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

A. S. Povarennykh, G. A. Sidorenko, L. S. Solntseva and
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16. Abstract

The far infrared spectra (500-60 cm^{-1}) of some simple sulfides and their analogs were studied. In all, 22 minerals with different structure types were investigated, out of which 14 are sulfides (galena, alabandite, pyrrhotite, sphalerite, wurtzite, cinnabar, realgar, orpiment, getcholite antimonite, molybdenite, pyrite, marcasite and heazlewoodite) 6 arsenides (niccolite, domeykite, arsenopyrite, lollingite, rammelsbergite and skutterudite), one telluride (tetradymite) and native arsenic. The main bands of infrared absorption spectra of the minerals are compared with the relative strength of the interatomic bonds σ and their interpretation is given.

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

A. S. Povarennykh, G. A. Sidorenko, L. S. Solntseva and
B. P. Solntsev
Kiev Institute of Geochemistry and Physics of Minerals of
the Academy of Sciences of the USSR, Moscow.
All-Union Scientific Research Institute of Mineral Raw Materials

The study of the infrared spectra of minerals in the normal range of wavelengths (from 4,000 to 400 cm^{-1}) 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]. /306*

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^{-1} 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 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^{-1}; the remaining bands of absorption, usually of insignificant intensity and located in the 1,100 cm^{-1} region, are not characteristic and do not have cognitive value.

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

It is evident that the recording of their infrared spectra of absorption in the long-wave region [from 400 to 50 cm^{-1}] 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 long-wave 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 /307
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^2; the infrared spectra were recorded in the interval from 500 to 60 cm^{-1}.

Infrared Spectra of Absorption of Some Sulfides and Arsenides 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 in the infrared spectra, making them of little significance. With a decrease in temperature, this effect of the electron "gas" should decrease gradually; for room temperature (about 300° 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^{-1} (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].

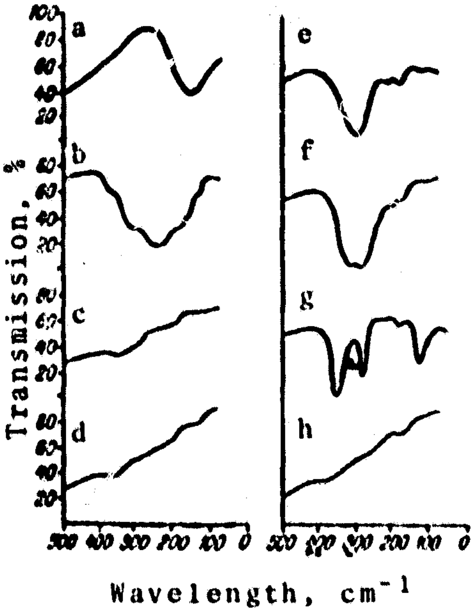

Fig. 1. Infrared spectra of absorption of sulfides and arsenides of uni- and divalent elements: a—galena; b—alabandite; c—pyrrhotite; d—niccolite; e—sphalerite; f—wurtzite; g—cinnabar; h—domeykite.

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^{-1} and two inflections at 300 and 180 cm^{-1} (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^{-1} (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 γ_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^{-1}), it has a fourth band with a peak at 120 cm^{-1} (Table 1), which is probably attributed to the deformational variations of the γ_4-bonds in the $NiAs_6$ polyhedra. The effect of an increase in the valency of /308 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.

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 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 1
Position of Bands of Absorption in Infrared Spectra of Some Sulfides and Arsenides of Uni- and Divalent Elements

Mineral, Its Formula, Location	Maxima of Absorption Bands, cm^{-1}					
	400	350	300	250	200	150
Galena PbS E. Rodopy (Bulgaria)	--	--	--	--	--	155 w
Alabandite MnS Sekerymb (Romania)	·	370 in	300 in	230 w	180 in	140 in
Pyrrhotite $Fe_{1-x}S_x$ Santalash (Kirg. SSSR)	--	360 w	280 w	--	180 w	--
Niccolite NiAs Shneeberg, Saxony (GDR)	--	370 w	285 in	--	190 in	120 w
Sphalerite ZnS Almaden (Spain)	--	--	298 w	220 w	185	--
Wurtzite ZnS* Carpaty (USSR)	--	335 in	316 296 w	215 w	190 in	--
Cinnabar HgS Khaydarkan (Cent. Asia)	--	345	283	--	180 w	120
Domeykite Cu_3As Tsvikau, Saxony (GDR)	--	370 w	280 in	--	180 w	--

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^{-1} (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 high-valency 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 /309 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_4S_4 (Fig. 2,a) is characterized by several intense bands of absorption with peaks at 373-368, 341 and 224 cm^{-1} 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 /310 at 341 cm^{-1}, in contrast to the doublet band at 373-368 cm^{-1}, 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_2S_3

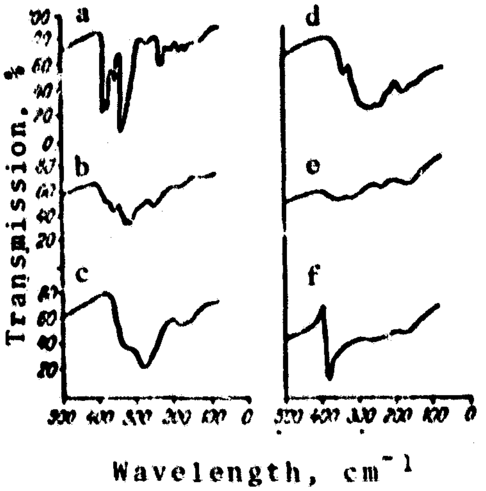

Fig. 2. Infrared spectra of absorption of sulfides and tellurides of tri- and tetravalent elements:

a—realgar; b—orpiment; c—getchelite; d—antimonite; e—tetradymite; f—molybdenite.

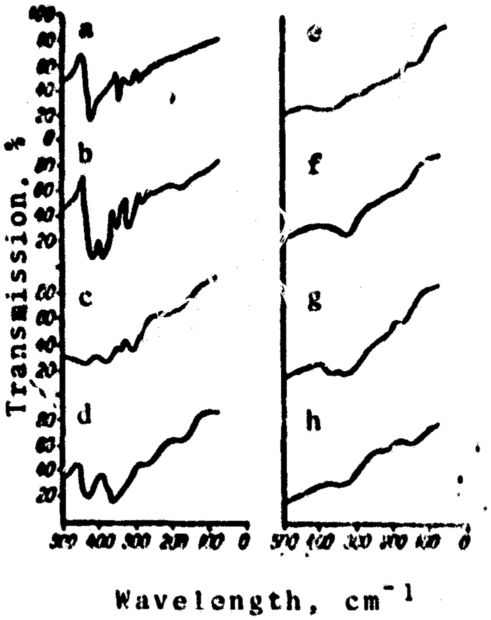

Fig. 3. Infrared spectra of absorption of sulfides and arsenides with a structure of the pyrite—marcasite type:

a—pyrite; b—marcasite; c—heazlewoodite; 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 Formula, Location	Maxima of Absorption Bands, cm⁻¹					
	400	350	300	250	200	150
Realgar, As_4S_4 Racha (Gruz. SSR)	373 d 368 d	359 341	374	224	210 d 201 d	[illegible] d 170 d [illegible] in
Orpiment As_2S_3 Yakutiya (RSFSR)	390 in 375	348 w	322 d 304 d	248	185 in	
Getchelite $AsSbS_3$ Khaydarkan (Cent. Asia)	—	330 in	273 w	—	180 w	[illegible] w
Antimonite Sb_2S_3 Baya-Siris (Romania)	—	335	272 w	240 w	[illegible] in [illegible] w	[illegible] w
Tetradymite Bi_2Te_2S Santalash (Kirg. SSR)	—	350 w	320 in	235 w	[illegible] w	
Molybdenite MoS_2 Koy-tash (Cent. Asia)	—	382	—	260 w	[illegible] w	

(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^{-1}) 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^{-1}.

The curve of the infrared spectrum of getchelite $AsSbS_3$ (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^{-1} (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 Sb_2S_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^{-1} (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 Bi_2Te_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^{-1} (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^{-1}, 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_2 (Fig. 3,a) has three distinctly expressed bands of absorption with peaks at 422, 349 and 294 cm^{-1} (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^{-1}, which are just barely noted on the curve of pyrite (peaks at 376 and 325 cm^{-1}) (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.

/311 On the curve of the infrared spectrum of heazlewoodite Ni_3S_2 (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^{-1} (Table 3).

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 Formula, Location	Maxima of Absorption Bands, cm^{-1}					
	400	350	300	250	200	150
Pyrite FeS_2 Berezov Field (Ural)	422	376 in 349	325 w 294	270 in	—	..
Marcasite FeS_2 Donbass (USSR)	420 d 398 d	335 328	293 255 in	—	180	—
Heczlewoodite Ni_3S_2 Trail Harbor (Tasmania)	(435)	(380w) 348	310 w	(280 in)	210 185	—
Arsenopyrite FeAsS Brich-Mulla (Uzb. SSR)	433	368	275 w	—	175	—
Lollingite $FeAs_2$ Eryayarvi (Finland)	—	370 w	280 w	—	180 in	130 in
Rammelsbergite $NiAs_2$ Bu-Azer (Morocco)	—	325 w	—	—	165 in	—
Skutterudite $Co_3(As_4)_3$ Bu-Azer (Morocco)	—	370 w	325 in 295 in	—	220 in 180 w	—
Arsenic As Shneeberg (GDR)	—	350 w	—	240 in	—	160 w

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 $FeAs_2$ and rammelsbergite $NiAs_2$ (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^{-1} for lollingite and 325 cm^{-1} 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^{-1}; the narrower band with a peak at 180 cm^{-1} (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^{-1} (Table 3).

Interpretation of the Basic Bands of Absorption of the Infrared Spectra of Sulfides and their Analogs

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 certain atomic polyhedra. Unfortunately, a sufficiently accurate cal- /312 culation 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:

$$\sigma = K \frac{W_k \cdot W_a}{CN \cdot d^2} \beta,$$

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; β is the coefficient of weakening of the bond, which depends 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 σ 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 Valence Variations

Inter-atomic bonds in RX_n polyhedra	Coordination number R	Inter-atomic distances $R-X$, Å	Valency of atoms R & X	Coefficient β	Mass of atom R	Relative strength of bonds $R—X$	Value of maximum ν_3, corresponding to variation of bonds $R-X$, cm
Pb—S	6	2,96	2 & 2	0,95	207,19	0,09	155
Mn—S	6	2,61	2 & 2	0,92	54,94	0,12	230
Fe—S pyrr	6	2,45	2 & 2	0,88	55,85	0,17	280 (?)
Fe—S pyr	6	2,27	2 & 2	0,80	55,85	0,31	349
Fe—(As, S) ars	6	2,29	3 & 3	0,80	55,85	0,38	368
Ni—As	6	2,43	3 & 3	0,80	58,71	0,40	370
Mo—S	6	2,38	4 & 2	0,90	95,94	0,39	382
Zn—S	4	2,35	2 & 2	1,00	65,37	0,32	298
Ni—S	4	2,28	2 & 2	0,81	58,71	0,29	310
As—S	3	2,24	3 & 2	0,80	74,92	0,58	373
Sb—S	3	2,52	3 & 2	0,80	121,75	0,43	272
As—As	3	2,51	3 & 3	0,80	74,92	0,76	350 (?)
S—S(Fe) pyr	1+3	2,10	2 & 2	1,00	32,06	0,15	422
S—As(Fe) ars	1+3	2,30	2 & 3	1,00	32,06	0,57	433
Hg—S	2	2,36	2 & 2	1,00	200,59	0,70	345

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

frequencies of the variations decrease (the bands of absorption are shifted to the right). /313

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 high-strength (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^{-1}, 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 middle of the main band of absorption into the low-frequency range (peak at 270 cm^{-1}) 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 sub- /314
stantially covalent minerals (with the addition of a metallic

TABLE 5

Attribution of the Most Important Bands of Absorption to the Variations ν_3 and ν_4 in the Infrared Spectra of Some Sulfides and Their Analogs

Mineral and Formula	Maxima of Absorption Bands, cm^{-1}	
	Valence Variations	Deformation Variations
Galena PbS	155	--
Alabandite MnS	230	—
Pyrrhotite $Fe_{1-x}S_x$	360; 280	--
Niccolite NiAs	370	120
Sphalerite ZnS	298	---
Würtzite ZnS	296	---
Cinnabar HgS	315; 283	120
Domeykite Cu_3As	370	180
Realgar As_4S_4	373, 368, 359, 341, 274	224, 210, 201, 182, 170
Orpiment As_2S_3	348, 322, 304, 218	185
Getchelite $AsSbS_3$	340; 273	185; 165
Antimonite Sb_2S_3	335, 272, 240, 2 0	180, 150
Tetradymite Bi_2Te_2S	350, 320	235; 175
Molybdenite MoS_2	382, 260	180
Pyrite FeS_2	422; 340	291
Marcasite FeS_2	420, 398; 355, 328	293, 255, 180
Heazlewoodite Ni_3S_2	310	185
Arsenopyrite FeAsS	433; 368	275; 178
Lollingite $FeAs_2$	370; 260	180; 130
Rammelsbergite $NiAs_2$	325	165
Skutterudite $Co_4(As_4)_3$	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—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 sulfides 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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