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OPTICAL ABSORPTION SPECTRA OF Cu^{2+} IN CHALCANTHITE AND MALACHITE

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Abstract

The optical absorption spectra of chalcanthite and malachite have been studied at room and liquid air temperatures. From the nature of the spectra, and large copper contents, the observed bands in both samples are attributed to Cu^{2+} in tetragonal symmetry. The crystal parameters which give a good fit to the observed band positions are, for chalcanthite and malachite respectively: *Dq*-1250, -1250; *Ds*-3240, -3245; *Dt*-710, -700; λ-830, -830.

The observed features and band shifts indicate that the vibronic interactions are greater in chalcanthite than in malachite.

Introduction

The structure of chalcanthite, triclinic $CuSO_4$: $5H_2O$, was determined by Beevers & Lipson (1934). The mineral contains two non-equivalent ionic groups per unit cell. The environment of each ion consists of four water molecules arranged in an approximate square with two polar sulphate oxygens at slightly greater distances from the Cu^{2+} central metal ion. The field experienced by the ions has a strongly tetragonal component along the axis joining the sulphate ion.

Malachite, $Cu_2(OH)_2 . CO_3$, is monoclinic and has four oxygens of O_h equally displaced at 1.98Å and two other oxygens at distances equal to 2.71Å from the central Cu^{2+} ion (Orgel 1960).

Although the optical absorption spectrum of chalcanthite has not been reported in the literature, the spectrum of malachite at room temperature was studied by Hunt & Salisbury (1971). They found only one broad band in the visible region at 8000Å and three others in the infrared at 2.29μ, 2.37μ, and 2.52μ. They attributed the band in the visible spectrum to a $^2E \rightarrow {}^2T_2$ transition of Cu^{2+} in O_h symmetry, and the three other bands to the CO_3'' radical. The only other study of a similar mineral is that of Newham & Santoro (1967), who reported that the reflectance spectrum of dioptase, $CuSiO_3 . H_2O$, showed one broad band at 13000 cm^{-1}. This was assigned to the transition $^2B_1 \rightarrow {}^2E$.

Experimental

The absorption spectra of chalcanthite (S. V. University Geology Museum) and malachite (Chamadala A. P., India) were recorded at room and liquid air temperatures on a medium quartz spectrograph in the wavelength region λ 9500-2000Å. As it was not possible to cut the crystals either parallel or perpendicular to their optic axes, they were cut at random from the massive samples. Crystals 1.5 mm thick for chalcanthite and 2.3 mm thick for malachite were found suitable for the study of their absorption spectra. Using polarized and unpolarized incident beams of radiation, spectra were recorded on Kodak IN, Ilford R.40 and Zenith plates in 20 to 30 minutes. Wavelengths and oscillator strengths of the bands were measured as detailed in Lakshman *et al.* (1972).

Theory

Divalent copper (Cu^{2+}) has an electronic structure $(A)3d^9$. In O_h symmetry the ground state electron configuration for Cu^{2+} is written $(t_2)^6(e)^3$ which gives rise to a ^2E state. When one electron from the t_2 orbit is promoted to the to the e orbit the resulting configuration $(t_2)^5$ $(e)^4$ gives rise to a ^2T state. Thus, one single transition (*i.e.* one single band) is expected for Cu^{2+} in O_h symmetry. As the ground state, ^2E, is often split under the Jahn-Teller effect, we can not have a regular octahedrally-coordinated Cu^{2+} complex (Ballhausen 1962).

In a tetragonal (quadrate) field, the ground ^2E would be split into two levels ($^2B_1$ and $^2A_1$) and similarly the upper $^2T_2$ would be split into two ($^2B_2$ and ^2E) levels. If, in addition, spin orbit interaction is taken into consideration, the ground ^2E would be split into two and the upper $^2T_2$ into three levels. The resulting energy levels for $O_{h'}$, D_{4h} and $D_{4h'}$ including spin orbit interaction, are given in Table 1.

The complete theory of the energy levels of Cu^{2+}, including spin orbit effect, has been given for various crystal symmetries by Liehr (1960). The energy matrices for quadrate fields are presented in Table 2.

Results and Analysis

Chalcanthite

Chalcanthite absorption spectra consist of four bands, of which two (at 12000 and 20166 cm^{-1}) are very prominent. The microphotometric profiles for these (90°K) are shown in Figure 1. The 12000 cm^{-1} band is the stronger of the pair; the other two weak bands occur at 16524 and 18177 cm^{-1}.

The wavelength and wave number data of the observed bands at room and liquid air temperatures are given in Table 3. At liquid air temperature the intense band at 12000 cm^{-1} exhibits a marked change in intensity for two mutually perpendicular orientations of the Nicol.

TABLE 1. ENERGY STATE CLASSIFICATIONS

Symmetry	O_h	D_{4h}	D_{4h} + spin orbit interaction
	A_1	A_1	Γ_6
	A_2	B_1	Γ_7
	E	$A_1 + B_1$	$\Gamma_6 + \Gamma_7$
	T_1	$A_2 + E$	$\Gamma_6 + \Gamma_6 + \Gamma_7$
	T_2	$B_2 + E$	$\Gamma_7 + \Gamma_6 + \Gamma_7$

TABLE 2. ENERGY MATRICES FOR THE CONFIGURATION d^9 IN A TETRAGONAL FIELD

$$\Gamma_6: \begin{vmatrix} \Gamma_8\ {}^2T_2 & \Gamma_8\ {}^2E \\ -\frac{\lambda}{2} -4Dv-Ds+4Dt-E & \sqrt{\frac{3}{2}}\lambda \\ & 6Dq-2Ds-6Dt-E \end{vmatrix} = 0$$

$$\Gamma_7: \begin{vmatrix} \Gamma_7\ {}^2T_2 & \Gamma_8\ {}^2T_2 & \Gamma_8\ {}^2E \\ \lambda-4Dq+\frac{7}{3}Dt-E & \frac{\sqrt{2}}{3}(3Ds-5Dt) & 0 \\ & -\frac{\lambda}{2} -4Dq+Ds+\frac{2}{3}Dt-E & \sqrt{\frac{3}{2}}\lambda \\ & & 6Dq+2Ds-Dt-E \end{vmatrix} = 0$$

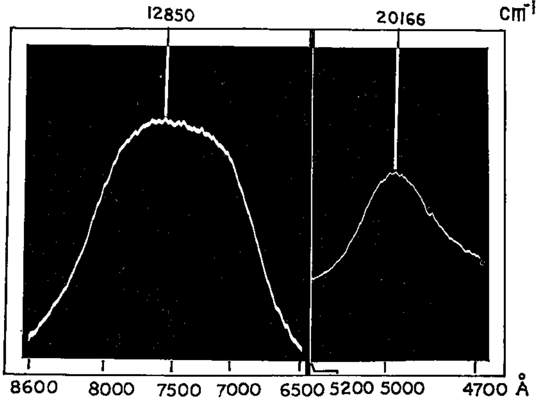

Fig. 1. Microphotometric profiles of the absorption spectrum of Cu^{2+} in chalcanthite at 90°K.

All these features indicate a distortion in symmetry, probably to one of D_{4h} symmetry. The energy level diagram for Cu^{2+} is shown both for O_h and D_{4h} fields in Figure 2. The ordering of energy levels is according to Holmes & McClure (1957).

The position of the band at 12000 cm^{-1} is an indication of near-octahedral symmetry in the crystal (Oye *et al.* 1964). The first three bands located at 12000 cm^{-1}, 16524 cm^{-1} and 18177 cm^{-1} have been assigned to ${}^2B_1 \rightarrow {}^2B_2$, ${}^2B_1 \rightarrow {}^2A_1$ and ${}^2B_1 \rightarrow {}^2E$ transitions respectively, as has been done by Holmes & McClure (1957) in the case of $CuSO_4 . 5H_2O$, from the magnitude and their relative positions.

The tetragonal field splitting parameters Ds and Dt are calculated as follows:

$$\begin{aligned} -3Ds + 5Dt &= 18177 - 12000 = \ \ 6177 \\ -4Ds - 5Dt &= 16524 \\ \hline -7Ds &= 22701 \end{aligned}$$

$$\therefore Ds \approx -3240\ cm^{-1}$$

$$\begin{aligned} 5Dt &= 6177 + 3Ds \\ &= 6177 - 9729 = -3552 \end{aligned}$$

$$\therefore Dt \approx -710\ cm^{-1}$$

Using these values of Ds and Dt and the free ion spin-orbit coupling constant, equal to -830 cm^{-1}, the energy matrices for Γ_6 and Γ_7 given

TABLE 3. ASSIGNMENTS FOR THE Cu^{2+} BANDS IN CHALCANTHITE

Band Positions				Assignments w.r.t. the ground state
300°K		90°K		
λ,Å	ν,cm^{-1}	λ,Å	ν,cm^{-1}	$\Gamma_7{}^a\ ({}^2E)$
8332.0	12000	7780.0	12850	$\Gamma_7{}^b\ ({}^2T_2)$
6050.0*	16524	6050.0*	16524	$\Gamma_6{}^a\ ({}^2E)$
5500.0*	18177	5500.0*	18177	$\Gamma_7{}^c\ ({}^2T_2)$
4957.5	20166	4957.5	20166	$\Gamma_a{}^b\ ({}^2T_2)$

*Comparator measurements

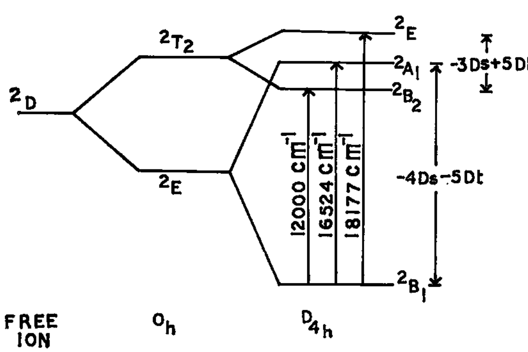

Fig. 2. Energy level diagram for Cu^{2+} in O_h and D_{4h} fields.

in Table 2 have been diagonalized for various values of Dq. The energy values thus obtained are plotted with respect to the ground Γ_7^a level against Dq values in Figure 3. A good fit of the experimentally-observed band positions is obtained for $Dq = -1250$ cm^{-1}.

The band positions are calculated with $Dq = -1250$ cm^{-1}, $Ds = -3240$ cm^{-1}, $Dt = -710$ cm^{-1}, $\lambda = -830$ cm^{-1} and are given along with the observed band positions (90°K), their oscillator strengths and corresponding transitions in Table 4.

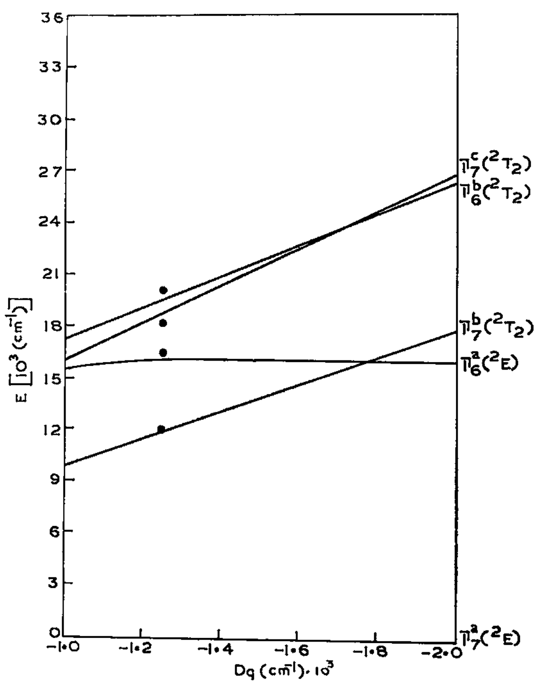

FIG. 3. Energy (inclusive of spin-orbit) level diagram of Cu^{2+} in chalcanthite in tetragonal symmetry plotted as a function of the crystal field parameter Dq, with $Ds = -3240$ cm^{-1}, $Dt = -710$ cm^{-1} and $\lambda = -830$ cm^{-1}. The solid circles show the experimental energies at 300°K.

TABLE 4. OBSERVED AND CALCULATED ENERGIES, OSCILLATOR STRENGTHS AND ASSIGNMENTS OF THE BANDS FOR Cu^{2+} IN CHALCANTHITE (Dq=-1250 cm^{-1}, Ds=-3240 cm^{-1}, Dt=-710 cm^{-1} and λ=-830 cm^{-1})

Transition from Γ_7^a (^2E)	Band Positions (cm^{-1}) observed at 300°K	calculated	Oscillator Strengths f x 10^4 300°K	90°K
Γ_7^b ($^2T_2$)	12000	11903	6.1	7.9
Γ_6^a (^2E)	16524	16124		
Γ_7^c ($^2T_2$)	18177	18727		
Γ_6^b ($^2T_2$)	20166	19404	0.13	0.26

The energy level scheme of Cu^{2+} in chalcanthite in D_{4h} symmetry, inclusive of spin-orbit interaction, is shown in Figure 4 along with the observed transitions and bands positions.

Since some of the band maxima measurements (measured on the comparator) are approximate, no attempt has been made to calculate the energies of the spin-orbit levels for various values of λ and select one which gave a good fit to the observed transitions and band positions.

Malachite

The malachite spectrum showed bands similar to those of chalcanthite. The only difference is that the first band on the red is at 12000 cm^{-1}

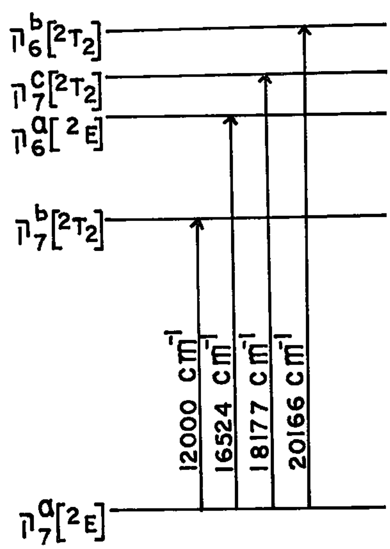

FIG. 4. Energy level scheme of Cu^{2+} in chalcanthite in D_{4h} symmetry inclusive of spin-orbit interaction. (The superscripts a, b and c are used by the authors to designate different levels).

TABLE 5. BAND MAXIMA, CRYSTAL AND TETRAGONAL FIELD PARAMETERS OF Cu^{2+} IN CHALCANTHITE AND MALACHITE.

	Chalcanthite ν(cm^{-1})	Malachite ν(cm^{-1})
I Band maxima		
$\Gamma_7^a(^2E) \rightarrow \Gamma_7^b$ ($^2T_2$)	12000	11919
Γ_6^a (^2E)	16524	16482
Γ_7^c ($^2T_2$)	18177	18160
Γ_6^b ($^2T_2$)	20166	20166
II Dq	-1250	-1250
III Ds	-3240	-3245
IV Dt	-710	-700
V λ	-830	-830

for chalcanthite and 11919 cm^{-1} for malachite. The intensity variation in polarized light is not as conspicuous as in chalcanthite.

The analysis carried out as in the case of chalcanthite gave the following crystal parameters: $Dq = -1250$ cm^{-1}, $Ds = -3245$ cm^{-1}, $Dt = -700$ cm^{-1} and $\lambda = -830$ cm^{-1}. Since these parameters are almost identical with those of chalcanthite, the detailed results of malachite are not presented here.

Discussion

The almost identical crystal parameters (Table 5) suggest that the crystal and tetragonal fields in both chalcanthite and malachite are similar. It has been observed that the intensity is concentrated in the two extreme bands 12000 cm^{-1} and 20166 cm^{-1} for chalcanthite, whereas in malachite the absorption is concentrated in three bands at 16524 cm^{-1}, 18160 cm^{-1} and 20166 cm^{-1} (these observed band positions are the same as in the chalcanthite). The first intense band at 12000 cm^{-1} in chalcanthite exhibits a large change in intensity for incident polarized light whereas no change has been observed for the weak band at 11919 cm^{-1} in malachite. When the crystals were cooled to liquid air temperature, a blue shift of about 850 cm^{-1} was observed for the red band in chalcanthite but no corresponding change was observed for malachite.

From the observed features it is concluded that the vibronic interactions in chalcanthite are much greater than those in malachite.

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