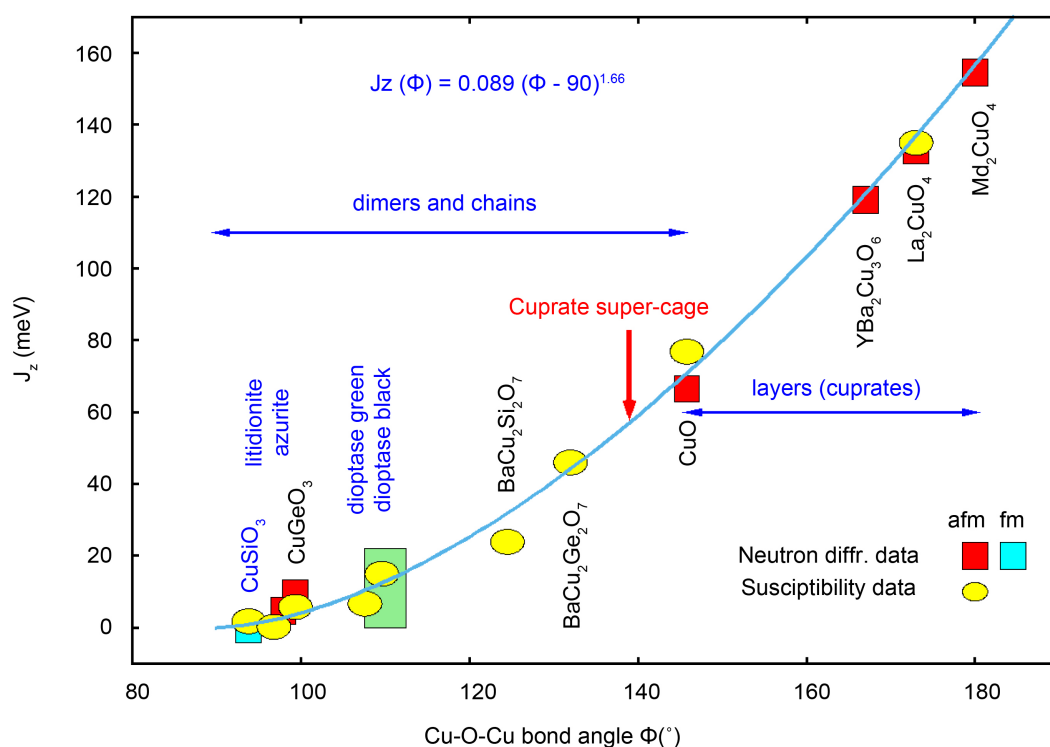


Figure 5. Principal superexchange interaction J_z versus Cu-O-Cu bond angle Φ [34] [35].

bond strength sum s_e of the four equatorial bonds. New values $R_0 = 1.713(9) \text{ \AA}$, $N = 5.76(16)$ were re-calculated for this work [37]. Results of a double-regression yielded for the cuprate group

$$\Delta_B (\text{cm}^{-1}) = (6658 \pm 38) \cdot s_e \quad (12a)$$

$$\text{respectively } \Delta_B (\text{cm}^{-1}) = (6269 \pm 21) \cdot (s_e + 1.38 \times 10^{-4} J_z) \quad (12b)$$

for both the diopside group and cuprates. Δ_B of the last mentioned group is 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 [33] 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^- 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 $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{CuO}_2$ is obviously strained.

Turning now to the calculation of splitting parameters Ds (Equation (9)) and Dt (Equation (10)) involving axial ligands one has to distinguish according to the *Nephelauxetic Effect* between pure oxo-ligands and such ones as H_2O or Cl^- with increased cationic charge and assumed higher Dq_a values [29]. H_2O (as equatorial ligands) are found in chalcantite, and hydroxyl groups in azurite and conicalcrite. The last compound has the most distorted “octahedron” and should show a pronounced splitting of the 2E_g term, which is not considered here.

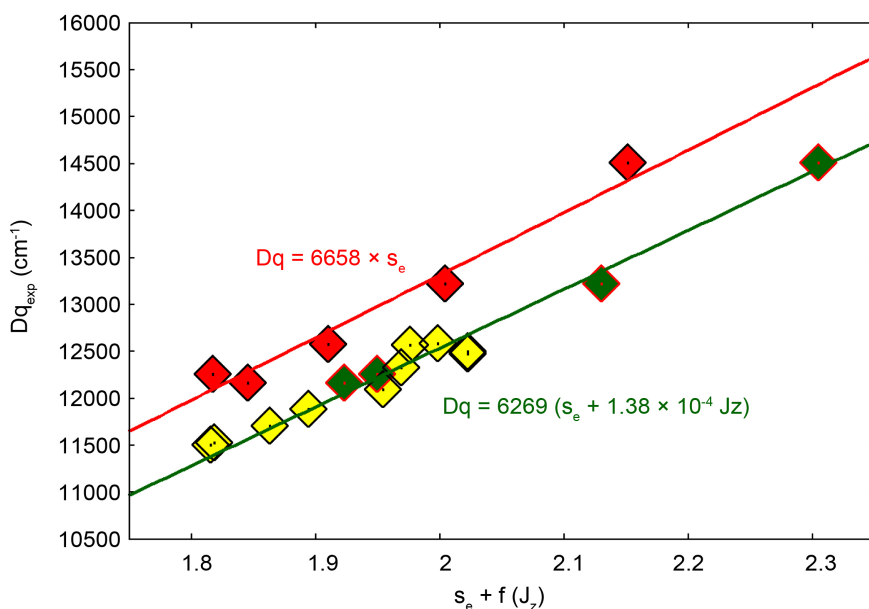


Figure 6. A linear relation between $Dq (\text{cm}^{-1})$ and the equatorial bond strength s_e in case of cuprates (red curve) corrected by a bond angle dependent (magnetic) contribution to show a single linear plot (green curve) with diopside group compounds (yellow) besides cuprates (now green).

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 diopside 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 Ds and Dt the Δ_E (Equation (2)) and Δ_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 form $f(\Delta) = \Delta_A / (2 \cdot \Delta_E - \Delta_B) = 2/3$, 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 bond length dependence. An empirical function $f(R) = \alpha_1 \cdot (R_a/R_e)$ may serve as a correction giving quotients $f(\Delta)/f(R)$ near unity when using $\alpha_1 = 0.59$ for diopside 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

$$\Delta_A = \alpha \cdot \left(\frac{\langle R_a \rangle}{\langle R_e \rangle} - \varepsilon \right), \text{ where } \alpha = (17892 \pm 60) \text{ cm}^{-1}, \quad (13)$$

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

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**.

An additional scaling η_l between 1.7 and 2.0 (Equation (10)) is needed to fit the Dt values of compounds with H_2O respectively Cl^- as axial bonds. Also, La_2CuO_4 needs such correction ($\eta_l = 1.71$) possibly caused by some O^- expected as axial ligands. Applied scaling factors were summarized as supplemented material in the **Table 7**.

Indeed, the connectedness of copper-ligand units, representing the number of shared copper-oxygen polyhedra, should be important for the dd excitation energy. Therefore, besides the equatorial ligand sums 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* [38], *X-ray* diffraction [39] and *NQR* measurements [40] that copper is statistically out of center of the CuO_2 plaquette, in this way the copper bond

Table 4. Comparison of experimental and calculated excitation energies and orbital ones in cm^{-1} . Δ_B is sorted from high values to low ones down the table; $f(\Delta) = \Delta_A / (2 \cdot \Delta_E - \Delta_B)$, $f(R) = \alpha_1 \cdot (R_a / R_e)$. Experimental and calculated Δ values are arranged one above the other.

Isolated CuO plaquettes, clusters and chains: Calculation with $Q_e^2 = 1.733$, $Q_s^2 = 0.761$, $\eta_s = 1.276$, $\eta_t = 1.738$, $\alpha_t = 0.59$												
Phase	Δ_B	Δ_E	Δ_A	Ds	Dq	Dt	Dt/Dq	Dt/Ds	$f(\Delta)$	$f(\Delta)/f(R)$	Ligands	
											equat.	axial
Cuprorivaite	12,590	15,760	18,530	3100	1259	1226	0.974	0.395	0.979	0.956	oxygen	no
	12,501	15,446	18,414	3051	1250	1241						
CuGeO ₃	12,570	13,970	13,970	2196	1257	1037	0.825	0.472	0.909	1.081	oxygen	oxygen
	12,439	14,209	14,324	2299	1244	1026						
Effenbergite	12,500	15,950	18,520	3139	1250	1139	0.955	0.380	0.955	0.930	oxygen	no
	12,566	15,895	18,591	3132	1257	1213						
Wesselite	12,480	16,050	18,520	3156	1248	1179	0.945	0.374	0.944	0.920	oxygen	no
	12,566	15,895	18,591	3132	1257	1213						
Diopside black	12,330	14,960	17,930	2937	1233	1236	1.003	0.421	1.019	1.013	oxygen	no
	12,324	15,057	17,850	2940	1232	1218						
Cu ₆ Ge ₆ O ₁₈	12,100	14,723	17,700	2903	1210	1217	1.006	0.419	1.020	1.017	oxygen	no
	12,123	14,845	17,606	2904	1212	1198						
Ge-Diopside	11,884	14,321	11,884	2046	1188	740	0.623	0.362	<u>0.709</u>	0.866	oxygen	H ₂ O
	11,929	14,434	12,084	2084	1193	750						
Azurite (1)	11,806	16,484	16,484	–	1181	–	0.770	0.317	0.809	1.024	OH ⁻ / oxygen	oxygen
	12,070	14,162	15,014	2444	1207	1048						
Azurite (2)	11,550	12,770	11,300	1789	1155	829	0.718	0.464	0.808	1.067	OH ⁻ / oxygen	oxygen
	11,589	12,924	11,669	1858	1159	848						
Litidionite	11,723	14,700	13,900	2411	1172	851	0.726	0.353	0.786	0.915	oxygen	oxygen
	11,794	14,465	13,917	2397	1179	866						
Lammerite (1)	11,780	13,744	14,356	2331	1178	1006	0.854	0.432	0.914	0.914	oxygen	oxygen
	11,735	13,744	14,357	2328	1174	1000						
Lammerite (2)	11,280	12,400	10,200	1617	1128	746	0.662	0.461	0.754	1.023	oxygen	oxygen
	11,231	12,425	10,279	1639	1123	745						
Chalcanthite (1)	11,407	12,600	8900	1442	1141	627	0.549	0.435	0.645	0.906	H ₂ O	oxygen
	11,135	12,302	8828	1428	1113	623						
Chalcanthite (2)	11,860	13,488	9735	1623	1186	648	0.547	0.399	0.644	0.875	H ₂ O	oxygen
	11,678	13,369	98,108	1643	1168	648						
Diopside green	11,508	14,398	10,700	1940	1151	588	0.511	0.303	<u>0.619</u>	0.801	oxygen	H ₂ O
	11,491	14,094	10,325	1847	1149	587						
Conichalcite	11,400	12,195	8585	1340	1140	645	0.566	0.481	0.661	0.940	OH ⁻	oxygen
	11,119	11,922	8449	1339	1141	658						
Y ₂ BaCuO ₅	10,700	13,200*)	14,700	2457	1070	974	0.911	0.397	0.936	0.904	oxygen	oxygen
	10,732	13,205	14,571	2435	1073	966						
Cuprates (undoped): Calculation with $Q_e^2 = 1.755$, $Q_s^2 = 0.936$, $\eta_s = 1.587$, $\eta_t = 2.18$, $\alpha_t = 0.70$												
Phase	Δ_B	Δ_E	Δ_A	Ds	Dq	Dt	Dt/Dq	Dt/Ds	$f(\Delta)$	$f(\Delta)/f(R)$	Ligands	
											equat.	axial
La ₂ CuO ₄	14,516	17,097	13,710	2327	1452	880	0.606	0.378	0.697	0.788	oxygen	O ⁻ ?
	14,308	16,833	13,664	2313	1431	883						
CaCuO ₂	13,226	15,726	21,370	3410	1323	1546	1.169	0.453	1.173	0.994	oxygen	no
	13,322	15,982	21,671	3476	1332	1554						
Sr _{0.5} Ca _{0.5} CuO ₂	12,581	15,565	21,452	3491	1258	1498	1.190	0.429	1.157	0.976	oxygen	no
	12,744	15,494	21,026	3397	1274	1488						
NdBa ₂ Cu ₃ O ₆	12,258	14,113	15,968	2546	1226	1157	0.944	0.454	1.000	1.072	oxygen	oxygen
	12,372	13,741	15,940	2473	1237	1210						
CuO (tenorite)	12,170	14,230	16,670	2676	1217	1193	0.981	0.446	1.023	1.027	oxygen	oxygen
	12,254	14,520	16,878	2735	1225	1188						
Sr ₂ CuO ₂ Cl ₂	12,097	14,839	15,887	2661	1210	1048	0.867	0.394	0.904	0.897	oxygen	Cl ⁻
	11,838	14,756	16,021	2706	1184	1040						

*) The broad band at 12,500 cm^{-1} is proven to split into two bands at about 10,700 cm^{-1} and 13,200 cm^{-1} , respectively.

Table 5. Experimental Δ_A energies versus calculated ones using the relation: $\Delta_A = 17,892 \cdot (\langle R_a \rangle / \langle R_e \rangle - \varepsilon)$ (cm^{-1}), $\varepsilon = 1/\sqrt{2}$ for dioptase group and $\varepsilon = 1/2$ for cuprates. Auxiliary bonds introduced in case of compounds with coordination number $CN = [4]$ are underlined.

Phase	CN	$\langle R_e \rangle$ (Å)	$\langle R_a \rangle$ (Å)	Δ_A (exp.)	Δ_A (calc.)
Cuprorivaite	[4]	1.9307	<u>3.35</u>	18,530	18,393
CuGeO ₃	[4 + 2]	1.9326	2.7549	12,920	12,854
Effenbergite	[4]	1.9265	<u>3.35</u>	18,520	18,460
Wesselite	[4]	1.9265	<u>3.35</u>	18,520	18,460
Dioptase black	[4]	1.9340	<u>3.30</u>	17,930	17,874
Cu ₆ Ge ₆ O ₁₈	[4]	1.9404	<u>3.30</u>	17,700	17,777
Ge-Dioptase	[4 + 2]	1.9474	2.6622	11,884	11,808
Azurite (1)	[4 + 2]	1.9434	2.9840	16,488 (?)	14,821
Azurite (2)	[4 + 1 + 1]	1.9593	2.5143	11,806	10,309
Litidionite	[4 + 2]	1.9525	2.8434	13,900	13,404
Lammerite (1)	[4 + 2]	1.9529	2.9230	14,350	14,128
Lammerite (2)	[4 + 1 + 1]	1.9703	2.4609	10,200	9695
Chalcanthite (1)	[4 + 2]	1.9759	2.3858	8900	8952
Chalcanthite (2)	[4 + 2]	1.9569	2.4400	9735	9657
Dioptase green	[4 + 2]	1.9613	2.5688	10,700	10,735
Conichalcite	[2 + 2 + 2]	1.9640	2.3403	8585	8668
Y ₂ BaCuO ₅	[4 + 1]	1.9899	2.196 + <u>3.90</u>	14,700	14,754
La ₂ CuO ₄	[4 + 2]	1.9043	2.4045	13,710	13,646
CaCuO ₂	[4]	1.9281	<u>3.26</u>	21,370	21,306
Sr _{0.5} Ca _{0.5} CuO ₂	[4]	1.9440	<u>3.30</u>	21,452	21,426
NdBa ₂ Cu ₃ O _{7.8}	[4 + 1]	1.9609	2.275 + <u>3.25</u>	15,968	16,260
CuO (tenorite)	[4 + 2]	1.9558	2.7842	16,670	16,524
Sr ₂ CuO ₂ Cl ₂	[4 + 2]	1.9864	2.8600	15,887	16,841

strength is reduced towards the 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 [51]).

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 formulas for the principal components g_{\parallel} and g_{\perp} , if the ground state is $^2B_{1g}$:

$$g_{\parallel} = g_e - \frac{8\lambda}{\Delta_B} - \frac{\lambda^2}{\Delta_E^2} - \frac{4\lambda^2}{\Delta_B \Delta_E}, \quad (14)$$

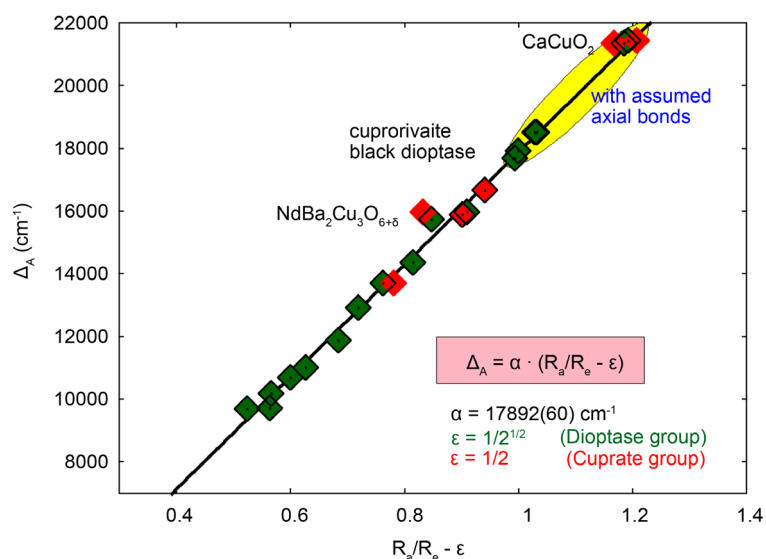


Figure 7. Δ_A excitation energies (cm^{-1}) depicted versus a function of axial to equatorial bond distances. Again the cuprate group excitations (in red) must be corrected by a (magnetic) contribution to reliably represent all data in a single regression line. Auxiliary axial bonds (see the yellow field)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

$$g_{\perp} = g_e - \frac{2\lambda}{\Delta_E} - \frac{\lambda^2}{\Delta_E^2}, \quad (15)$$

where $g_e = 2.0023$ is the g -value for the free electron, and λ is the spin-orbital coupling parameter, which yields for the free Cu^{2+} ion $\lambda_o = 829 \text{ cm}^{-1}$ [60].

The k values are the spin orbital reduction factors used to scale the coupling parameters to the free Cu^{2+} ion value, $k = \lambda/\lambda_o$. This parameter reduction is attributed to covalence effects. **Table 6** compares the results for diopside and Ge-diopside, 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 diopside related compounds.

Notation	Diopside	Ge-Diopside
Δ_B	11,508	11,884
Δ_E	14,395	14,321
Δ_A	10,700	11,884
$g_{ }$	2.3601	2.3780
g_{\perp}	2.0511	2.0970
$\lambda_{ }$	-504.08	-545.53
$k_{ }$	0.608	0.658
λ_{\perp}	-346.91	-662.63
k_{\perp}	0.418	0.799

5. Conclusion

As shown, a comparative reappraisal of 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 $\text{Cu}_6(\text{Ge,Si})_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ 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. Especially it should be investigated whether a *Zhang-Rice* excitation like that observed for CuGeO_3 can be confirmed for the hydrated compounds of the dioptase family, too. In addition, the proposed assignment of the *dd* excitations of the green phase YBa_2CuO_5 should be supported by a CuL_3 resonant X-ray scattering investigation.

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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 diopside group compounds.

Scaling factor notation	Cuprates	Diopside group	Ratio
Q_c^2	1.755	1.733	1.013
Q_a^2	0.936	0.761	1.230
η_s	1.587	1.276	1.244
η_t	2.180	1.738	1.254



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