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#### NASA TECHNICAL MEMORANDUM

#### INFRARED SPECTRA OF SOME SULFIDES AND THEIR ANALOGS OF BINARY COMPOSITION IN THE LONG-WAVE REGION

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| 16. Above: The far infrared spectra (500-60 cm <sup>-1</sup> ) of some simple<br>sulfides and their analogs were studied. In all, 22 minerals<br>with different structure types were investigated, out of<br>which 14 are sulfides (galena, alabandite, pyrrhotite,<br>sphalerite, wurtzite, cinnabar, realgar, orpiment, getchclite<br>antimonite, molybdenite, pyrite, marcasite and heazlewoodite)<br>6 arsenides (niccolit, domeykite, arsenopyrite, lollingite,<br>rammelsbergite and skutterudite), one telluride (tetradymite)<br>and native arsenic. The main bands of infrared absorption<br>spectra of the minerals are compared with the relative<br>strength of the interatomic bonds o and their interpretation<br>is given. |                            |   |  |  |  |  |  |
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#### INFRARED SPECTRA OF SOME SULFIDES AND THEIR ANALOGS OF BINARY COMPOSITION IN THE LONG-WAVE REGION

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The study of the infrared spectra of minerals in the normal range of wavelengths (from 4,000 to 400 cm<sup>-1</sup>) has a number of substantial shortcomings. The impossibility of recording of the most important bands of absorption in the spectra of a considerable number of minerals, which possess low interatomic bond strength, should be considered the chief shortcoming. These include primarily mineral facies of binary composition, which belong to the classes of chlorides and fluorides, sulfides, arsenides and tellurides, and also a considerable part of the class of oxides, especially low-valence elements [2, 17].

The situation is exceptionally poor with sulfides and their analogs, for which the basic bands of absorption in the infrared spectra are located in the low-frequency (long-wave) range, usually below the 400 cm<sup>-1</sup> boundary. For this reason, the sulfides in the normal region of the infrared spectrum which have been studied prior to now [1, 11, 15, 16, 17] provide a clearly non-indicative picture, insofar as, in this interval  $(4.000-400 \text{ cm}^{-1})$ , they possess only very high, but sufficiently uniform, absorption of infrared beams. This is most clearly noticeable in studies [1, 15], where data are presented on the study of many sulfides of both simple (binary) and complex composition. Distinct bands of absorption [1, 17] are observed only for some minerals (pyrite. marcasite and arsenopyrite) in the region close to 400 cm<sup>-1</sup>; the remaining bands of absorption, usually of insignificant intensity and located in the 1,100  $\rm cm^{-1}$ region, are not characteristic and do not have cognitive value.

\*Numbers in the margin indicate pagination in the foreign text.

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It is evident that the recording of their infrared spectra of absorption in the long-wave region [from 400 to 50 cm<sup>-1</sup>] will be uniquely productive for sulfides, just as for halides [6]. For some natural and synthetic sulfides, such studies have been recently carried out; very interesting and important results were obtained [9, 10, 13]. It is natural that the use of longwave infrared spectroscopy may be expanded considerably, and utilized for the characteristics of all of those minerals, the composition of which contains large cations with low valency, as was recently shown in some carbonates [7].

Our goal is the systematic study of all of the most important natural sulfides, beginning from simple (binary composition) to complex compounds (with three and four types of atoms). Studied in the present article are the infrared spectra of 22 minerals of primarily binary composition, of which 14 are sulfides, 6 arsenides, one telluride, and one belongs to the class of simple substances (native arsenic). The study was carried out on the FIS-1 infrared spectrophotometer (Hitachi, Japan). The thickness of the mineral layer was from 3 to 5 mg/cm<sup>2</sup>; the infrared spectra were recorded in the interval from 500 to 60 cm<sup>-1</sup>.

#### <u>Infrared Spectra of Absorption of Some Sulfides and Arsenides</u> of Uni- and Divalent Elements

In this group, which consists of representatives of eight mineral facies, minerals with coordination structures and substantially covalent bonds dominate. The group includes the coordination structures—galena, alabandite, pyrrhotite, niccolite, sphalerite, wurtzite, domeykite and cinnabar, which possesses a chain structure.

Among them, pyrrhotite is distinguished by the greatest portion of the metallic bond, which substantially affects the shape of the curve of their infrared spectra. The scattering and absorption of the infrared rays by free electrons leads to smoothing, and partially to "blurring", of the bands of absorption



Wavelength,  $cm^{-1}$ 

Fig. 1. Infrared spectra of absorption of sulfides and arsenides of uni- and divalent elements: a-galena; b-alabandite; c-pyrhotite; d-niccolite; e-sphalerite; fwurtzite; g-cinnabar; h-domeykite. in the infrared spectra, making them of little significance. With a decrease in temperature, this effect of the electron "gas" should decrease gradualky; for room temperature (about  $300^{\circ}$  K), it is rather great, and severely distorts the picture of the interatomic bonds.

The curve of the infrared spectrum of galena PbS (Fig. 1,a) has one wide and rather deep band of absorption in this range, with a peak at 155 cm<sup>-1</sup> (Table 1). This position of the basic band of absorption of the galena, which is most shifted into the low-frequency region of the spectrum, as compared with other sulfides, is easily explained by the large interatomic distances and the mass of the lead atom [5].

The curve of the infrared spectrum of alabandite MnS (Fig. 1,b) has a more complex configuration of the band of absorption with a peak at 230 cm<sup>-1</sup> and two inflections at 300 and 180 cm<sup>-1</sup> (Table 1). In addition, there are two slight inflections (steps) on the edges of this main band of absorption, the nature of which is unknown.

There are three wide bands of absorption with peaks at 360, 280 and 180 cm<sup>-1</sup> (Table 1) on the curve of the infrared spectrum of pyrrhotite  $Fe_{1-x}S_x$  (Fig. 1,c), with the first of them, which should be taken for the band of valent variations of the  $\gamma_3$ -bonds in the  $Fe^{III}S_6$  polyhedra, being the most distinctly manifested.

The curve of the infrared spectrum of niccolite (Fig. 1,d), which is isostructural with pyrrhotite, is nearly completely analogous to it, and, in addition to three bands of absorption, located in those same places (370, 285 and 190 cm<sup>-1</sup>), it has a fourth band with a peak at 120 cm<sup>-1</sup> (Table 1), which is probably attributed to the deformational variations of the  $\gamma_{4}$ -bonds in the NiAs<sub>6</sub> polyhedra. The effect of an increase in the valency of the Ni, as compared with the Fe in pyrrhotite, is compensated by an increase in the mass of the "anion" (S-As), and, therefore, the bands of absorption in the niccolite are located roughly in the same places as in pyrrhotite.

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The curves of the infrared spectra of polymorphous facies of ZnS—sphalerite (Fig. 1,e) and wurtzite (Fig. 1,f)—are identical, and are characterized by a single intense wide band of absorption with a peak in the region of  $300 \text{ cm}^{-1}$  (Table 1). The slight branching of this band for wurtzite is associated with the presence in it of a substantial number of atoms of isomorphous iron, just as we observed for ferrous sphalerite.

| TABLE I |           |           |          |        |           |             |   |
|---------|-----------|-----------|----------|--------|-----------|-------------|---|
| Pos     | sition of | Bands of  | Absorpti | ion in | Infrared  | Spectra of  |   |
| Some    | Sulfides  | and Arsei | nides of | Uni- a | and Dival | ent Element | S |

| Mineral. Its Formula.                       | Maxhma of Absorption Bands, cm <sup>-1</sup> |         |                                 |           |          |           |  |
|---|--|---------|---------------------------------|-----------|----------|-----------|--|
| Location                                    | -100)  | 350     | 300                             | 250       | 200      | 150       |  |
| Galena PbS                                  |  |         | * 1998 - AL 2 Stationary (1998) | - 40 Art  |          | 155 W     |  |
| Alabandite, MnS                             |  | 370 i n | 300 in                          | 230 W     | -180 in  | 140 in    |  |
| Pyrrhotite $Fe_{1-x}S_x$                    |  | 360 W   | 280 W                           | ,a.,e     | 180 W    |           |  |
| Santalash (Kirg, SSSR)<br>Niccolite NiAs    |  | 370 W   | 285 in                          | است.<br>ا | 190 ìn   | 120 W     |  |
| Shnecherg, Saxony (GDR)<br>Sphalerite 2nS   |  | · · ·   | 298 w                           | 220 W     | 185      | h- 14     |  |
| Almaden (Spain)<br>Wurtzite ZnS*            |  | 335 i n | 316                             | 215 W     | -190 i.n | \$~a -    |  |
| Carpaty (USSR)<br>Cinnabar Hgs              | ***  | 345     | 286 W                           |           | 180 W    | 120       |  |
| -Khaydarkan (Cent. Asia)<br>Domeykite Cu3As |  | 370- w  | <b>280</b> in                   |           | 180 W    | , <b></b> |  |
| Tsvikau, Saxony (GDR)                       |  |         |                                 |           |          |           |  |

#### Note to tables 1-3. The most intense bands of absorption are set up as half-dark; w-wide, in-inflection, d-doublet. Wurtzite, containing about 7% iron, is marked with an asterisk.

The curve of the infrared spectrum of cinnabar and HgS (Fig. 1,g) possesses three intense bands of absorption with peaks at 345, 283 and 120 cm<sup>-1</sup> (Table 1). In accordance with the characteristics of its chain structure [8], the two first bands are evidently attributed to the valency variations of the Hg--S bonds in the chains (distance Hg-S=2.36 Å) and between them (Hg-S=3.1-3.3 Å), and the last band probably corresponds to the deformation variations of the shortest Hg--S bonds.

The curve of the infrared spectrum of domeykite  $Cu_3As$ (Fig. 1,h) is reminiscent of the curves of pyrrhotite and niccolite, both in the weak intensity of the bands of absorption and in their location in the spectrum (Table 1).

### Infrared Spectra of Absorption of Some Sulfides and Tellurides of Tri- and Tetravalent Elements

Studied in this group are representatives of six mineral facies, among which, as is generally characteristic of highvalency elements of the class of sulfides and their analogs [4], there are no minerals with coordination structures. Chiefly represented here are facies with chain and laminar structures, and only realgar is related to the typical molecular structures with a circular motif at the base [12]. All of these minerals have substantially covalent bonds between the atoms, and only in molybdenite, and especially tetradymite, is the fraction of the metallic bond detected.

The curve of the infrared spectrum of realgar As<sub>4</sub>S<sub>4</sub> (Fig. 2,a) is characterized by several intense bands of absorption with peaks at 373-368, 341 and 224 cm<sup>-1</sup> and many weaker harmonics (Table 2). All of these bands are in good accordance with the data in [9], but, evidently, the band of absorption with a peak at 341 cm<sup>-1</sup>, in contrast to the doublet band at 373-368 cm<sup>-1</sup>, should be associated with the valency variations of the longer As—As bonds, rather than the As—S bonds [4, 12].

The curve of the infrared spectrum of laminar orpiment As<sub>2</sub>S<sub>3</sub>

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Wavelength, cm<sup>-1</sup>

Fig. 2. Infrared spectra of absorption of sulfides and tellurides of tri- and tetravalent elements:

a-realgar; b-orpiment; cgetchelite; d-antimonite; e-tetradymite; f-molybdenite.



Wavelength,  $cm^{-1}$ 

Fig. 3. Infrared spectra of absorption of sulfides and arsenides with a structure of the pyrite-marcasite type:

a-pyrite; b-marcasite; cheazlewoodite; d-arsenopyrite; e-lollingite; f-rammelsbergite; g-skutterudite; h-arsenic.

## TABLE 2

Position of Bands of Absorption in Infrared Spectra of Some Sulfides and Tellurides of Tri- and Tetravalent Elements

| Mineral Its   | Maxima of Absorption Bands, cm <sup>-1</sup> |            |                |       |                |                |  |
|---|--|------------|----------------|-------|----------------|----------------|--|
| Formula, Location   | 400  | 350        | 300            | 250   | 200            | 1.0            |  |
| Realgar, As4S4<br>Racha (Gruz. SSR)                                   | 373 d<br>368 d                               | 359<br>341 | 374            | 224   | 210 d<br>201 d | 159 d<br>178 d |  |
| Orpiment As2S3<br>Yakutiya (RSFSR)                                    | 390 i n<br>375                               | 348 W      | 322 d<br>304 d | 243   | 185 i.n        | 1              |  |
| Getchelitê AsSb\$3<br>Khavdarkan (Cont Asia)                          |  | 330 i n    | 273 W          |       | 180 W -        | ' W            |  |
| Antimonite Sb2S3  |  | 335        | 272 W          | 240 W | in in          | E W            |  |
| Baya-Siris (Romania)<br>Tetradymite Bi <sub>2</sub> Te <sub>2</sub> S |  | 350 W      | 320 i n        | 235 W | Er W           |                |  |
| Santalash (Kirg. ŠSR)<br>Molybdenite MoS2                             |  | 382        |                | 260 W | 120 W          |                |  |
| Koy-tash (Cent. Asia)   |  |            |                |       |                | 1              |  |

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(Fig. 2,b) differs appreciably from the curve of realgar in intensity and location of the bands of absorption (Table 2). The intensity of the bands associated with valency variations is sharply reduced, which, generally speaking, is quite characteristic for laminar structures; in this case, all of the bands are shifted slightly (by 10-15 cm<sup>-1</sup>) into the high-frequency region of the spectrum. Granted, the deepest band of absorption, which may be attributed to valency variations of the As—S bonds, is located in the region of 300 cm<sup>-1</sup>.

The curve of the infrared spectrum of getchelite AsSbS; (Fig. 2,c), which is close in its structural characteristics to orpiment [3], possesses a quite simple configuration with the main band of absorption in the region of 270 cm<sup>-1</sup> (Table 2). This makes it more similar, however, to the infrared spectrum of antimonite, and not orpiment, which is possibly associated with the ordered location of the Sb atoms in the getchelite structure.

The curve of the infrared spectrum of antimonite  $\text{Sb}_2\text{S}_3$ (Fig. 2,d) also has weak and rather broad bands of absorption of the valency variations with peaks at 335, 272, 240 and 220 cm<sup>-1</sup> (Table 2), which are sufficiently well linked with the four basic groups of interatomic Sb—S distances [4].

The bands of absorption are very weakly expressed on the curve of the infrared spectrum of tetradymite  $\operatorname{Bi}_2\operatorname{Te}_2S$  (Fig. 2,e), just like in other minerals with a metallic fraction of the bond— pyrrhotite, niccolite, domeykite (Fig. 1). Here, we see four broad bands with peaks at 350, 320, 235 and 175 cm<sup>-1</sup> (Table 2), to which two types of interatomic distances between Bi, Te and S correspond [4].

The curve of the infrared spectrum of molybdenite  $MoS_2$ (Fig. 2,f) has a single intense and two weak bands of absorption with peaks at 382, 260 and 180 cm<sup>-1</sup>, respectively (Table 2). The simple form of the curve of the infrared spectrum is brought about by the simple and highly-symmetrical structure of the molybdenite [4].

### Infrared Spectra of Absorption of Some Sulfides and Arsenides with a Pyrite-Marcasite Structure

Studied in this group were representatives of eight mineral facies, among which five have a structure of the pyrite-marcasite type: pyrite, marcasite, arsenopyrite, lollingite and rammelsbergite, two-heazlewoodite and skutterudite-have specific structures, and the last-native arsenic-belongs to minerals with a "channeled" laminar structure. All of the arsenides and arsenic possess a considerable fraction of the metallic bond, and are characterized by weakly-pronounced bands of absorption on the curves of the infrared spectra.

The curve of the infrared spectrum of pyrite FeS<sub>2</sub> (Fig. 3.a) has three distinctly expressed bands of absorption with peaks at 422, 349 and 294 cm<sup>-1</sup> (Table 3). The value of the peak of the most intense band, which corresponds to valency variations of the S-S bonds, differs slightly from the value given in study [17].

The curve of the infrared spectrum of marcasite  $FeS_2$ (Fig. 3,b) has a more complex configuration, with a sharp increase in the intensity of the two bands with peaks at 398 and 328 cm<sup>-1</sup>, which are just barely noted on the curve of pyrite (peaks at 376 and 325 cm<sup>-1</sup>) (Table 3). This is brought about primarily by a reduction in the symmetry in the structure of the marcasite, a change in the interatomic distances and removal of the degeneration of the basic variations of the lattice.

On the curve of the infrared spectrum of heazlewoodite Ni<sub>3</sub>S<sub>2</sub> (Fig. 3,c), in addition to the inherent bands of absorption, there are parasitic bands, owing to admixtures of Bravoite and weissite, from which it is impossible to completely separate. The basic band, which corresponds to valency variations of the Ni-S bonds in the coordination structure of this mineral [4], has a peak at 310 cm<sup>-1</sup> (Table 3). /311

The curve of the infrared spectrum of arsenopyrite FeAsS (Fig. 3.d) has a general similarity to the curve of marcasite,

TABLE 3

Position of Bands of Absorption in Infrared Spectra of Some Sulfides and Arsenides with a Pyrite-Marcasite Structure

| Mineral. Its                                 | Maxima of Absorption Bands, cm <sup>-1</sup> |                |                |          |            |         |  |
|--|--|----------------|----------------|----------|------------|---------|--|
| Formula, Loca-<br>tion                       | 400  | 350            | 300            | 250      | 200        | 2540    |  |
| Pyrite FeS2<br>Berezov Field (Ural)          | 422  | 376 i n<br>349 | 325 w<br>294   | 270 i n  |            | ¢ 100   |  |
| Marcasito Fes/                               | 420 d<br>398 d                               | 335<br>328     | 293<br>255 i n |          | 180        |         |  |
| Heazlewoodite Ni <sub>3</sub> S <sub>2</sub> | (435)  | (150W)<br>348  | 310 W          | (280i n) | 210<br>185 |         |  |
| Trail Harbor (Tasmania<br>Arsenonyrite FeasS | 433  | 368            | 275 W          |          | 175        | <b></b> |  |
| Lollingite FeAs2                             |  | 370 W          | 280 W          |          | 180 i n    | 130 in  |  |
| Rammolsbergite NiAs <sub>2</sub>             |  | 325 W          |                |          | 165 i n    | -       |  |
| Bu-Azer (Morocco)<br>Skutterudite Co3(As4)3  |  | 370 W          | 325 i n        |          | 220 i n    |         |  |
| Bu-Azer (Morocco)<br>Arsenic As              | -  | 350 W          | 2,011          | 240 i n  | 180 W      | 160 W   |  |
| Shneeberg (GDR)                              |  |                |                |          |            |         |  |

Note. In parentheses -- maxima of the bands of absorption of the admixture minerals -- bravoite and weissite.

but with a lesser number and sharpness of the bands of absorption than in the latter (Table 3), which is evidently brought about by the increased fraction of the metallicity of the bonds.

The curves of the infrared spectra of lollingite  $\text{FeAs}_2$ and rammelsbergite NiAs<sub>2</sub> (Fig. 3,e and f) are little-pronounced: the bands of absorption are blurred and broad. The characteristic band of each differs slightly in its maximum, which is 370 cm<sup>-1</sup> for lollingite and 325 cm<sup>-1</sup> for rammelsbergite (Table 3).

On the curve of the infrared spectrum of skutterudite  $Co_{4}[As_{4}]_{3}$  (Fig. 3,g), the basic band of absorption is broad, with two maxima at 370 and 325 cm<sup>-1</sup>; the narrower band with a peak at 180 cm<sup>-1</sup> (Table 3) is evidently attributed to deformational variations of the Co—As bonds.

The last curve of the infrared spectrum belongs to arsenic

(Fig. 3,h), and also has a rather "smoothed" and simple form; noted on it are only three bands of absorption with peaks at 350. 240 and 160 cm<sup>-1</sup> (Table 3).

### <u>Interpretation of the Basic Bands of Absorption of the Infrared</u> <u>Spectra of Solfides and their Analogs</u>

Knowledge of the structure of the studied minerals and the basic crystal chemical factors which determine the strength of the interatomic bonds [5] makes it possible for us to correlate the most important bands of absorption on the curves of the infrared spectra of these minerals to the variations of vertain atomic polyhedra. Unfortunately, a sufficiently accurate calculation of the values of the frequencies of the characteristic bands of absorption, according to the formula of one of the authors in [5], can not be applied to these minerals, insofar as the degree of polymerization of the atomic polyhedra, which strongly affects absorption, is sharply different in them. In addition, it is impossible, with sufficient accuracy, to take into account the effect of the valent electrons which do not take part in the bond, which increase the forces of interatomic repulsion, just like the effect of the mass of the atoms, and especially the heavy atoms, which is not as simple as for many complex oxygen compounds.

For this reason, for interpretation of the curves of the infrared spectra of the studied minerals, we made use of the magnitudes of the relative strength of the interatomic bond in the corresponding coordination polyhedra [4], which is calculated according to the following formula:

$$\sigma := K \frac{W_* \cdot W_*}{CN \cdot d^2} \beta,$$

where K is the strength coefficient of the bond, which depends on the degree of covalence;  $W_k$  and  $W_a$  are the valence of the "cations" and "anions"; CN is the coordination number; d is the interatomic distances;  $\beta$  is the coefficient of weakening of the bond, which de-

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pends on the number and state of the valent electrons which do not take part in the bond.

Compared in table 4 are the maxima of the bands of absorption of the valence variations with the magnitudes of the relative strength of the bond of the corresponding atomic polyhedra. Observed on the whole is a rather well-pronounced cymbate dependence between the frequencies of the characteristic bands of absorption and the strength of the bonds  $\sigma$  in the polyhedra. The existing specific deviations from this dependence, for example for the polyhedra of zinc, antimony and mercury, may be easily explained if one takes into account the mass (atomic weight) of these three elements, with an increase in which, as is common knowledge, the

|                    | TABLE 4                                       |          |
|--------------------|---|----------|
| Interrelationship  | of Crystal Chemical Factors and               | Relative |
| Strength of R-X    | Bonds in Various Polyhedra with<br>Variations | Valence  |
| and the second and |   |          |

| Inter-<br>atomic<br>bonds<br>in <sub>RXn</sub><br>polyhedra  | cord-<br>ina-<br>tion<br>num-<br>ber<br>R                    | Inter-<br>atomic<br>dist-<br>ances<br>R-X,Å  | Valen-<br>cy<br>of<br>atoms<br><i>k</i> & <i>X</i> | Coef-<br>fic-<br>ient<br>ß  | Mass<br>of s<br>atom<br>R   | Rela-<br>tive<br>trengt<br>of<br>bonds<br><i>R-X</i>   | Value of maxi-<br>mum $v_3$ , corres-<br>h ponding to vari-<br>ation of bonds                                 |
|--|--|--|--|---|---|--|---|
| Ph S<br>Mn - S<br>Fe S pyrr<br>Fe ( $AS$ , Sars)<br>Ni - As<br>Mn - S<br>Ni - S<br>Ni - S<br>Ni - S<br>Ni - S<br>Sb - S<br>As - As<br>S - S(Fe) pyr<br>S - As(Fer ars) | 6<br>6<br>6<br>6<br>6<br>4<br>4<br>3<br>3<br>1+3<br>1-3<br>2 | 2,96<br>2,61<br>2,45<br>2,27<br>2,23<br>2,43<br>2,38<br>2,38<br>2,38<br>2,38<br>2,38<br>2,24<br>2,52<br>2,51<br>2,51<br>2,50<br>2,30<br>2,36 | 222233222233222<br>66666666666666666666666         | 0,95<br>0,92<br>0,88<br>0,80<br>0,80<br>0,80<br>0,80<br>0,80<br>0,80<br>0,8 | 207,19<br>51,94<br>55,85<br>55,85<br>55,85<br>55,85<br>55,85<br>55,85<br>55,85<br>55,85<br>56,71<br>74,92<br>121,75<br>74,92<br>121,75<br>74,92<br>121,75<br>74,92<br>32,16<br>32,06<br>20,59 | 0,09<br>0,12<br>0,17<br>0,31<br>0,38<br>0,40<br>0,39<br>0,32<br>0,29<br>0,58<br>0,43<br>0,76<br>0,45<br>0,57<br>0,70 | 155<br>230<br>280 (?)<br>349<br>368<br>370<br>382<br>298<br>310<br>373<br>272<br>350 (?)<br>422<br>433<br>345 |

Note. Pyrr. -- pyrrhotite, pyr. -- pyrite, ars. -- arsenopyrite.

frequencies of the variations decrease (the bands of absorption are shifted to the right).

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Being supported by the correspondence of the bands of absorption of the valence variations and the magnitudes of the strength of the interatomic bonds, one can more reliably interpret the curves of the infrared spectra of a number of studied sulfides and their analogs. Thus, for galena, the sole broad band in the spectrum corresponds to the valence variations of the Pb-S bonds: the deformation variations of these bonds are absent in the studied range of its infrared spectrum. The very same picture is characteristic for three other sulfides with a low bond strength-alabandite, sphalerite and wurtzite (Fig. 1). But yet another picture is observed for cinnabar with its highstrength (because of the double coordination of the mercury atoms) bonds. Picked out on its curve of absorption are two sharply different bands of valence variations with peaks at 345 and 283 cm<sup>-1</sup>, while a third band, slightly less intense, corresponds to deformation variations of the -Hg-S-Hg-S- chains.

Detected for realgar and orpiment, studied by R. Forneris [9], are bands of absorption which correspond both to valence and deformation variations of the As—S bonds. However, because of the low symmetry of the minerals and the incomplete identity of the As—S distances and S—As—S angles (and As—S—As, accordingly) [12, 14], both those and other bonds have a complex structure.

Clearly evident on the curves of getchelite and antimonite (Fig. 2,c and d) are the broadening and shifting of the mi``le of the main band of absorption into the low-frequency range (peak at 270 cm<sup>-1</sup>) and the considerably lesser manifestation of the bands which correspond to the deformation variations.

On the other hand, for molybdenite (Fig. 2,f), bands of absorption of both valence and deformation variations are clearly displayed.

There is special interest in the infrared spectra of substantially covalent minerals (with the addition of a metallic /314

TABLE 5Attribution of the Most Important Bands of Absemption to the<br/>Variations v3 and v4 in the Infrared Spectra of Some Sul-<br/>fides and Their Analogs

| Mineral and                               | Maxima of Absorption Bands, cm <sup>-1</sup> |                         |  |  |  |  |
|---|--|-------------------------|--|--|--|--|
| Formula                                   | Valence Vari-                                | Deformation             |  |  |  |  |
|   | ations                                       | Variations              |  |  |  |  |
| Galena PbS                                | 155  |                         |  |  |  |  |
| Alabandite MnS                            | 230  |                         |  |  |  |  |
| Pyrrhotite FeS                            | 360; 280                                     |                         |  |  |  |  |
| Niccolite NiAsl <sup>-x</sup> x           | 370  | 120                     |  |  |  |  |
| Sphalerite ZnS                            | 298  |                         |  |  |  |  |
| Wurtzite ZnS                              | 206  |                         |  |  |  |  |
| Cinnabar HgS                              | 345; 283                                     | 120                     |  |  |  |  |
| Domeykite Cu <sub>3</sub> As              | 379  |                         |  |  |  |  |
| Realger As <sub>4</sub> S <sub>4</sub>    | 373, 368, 359, 341, 274                      | 224, 210, 201, 182, 170 |  |  |  |  |
| Qrpimeny As <sub>2</sub> S <sub>3</sub>   | 348, 322, 304, 248                           |                         |  |  |  |  |
| Getchelite As5bS3                         | 360; 273                                     | 160, 100                |  |  |  |  |
| Antimonive SD <sub>2</sub> S <sub>3</sub> | AK), 272, 240, 2 U                           | 035.175                 |  |  |  |  |
| Tetradymite BizTe2S                       | 1000, 0.49<br>200 000                        | 180                     |  |  |  |  |
| Molybdenite MoS <sub>2</sub>              | 1 072, 200<br>4090 - 1444                    | 201                     |  |  |  |  |
| Pyrite FeS2                               | 400 005 355 398                              | 293, 255, 180           |  |  |  |  |
| Marcasite FeS2                            | 310  | 185                     |  |  |  |  |
| Arcononvrite Foles                        | 433: 368                                     | 275: 178                |  |  |  |  |
| Lollingite PeAs2                          | 370: 260                                     | 180:130                 |  |  |  |  |
| Pammal changita Ni Aca                    | 325  | 165                     |  |  |  |  |
| Skutterudite Co. (As.)                    | 370; 325                                     | 220, 130                |  |  |  |  |
| Arsenic As                                | 350  | 160                     |  |  |  |  |

bond) with structures of the pyrite-marcasite type (Fig. 3, Table 3). Here, as shown by A. Gillieson [10], pyrite and the minerals which are isostructural with it display two bands of absorption, which correspond to valence variations of the S- $\infty$ S and Fe-S bonds, and one band which corresponds to deformation variations of the Fe-S-S.

For marcasite and its analogs, as a result of the substantial structural rearrangement, as compared with pyrite (the change in the interatomic distances, acquisition of a sub-chain "rutile-like" motif), which leads to an appreciable difference in the interatomic distances and the angles of Fe-S-S, all three types of bands turn out to be doubled, that is, they acquire a

doublet nature. Granted, even beginning from the infrared spectra of arsenopyrite and switching to arsenides with a marcasite structure, the doublets of the bands of absorption are removed, and the bands of absorption themselves, because of the effect of the metallic bonds, broaden considerably, becoming indistinct and weakly resolved.

An attempt is made in table 5 to interpret the most important bands of absorption of the infrared spectra of the sullides and minerals close to them that we studied. For some of them, where these bands are weakly pronounced, such a correlation has an approximate nature to a certain extent. This correlation will probably be made more specific in the near future, if we manage to successfully use low temperatures for the recording of infrared spectra.

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