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## FAR-INFRARED STUDIES OF SOME TETRAHEDRITES AND TENNANTITES

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**Abstract.** Fourier transform spectrometer was used to record far-infrared absorption spectra of 3 tetrahedrites and 2 tennantites. Absorption bands in the range of wave numbers 155—170 and 245—265  $\text{cm}^{-1}$  were attributed to vibrations of the Cu sublattices, the bands 300—315 and 323—345  $\text{cm}^{-1}$  to the sublattices of S atoms. The bands corresponding to vibrations of the As and Sb sublattices lie above 350  $\text{cm}^{-1}$ .

### INTRODUCTION

There are relatively few publications concerning the infrared absorption spectra of sulphide minerals (Moenke 1974). In general, specifically when dealing with complex sulphides, their authors confine themselves to recording a spectrum, making no attempts at its precise interpretation. This is because the absorption bands of those minerals fall predominantly in the far-infrared range in which experimental difficulties are encountered due to weak signals recorded. Far-infrared absorption spectra of some complex lead sulphides (sulphosalts) were recorded by Povarennykh *et al.* (1971).

Due to the application of Fourier spectrometer, which secures a considerably higher signal-to-noise ratio compared with dispersion spectrometers, the present authors obtained good-quality absorption spectra of some tetrahedrites and tennantites.

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## MATERIAL AND METHODS

Investigations were carried out on 3 tetrahedrites and 2 tennantites, viz.:

- Kapnik tetrahedrite (Hungary),
- Harz tetrahedrite (GDR),
- Banská Štiavnica tetrahedrite (Tschechoslovakia),
- Miedzianka tennantite (Góry Świętokrzyskie Mts., Poland),
- Lubin tennantite (Lower Silesia, Poland).

Table 1  
Far IR absorption bands of tetrahedrites and tennantites

Specimen	Assignment of sublattice vibration				
	Cu		S	As, Sb (?)	
Tetrahedrite Harz	170	245	300	323	363
Tetrahedrite Banská Štiavnica	160	247	302	330	382
Tetrahedrite Kapnik	155	250	303	330	365 382
Tennantite Miedzianka	166	262	312	345	375
Tennantite Lubin	166	265	315	342	375

Samples 1, 2 and 3 come from the collections of the Department of Mineralogy and Geochemistry of the Academy of Mining and Metallurgy in Cracow. Samples 4 and 5 were kindly presented to the authors by Dr W. Salamon, for which thanks go to him.

Control chemical and mineralogical analyses have ruled out the presence of any significant admixtures of other minerals. Zinc which was detected by emission spectroscopic method in samples 1, 2, 3 and 4 in an amount of ca. 1% may appear as an isomorphous admixture or as sphalerite. Moreover, an insignificant admixture of galena is possible in samples 1 and 2.

Absorption spectra were recorded in the range of wave numbers 100—450  $\text{cm}^{-1}$  with a FTS-14V Digilab Fourier spectrometer, using a conventional globar source of infrared radiation, a mylar beam splitter (6  $\mu$  in thickness) and a TGS detector of the pyroelectric bolometer type. The sample in the form of Nujol mulls was placed between polyethylene windows. The measurement parameters used were: resolution 4  $\text{cm}^{-1}$ , sampling interval 2  $\text{cm}^{-1}$ , number of scans 100. The Fourier transform was calculated with double precision, using 32-bit words.

## RESULTS AND DISCUSSION

Tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  and tennantite  $\text{Cu}_{12}\text{As}_4\text{S}_{13}$  have a similar structure which can be regarded as the sphalerite-type superstructure, the edge of the unit cell in the sulphosalts studied being twice as long. X-ray diffraction investigations of Pauling and Neuman (1934) and Wuensch *et al.*

(1964, 1966) have shown that the minerals in question possess the space group  $I\bar{4}3m (T_d^3)$  and a body-centred cell containing two  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  or  $\text{Cu}_{12}\text{As}_4\text{S}_{13}$  molecules.

Tetrahedrite and tennantite crystals are isodesmic, therefore they contain no molecular groupings. It follows from that fact that all atomic vibrations in these crystals are to be treated as lattice vibrations, with no division into intramolecular and lattice vibrations. Of two types of lattice vibrations, translation and rotation (libration), only the former come into play since rotation is peculiar to molecular groups alone.

Lattice vibrations display low-energy vibrational transitions. Consequently, absorption of far-infrared radiation (10—400  $\text{cm}^{-1}$ ) and lack of distinct absorption bands in the middle-infrared range (400—4000  $\text{cm}^{-1}$ ) are to be expected. In fact, no absorption bands in range  $> 450 \text{ cm}^{-1}$  have been recorded in the spectra of the minerals studied.

Translational lattice vibrations can be considered as displacements of the atomic (ionic) sublattices with respect to one another.

According to the data obtained by Wuensch, in the unit cells of tetrahedrite and tennantite the copper atoms occupy 12 lattice points of the symmetry 4 ( $S_4$ ) and 12 points of the symmetry  $mm (C_{2v})$ . Two points of the highest symmetry  $43m (T_d)$  are occupied by sulphur atoms whereas the remaining S atoms lie in the plane of symmetry, i.e. they have a position  $m (C_s)$ . Antimony and arsenic atoms show the symmetry 3m ( $C_{3v}$ ). For a structure of that type the distribution of reducible representation of normal vibrations of the unit cells of tetrahedrite and tennantite can readily be determined using Bahagavantham's and Venkatrayudu's method (1969):

$$4A_1 + 2A_2 + 6E + 9F_1 + 14F_2$$

Of all the above types, only the triply degenerated vibrations of the  $F_2$  type are infrared-active, yet one of them, produced by the sulphur lattice in tetrahedral coordination  $T_d$ , is an acoustic vibration and for the wave vector  $k = 0$  (the centre of Brillouin zone) its frequency equals zero. The remaining thirteen  $F_2$  vibrations should yield infrared absorption bands: 6 bands due to Cu atoms, 5 to S atoms, 2 to Sb or As atoms.

Figures 1 and 2 show spectra of tetrahedrites and tennantites recorded in the absorbance scale ( $-\lg T$ ) in the range of 100—450  $\text{cm}^{-1}$ . In figure 2 an absorption spectrum of chalcopyrite  $\text{CuFeS}_2$  is also presented, which was recorded to facilitate the interpretation of tetrahedrite-tennantite spectra.

A comparison of the spectra obtained with those of some simple sulphides with a similar structure, e.g. chalcopyrite  $\text{CuFeS}_2$  or sphalerite  $\text{ZnS}$  which is isostructural with tetrahedrite-tennantite, shows that the fundamental absorption bands can be tentatively attributed to vibrations of respective sublattices. Thus, vibrations of the sublattice of sulphur atoms seem to be responsible for the most intense bands in the range 300—345  $\text{cm}^{-1}$ . This statement has been based on the fact that a strong band that appears in that region in the spectrum of sphalerite (Nyquist, Kagel 1971) may be only due to the sublattices of sulphur atoms. In view of their local symmetry, zinc atoms do not produce infrared-active vibrations. On account of their similarity to the spectra of other copper sulphides,

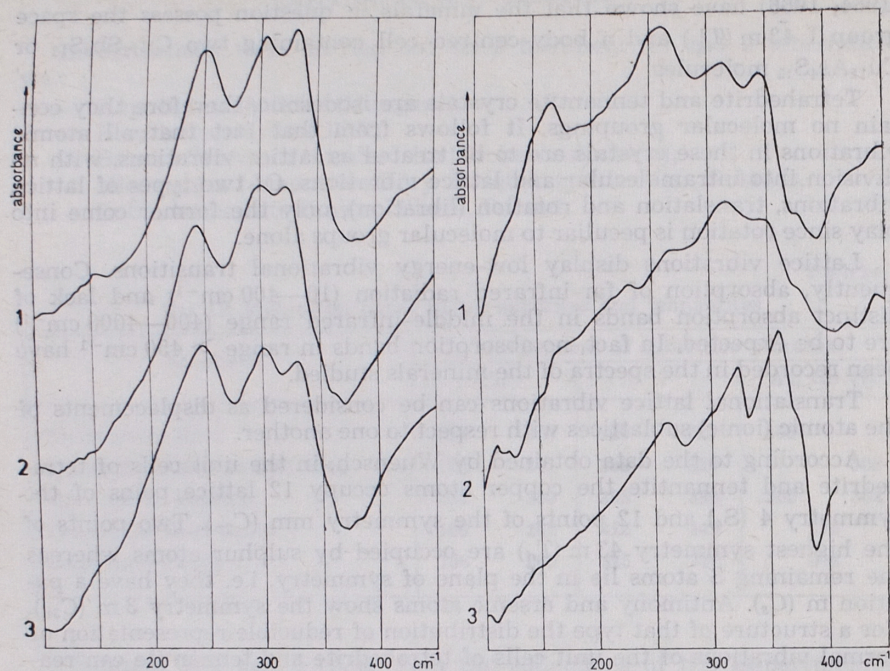


Fig. 1. Far-infrared spectra of tetrahedrites from  
1 — Kapnik, 2 — Harz, 3 — Banská Štiavnica

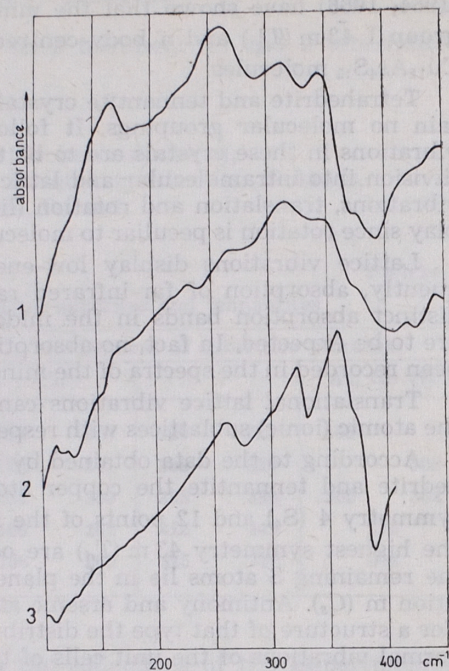


Fig. 2. Far-infrared spectra of  
1 — tennantite from Miedzianka, 2 — tennantite from Lubin 3 — chalcopyrite

the absorption bands  $155\text{--}170\text{ cm}^{-1}$  and  $245\text{--}265\text{ cm}^{-1}$  are to be attributed to vibrations of the Cu sublattices. The remaining weakest bands at higher wave numbers are presumably due to As and Sb atoms. Some less pronounced bands ( $230, 350, 418, 440\text{ cm}^{-1}$ ) have not been ascribed to normal vibrations since they may be produced by foreign admixtures in the crystal lattice or the resultant lattice defects.

From the spectra of tetrahedrites and tennantites it is evident that tennantite bands are displaced to higher wave numbers compared with the analogous tetrahedrite bands. This behaviour may be due to the different effect of As or Sb ions on the vibrations of other atoms. Furtheron, the slight variations in the position of absorption bands of different tetrahedrites and different tennantites may be caused by little but different substitution in their crystal lattice.

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### BADANIA SPEKTROSKOPOWE W ZAKRESIE DALEKIEJ PODCZERWIENI MINERAŁÓW GRUPY TETRAEDRYTU-TENNANTYTU

#### Streszczenie

Przy zastosowaniu spektrometru fourierowskiego FTS-14V Digilab zarejestrowano widma absorpcyjne 3 okazów tetraedrytu i 2 okazów tennantytu w zakresie liczb falowych  $100\text{--}450\text{ cm}^{-1}$ . Pasma absorpcji w zakresie  $155\text{--}170$  oraz  $245\text{--}265\text{ cm}^{-1}$  przypisano drganiom podsieci atomów Cu, pasma  $300\text{--}315$  i  $323\text{--}345\text{ cm}^{-1}$  podsieci atomów S. Pasma odpowiadające drganiom podsieci As i Sb leżą powyżej  $350\text{ cm}^{-1}$ .

#### OBJAŚNIENIA FIGUR

- Fig. 1. Widma absorpcyjne w dalekiej podczerwieni tetraedrytów  
1 — Kapnik, 2 — Harz, 3 — Banská Štiavnica  
Fig. 2. Widma adsorpcyjne w dalekiej podczerwieni  
1 — tennantytu z Miedzianki, 2 — tennantytu z Lubina, 3 — chalkopiryty

Мирослав ХАНДКЕ, Витольд ЖАБИЊСКИ

### ДЛИННОВОЛНОВЫЕ ИНФРАКРАСНЫЕ СПЕКТРЫ МИНЕРАЛОВ ИЗ ГРУППЫ ТЕТРАЭДРИТА-ТЕННАНТИТА

#### Резюме

Используя фурьеровский спектрометр FTS-14V Digilab были зарегистрированы длинноволновые ИК-спектры поглощения 3 образцов тетраэдрита и 2 образцов теннантита в диапазоне волновых чисел  $100\text{--}$

—450  $\text{cm}^{-1}$ . Полосы поглощения в диапазоне 155—170 и 245—265  $\text{cm}^{-1}$  были приписаны колебаниям субрешетки атомов  $\text{Cu}$ , полосы 300—315 и 323—345  $\text{cm}^{-1}$  — субрешетки атомов  $\text{S}$ . Полосы отвечающие колебаниям суб решетки  $\text{As}$  и  $\text{Sb}$  находятся выше 350  $\text{cm}^{-1}$ .

### ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. ИК-спектры поглощения тетраэдритов

1 — Капник, 2 — Гарц, 3 — Банска Штявница

Фиг. 2. ИК-спектры поглощения теннантитов (4, 5) и халькопирита (6)

1 — теннантит из Медзянки, 2 — теннантит из Любина, 3 — халькопирит