

INFRARED SPECTRA-CRYSTAL STRUCTURE CORRELATIONS: II. COMPARISON OF SIMPLE POLYMORPHIC MINERALS

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ABSTRACT

Comparisons have been made between the infrared spectra of eight pairs of minerals related by polymorphic transformations. Polymorphs related by minor structural rearrangements without change in coordination or bond type have very similar spectra. Changes in structural arrangement or bond type are strongly reflected in the spectra. The shifts in the principal metal-oxygen stretching frequencies are directly related to changes in the metal oxygen distances, and to a limited degree, these distances can be calculated from the infrared spectrum. A relation is also derived which gives a straight line fit between the O-H · · · O distances in hydroxylated minerals and the O-H stretching frequency.

INTRODUCTION

Although many infrared spectra of minerals have been measured, relatively little progress has been made in the interpretation of the spectra and in correlating them with the crystal structure of the solid. Most progress to date has been with the silicates and minerals with well-characterized functional groups. For the silicates the method of isomorphous substitution developed by Stubican and Roy (1961 a, b, c) and Tarte (1962, 1963 a, b) allows one to assign particular infrared bands to specific metal-oxygen stretching modes. This method has been particularly successful with the layer lattice silicates. Minerals with well-defined, usually covalently bonded, anion groups such as the hydroxides, carbonates, sulfates and nitrates are also particularly amenable to infrared interpretation. This is because the anion group retains much of the character of the free ion and the infrared spectral analysis can be taken directly from the assignments of the free ion. Also because of the tight covalent bonding, the internal vibrations of the anion group lie at much higher frequencies than the lattice vibrations and are thus easy to distinguish from the latter. Minerals of which the internal vibrations have been studied include brucite and portlandite (see for example, Mitra 1962); many carbonates (Adler and Kerr, 1962, 1963a) and some sulphates (Omori and Kerr 1963). The study of the removal of degeneracy of the internal vibration modes can be made to yield considerable information about the symmetry of the anion group and its environment (Adler and Kerr, 1963b).

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TABLE 1. LIST OF MINERALS EXAMINED

Mineral		Sources or Preparation
As ₂ O ₃	Arsenolite	Fisher certified reagent
	Claudetite	Prepared from arsenolite at 20 k-bars at 350° C. in anvil apparatus
AlOOH	Boehmite	Prepared by hydrothermal hydrolysis of metallic aluminum at 400 bars and 375° C.
	Diaspore	Chester, Mass., Genth Collection No. 256, Pennsylvania State University
FeOOH	Lepidocrocite	Beibert, Hesse Cassel, Germany, Mineral Industries Museum No. 257-2, Pennsylvania State University
	Goethite	Horhausen, Nassau, Genth Collection No. 259, Pennsylvania State University
FeS ₂	Pyrite	Sedimentary pyrite from Big Clifty Formation, Cub Run Kentucky
	Marcasite	Bautsch Mine, Jo Daviss Co., Ill.
MnO ₂	Pyrolusite	Stock
	Ramsdellite	Chisholm, Minn. Described by Klingsberg and Roy (1958)
PbO	Litharge	Prepared from mixed phase reagent grade PbO by hydrothermal reaction at 1000 bars and 350° C.
	Massicot	Stock
Sb ₂ O ₃	Senarmontite	Stock
	Valentinite	Prepared from reagent grade Sb ₂ O ₃ by hydrothermal reaction at 1000 bars and 600° C.
TiO ₂	Rutile	Prepared by heating reagent grade TiO ₂ to 1200° C. in air
	Anatase	Stock

Infrared spectroscopy has also proved a useful tool for obtaining information about the coordination number of ions in simple crystal structures (Dachille and Roy, 1959). This technique has been used mainly for the silica polymorphs coesite and stishovite (Dachille and Roy, 1959, Austin *et al.*, 1960, Sclar *et al.*, 1962, Lyon, 1962) and for the quartz-rutile transformation in germania (Lippincott *et al.*, 1958, Dachille and Roy, 1959, Obukhov-Denisov *et al.*, 1960). Few other comparisons of the infrared spectra of simple solids related by polymorphic transformations occur in the literature. It is of interest, therefore, to examine the spectra of polymorphs of simple oxides to determine whether or not one may obtain useful structural information directly from the infrared spectrum.

It has been shown elsewhere (White and Roy, 1964) that the infrared spectral characteristics of many simple structure-type oxides can be re-

lated directly to the coordination number and interatomic distances. In the present paper these concepts are extended to more complex structures and specifically to pairs of structures related by polymorphic transformations.

EXPERIMENTAL

All spectra were obtained on a Perkin-Elmer Model 21 spectrometer equipped with NaCl and KBr optics. Because of the broad bands obtained in most spectra, peak positions are not likely accurate to more than $\pm 5 \text{ cm}^{-1}$ even for the sharp peaks.

Samples were ground either in an agate mortar or in a "wiggle-bug" vibrating mixer. About one milligram of mineral was used. Both the pressed KBr pellet technique and the Nujol (mineral oil) mull technique were used with about equal success, however, the spectra shown in the figures were all obtained in KBr discs.

Both natural and synthetic minerals were used in preparing the spectra; in each case the sample was carefully checked by *x*-ray diffraction for phase purity. The importance of establishing phase purity in such studies cannot be exaggerated since a few per cent impurity may produce additional peaks.

RELATION OF METAL-OXYGEN FREQUENCIES WITH METAL-OXYGEN DISTANCES

In the first paper of this series (White and Roy, 1964) the infrared spectra of a large number of simple structure-type oxides and fluorides were obtained. From a semi-theoretical analysis, it was found that the frequency factor (defined as $F = \bar{\nu}^2 \mu / Z_1 Z_2$ where $\bar{\nu}$ is the main metal oxygen stretching frequency, μ is the reduced mass of the metal-anion pair, and $Z_1 Z_2$ is the product of the effective charges of the cation and anion) is linearly related to the inverse cube of the cation-anion distance. When the highest frequency stretching modes of the materials examined were plotted against the inverse cube of the cation-anion distance, it was found that the data did follow a distinct linear trend but with considerable scatter. However, the compounds with the same coordination fell into isolated sections of the curve. This relationship is reproduced in Fig. 1. The straight line shown is fitted through the experimental points rather than a theoretical curve. This relationship will be further tested with the data of this paper.

POLYMORPHS RELATED BY MINOR STRUCTURAL REARRANGEMENTS

It is usually a valid assumption that the position of infrared bands in crystals depends mainly on nearest neighbor interactions. If this assump-

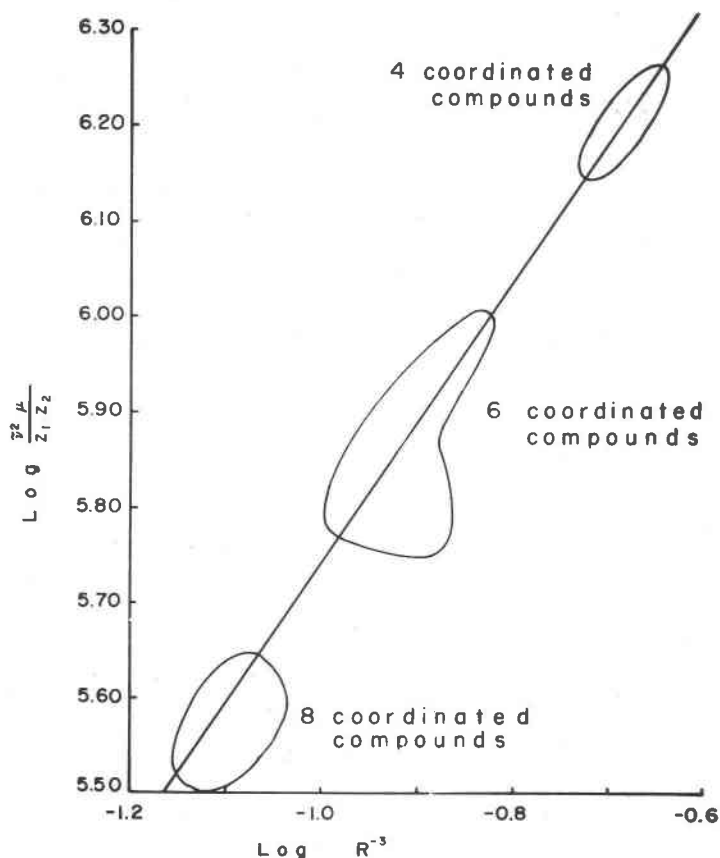


FIG. 1. Relationship between the frequency factor for the highest frequency metal-anion stretching mode and the metal-anion bond length. $\bar{\nu}$ is the metal-anion frequency in wavenumber, μ is the reduced mass, and $Z_1 Z_2$ is the product of the cation and anion charges. The enclosed areas show the scatter of points obtained for compounds with different coordination numbers.

tion is true, the infrared spectra of polymorphs in which the structural changes are minor and do not involve changes in the coordination of nearest neighbors or changes in bond type should be very similar. This assumption was checked by obtaining the spectra of the polymorphs of TiO_2 , MnO_2 and FeS_2 .

Infrared spectra of the TiO_2 polymorphs. The spectra of two of the three TiO_2 polymorphs, rutile and anatase, are given in Fig. 2. According to Von Hippel *et al.* (1962), the strong absorption feature centered at 625 wave-numbers is the E_u asymmetric stretching mode of the TiO_6 octa-

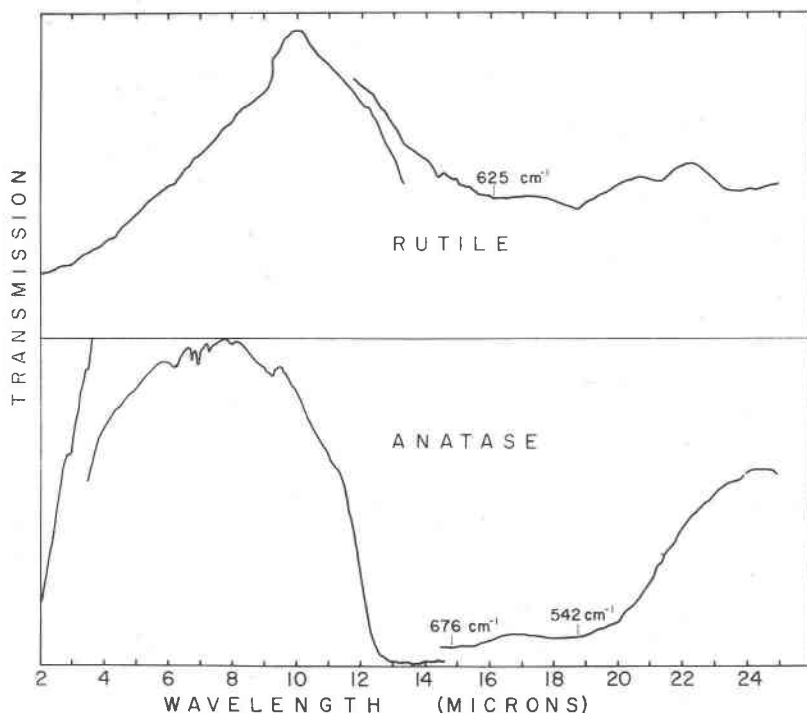


FIG. 2. Infrared spectra for the TiO₂ polymorphs rutile and anatase.

hedra. In the anatase spectrum this band is apparently split into two broad peaks centered at 676 cm^{-1} and 542 cm^{-1} . In the spectrum of brookite (Bayer, 1962) the band becomes even broader and is apparently composed of a number of closely spaced peaks. This would be expected because of the lower symmetry of the brookite structure. However, it is not clear why anatase should have a split band since it has the same point group as rutile (D_{4h}) and has only two metal-oxygen distances.

The general conclusion, however, is immediately clear. The spectra of the three TiO₂ polymorphs are different only in minor ways, such as the degree of splitting. Since this polymorphic relation involves only slight rearrangements of TiO₆ octahedra with no changes in either bond type or primary coordination, there is no gross change in the spectrum.

Infrared spectra of the MnO₂ polymorphs. The infrared spectra of two of the MnO₂ polymorphs, pyrolusite and ramsdellite are given in Fig. 3. The spectra of a number of the less-well-defined MnO₂ phases were also obtained but although the spectra show the same general absorption

features, the bands are less distinct and they are not reproduced here. Pyrolusite with the rutile structure has a single broad band at 606 cm^{-1} . The lower symmetry of the orthorhombic ramsdellite (Bystrom, 1949) is reflected in the infrared spectrum. The main absorption band is now split into four rather ill-defined components. The breadth of the peak has increased but the average frequency remains at approximately the same value as for rutile, suggesting that there has been little change in the metal-oxygen distances.

Infrared spectrum of FeS_2 . The infrared spectra of the two FeS_2 polymorphs pyrite and marcasite are given in Fig. 4. Since sulfur is much heavier than oxygen, the cation-anion stretching frequencies would be expected to appear at much lower energies than in oxide minerals. This is indeed the case. The spectrum of each mineral is devoid of major features except for a band near 400 cm^{-1} . In the pyrite spectrum, the band appears at 418 cm^{-1} with a shoulder on the low energy side at 412 cm^{-1} . In the marcasite spectrum, the main absorption band is at 422 cm^{-1} , with a high frequency shoulder at 480 cm^{-1} . The bands are quite sharp.

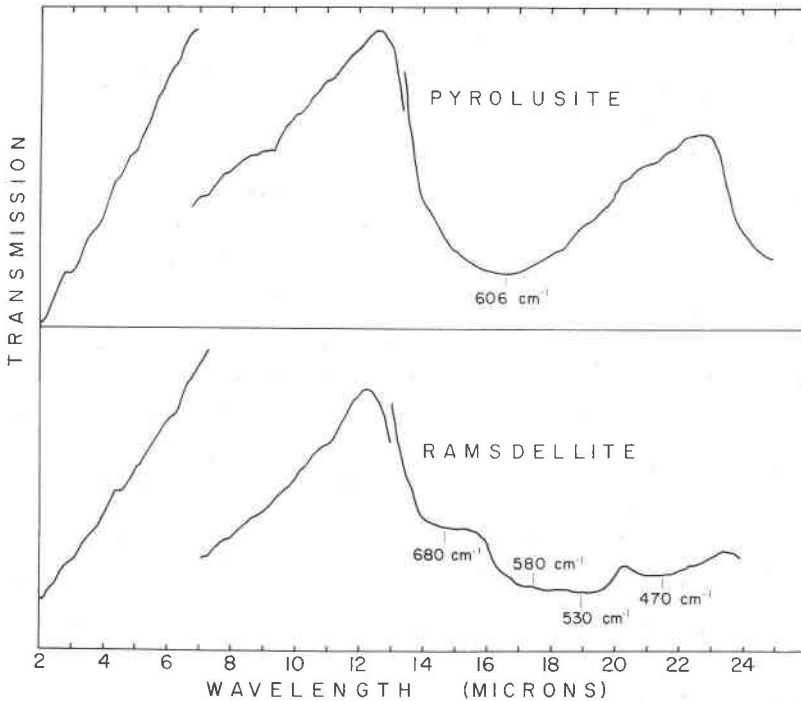


FIG. 3. Infrared spectra for the MnO_2 polymorphs pyrolusite and ramsdellite.

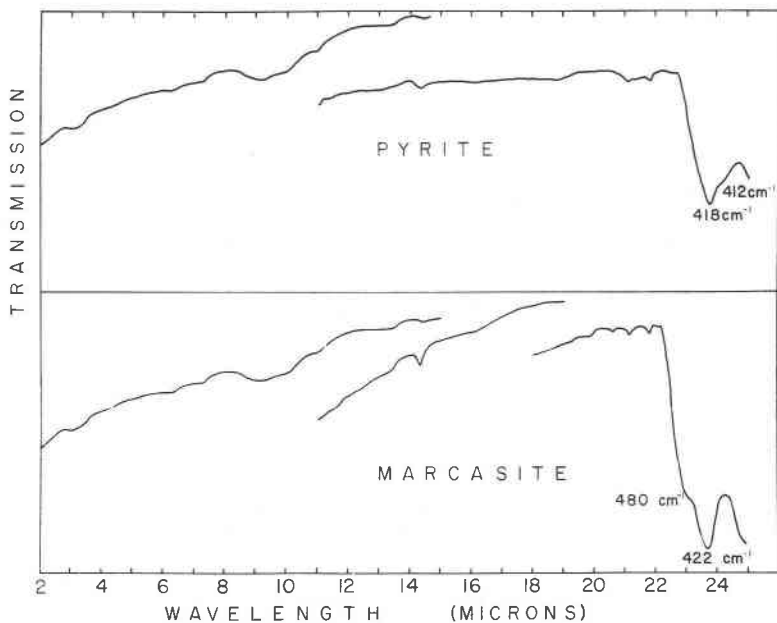


FIG. 4. Infrared spectra for the FeS_2 polymorphs pyrite and marcasite.

There are two possibilities for the assignment of these bands: the Fe-S stretching vibration and the S-S stretching vibration. In oxides, the O-O stretching modes would not be expected to be observable in the available spectral range because of the large oxygen-oxygen distances in most oxides and the small force constants derived from the weak oxygen-oxygen interactions. However, pyrite and marcasite are essentially NaCl structures of Fe and S_2 groups and the S-S distances are 2.14 and 2.21 Å, respectively (Wyckoff, 1951). Bellamy (1959) notes that the S-S stretching frequency in organic sulfides occurs between 400 and 500 cm^{-1} for those compounds that have so far been studied. If one assumes that the curve given in Fig. 1 is approximately valid and calculates the expected Fe-S stretching frequencies on the basis of the known metal-sulfur distances (2.26 in pyrite, 2.24 in marcasite, Wyckoff, 1951) the values 298 $^{-1}$ for pyrite and 302 cm^{-1} for marcasite are obtained. These numbers are in rough agreement with the work of Mitsubishi *et al.* (1958) who found the main stretching frequencies of ZnS and CdS to be 300 cm^{-1} and 270 cm^{-1} respectively although in these two cases the metal oxygen distances are somewhat larger. Thus one would tentatively conclude that the bands observed in the infrared spectra of pyrite and marcasite are due to sulfur-sulfur stretching vibrations and that their position is approximately

what would be expected for strong sulfur-sulfur bonding in the sulfide structure. This does leave unexplained the observation that the sulfur-sulfur distances are just about what would be expected from the sum of the neutral atom radii. One would have expected some shortening of the sulfur-sulfur bond if covalent bonding is present.

POLYMORPHS WITH CONSIDERABLE STRUCTURAL REARRANGEMENT

Infrared spectra of the $AlOOH$ and $FeOOH$ Polymorphs. The infrared spectra of the two pairs of polymorphically related minerals boehmite and lepidocrocite and diaspore and goethite are given in Fig. 5. The spectra are sharp and distinct with narrow bands in the high frequency region and a series of broad bands in the low frequency region. It can be immediately noted that the spectral similarities are between the materials with the same polymorphic form rather than the same chemical composition. Thus boehmite and lepidocrocite have nearly identical spectra and diaspore and goethite have very similar spectra, while there are marked differences between boehmite and diaspore. The frequencies of the spectral bands are listed in Table 2. One striking feature is that the replacement of iron for aluminum in the diaspore structure causes a very marked shift of the bands of longer wavelengths while the same replacement in the boehmite structure has almost no effect.

It is possible to interpret most of the features in these spectra. There are two main structural groups in these polymorphs that contribute to the infrared absorption. These are the internal vibrations of the O-H functional group, and the vibrations of the AlO_6 and FeO_6 structural building blocks. The strong bands which occur between 2800 and 3200 cm^{-1} are certainly the O-H stretching modes. No other functional group vibration occurs in this spectral region. The two sharp peaks at 2105 and 1980 cm^{-1} in the diaspore spectrum are likely the second harmonics of the two strong peaks at 1075 and 960 cm^{-1} . No explanation is offered for the weak bands at 1149 and 1145 wave-numbers in boehmite and lepidocrocite. The strong bands at 1063 and 1013 in boehmite and lepidocrocite are probably due to O-H bending modes. These values are a little higher than the O-H bending mode in quartz 915 cm^{-1} (Kats, 1962), and the range of 850 to 950 cm^{-1} reported by Stubican and Roy (1961), for dioctahedral layer silicates. In sharp contrast, the O-H bending modes in diaspore and goethite are apparently the strong bands at 1075 and 882 cm^{-1} . Here there is a distinct shift to lower wave-numbers when iron is substituted for aluminum, but the band positions are still considerably higher than those reported by Stubican and Roy, (1961) for what they termed O-H $\cdot\cdot$ Al and O-H $\cdot\cdot$ Fe bonds. However, the alternative would be to assign these bands to Al-O and Fe-O stretching modes which seems

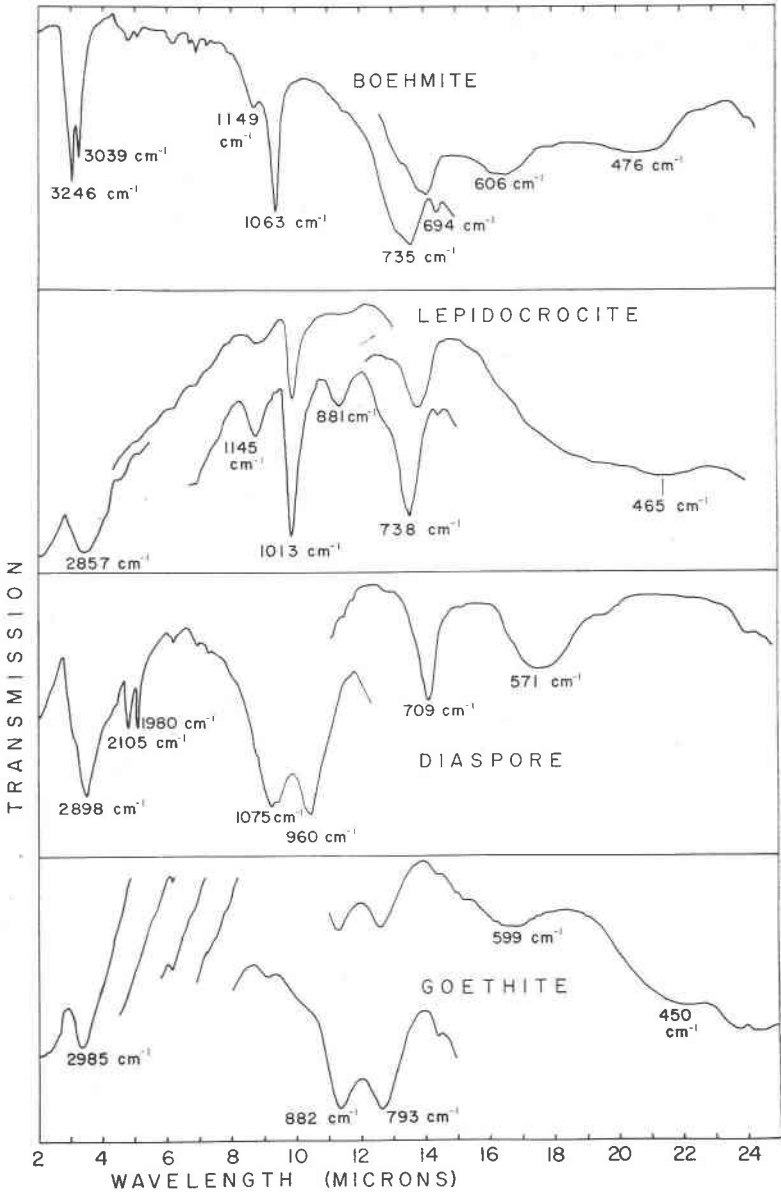


FIG. 5. Infrared spectra for the AlOOH and FeOOH polymorphs boehmite, lepidocrocite, diaspore, and goethite.

TABLE 2. BAND FREQUENCIES OF AlOOH AND FeOOH POLYMORPHS

Boehmite			Lepidocrocite			Interpretation
(cm^{-1})	Intensity	Character	cm^{-1}	Intensity	Character	
3246	S	Sh	2857	S	B	O-H stretch
3039	S	Sh				O-H stretch
1149	W		1145	W		
1063	S		1013	S		O-H bending
			881	W		
735	S		738	S		Me-O stretch
694	W					
606	M	B				(?)
476	M	B	465	M	V.B.	(?)
Diaspore			Goethite			
2898	S		2985	S		O-H stretch
2105	W	Sh				2×1075
1980	W	Sh				2×960
1075	S		882	S		-OH bending
960	S		793	S		Me-O stretch
709	S		599	M	B	Me-O stretch
571	M	B	450	M	B	(?)

S = Strong Sh = Sharp
 M = Medium B = Broad
 W = Weak VB = Very Broad

even less likely. The weak band in lepidocrocite at 881 cm^{-1} is due to about 10% goethite impurity (observable in the x -ray powder pattern of the specimen).

The remainder of the bands in the four compounds arise from lattice vibrations in the aluminum and iron octahedra, since these are the only structural units present. The octahedra are not perfectly symmetrical in either the boehmite or diaspore structures and perhaps the various metal-oxygen distances could be calculated using the relationship in Fig. 1. Accordingly, the value of the frequency factor for each band was calculated and a hypothetical metal-oxygen distance determined from Fig. 1. These values are tabulated and compared with the metal-oxygen distances determined by x -ray diffraction in Table 3. The results do not justify very extensive conclusions. The two highest frequency bands yield metal-oxygen distances which correspond very roughly to the observed distances so that it seems likely that these two bands do indeed refer to Al-O and Fe-O stretching frequencies. The values are close enough

TABLE 3. COMPARISON OF CALCULATED WITH OBSERVED METAL-OXYGEN DISTANCES IN ALUMINUM AND IRON HYDRATE MINERALS

Mineral	Me-O (obs.)	Me-O (calc.)	Mineral	Me-O (obs.)	Me-O (calc.)
Boehmite	1.87 (2)	1.95	Diaspore	1.84 (1)	1.72
	1.88 (2)	2.10		1.86 (2)	1.97
	1.99 (2)	2.35		1.99 (2)	1.97
		2.03 (1)		2.16	
Lepidocrocite	1.94 (2)	1.84	Goethite	1.89 (1)	1.78
	2.05 (2)			2.02 (2)	2.02
	2.13 (2)	2.26		2.05 (2)	2.02
		2.12 (1)		2.30	

Numbers in parenthesis refer to number of Me-O bonds of the given length.

Observed metal-oxygen distances taken from literature: boehmite, Milligan and McAtee (1956); lepidocrocite, Wyckhoff (1951); diaspore and goethite, Hoppe (1941).

to give the right coordination number for the cation but are not close enough to be of much help in calculating interatomic distances. The lowest frequency band yields a metal-oxygen distance so much larger than any observed distances that it seems unlikely that this band is a pure stretching mode.

It is possible to make an additional interpretation of the O-H stretching frequencies. Several workers (Rundle and Parasol, 1952, Lord and Merrifield, 1953, and Glemser and Hartert, 1956) have previously noted a relationship between the O-H stretching frequency and the length of the O-H...O hydrogen bond. Glemser and Hartert (1956) have provided the most complete data to date and have published the frequencies of a series of metal hydroxides. However, their data were plotted in terms of wavelength as a function of bond length yielding a very strongly curving function which is not very useful for comparison with other materials. It has been possible to fit the available data to a function of the form:

$$(\tilde{\nu}_0 - \tilde{\nu}) = BR^n$$

A very good straight line fit is obtained (Fig. 6). There is an expected scatter at small values of the frequency differences since this is a small difference term between fairly large numbers. The quantity $\tilde{\nu}_0$ can be interpreted as the frequency that the O-H band would have if it were completely unperturbed. The exponent n is a repulsion parameter since the observed frequency shift from the free ion value is a measure of the interaction of the hydroxyl group with its surroundings. From the slope of Fig. 6, $n = 17.5$. The proportionality constant B has a value of 94,000 determined from the intercept of Fig. 6. The value of $\tilde{\nu}_0$ is found on a best

fit basis to be 3614 cm^{-1} . The fit of the data of Lord and Merrifield is probably quite good considering that their measurements were made on a series of organic compounds and are being compared with data for metal hydroxides.

This relationship can now be applied to the somewhat unusual boehmite spectrum. Only boehmite has a split O-H stretching mode. The frequencies are unusually high and if the relationship in Fig. 6 is assumed to apply one obtains O-H \cdots O distances of 2.86 and 2.75 Å. The split peak thus implies that there are two well-defined O-H \cdots O distances in boehmite instead of the one found by *x*-ray methods. Secondly, the bond distance is considerably larger than either of the two values reported in the literature. 2.47 has been reported by Reicherz and Yost (1946) and 2.69 by Milligan and McAtee (1956). The infrared data do agree with the

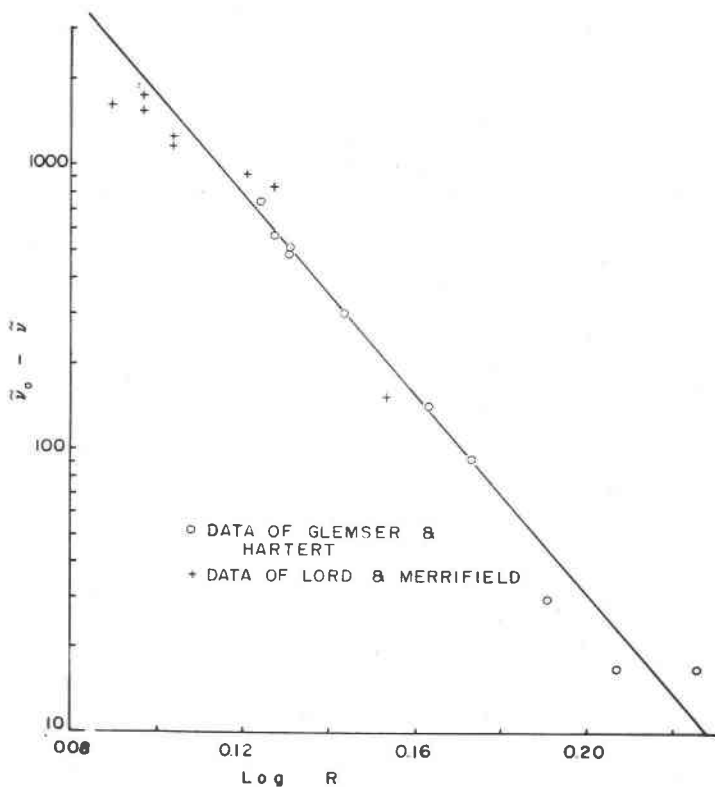


FIG. 6. Relationship between O-H stretching frequency (in wave numbers) and O-H \cdots O bond distances based on the data of Lord and Merrifield (1953) and Glemser and Hartert (1956). The abscissa is plotted as $R(\text{O-H})$, (in angstroms) a hypothetical O-H bond length equal to one half the *x*-ray determined O-O distance.

NMR study of Holm (1958) in that the bond length is greater than the 2.54 critical value above which the hydrogen bond is asymmetric. The infrared evidence would suggest that boehmite is not quite isostructural with lepidocrocite, that there are two O-H...O distances in the structure, and that the layers are sufficiently separated that only a very weak hydrogen bond is formed.

Infrared spectra of the PbO polymorphs. The infrared spectra of the two polymorphs of PbO, litharge and massicot are given in Fig. 7. These two

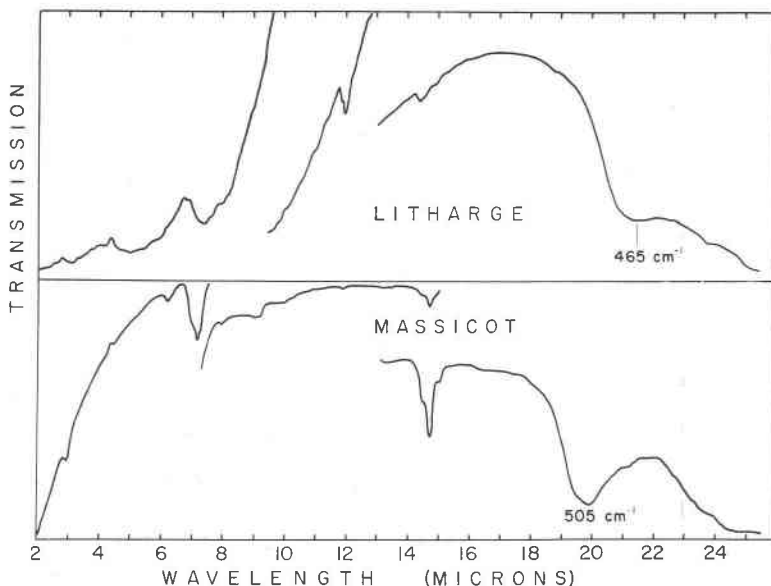


FIG. 7. Infrared spectra for the PbO polymorphs litharge and massicot.

materials form an example of structurally simple polymorphs which are related by a considerable change in structural arrangement. Litharge, the tetragonal form of PbO, consists of a pyramidal structure with four oxygens forming the base and a Pb-ion at the apex. The actual coordination is 8, but the bonds are such that four of the Pb-O bonds are much stronger than the others. Massicot, the orthorhombic form of the Pb-O consists of chains which form a layer structure. There is strong bonding along the chains but weak bonding between the layers (Leciejewicz, 1960, 1961) (Kay, 1961).

The spectra show only one strong absorption band for each mineral at 465 cm⁻¹ for litharge and 505 cm⁻¹ for massicot. These bands are almost

certainly caused by lead-oxygen stretching vibrations. The weak bands in the higher frequency part of the spectrum are due to traces of lead carbonates which appear as an impurity during the grinding process in preparing the specimens.

If one assumes that all eight Pb-O bonds are of equal strength (an assumption inherent in the derivation of the frequency factor-bond length relationship of Fig. 1) one obtains bond lengths which are much smaller than the observed lengths. However, if account is taken of the known structure, it can be seen that only half of the lead-oxygen bonds are strong bonds. These are the ones that form the sides of the PbO_4 pyramid. This should have the effect of doubling the effective charge per bond. If the Z_1Z_2 term is doubled in the frequency factor and the metal oxygen distance calculated on this basis, very good agreement is obtained. The data are as follows:

	Pb-O (calculated)	Pb-O assuming double bond strength	Pb-O observed
Litharge	2.00 Å	2.32 Å	2.30 Å
Massicot	1.83 Å	2.22 Å	2.21 Å

Thus the infrared data can be rationalized with the known structure but does not *a priori* provide a way of determining what the structure is.

POLYMORPHS RELATED BY A CHANGE IN BOND TYPE

Since the infrared spectrum is determined not only by the site symmetry of the vibrating units but also by the force constants of the bonds, polymorphs which retain their primary coordination but undergo a fairly drastic change in bond type would be expected to have distinctly different infrared spectra. This hypothesis is examined in the following section.

Infrared spectra of the As_2O_3 and Sb_2O_3 polymorphs. The infrared spectra of the two polymorphic pairs of As_2O_3 and Sb_2O_3 , arsenolite and senarmontite and claudetite and valentinite are given in Fig. 8. Arsenolite and senarmontite are the cubic forms of As_2O_3 and Sb_2O_3 , respectively. Claudetite and valentinite are closely related structurally although claudetite is monoclinic and valentinite is orthorhombic. The cubic polymorphs are composed of a molecular lattice of As_4O_6 and Sb_4O_6 molecules. The other polymorphs have a chain structure with strong bonding along the chains and weak bonding across the layers of chains.

The most dominant feature of the arsenolite and senarmontite spectra are the metal-oxygen stretching modes at 795 cm^{-1} and 740 cm^{-1} respectively. Arsenolite has an additional strong band at 477 cm^{-1} . The equivalent peak in senarmontite appears to be beyond the range of the

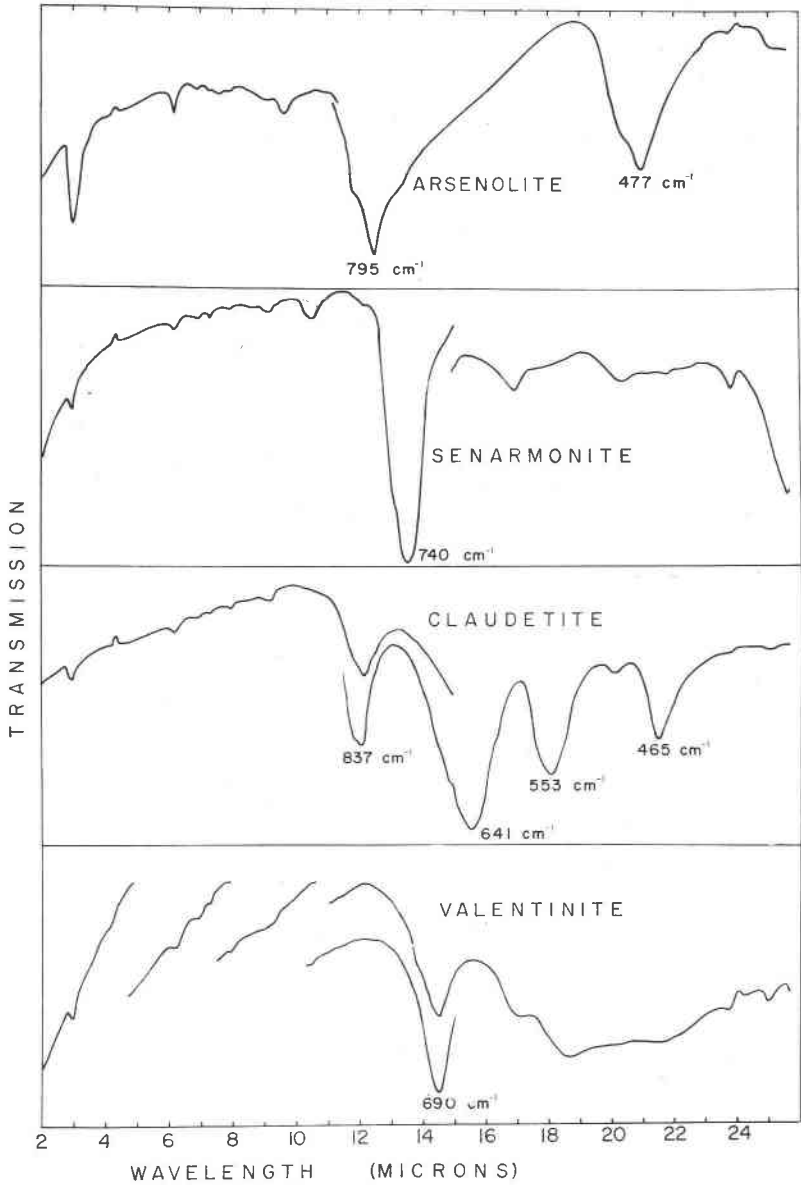


FIG. 8. Infrared spectra for the As_2O_3 and Sb_2O_3 polymorphs arsenolite, senarmonite, claudetite, and valentinite.

available instrument. The spectra of the two compounds with the same structure appear to be quite similar. The shift of the antimony-oxygen band to lower frequencies because of the heavier antimony ion is actually rather slight because although antimony is much heavier than arsenic, the reduced masses are not very different. (As-O, 13.2; Sb-O, 14.2) It is for this reason that the mass shift dominates the spectra compounds of light elements but has very little effect on the spectra of heavy metal oxides.

The spectrum of claudetite is characterized by four strong bands at 837, 641, 553 and 465 cm^{-1} . These have symmetric band contours and are well-resolved. They are much more reminiscent of the spectra of organic compounds (well-defined molecules) than of ionic compounds. The spectrum of valentinite, in contrast, except for the single sharp band at 690 cm^{-1} is more diffuse, although an equivalent to each of the claudetite bands can be found. This probably reflects the increased ionic character of Sb_2O_3 over As_2O_3 and thus in this case the spectra of two similar structure types are not entirely similar.

A calculation of the metal-oxygen distances using the methods previously outlined gives results in moderately good agreement with those reported by x-ray methods. These results are given below:

	Me-O (calc.)	Me-O (obs)
Arsenolite	1.75 Å	1.80 Å
Claudetite	1.72 Å	1.80 Å
Senarmontite	1.78 Å	1.82 Å
Valentinite	1.83 Å	1.82 Å

The values calculated for the frequency factor place arsenolite and senarmontite squarely in the field of the 4-coordinated compounds in Figure 1. The structures of these compounds (Becker *et al.*, 1962) are built up of arrangements of tetrahedra.

CONCLUSIONS

The results of this examination of the infrared spectra of minerals related by polymorphic transition can be summarized as follows:

- (a) The spectra of compounds with the same structure type are nearly identical except for the expected shifts due to different atomic masses and different metal oxygen distances. Spectra of polymorphs of the same compound are therefore not identical.
- (b) If the polymorphic transformation involves only minor structural rearrangements and no change in primary coordination, the spectra will be very similar.
- (c) Polymorphic transformations which involve either changes in

primary coordination or major changes in bond type are reflected by gross changes in the infrared spectrum. Thus infrared spectroscopy is an extremely valuable tool for obtaining this basic information about a new polymorph without waiting for a detailed structure analysis.

- (d) A relation has been derived which relates hydrogen bond lengths to the position of the O-H stretching frequency in hydrated minerals. This relationship needs much additional checking but appears to be *potentially* capable of providing accurate O-H...O distances.
- (e) The relationship between metal-oxygen stretching frequency and metal-oxygen distance has been tested on a number of new cases. While the relationship appears capable of providing first approximations to interatomic distances, it is not yet trustworthy and additional work is needed.

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