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Characterization of conichalcite by SEM, FTIR, Raman and electronic reflectance spectroscopy

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ABSTRACT

The mineral conichalcite from the western part of Bagdad mine, Bagdad, Eureka District, Yavapai County, Arizona, USA has been characterized by electronic, near-infrared (NIR), Raman and infrared (IR) spectroscopy. Scanning electron microscopy (SEM) images show that the mineral consists of bundles of fibres. Calculations based on the results of the energy dispersive X-ray analyses on a stoichiometric basis show the substitution of arsenate by 12 wt.% of phosphate in the mineral. Raman and IR bands are assigned in terms of the fundamental modes of AsO_4^{3-} and PO_4^{3-} molecules and are related to the mineral structure. Near-IR reflectance spectroscopy shows the presence of adsorbed water and hydroxyl units in the mineral. The Cu(II) coordination polyhedron in conichalcite can have at best pseudo-tetragonal geometry. The crystal field and tetragonal field parameters of the Cu(II) complex were calculated and found to agree well with the values reported for known tetragonal distortion octahedral complexes.

Keywords: conichalcite, adelite, austenite, duftite, SEM and EDX analyses, FTIR, Raman spectroscopy, electronic reflectance spectroscopy.

Introduction

Conichalcite, $CaCuAsO_4OH$, forms in the oxidation zone of copper ore bodies. It is a member of the adelite group of minerals which also includes such species as austenite, adelite and duftite. In general, members of the group have the formula $AB^{2+}(XO_4)(OH)$ where cation A may be Ca or Pb and cation B may be Zn, Mg, Fe, Co, Ni, Cu or selected combinations of these atoms and X is As^{5+} or P^{5+}. These isostructural minerals crystallize in the orthorhombic space group $P2_12_12_1$.

The crystal structure of conichalcite was first determined by Qurashi and Barnes (1963) originally in *Pnma* with final refinement in $P2_12_12_1$. Later it was refined by Radcliffe and Simmons (1971) with unit-cell parameters, a = 0.7393, b = 0.9220 and c = 0.5830 nm. The structure of conichalcite consists of a three-dimensional assemblage of distorted AsO_4 tetrahedra, $CuO_4(OH)_2$ tetragonal bipyramids and $CaO_7(OH)$ square antiprisms, sharing corners and edges.

Available chemical data show the formation of solid solutions between austinite and conichalcite (Jambor *et al.*, 1980; Taggart and Foord, 1980; Keller *et al.*, 1981, 1982). A complete solid solution also exists between conichalcite and duftite (Jambor *et al.*, 1980).

The Raman spectra of tetrahedral anions in aqueous systems are well known. For the arsenate anion, the symmetric stretching vibration (ν_1) occurs at 810 cm^{-1} which coincides with the asymmetric stretching mode (ν_3). The two bending modes (ν_2) and (ν_4) are observed at 342 and at 398 cm^{-1}, respectively (Frost *et al.*, 2002, 2003*b*; Martens *et al.*, 2003*a,c*, 2004; Frost and Weier, 2004*b*). Of all the spectra for tetrahedral oxyanions, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanion spectra.

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Several spectra of arsenates including the basic copper arsenates olivenite and euchroite were reported by Farmer (1974) but no examples of the adelite group of minerals (including conichalcite) were shown. The IR spectra of the minerals conichalcite, austinite, olivenite and adamite have been reported (Sumin De Portilla, 1974). Recent studies have been carried out on arsenate minerals (Frost *et al.*, 2002, 2003*b*; Martens *et al.*, 2003*a,c*, 2004; Frost and Weier, 2004*b*).

If the point symmetry of the arsenate group is lower than the ideal tetrahedral symmetry (T_d) then the degeneracies will be broken and splitting of the Raman bands will occur. In the adelite group the point symmetry of the arsenate group is C_1 and the factor-group analysis predicts that 18 distinct Raman active modes will occur. Spectroscopic studies of the adelite group of minerals have been limited, although a Raman study of the adelite group including an Australian conichalcite has been published (Martens *et al.*, 2003*b*). In this study we examine conichalcite from a different locality (Bagdad Mine, Arizona) by Raman, Fourier transform infrared (FTIR) spectroscopy and also by electronic reflectance spectroscopy with a view to correlating the spectral behaviour with the known structure of the mineral.

The electronic spectral studies were not carried out with the specific aim of examining the effects of cations and their symmetry on any of these minerals. It would be quite interesting to study the electronic spectra of the divalent copper that is present in conichalcite. The most common electronic process revealed in the spectra of minerals is due to unfilled electron shells of transition elements and Fe is the most common transition element in minerals. The d^9 configuration makes Cu(II) subject to Jahn-Teller distortion if placed in an environment of cubic (i.e. regular octahedral or tetrahedral) symmetry, and this has a profound effect on all its stereochemistry. The Cu(II) is never observed in regular environments and is usually subject to distortion. The typical distortion is an elongation along one four-fold axis, so that there is a planar array of four short Cu−L bonds and two *trans* long ones. There are numerous cases in which apparently octahedral Cu(II) complexes execute a dynamic (pulsating) Jahn-Teller behaviour, where the direction of the elongation varies rapidly. Since spectral properties vary from one mineral to another due to variation in structure and composition (Burns, 1970), the present study focuses on a conichalcite ($CaCuAsO_4OH$) from Bagdad mine. Results are given in the present paper of comprehensive investigations of vibrational spectra, including Raman and IR along with the electronic spectra, and are explained in terms of the structure of anions and cations in the mineral.

Experimental

Samples

The conichalcite used in this study was a grass green-coloured mineral, from the personal collection of one of the authors (RLF). It originated from the western part of Bagdad mine, Arizona. The mineral was made into powder and used for the study of electronic reflectance spectroscopy in the UV-Vis region.

Scanning electron microscopy

Scanning electron microscopes were employed for both EDXA (Joel 840 electron probe microanalyser) and secondary electron imaging (Joel 35CF). Samples for analysis were prepared by embedding in araldite, polishing with diamond paste on a Lamplan polishing cloth with water as the lubricant and coated with carbon.

Raman microprobe spectroscopy

A small conichalcite crystal of ~1 mm^2 was fixed and oriented on the stage of an Olympus BHSM microscope, equipped with 10× and 50× objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range 100−4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation light was scrambled. Details of the experimental technique were reported previously (Frost *et al.*, 2002, 2003*b*, 2004; Martens *et al.*, 2003*a,c*, 2004; Frost, 2004*a,b*).

IR and NIR spectroscopy

The IR spectrum was obtained using a Nicolet Nexus 870 FTIR spectrometer with a Smart Endurance single-bounce diamond ATR cell.

The spectrum was obtained over the 4000−500 cm^{-1} region by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. The NIR spectrum was collected on a Nicolet Nexus FTIR spectrometer fitted with a Nicolet Near-IR Fibreport accessory. A white light source was employed with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 11000 to 4000 cm^{-1} by the co-addition of 64 scans at the resolution of 8 cm^{-1}. A mirror velocity of 1.2659 m/s was used. The spectra were transformed using the Kubelka-Munk algorithm for comparison with that of absorption spectra. Spectral manipulations such as baseline adjustment, smoothening and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 >0.995.

UV-Vis spectroscopy

UV-Vis spectroscopy is an ideal tool for the study of coloured minerals containing transition metals. Spectra of d−d transitions mainly fall in this region and can be studied either by absorption or by reflection. The technique of reflectance spectroscopy is most suitable for minerals including dark coloured and or non-transparent materials. Reflectance spectroscopy is the study of light as a function of wavelength that has been reflected or scattered from a solid, liquid or gas. As photons enter a mineral, some are reflected from grain surfaces, some pass through the grain, and some are absorbed. Those photons reflected from grain surfaces or refracted through a particle are said to be scattered. Scattered photons may encounter another grain or be scattered away from the surface so they may be detected and measured. The variety of absorption processes and their wavelength dependence allow us to derive information about the chemistry of a mineral from its reflected light. Use of the reflectance spectroscopy technique is growing rapidly and can be used to derive significant information about mineralogy and with little or no sample preparation. A Varian Cary 3 UV-Visible spectrophotometer, equipped with Diffuse Reflectance Accessory (DRA) was employed to record the electronic spectra of the samples in the region between 200 and 900 nm. This technique allows the study of the reflectance spectra of the samples in powder form. The DRA consists of a 73 mm diameter integrating sphere, featuring an inbuilt high-performance photomultiplier. The sample was mounted on coarse filter paper (#1) by resuspending the sample and submerging the filter paper into the suspension. Initially a base line was recorded using two pressed polytetrafluoroethylene disks (PTFE) as reference disks. Next, the sample was mounted flat over the sample port and the reflectance spectrum of the sample, relative to the reference disks, was collected by the integrating sphere. By placing the sample flat, any specular components of reflectance should be directed out of the DRA entrance port, as the angle of incidence is 0º. The diffuse reflectance measurements were converted into absorption (arbitrary units) using the Kubelka-Munk function ($f(R_\infty) = (1 - R_\infty)^2/2R_\infty$). Data manipulation was performed using Microsoft Excel®.

Results and discussion

SEM analysis of conichalcite

Images of conichalcite taken at a number of magnifications are shown in Fig. 1. The figure clearly shows parallel aggregates of fibres that are pseudomorphing crystals which appear as bundles of thin prismatic crystals. The peaks of the EDX spectrum have been deconvoluted and calibrated to produce the analyses given in Table 1 which

TABLE 1. EDX analyses of conchalcite crystals.

Atom	Wt.%			
	Grain 1	Grain 2	Grain 3	Grain 4
O	34.08	34.91	26.67	42.35
Si	0.52	1.05	0.89	0
As	25.01	23.75	27.72	21.47
P	0.93	0.93	0.76	1.23
Ca	13.09	13.24	14.62	13.18
Cu	26.37	26.13	29.33	21.76

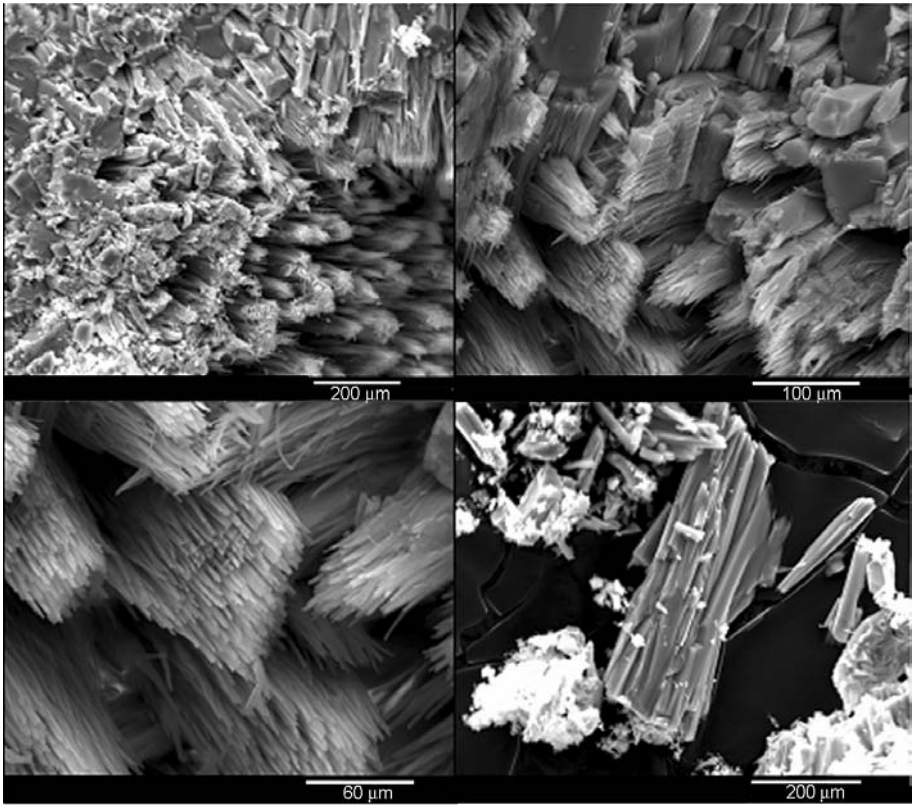


FIG. 1. SEM images of conichalcite crystals.

show that the conichalcite contains some isomorphic substitution of phosphate for arsenate. The amount of substitution is 12 mol.%. Thus, the chemical formula for conichalcite is $[(CaCu^{2+}(AsO_4)_{0.88}(PO_4)_{0.12}(OH)]$.

Vibrational analysis

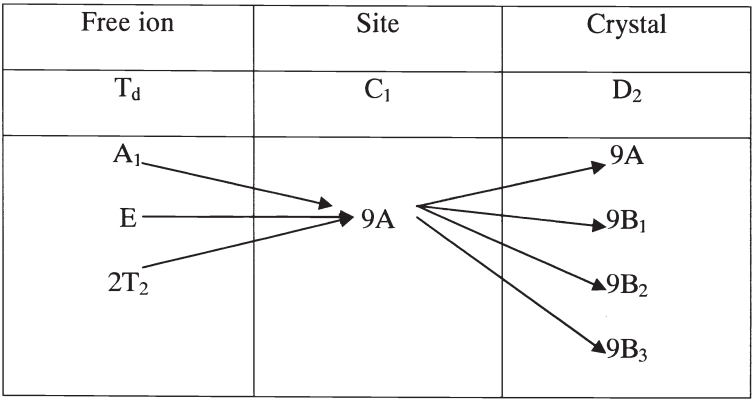
Factor group analysis

The adelite group of minerals is isostructural and exhibits $P2_12_12_1$ symmetry. Hence the factor-group analysis is the same for all the minerals in this family. Factor group analysis yields 36 internal modes for the arsenate ion and 69 lattice vibrations in conichalcite, with $\Gamma = 27A + 26B_1 + 26B_2 + 26B_3$. The theoretical vibrational analysis of conichalcite is shown in Tables 2 and 3. The A_1 symmetry of the free ion gives rise to four bands for the arsenate ion in the conichalcite crystal with A, B_1, B_2, B_3 symmetry. This implies there are four vibrations, which are Raman active. The A modes are Raman active and the B modes are both Raman and IR active. The T_2 symmetry of the free ion provides four bands for the arsenate ion in the conichalcite crystal with A, B_1, B_2, B_3 symmetry. The ν_3 mode (T_2) splits up into three components under site symmetry C_1; thus four anions in the unit cell give 4×3 ν_3 vibrations distributed into the four symmetry species of $222-D_2$'. This means that there are 12 antisymmetric vibrations, which should be Raman active. The free arsenate ion has tetrahedral symmetry and thus should have four bands of which two are IR active with values of ν_3 (T_2) 887 cm^{-1} and ν_4 (T_2) 463 cm^{-1}. The Raman active modes are observed at 837 (A_1) and 349 (E) cm^{-1} (Farmer, 1974).

Vibrational spectra

The spectral features observed both in Raman and IR spectra of the conichalcite can be divided into four regions as follows: (1) hydroxyl stretching (3800–2600 cm^{-1}); (2) mid-IR (MIR) region

TABLE 2. Vibrational analysis of the internal modes of the anions in the unit cell in conichalcite.



(2200−1200 cm^{-1}); (3) $(AsO_4)^{3-}$ and $(PO_4)^{3-}$ stretching (1100−700 cm^{-1}), and (4) low-wavenumber region, $(AsO_4)^{3-}$ and $(PO_4)^{3-}$ bending (600−100 cm^{-1}) regions.

Hydroxyl-stretching region

Infrared and Raman spectra of the hydroxyl-stretching region of conichalcite are shown in Fig. 2. The results of the analyses of the spectra are given in Table 4 and compared with the study by Martens *et al.* (2003*b*), which reported Raman spectra for the adelite-group members austenite and a zincian conichalcite from Lorena mine, Cloncurry, Queensland, Australia. The most intense band at ~3150 cm^{-1} both in IR and Raman spectra is characteristic of OH stretching. On either side of this, four symmetrical bands are located around 3300, 3250, 3050 and 2900 cm^{-1}. However, the band positions and their intensities differ slightly. The differences in the band positions for this mineral are attributed to the changes in composition depending on the amount of Cu in the mineral. These observations agree with the chemistry and crystal structure of the mineral of the adelite group (Hawthorne, 1976, 1990; Clark *et al.*, 1997; Kharisun *et al.*, 1998). Replacement of the Zn in austinite by the Cu in conichalcite causes a shift of the 3250 cm^{-1} band of austinite to the lower wavenumber of 3125 cm^{-1} (see Table 4).

Figure 3 shows the MIR region 2200−1200 cm^{-1} where hydroxyl deformation modes of water are found at ~ 1600 cm^{-1} and overtones of phosphate and arsenate ions appeared around 2000 and 1400 cm^{-1}. Minerals containing physically adsorbed water give rise to strong bands at 3450 cm^{-1}, the water hydroxyl-stretching vibration, and at ~1600 cm^{-1}, the water-bonding vibrations (Frost *et al.*, 1998, 2003*a*; Martens *et al.*, 2004). In the present sample, two well resolved bands at 1644 and 1823 cm^{-1} are indicative of chemically bonded water in the mineral. One strong band centred at 2079 cm^{-1} may be an overtone of the antisymmetric mode of the PO_4^{3-} ion (ν_3). The low-wavenumber bands from 1300 to 1500 cm^{-1} show structure both in IR and Raman and may be attributed to overtones of the arsenate ion.

TABLE 3. Vibrational analysis of the lattice modes in conichalcite.

Site	Crystal	Translational	Total
C_1	D_2		
18A	18A		18A
	$18B_1$	B_1	$17B_1$
	$18B_2$	B_2	$17B_2$
	$18B_3$	B_3	$17B_3$

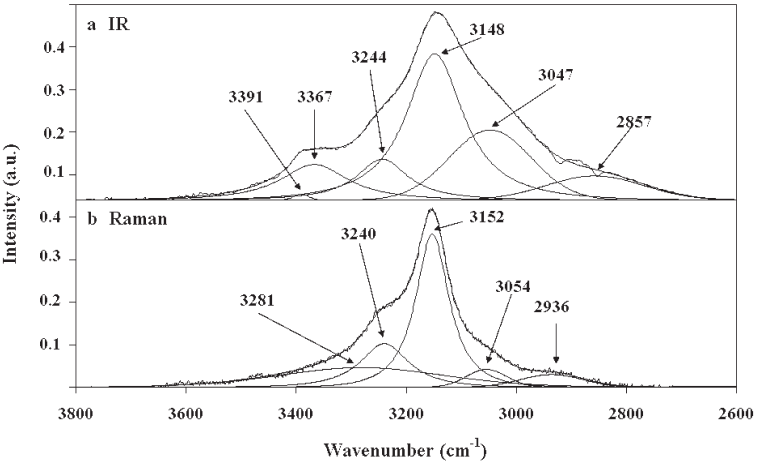


FIG. 2. Raman and IR spectra of conichalcite in the OH-stretching region.

TABLE 4. Raman and IR spectroscopic data (cm^{-1}) of selected arsenate minerals.

Conichalcite* $CaCu^{2+}(AsO_4)(PO_4)(OH)$ This work		Conichalcite† $CaCu^{2+}(AsO_4)(OH)$ Published	Austinite $CaZn(AsO_4)(OH)$ Published
IR	Raman	Raman	Raman
3391			
3367s	3281		
3244	3240s	3233	3350
3148m	3152m	3158	3265
3047s	3054w	3086	
2857	2936s		
2079m	2077w		
2023s	2077		
1867			
1823m			
1776s			
1644w	1600m		
1468s	1523s		
1455c			
1414c			
1377c			
1361m	1335m		
1312s			
1164			
1100s			
1060s			
1052m	1050vw		
1040c			
1020s			
962c	955vw		
931m	911vw		
902c			
888w	869w		
841c	847w		
814w	834m	832	911

TABLE 4. (*contd.*)

Conichalcite* $CaCu^{2+}(AsO_4)(PO_4)(OH)$ This work		Conichalcite† $CaCu^{2+}(AsO_4)(OH)$ Published	Austinite‡ $CaZn(AsO_4)(OH)$ Published
IR	Raman	Raman	Raman
806c	822c	821	889
787w	812c	811	859
769c	780w	781	844
752m	754vw	750	818
693s			806
666w			738
573c			708
565m	538w		538
529c	534c	534	494
	486m	463	478
	450vw		457
	444m	446	420
	427s	430	
	364s	389	409
	358w	358	374
	335c	335	322
	324m	328	308
	287c	286	275
	276s	274	252
	221s		231
	206m	206	209
	198s	180	175
	178c	165	139
	162c	150	129
		123	

* Conichalcite from the western part of Bagdad mine, Arizona (this work)
† Conichalcite from Lorena mine, Cloncurry, Queensland, Australia (Martens *et al*., 2003)
‡ Austinite from Lorena mine, Cloncurry, Queensland, Australia (Martens *et al*., 2003)
Abbreviations of the bands character: m – major; s – shoulder; w – weak; vw – very weak; c – component

Arsenate and phosphate vibrations

The vibrational stretching in the 1200–530 cm^{-1} region of conichalcite is shown in Fig. 4. The presence of AsO_4^{3-} and PO_4^{3-} bands are identified in this region. The Raman spectrum displays two weak bands at ~950 cm^{-1}; but are strong in the IR spectrum at 962, 931 and 902 cm^{-1}. This group of bands is attributed to the hydroxyl-stretching deformation modes of OH bonded to Ca or Cu. Sumin De Portilla (1974) also suggested that bands observed at 980 and 1010 cm^{-1} are due to hydroxyl deformation modes. A previous study showed that the $\nu_1(A_1)$ and $\nu_3(T_2)$ modes of the free arsenate ion bands are at 837 and 878 cm^{-1} in the Raman spectrum (Griffith, 1970). The major Raman band at 834 cm^{-1} and its components at 822 and 812 cm^{-1} are assigned to the AsO_4^{3-} symmetric stretching vibrations (ν_1). The ν_1 mode is also activated fairly well in IR at 841 cm^{-1}. The $\nu_3(F_2)$ mode is active both in IR and Raman. It is observed as a weak band at 780 cm^{-1} in Raman but it is strong in IR, located at 752 cm^{-1}, with components at 769, 787 and 806 cm^{-1}. Raman spectra of the phosphate oxyanions in an aqueous system show a symmetric stretching mode (ν_1) at 938 cm^{-1}, the antisymmetric mode (ν_3) at 1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} (Farmer, 1974). The major band in IR at 1052 cm^{-1} with

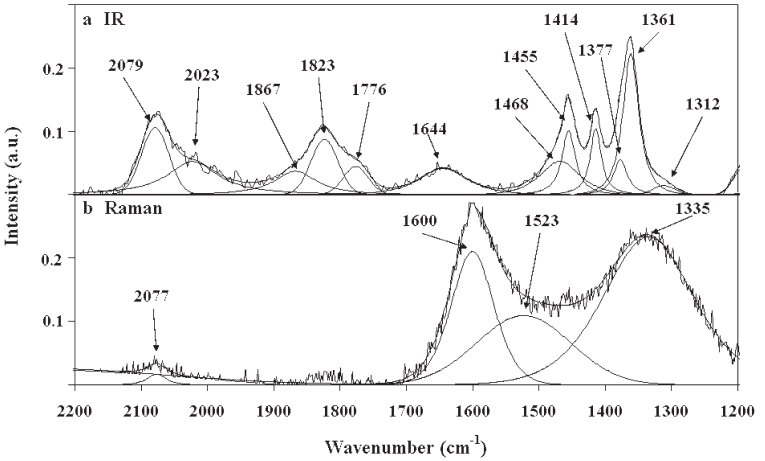


FIG. 3. Raman and IR spectra of conichalcite in the 2200−1200 cm^{-1} region.

three shoulders and a component at 1100, 1060, 1020 and 1040 cm^{-1} is identified as the ν_3 mode of the phosphate oxyanion. This complex band profile observed around 1052 cm^{-1} is in excellent agreement with the complex band profile at ~1100 cm^{-1} in a number of natural zinc phosphate minerals (Frost, 2004*a*). But this mode is weak in the Raman spectrum at 1050 cm^{-1}. The reason might be a low concentration of phosphate ion partially substituted by an arsenate ion in the present conichalcite sample. CuO-stretching vibrations were noticed in duftite of the adelite group at 549 and 512 cm^{-1} (Martens *et al.*, 2003). The low-wavenumber bands of IR shown here at 573 and 565 cm^{-1} are assigned to CuO-stretching vibrations.

Low-wavenumber region (600−100 cm^{-1})

Farmer (1974) reported the bending modes of the phosphate ion in autunites (ν_4) at 615 and 545 cm^{-1}. The PO_4^{3-} ν_4 mode was also observed by Raman spectra in saléeite, a mineral of uranyl phosphate at 612 and 573 cm^{-1} (Frost and Weier, 2004*a,b*) and, for another aluminium phosphate mineral, augelite, for which at 635 cm^{-1} an intense band with component bands at 643 and 615 cm^{-1} (Frost and Weier, 2004*c*) was also recorded. The low-wavenumber region of the Raman spectrum of conichalcite is shown in Fig. 5. Two Raman bands at 538 and 534 cm^{-1} and an IR band at 529 cm^{-1} are attributed to the ν_4 mode of PO_4^{3-}. The free AsO_4^{3-} ion exhibits $\nu_2(E)$ and $\nu_4(T_2)$ modes at 349 and 463 cm^{-1}

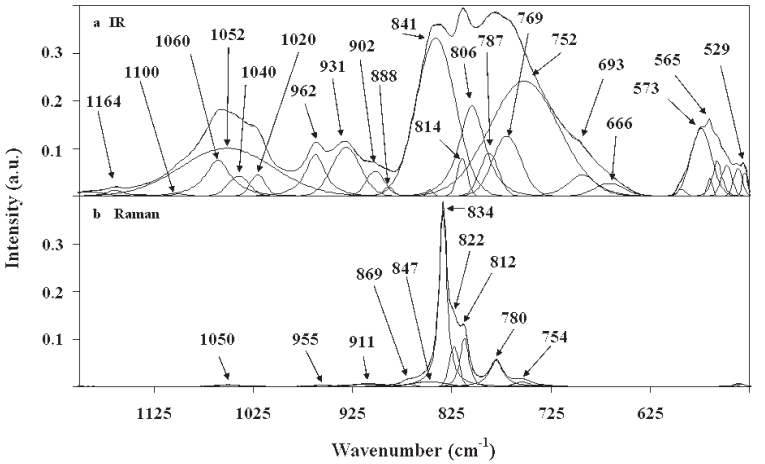


FIG. 4. Raman and IR spectra of conichalcite in the $(AsO_4)^{3-}$ and $(PO_4)^{3-}$-stretching region.

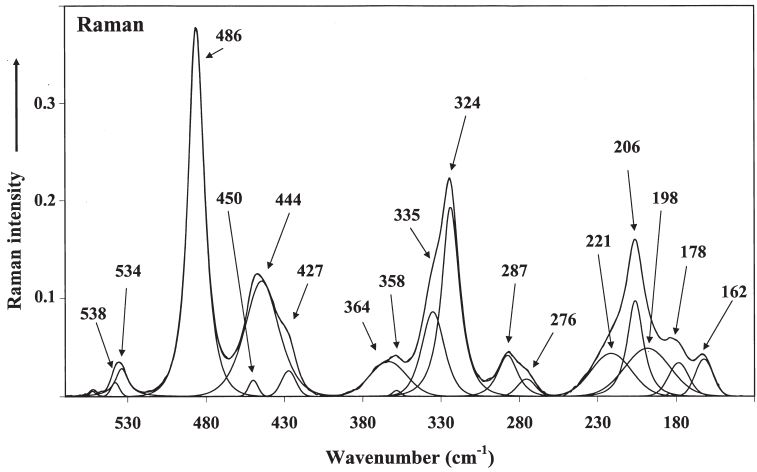


FIG. 5. Raman spectrum of the low wavenumber region (600−100 cm^{-1}).

(Griffith, 1970). Conichalcite shows three intense groups of bands at ~500, 300 and 200 cm^{-1}. In the first group, the most intense band at 486 cm^{-1} with a doublet at 444 and 427 cm^{-1} is due to the splitting of the $\nu_4(T_2)$ mode while the middle group dominated by a sharp peak at 324 cm^{-1} but, with a number of component bands, is linked to the ν_2 bending-mode vibrations of $(AsO_4)^{3-}$. Two bands, at 287 and 276 cm^{-1}, may be assigned to OCuO-bending modes. Other bands observed at 206 cm^{-1} with components at 198, 178 and 162 cm^{-1} can be described as lattice vibrations.

Electronic (reflectance) spectra

The electronic spectra of six-coordinated Cu(II) complexes are analysed assuming approximate 4/*mmm* (D_{2h}) or 4*mm* (C_{4v}) point symmetry for the Cu^{2+} ion and its ligands. The e_g and t_{2g} levels of the free ion term; ^2D are further split into B_{1g}, A_{1g}, B_{2g} and E_g levels, respectively. Therefore, three spin-allowed transitions are expected for Cu(II) in the NIR and visible regions (Lever, 1984). The bands are resolved by Gaussian analysis and assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions in order of increasing energy. The sequence of energy levels depends on the amount of distortion due to ligand field and Jahn-Teller effects (Ferguson *et al.*, 1975).

The electronic (reflectance) spectra of conichalcite (Fig. 6) show a very strong band centred at ~10,000−7000 cm^{-1} with a well defined shoulder at 11,000−10,000 cm^{-1} in the high-energy NIR region of 11,000−6500 cm^{-1} (Fig. 6) and a broad feature in the visible spectrum centered at ~18,000−11,000 cm^{-1} (550−900 nm; Fig. 6*a*). Near-IR reflectance spectroscopy has also been used to show the presence of water and hydroxyl units in the mineral. The spectrum in the NIR region, 7000−4000 cm^{-1}, is shown in Fig. 7. Two bands at 7060 (Fig. 6*b*) and 6452 cm^{-1} are attributed to the first overtone of the fundamental hydroxyl-stretch mode. The other two main bands at 6000−5000 cm^{-1} are assigned to water-combination modes of the hydroxyl fundamentals of water. The sharp band located at 4143 cm^{-1} with structure is assigned to the combination of the stretching and deformation modes of the *M*-OH units of conichalcite (Frost and Erickson, 2005).

The three broad intense spin-allowed d−d transitions of Cu(II) in the present mineral are identical with λ_{max} differently centered for several Cu(II) complex compounds (Hathaway and Billing, 1970; Hathaway, 1984; Reddy *et al.*, 1987; Ciobanu *et al.*, 2003; Reddy *et al.*, 2004) in tetragonally distorted octahedral coordination. As shown in the Fig. 6, conichalcite displays three bands. The first band at 10575 cm^{-1} shows an additional band at 9280 cm^{-1}. The broad band is centred at 8585 cm^{-1} with two components at 8680 and 8000 cm^{-1}. The visible region band at 13,965 cm^{-1} also splits into two with maxima at 15,313 and 12,500 cm^{-1}. As expected, the three spin-allowed bands are broad and intense. The Gaussian band-fitting shows further splitting. The

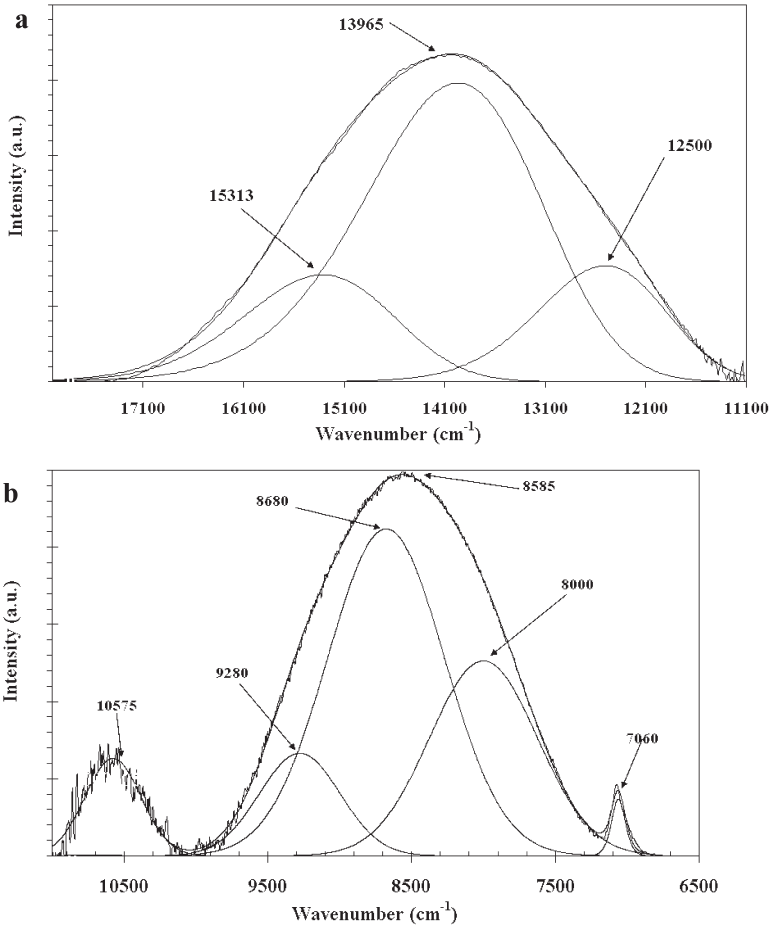


FIG. 6. Electronic spectra of conichalcite: (a) visible region; (b) NIR region.

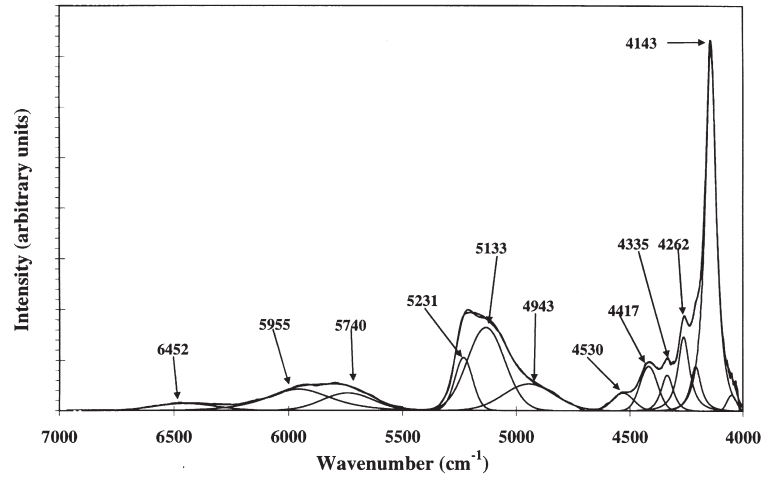


FIG. 7. NIR spectrum of conichalcite in the 4000 to 7000 cm^{-1} region.

TABLE 5. Comparison of octahedral and tetragonal field parameters (cm^{-1}) of Cu^{2+} in selected minerals.

Mineral	Dq	Ds	Dt	Reference
Brochanthite $[Cu_4^{2+}(SO_4)(OH)_6]$	1050	1730	285	Reddy *et al.* (1987)
Connellite $[Cu_{36}^{2+}Cl_6(SO_4)_2(OH)_{62}.12H_2O]$	1205	1525	450	Sreeramulu *et al.* (1990)
Cornetite $[Cu_3^{2+}(PO_4)(OH)_3]$	1257	1434	380	Venkateramanaiah *et al.* (1996)
Chrysocolla $[Cu^{2+},Al)_2\ H_2Si_2O_5(OH)_4.nH_2O]$	1063	1697	268	Ravikumar *et al.* (1998)
Smithsonite $[(Zn,Cu^{2+})(CO_3)]$	1250	1770	338	Reddy *et al.* (2004)
Conichalcite $[CaCu^{2+}(ASO_4)(OH)]$	1058	1711	348	This work

assignments of the bands are made as follows:

$^2B_{1g} \rightarrow {}^2A_{1g} = 4Ds + 5Dt = 8585\ cm^{-1}$
$^2B_{1g} \rightarrow {}^2B_{2g} = 10Dq = 10{,}575\ cm^{-1}$
$^2B_{1g} \rightarrow {}^2E_g = 10Dq + 3Ds - 5Dt = 13{,}965\ cm^{-1}$

The crystal field (Dq) and tetragonal field (Ds and Dt) parameters derived from the observed data are Dq = 1058 Ds = 1711 and Dt = $348cm^{-1}$. The values of Dq and Dt in tetragonal field will have the same sign for an axial elongation and opposite sign if Cu(II) experiences axial compression (Hathaway and Billing, 1970). The same sign of Dq and Dt values confirms Cu(II) symmetry distortion from octahedral to elongated tetragonal field in conichalcite. The crystal field and tetragonal field parameters of Cu(II) derived from the electronic spectra of conichalcite agree well with the values reported for other tetragonal distorted octahedral Cu^{2+} complexes (Table 5).

Conclusions

Electronic and vibrational spectroscopic data are reported for the mineral conichalcite. The presence of a phosphate ion as an impurity was found in the mineral by EDX analyses and reflected by the ν_3 and ν_4 modes of PO_4^{3-} in both the IR and Raman spectra. The presence of water and hydroxyl units in the mineral was found from spectral features observed in both IR and NIR spectra. Substitution of the Cu in conichalcite for the Zn in austinite causes a shift of bands to lower wavenumbers. The three spin-allowed electronic bands of Cu(II) are consistent with tetragonally elongated coordination of the Cu polyhedra.

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