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INFRA-RED (IR-SPECTRA) OF CERTAIN SULPHIDES AND  
ANALOGOUS BINARY COMPOUNDS IN THE LONG-WAVE REGION

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The study of the IR-spectra of minerals in the usual range of wave-length (from 4000 to 400  $\text{cm}^{-1}$ ) has many substantial defects. The chief of them should be considered to be the impossibility of assigning the main absorption bands in the spectra of a significant number of minerals, possessing weak interatomic bonds. Directly pertaining to them are the mineral forms of binary compounds belonging to the class of chlorides and fluorides, sulphides, arsenides and tellurides, also a considerable proportion of the class of acids, notably of low-valence elements.

Unusually bad is the position with sulphides and their analogs for which the principal absorption bands in the IR-spectra are broad and low-frequency (long-wave) bands, usually below the 400- $\text{cm}^{-1}$  limit. No doubt for this reason and up to the present, investigations of sulphides in the ordinary region of IR-spectra (1,11,15,16,17) have yielded an uninformative picture inasmuch as, in this mineral (4000 to 400  $\text{cm}^{-1}$ ), they possess only a very high but uniform absorption of infra-red light. This is most distinctly seen from papers (1,15) where the data are presented in the investigation of a great many of the sulphides, both for the simple (binary) and the complex compounds. Only for certain minerals (pyrite, marcasite and arsenopyrite) in the region near 400  $\text{cm}^{-1}$  are distinct absorption bands observed (1,17); the

remaining absorption bands are generally of low intensity and are situated in the  $1100\text{-cm}^{-1}$  region, neither appearing characteristic nor being relevant to this investigation.

It is obvious that there will be as good results for sulphides as for halides (6), in the recording of their IR-absorption spectra in the long-wave region (from  $400$  to  $50\text{ cm}^{-1}$ ). For certain natural and synthetic sulphides such surveys were recently made; very interesting and significant results were obtained (9,10,13). It is clear that the application of long-wave IR-spectroscopy may be considerably expanded and developed for the characterization of all these minerals and to compounds in which there exist large low-valence cations, as was recently shown in certain carbonates (7).

Our objective was systematic study of the most important natural sulphides, going from the ordinary (binary compounds) to the complex compounds (with three or four kinds of atoms). In this investigation of the IR-spectra of twenty-two minerals, chiefly binary compounds, 14 sulphides, 6 arsenides, 1 telluride, and one belonging to the elemental class (native arsenic) were determined. The infra-red spectrometer FIS-1 (Hitachi, Japan) were used for the investigation. The thickness of the mineral sections was  $3\text{-}5\text{ mg/cm}^2$ ; IR-spectra were recorded in the interval from  $500$  and  $60\text{ cm}^{-1}$ .

#### Infra-Red Absorption Spectra of Certain Sulphides and Arsenides of Univalent and Bivalent Elements

In this group, consisting of representatives of eight mineral species, there predominate minerals with co-ordination structures and bonds of essentially covalent type. Here are described those so co-ordinated - galena, alabandine, pyrrhotite, niccolite, sphalerite, wurtzite, domeykite, and cinnabar - which have chain structure.

Among these, pyrrhotite is distinguished by the longest metallic bonds, a fact which is very clearly indicated by the shape of the curves of its IR-spectra. The dispersion and absorption by free electrons of the infra-red rays smooth out and

partly smear out the absorption bands of the IR-spectra. With reduction in temperature, this effect of the electron "gas" gradually lessens but, even at room temperature (about 300 °K), it is fairly large and greatly distorts the picture of the interatomic bonds.

The IR-spectra of galena PbS (Figure 1a) has in this region one broad and very strong absorption band with its peak at  $155 \text{ cm}^{-1}$  (Table 1). In comparison with other sulphides, the most displaced to the low-frequency region of the spectrum is the main absorption band of galena, a fact which is readily explained by the large interatomic distance and the mass of the lead atoms (5).

The IR-spectrum of alabandine MnS (Figure 1b) has a more complex contour of the absorption band, with a peak (at)  $230 \text{ cm}^{-1}$  and two shoulders (at) 300 and  $180 \text{ cm}^{-1}$  (Table 1). Furthermore, two more small shoulders (cause unknown) exist in the sides of this main absorption band.

In the IR-spectrum of pyrrhotite,  $\text{Fe}_{1-x}\text{S}$  (Figure 1c), there are three broad absorption bands with peaks (at) 360, 280, and  $180 \text{ cm}^{-1}$  (Table 1); the most clearly apparent is the first of them (10), which is assumed to be the  $\nu_3$  valence vibration band of the bonds in the  $\text{Fe}^{3+}\text{S}_6$  polyhedron.

The IR-spectrum of niccolite, isosteric with pyrrhotite, (Figure 1d), is almost completely its analog and, besides three absorption bands situated in the same positions (370, 285 and  $190 \text{ cm}^{-1}$ , has a fourth band with a peak at  $120 \text{ cm}^{-1}$  (Table 1) which possibly pertains to the  $\nu_4$ -deformation vibration of the bonds in the polyhedron  $\text{NiAs}_6$ . The effect of the increased valency of Ni in comparison with Fe in pyrrhotite is balanced by the increased mass of the "anion" (S  $\rightarrow$  As); therefore, the absorption bands in niccolite are located approximately in the same positions as they are in pyrrhotite.

The IR-spectra of the polymorphous forms of ZnS - sphalerite (Figure 1e) and wurtzite (Figure 1f) - are identical and characterized by one strong broad absorption band with (its) peak in the region (of)  $300 \text{ cm}^{-1}$  (Table 1). The trifling splitting of this band in wurtzite is connected with the presence of a

considerable number of atoms of isomorphous iron such as were also observed by us in ferruginous sphalerite.

The IR-spectrum of cinnabar, HgS (Figure 1g) has three strong absorption bands with peaks (at) 345, 283, and 120  $\text{cm}^{-1}$  (Table 1). In accordance with the peculiar chain of its structure (8), the two main bands are apparently related to the valence vibration of the Hg-S bond in the chains (Hg-S distance = 2.36 Å) and among those (Hg-S = 3.1-3.3 Å), but the last probably corresponds to the deformation vibrations of the shorter (13) Hg-S bonds.

The IR-spectrum of domekyite,  $\text{Cu}^3\text{As}$  (Figure 1h) resembles those of pyrrotite and niccolite both in the weak intensity of the absorption bands and in their spectral position (Table 1).

#### IR-Spectral Absorption of Certain Sulphides and Tellurides of Tri- and Quadrivalent Elements

In this group were surveyed six representative mineral forms among which, as is usual in the case of high-valency element class of sulphides and their analogs (4), there are no minerals with co-ordinated structures. Here were represented, for the most part, forms with chain and laminar structures, whereas only realgar has the typical, ring modular structure (12). All these minerals have substantially covalent bonds between atoms, and only molybdenite and, particularly, tetradyrite display a number of metallic bonds.

The IR-spectrum of realgar  $\text{As}_4\text{S}_4$  (Figure 2a) is characterized by several strong absorption bands with peaks (at) 373-368, 341 and 224  $\text{cm}^{-1}$ , and many more weak harmonics (Table 2). All these bands are in good agreement with the data of reference (9) but, apparently, the observed absorption bands with peaks (at) 341  $\text{cm}^{-1}$  should be connected with the difference of the doublet bands (at) 373-368  $\text{cm}^{-1}$  and with the valence vibrations not of the As-S bond but rather of the longer As-As bonds (4,12).

The IR-spectrum of laminated orpiment,  $\text{As}_2\text{S}_3$  (Figure 2b) differs markedly from the realgar curves in intensity and position of the absorption bands (Table 2). The intensities of the bands connected with the valence vibrations are sharply reduced, a fact which is in general quite characteristic of laminated structures; in addition, all the bands are somewhat displaced (by 10 to 15  $\text{cm}^{-1}$ ) to the high-frequency region of the spectrum. In fact, the strongest absorption bands, related probably to the valence vibrations of the As-S bond, are situated in the 300- $\text{cm}^{-1}$  region.

The IR-spectrum of getchelite,  $\text{AsSbS}_3$  (Figure 2c), is of similar form to that of orpiment (3) and has a very simple shape with the main absorption band in the 270- $\text{cm}^{-1}$  region (Table 2). Even then it is more like the IR-spectrum of antimonite than that of orpiment, a circumstance possibly linked to the regular arrangement of the antimony atoms in the structure of getchelite.

The IR-spectrum of antimonite  $\text{Sb}_2\text{S}_3$  (Figure 2d) also possesses weak and quite broad absorption bands for the valence vibrations, with peaks (at) 335, 272, 240, and 220  $\text{cm}^{-1}$  (Table 2) which can be adequately related to the four fundamental interatomic distances Sb-S (4) for the group.

In the IR-spectrum of tetradymite  $\text{Bi}_2\text{Te}_2\text{S}$  (Figure 2e), the absorption bands appear very weakly; like (those) in other minerals with metallic bond assignment - pyrrhotite, niccolite, domeykite (Figure 1). Here we see four broad bands with peaks (at) 350, 320, 235, and 175  $\text{cm}^{-1}$  (Table 2) which correspond to the two types of interatomic distances between Bi, Te, and S (4).

The IR-spectrum of molybdenite  $\text{MoS}_2$  (Figure 2f) has one intense and two weak absorption bands with peaks (at) 382, 260, and 180  $\text{cm}^{-1}$ , respectively (Table 2). The simple form of the IR-spectrum is explained by the simple and highly symmetrical structure of molybdenite (4).

The IR-Absorption Spectra of Some Sulphides and Arsenides with the Pyrite-Marcasite Structure

In this group will be studied eight representatives of mineral species among which five (pyrite, marcasite, arsenopyrite, loellingite, and rammelsbergite) have the pyrite-marcasite structure; two - heazlewoodite and skutterudite - which possess unique structures; and, finally, native arsenic which belongs to the minerals with "channelled" laminar structure. All arsenides and arsenic have a considerable proportion of metallic bonds and are distinguished by indistinct absorption bands in their IR-spectra.

The IR-spectrum of pyrite  $\text{FeS}_2$  (Figure 3a) possesses three distinctly formed absorption bands with peaks (at) 422, 349, and  $294 \text{ cm}^{-1}$  (Table 3). The magnitudes of the peaks, particularly of the intense band corresponding to the valence vibration of the S-S bond, are similar to the magnitudes quoted in (17).

The IR-spectral curves of marcasite  $\text{FeS}_2$  (Figure 3b) have a more complex configuration with sharply increased intensities for the two bands with peaks (at) 398 and  $328 \text{ cm}^{-1}$  which are almost invisible in the pyrite curves (peaks (at) 376, and  $325 \text{ cm}^{-1}$ ) (Table 3). This is explained in the first place by the lower symmetry of the marcasite structure, by the change in the interatomic distances, and by the reduction in the degeneracy of the fundamental vibrations of the lattice.

In the IR-spectrum of heazlewoodite  $\text{Ni}_3\text{S}_2$  (Figure 3c), besides (its) own absorption bands, (there) are parasitic bands to contamination by bravoite and vaesite from which it is impossible to separate it completely. The main band corresponding to the valence vibrations of the Ni-S bonds in the co-ordination structure of this mineral (4) has two maxima (at)  $310 \text{ cm}^{-1}$  (Table 3).

The IR-spectrum of arsenopyrite  $\text{FeAsS}$  (Figure 3f) has a general similarity to the marcasite curves but has fewer peaks and an absorption peak sharpness (Table 3) which seemingly is explained by the increasing degree of metallicity of the bonds.

The IR-spectra of loellingite  $\text{FeAs}_2$  and rammelsbergite  $\text{NiAs}_2$  (Figures 3g and h) are poorly formed: the absorption bands are broad and not sharply defined. Characteristic bands of each differ in their maxima;  $370 \text{ cm}^{-1}$  for loellingite and  $325 \text{ cm}^{-1}$  for rammelsbergite (Table 3).

In the IR-spectral curves of skutterudite  $\text{Co}_4(\text{As}_4)_3$  (Figure 3i), the main absorption band is broad and has two maxima (at)  $370$  and  $325 \text{ cm}^{-1}$ ; a less broad band with a peak at  $180 \text{ cm}^{-1}$  (Table 3) is obviously related to the deformation vibrations of the Co-As bonds.

The final IR-spectrum belongs to arsenic (Figure 3j) and also has a considerably smoothed out appearance; it has just three absorption bands with peaks (at)  $350$ ,  $240$ , and  $160 \text{ cm}^{-1}$  (Table 3).

#### The Interpretation of the Principal IR Absorption Bands of the Sulphides and Their Analogs

The knowledge of the structure of the minerals investigated and their principal crystallographic parameters, factors (24) by which the strength of the interatomic bonds (5) is determined, allows us to (25) connect the more important absorption bands in the IR spectra of these minerals with the vibrations of specific atomic polyhedra. Unfortunately, sufficiently exact calculations of frequency values of characteristic absorption bands of these minerals, using the formula of one of the authors (5), cannot be applied because of the marked difference in the degree of polymerization of the atomic polyhedra which strongly influences the absorption. Furthermore, it is impossible with adequate precision to allow for the effect of valence electrons, not participating in the bond (26), in increasing the strength of the interatomic repulsion, as well as for the effect of the atomic masses, particularly the heavy (ones), which is not as simple as in many complex oxygen compounds.

For this reason, in the interpretation of the IR-spectra of the minerals investigated, I used the values of the relative strengths of the interatomic bonds of the corresponding co-ordinated polyhedra (4) which are calculated by the following formula:

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

where k - coefficient of bond strength, depending on the degree of covalency;

$W_k$  &  $W_a$  - valency of the "cations and anions";

CN - co-ordinating number;

d - interatomic distance;

$\beta$  - coefficient of bond weakening, depending on the number and ratio of the non-bonding to the valency-bond electrons.

In Table 4, the maxima of the absorption bands of the valence vibrations are compared with the values of the relative strengths of the bond of the corresponding atomic polyhedra. On the whole, there is seen a fairly clearly indicated correlation between the frequencies of the characteristic absorption bands and the bond strength of the " $\sigma$ " of the polyhedra. Existing isolated divergences from such relationships, for example the polyhedra of zinc, antimony, and mercury, can be easily explained, if allowance is made for the mass (atomic weight) of these three elements, which increase as the vibration frequencies decrease (the absorption bands are displaced to the right\*).

On the basis of the correspondence of the absorption bands of the valence vibrations and the values of the interatomic bond strengths, it is possible to interpret more positively the IR-spectra of the series of sulphides investigated and their analogy. Thus, in galena, the only single broad absorption band in the spectrum corresponds to the valence vibrations of the Pb-S bond: the deformation vibrations of this bond are not

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\*Translator's Note: "To the right" means longer wavelength and lower frequencies.



present in the range studied for this IR-spectrum. A similar picture is characteristic of the three other sulphides with weak bond strengths - alabandine, sphalerite and wurtzite (Figure 1). But, for cinnabar with its highly stable bonds (thanks to the double co-ordination of the mercury atoms), there is observed yet another picture. In its absorption curve, there are seen two markedly different bands for the valence vibrations with peaks (at) 345 and 283  $\text{cm}^{-1}$ , but a third band, somewhat less intense, corresponds to the deformation vibrations of the -Hg-S-Hg-S- chains.

For realgar and orpiment, absorption bands appear in the investigations of R. Formeris (9) and correspond to both valence and deformation vibrations of the As-S bonds. Nevertheless, thanks to the low symmetry of the minerals and the imperfect identity of the As-S distances and the S-As-S angles (and consequently the As-S-As) (12,14), these and other bands have a complex structure.

In the spectra of getchelite and antimonite (Figures 2c and d) there are clearly visible broadening and displacement of the central main absorption bands to the low-frequency region (peak at 270  $\text{cm}^{-1}$ ) and considerably smaller development of bands corresponding to deformation vibrations.

On the contrary, for molybdenite (Figure 2f), there are distinct absorption bands both for valence and for deformation vibrations.

Particular interest is presented by the IR-spectra of essentially covalent minerals (mixed with metallic bonds) with structures like pyrite and marcasite (Figure 3, Table 3). Here, as shown by A.H. Gillieson (10), for pyrite and minerals isostructural with it, there can be distinguished two absorption bands, corresponding to the valence vibrations of the S-S and the Fe-S bonds, and one band corresponding to the deformation vibration of Fe-S-S.

For marcasite and its analogs, as a result of the significant structural re-ordering in comparison with pyrite (the change of the interatomic distances, the acquisition of

the "rutile-like" sub-chain are reasons), and, taking into account the marked difference in the interatomic distances and Fe-S-S angles, all three types of bands appear double, i.e., have acquired doublet character. Starting from the IR-spectra of arsenopyrite, in the transition to arsenides of marcasite structure, the doublet absorption bands disappear (30) and absorption bands, thanks to the influence of the metallic bonds, are much broadened to become an indistinct but admitted spectrum.

In Table 5, an attempt is made at the interpretation of the principal absorption IR-spectral bands of the sulphides and similar minerals studied by us. For certain of them where bands appeared but weakly, such binding has to some extent an approximate character. It might result in greater precision if in the future we were able to use low temperatures during the recording of the IR-spectra.

TABLE 1

Position of Absorption Bands of the IR-Spectra of Certain Sulphides and Arsenides of Mono- and Divalent Elements

| Mineral, formula<br>deposit                                                 | Maxima of absorption peaks, cm <sup>-1</sup> |         |               |       |        |        |
|-----------------------------------------------------------------------------|----------------------------------------------|---------|---------------|-------|--------|--------|
|                                                                             | 400                                          | 350     | 300           | 250   | 200    | 150    |
| Galena, PbS-<br>East Rodopi<br>(Bulgaria)                                   | -                                            | -       | -             | -     | -      | 155 b  |
| Alabandine, MnS<br>Sekerimb, (Rumania)                                      | -                                            | 370 sh  | 300 sh        | 230 b | 180 sh | 140 sh |
| Pyrrhotite, Fe <sub>1-x</sub> S <sub>x</sub><br>Santalach,<br>(Khirg, USSR) | -                                            | 360 b   | 280 b         | -     | 180 b  | -      |
| Niccolite, NiAs<br>Schneeberg,<br>(Saxony, DDR)                             | -                                            | 370 b   | 285 sh        | -     | 190 sh | 120 b  |
| Sphalerite, ZnS<br>Almaden, (Spain)                                         | -                                            | -       | 298 b         | 220 b | 185    | -      |
| Wurtzite, ZnS*<br>Karpati, (USSR)                                           | -                                            | 335 sh  | 316,<br>296 b | 215 b | 190 sh | -      |
| Cinnabar, HgS<br>Haidarkan<br>(Central Asia)                                | -                                            | 345 (?) | 283           | -     | 180 b  | 120    |
| Domeykite, Cu <sub>3</sub> As<br>Zwickau,<br>(Saxony, DDR)                  | -                                            | 370 b   | 280 sh        | -     | 180 b  | -      |
| -                                                                           | -                                            | -       | -             | -     | -      | -      |

Footnote for Tables 1 to 3: Most intense absorption bands are shown in heavy type. b = broad, sh = shoulder, d = doublet. The asterisked wurtzite, contained approximately 7% iron.

TABLE 2

Position of Absorption Bands of the IR-Spectra of Certain Sulphides and Tellurides of Tri- and Quadrivalent Elements

| Mineral, formula<br>deposit                                              | Maxima of absorption bands, $\text{cm}^{-1}$ |            |                |       |                 |                          |
|--------------------------------------------------------------------------|----------------------------------------------|------------|----------------|-------|-----------------|--------------------------|
|                                                                          | 400                                          | 350        | 300            | 250   | 200             | 150                      |
| Realgar, $\text{As}_4\text{S}_4$<br>Racha (Georgian SSR)                 | 373 d<br>368 d                               | 359<br>341 | 374            | 224   | 210 d<br>204 d  | 182 d<br>170 d<br>140 sh |
| Orpiment, $\text{As}_2\text{S}_3$<br>Yakutia (RSFSR)                     | 390 sh<br>375                                | 348 b      | 322 d<br>304 d | 248   | 185 sh          | -                        |
| Getchelite, $\text{AsSbS}_3$<br>Haidarkan, (Central Asia)                | -                                            | 330 sh     | 273 b          | -     | 180 b           | 165 b                    |
| Antimonite, $\text{Sb}_2\text{S}_3$<br>Baya-Sprrie (Rumania)             | -                                            | 335        | 272 b          | 240 b | 220 sh<br>180 b | 130 b                    |
| Tetradimite, $\text{Bi}_2\text{Te}_2\text{S}$<br>Santalach (Khirgiz SSR) | -                                            | 350 b      | 320 sh         | 235 b | 175 b           | -                        |
| Molybdenite, $\text{MoS}_2$<br>Koi-Tash (Central Asia)                   | -                                            | 382        | -              | 260 b | 180 b           | -                        |

TABLE 3

Position of Absorption Bands of the IR-Spectra of Certain Sulphides and Arsenides with the Pyrite-Marcasite Structure

| Mineral, formula<br>deposit                                       | Maxima of absorption bands, $\text{cm}^{-1}$ |                |                  |        |                 |        |
|-------------------------------------------------------------------|----------------------------------------------|----------------|------------------|--------|-----------------|--------|
|                                                                   | 400                                          | 350            | 300              | 250    | 200             | 150    |
| Pyrite, $\text{FeS}_2$<br>Berezov Mine (Urals)                    | 422                                          | 376 sh<br>349  | 325 b<br>294     | 270 sh | -               | -      |
| Marcasite, $\text{FeS}_2$<br>Donbass (SSR)                        | 420 d<br>398 d                               | 355<br>328     | 293<br>255 sh    | -      | 180             | -      |
| Heazlewoodite, $\text{Ni}_3\text{S}_2$<br>Trail Harbor (Tasmania) | (435)                                        | (380 b)<br>348 | 310 b            | 280 sh | 210<br>185      | -      |
| Arsenopyrite, $\text{FeAsS}$<br>Brich-Mulla (Uzbek SSR)           | 433                                          | 368            | 275 b            | -      | 178             | -      |
| Loellingite, $\text{FeAs}_2$<br>Eryajarvi (Finland)               | -                                            | 370 b          | 280 b            | -      | 180 sh          | 130 sh |
| Rammelsbergite, $\text{NiAs}_2$<br>Bu-Azer, (Morocco)             | -                                            | 325 b          | -                | -      | 165 sh          | -      |
| Skutterudite, $\text{Co}(\text{As}_4)_3$<br>Bu-Azer, (Morocco)    | -                                            | 370 b          | 325 sh<br>295 sh | -      | 220 sh<br>180 b | -      |
| Arsenic, As<br>Schneeberg, (DDR)                                  | -                                            | 350 b          | -                | 240 sh | -               | 160 b  |

TABLE 4

Relation between Associated Crystallographic Factors and Comparative  
Stability of Bond R-X of Various Polyhedra with Valence Vibration

| Interatomic bonds<br>of polyhedra $RX_R$ | Co-ordination<br>No. R | Interatomic<br>Distance<br>R-X, A | Valency<br>of Atoms<br>R & X | Coefficient<br>$\beta$ | Atomic<br>Mass<br>R | Stability<br>of bond<br>R-X | Maximum values<br>$v_3$ , corresponding<br>to vibration of<br>bond R-X, $cm^{-1}$ |
|------------------------------------------|------------------------|-----------------------------------|------------------------------|------------------------|---------------------|-----------------------------|-----------------------------------------------------------------------------------|
| 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<br>pyrrhotite                       | 6                      | 2.45                              | 2 : 2                        | 0.88                   | 55.85               | 0.17                        | 280 (?)                                                                           |
| Fe-S<br>pyrite                           | 6                      | 2.27                              | 2 : 2                        | 0.80                   | 55.85               | 0.31                        | 349                                                                               |
| Fe-(As, S,<br>arseno-pyrite)             | 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                        | 0.84                   | 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)<br>pyrite                        | 1 + 3                  | 2.10                              | 2 : 2                        | 1.00                   | 32.06               | 0.45                        | 422                                                                               |
| S-As(Fe)<br>arseno-pyrite                | 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                                                                               |

TABLE 5

Assignment of Important Absorption Bands with Vibrations  $\nu_3$  and  $\nu_4$  of the IR-Spectra of Certain Sulphides and Their Analogs

| Mineral & formula                            | Maxima of absorption bands, $\text{cm}^{-1}$ |                         |
|----------------------------------------------|----------------------------------------------|-------------------------|
|                                              | Valence vibrations                           | Deformation vibrations  |
| Galena PbS                                   | 155                                          | -                       |
| Alabandine MnS                               | 230                                          | -                       |
| Pyrrhotite $\text{Fe}_{1-x}\text{S}_x$       | 360 : 280                                    | -                       |
| Nickelite NiAs                               | 370                                          | 120                     |
| Sphalerite ZnS                               | 298                                          | -                       |
| Wurtzite ZnS                                 | 296                                          | -                       |
| Cinnabar HgS                                 | 345 : 283                                    | 120                     |
| Domeykite $\text{Cu}_3\text{As}$             | 370                                          | 180                     |
| Realgar $\text{As}_4\text{S}_4$              | 373, 368, 359, 341, 274                      | 224, 210, 204, 182, 170 |
| Orpiment $\text{As}_2\text{S}_3$             | 348, 322, 304, 248                           | 185                     |
| Getchelite $\text{AsSbS}_3$                  | 330, 273                                     | 185, 165                |
| Antimonite $\text{Sb}_2\text{S}_3$           | 335, 272, 240, 210                           | 180, 130                |
| Tetradymite $\text{Bi}_2\text{Te}_2\text{S}$ | 350, 320                                     | 235, 175                |
| Molybdenite $\text{MoS}_2$                   | 382, 260                                     | 180                     |
| Pyrite $\text{FeS}_2$                        | 422, 349                                     | 294                     |
| Marcasite $\text{FeS}_2$                     | 420, 398, 355, 328                           | 293, 255, 180           |
| Heazlewoodite $\text{Ni}_3\text{S}_2$        | 310                                          | 185                     |
| Arsenopyrite $\text{FeAsS}$                  | 433, 368                                     | 275, 178                |
| Loellingite $\text{FeAs}_2$                  | 370, 280                                     | 180, 130                |
| Rammelsbergite $\text{NiAs}_2$               | 325                                          | 165                     |
| Skutterudite $\text{Co}_4(\text{As}_4)_3$    | 370, 325                                     | 220, 180                |
| Native Arsenic As                            | 350                                          | 160                     |

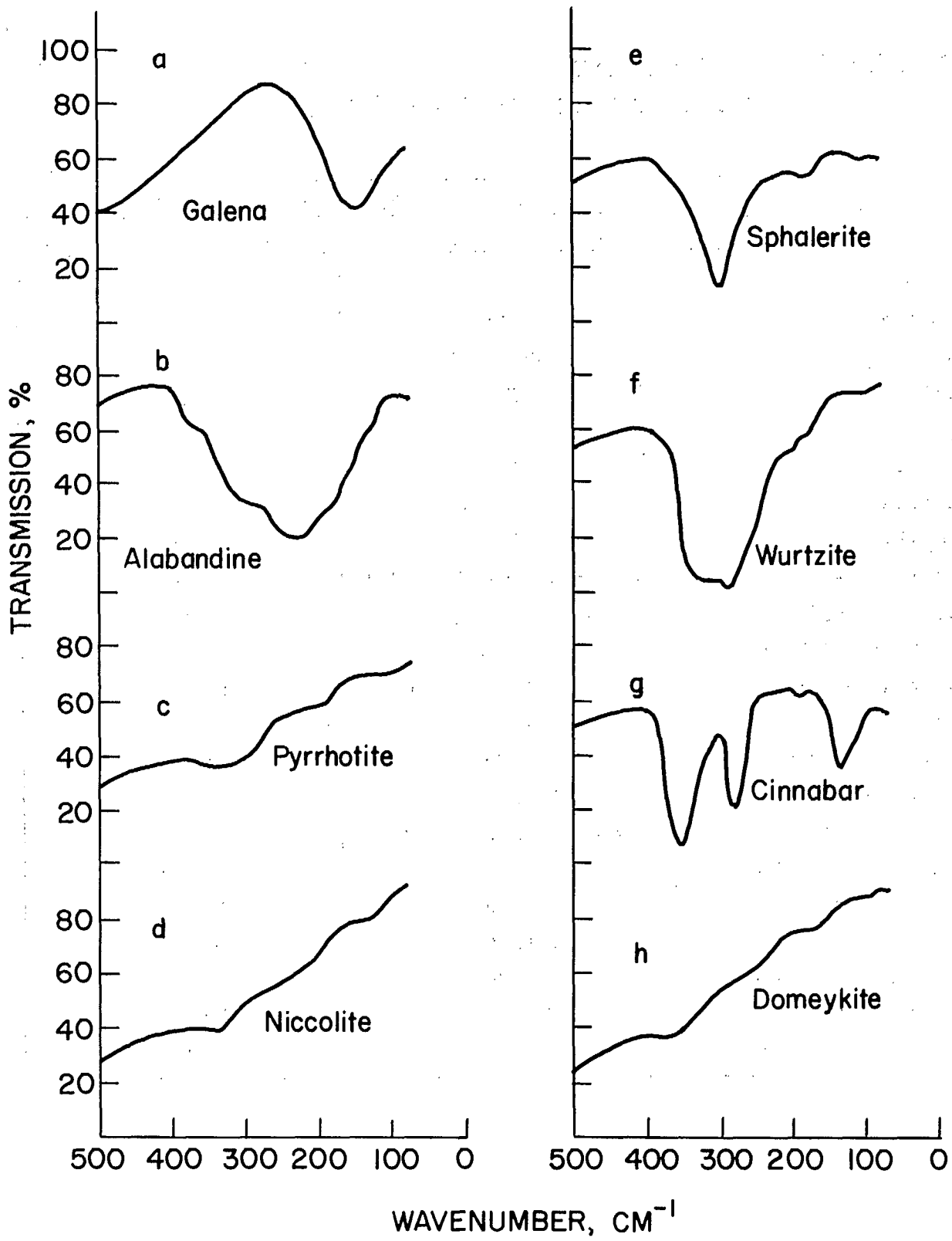


FIGURE 1



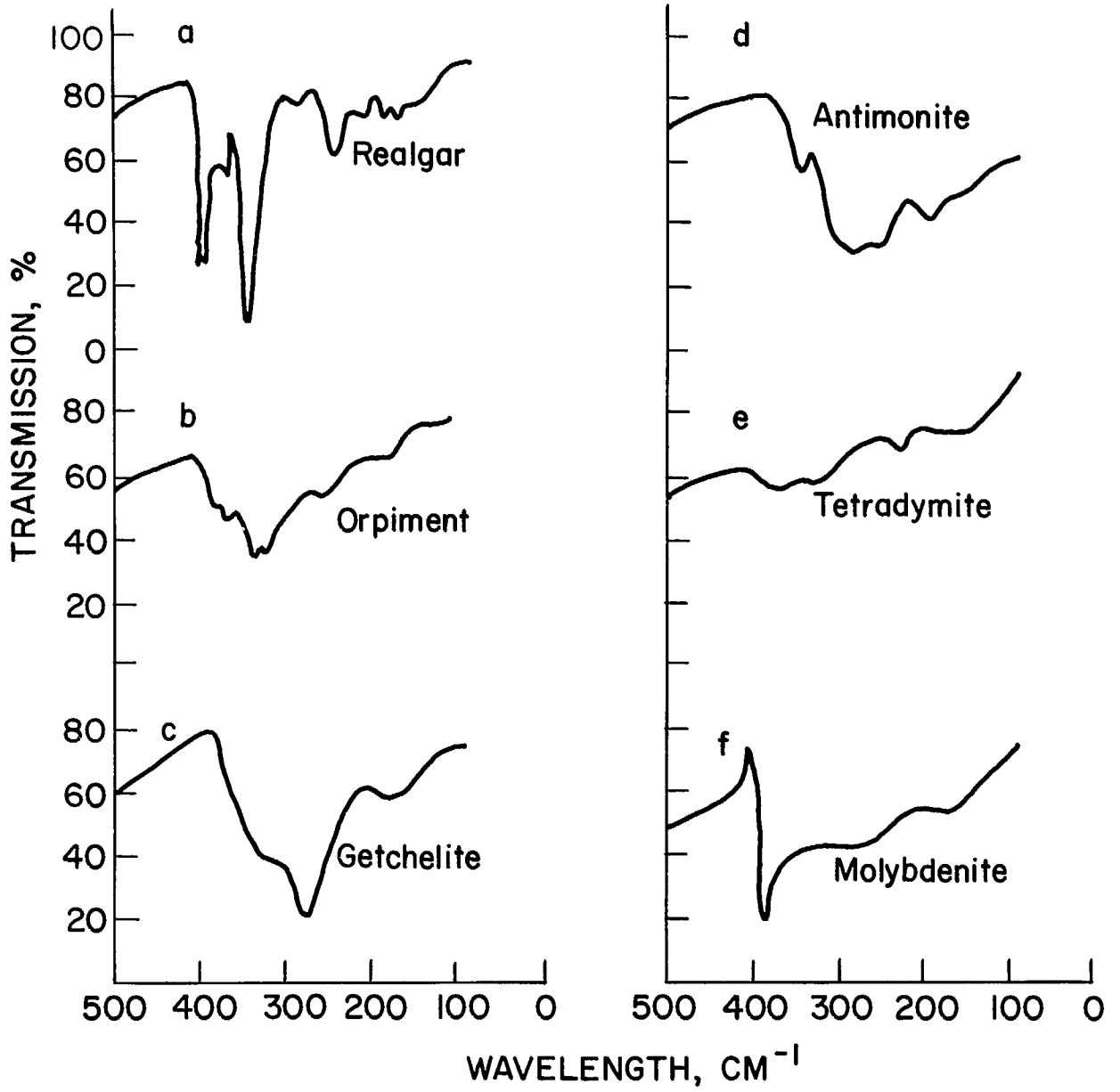


FIGURE 2

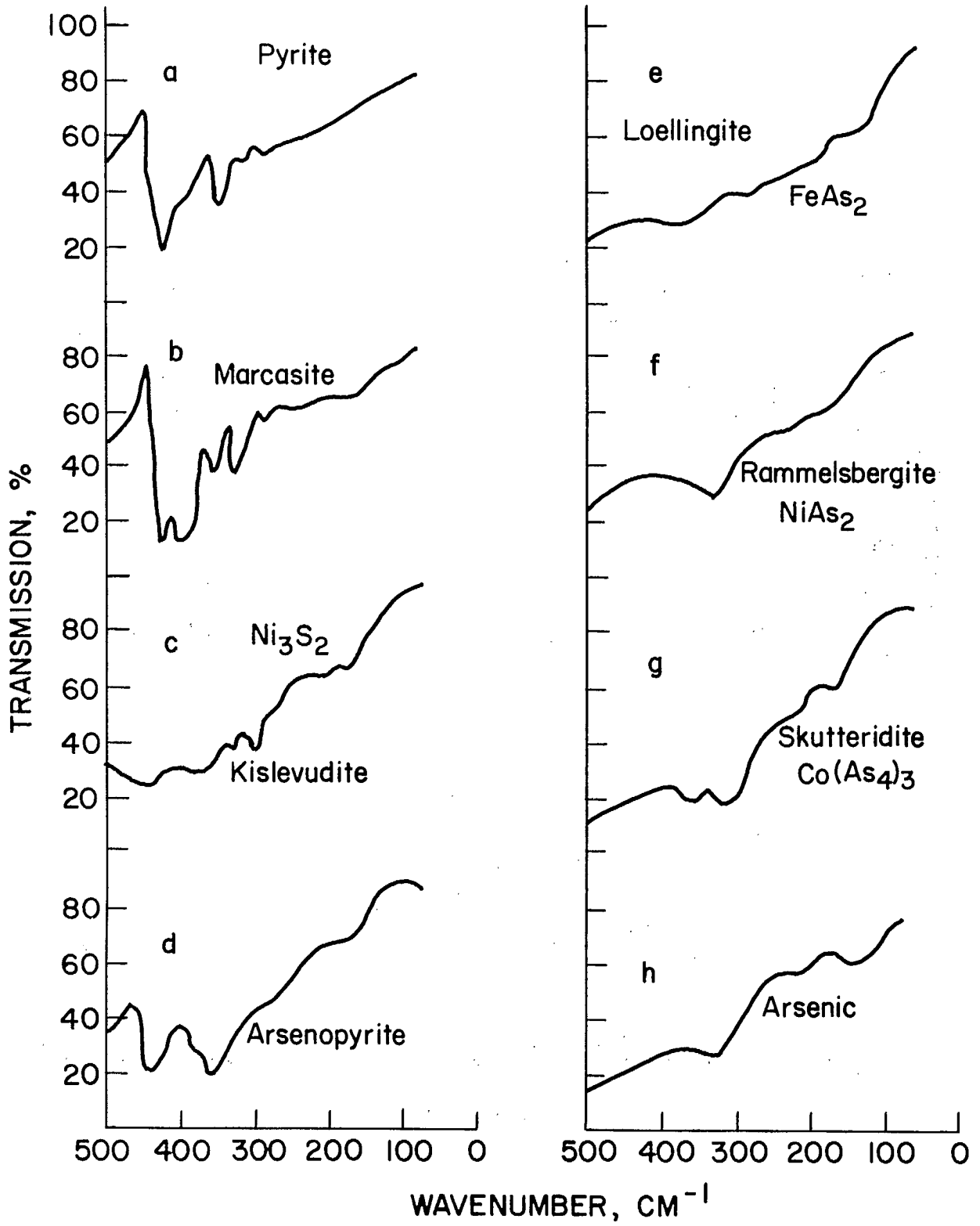


FIGURE 3