The nature of hydrogen bonds and water in legrandite by IR spectroscopy

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Abstract

Infrared (IR) spectroscopy and differential thermal analysis (DTA) have been used to study the nature and role of the hydrogen bonds in legrandite, which has the proposed formula $(ZnOH)_2(HOAsO_3)$. The IR spectra of legrandite and the Zn arsenates, adamine and austinite, combined with DTA data for legrandite seem to indicate that there are no water molecules in the structure of legrandite and that an oxygen atom of the arsenate anion is protonated, forming $(HOAsO_3)^{2-}$ groups in the structure of the mineral. The presence of acid anions seems to be characteristic of arsenates that contain water in their structures. A correlation table for frequencies of IR-absorption bands for legrandite, adamine, and austinite is given.

Introduction

Legrandite is a rare arsenate mineral, with a formula commonly given as $Zn_2(OH)(AsO_4)H_2O$. Its structure, as established by Pusharovskii (Pusharovskii, Pobedimskaya, and Belov, 1971, 1972), consists of walls of Zn-polyhedra of four different kinds. The coordination polyhedra of $Zn_{1,2,3}$ atoms are pseudo-trigonal bipyramids while those for Zn_4 atoms are slightly deformed octahedra. Adamine has a similar structure with Zn-octahedra and pseudotrigonal bipyramids (Kokkoros, 1937).

Two types of As tetrahedra link the Zn-polyhedral walls. The close arrangement of water molecules opens the possibility of H-bond formation between neighboring layers parallel to the (100) cleavage. The chemical composition of legrandite suggests two possible structural formulas—$Zn_2(OH)(AsO_4) \cdot H_2O$ and $(ZnOH)_2(HOAsO_3)$—which are not distinguished by X-ray data.

Raman spectra of arsenic acid in the 3000 cm^{-1} to 3670 cm^{-1} region show that the structure $OAs(OH)_3$ predominates over the acid form H_3AsO_4 (Gupta and Guna, 1948). IR spectra of phosphates and arsenates containing PO_4^{3-} and AsO_4^{3-} groups differ from those of compounds containing $HOPO_3^{2-}$ and $HOAsO_3^{2-}$. This is due to changes in the electron clouds, to changes in the symmetry of the anions, and to the presence in the latter anions of OH^- groups capable of forming H bonds. When the structures contain OH^- groups, the symmetry of the anions is lowered

from T_d to C_{2v}, as can be seen from the splitting of the ν_3 and ν_4 bands and the appearance of a ν_1 band (sometimes a ν_2 band also appears). The OH^- groups also cause the appearance of stretching frequencies in the 2400 cm^{-1} to 3300 cm^{-1} region and of deformation frequencies in the 300 cm^{-1} to 1300 cm^{-1} region (Blinc and Hadži, 1958). The spectra of groups having C_{2v} symmetry show the ν_3 and ν_4 frequencies as a wide band with three components. The bands $\nu_1(AsO_4)$ and $\nu_2(AsO_4)$ appear in the 720 cm^{-1} to 730 cm^{-1} region and at 370 cm^{-1} respectively. The vibrations of As–OH and P–OH bonds give rise to four absorption bands in the 1200 cm^{-1} to 2900 cm^{-1} region. The high-frequency bands are due to stretching vibrations of the OH^- groups and the low frequency bands are due to deformation vibrations of these groups (Blinc and Hadži, 1958).

Ryskin and Stavitskaya (1959) and Stekhanov and Klotchikhin (1960) interpret the spectra assuming the presence of water molecules. However, Tarte and Paques-Ledent (1968) consider that the amphoterical nature of water allows the water molecules to act as proton and electron donors at the same time, thus allowing the molecules to form H-bonds and to coordinate with metals that have electron acceptor properties. Either interpretation may be correct, depending on the structure of the hydrated mineral.

IR data on phosphates and arsenates with acid anions (Blinc and Hadži, 1958, 1960; Hadži, 1965) show that four absorption bands in the 1200 cm^{-1} to 3100 cm^{-1} region are characteristic of acid anions.

These bands are due to vibrations of the OH . . . A bond (where A = As,P) and have been labeled as A, B, C, and D bands. Analogous bands have been reported for acid germanates and acid silicates (Ryskin, Stavitskaya, and Toropov, 1960; Ryskin and Stavitskaya, 1960; Stavitskaya and Ryskin, 1969). These four bands, which indicate the presence of acid anions in the crystal structure, also occur in the IR spectra of pharmacolite (Portilla, Zaitsev, and Yakhontova, 1971) and picropharmacolite (Sumin de Portilla, 1974).

Experimental method

Preliminary X-ray studies of semi-transparent honey-yellow crystals—which occur in fan-like form on an ochre base on monheimite-limonite at Ojuela in Mapimi, Mexico—agreed with results of previous studies of legrandite by Drugman and Hey (1932), Desautels and Clarke (1964), and Finney (1964), Finney's samples being from this same deposit.

Samples for IR spectroscopy were prepared as pressed tablets of KBr or as emulsions with nujol. The spectra, recorded on a Zeiss UR-20 infrared spectrophotometer (GDR), cover the IR region from 400 cm^{-1} to 3800 cm^{-1} (Fig. 1). Deuteration and dehydration of the samples were carried out in an autoclave at temperatures up to 150°C and 500°C respectively. The autoclave was completely filled with D$_2$O for deuteration.

Results

In the region of the $\nu_3(T_2)$ stretching vibration of the arsenate anion, the IR spectra of legrandite show a poorly resolved wide band between 785 cm^{-1} and 810 cm^{-1} with maxima at 790 cm^{-1}, 825 cm^{-1}, and 880 cm^{-1}. The $\nu_1(A_1)$ band has the shape of a shoulder at 730 cm^{-1}. Nujol also shows a δ band at this frequency but it has a considerably lower intensity. The deformation vibrations region $\nu_4(T_2)$ shows three bands: 400 cm^{-1}, 455 cm^{-1}, and 485 cm^{-1}. The splitting of the $\nu_3(T_2)$ and $\nu_4(T_2)$ band of the arsenate anion indicate that its site symmetry is C_{2v}(Mayantz, 1960). This agrees with the X-ray analysis of Pusharovskii (Pusharovskii, Pobedimskaya and Belov, 1971, 1972).

The intense band at 520 cm^{-1} may be due to vibrations of the Zn–O bond. Analogous bands appear in the IR spectra of adamine (515 cm^{-1} and 535 cm^{-1}) and austinite (525 cm^{-1}) (Sumin de Portilla, 1974b).

The 930 cm^{-1} band as well as the 1030 cm^{-1}, 1150 cm^{-1}, 2050 cm^{-1}, 2450 cm^{-1}, 2730 cm^{-1}, 3120 cm^{-1}, 3300 cm^{-1}, and 3380 cm^{-1} absorption bands are due to vibrations of the OH$^-$ groups. This is proved by the shift of these bands and their changes in intensity after deuteration of the sample.

To make a correlation table for the absorption bands in the spectra of legrandite, adamine, and austinite (Table 1), we compared the data for phar-
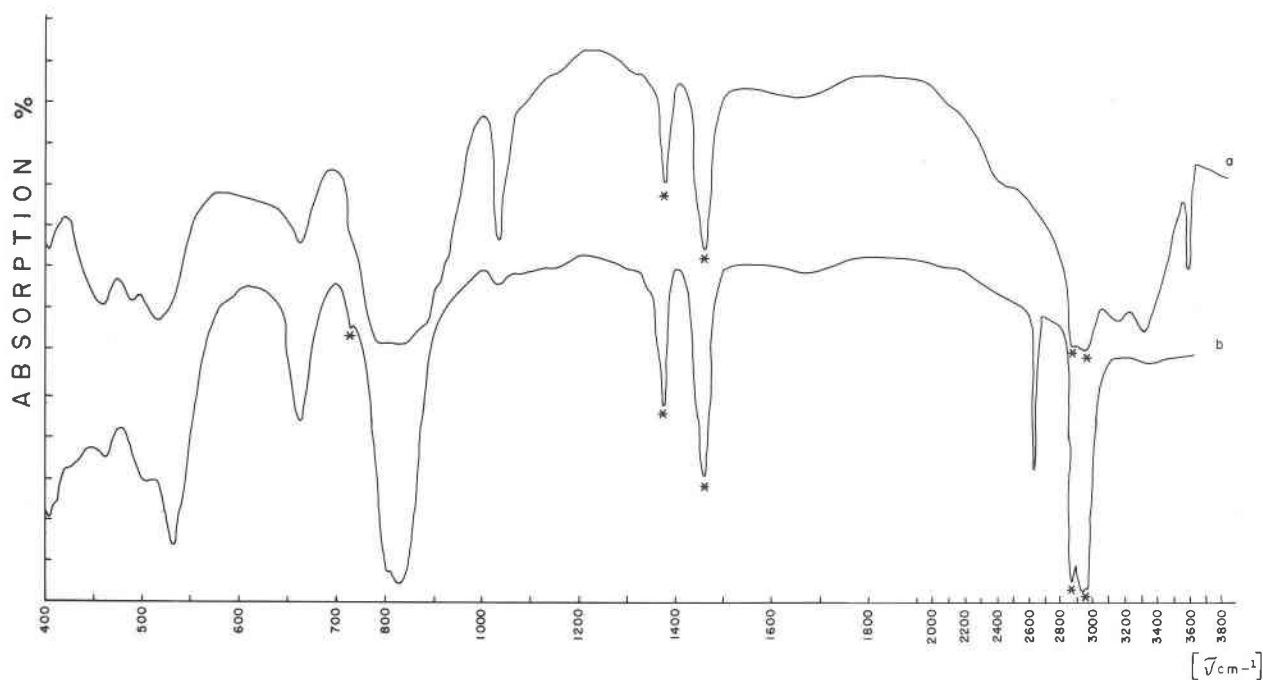

FIG. 1. IR-spectra. a) legrandite from Ojuela (Mapimi); b) deuterated sample; * band of nujol.

TABLE. Correlation of Frequencies of IR Absorption Bands for Legrandite, Adamine, and Austinite

Mineral	$(AsO_4)^{3-}$			Zn-O	Zn – OH		$\nu(As - OH)$				Overtone	Other
	$\nu_1(A_1)$	$\nu_3(T_2)$	$\nu_4(T_2)$		$\nu OH(OD)$	$\delta OH(OD)$	A	B	C	D	2ν (AsO_4)	Bands
Legrandite	730	790	400	520	3580	930	2730	2450	2050	1150	1650	670
$(ZnOH)_2(HOAsO_3)$		825	455		(2625)	(665)						
					3300	1030						
		880	485		(3120)	(800)						
Adamine	740	800	400	515	3580	900	2900				1650	
$Zn_2(OH)(AsO_4)$		820	485	535								
		860										
Austinite	750	800	410	525	3550	915		2450	1940		1650	
$CaZn(OH)(AsO_4)$		845	430	570	3300	980						
			465			1010						

( ) – *deuterated bands*

macolite—which has an $(HOAsO_3)^{2-}$ anion and OH^- groups coordinated with metals in its structure (Portilla *et al*, 1971—with the data for adamine and austinite, which lack the $(OHAsO_3)^{2-}$ anion (Sumin de Portilla, 1974b), having only OH groups coordinated with metals. The 1150 cm^{-1}, 2050 cm^{-1}, 2450 cm^{-1}, and 2730 cm^{-1} bands are probably related to H bonds in As–OH . . .O. We consider that the wide and very intense 3120 cm^{-1} band is related to stretching vibrations of hydroxyls with H bonds. The very weak 1650 cm^{-1} band does not change after deuteration or dehydration of the sample and is probably an overtone of the $\nu_3(T_2)$ band.

The 930 cm^{-1} and 1030 cm^{-1} bands lie in the region of metal–OH deformation vibrations and may be related to Zn–OH bonds. Two intense narrow bands at 3300 cm^{-1} and 3580 cm^{-1} lie in the region of hydroxyl stretching vibrations and are probably related to the presence of these groups. If so, the existence of *two* such bands indicates that different kinds of hydroxyls coordinate with metal atoms in the structure of legrandite. The 3580 cm^{-1} band is characteristic of hydroxyls with very weak H bonds. The lower frequency 3300 cm^{-1} band may indicate OH^- groups with somewhat stronger H bonds.

It is difficult to correlate the 670 cm^{-1} band because the $\nu_4(T_2)$ band of the arsenate anion covers the 400 to 490 cm^{-1} region and also because the $\delta_{oh}=930$ cm^{-1} band shifts to 670 cm^{-1} after deuteration of the sample. The correlation of the 670 cm^{-1} band with δ (OH) vibrations is excluded since the IR spectra of dehydrated legrandite do not show any significant change of this band. Ryskin *et al.* (1960) and Ryskin

and Stavitskaya (1960) reported that the IR spectra of acid phosphates and silicates also show a similar sharp and intense band (at 625 cm^{-1} in the spectra of $K_2HPO_4 \cdot 3H_2O$). No definite interpretation was given for this band.

Discussion

The two hydroxyl bands at 3300 cm^{-1} and 3580 cm^{-1} in the spectra of legrandite may indicate two different kinds of hydroxyl groups in the structure of this mineral. The main difference between these hydroxyls is the strength of the H bonds that they form. The 3580 cm^{-1} band is due to stretching vibrations of a virtually free hydroxyl group. Both kinds of hydroxyls are probably coordinated with Zn atoms that lie in different positions in the crystal structure. The three wide bands at 2050 cm^{-1}, 2450 cm^{-1}, and 2730 cm^{-1} are probably related to stretching vibrations of OH^- groups coordinated with As atoms and linked by strong H bonds to oxygen atoms. The IR spectra of acid salts of different metals show analogous bands (Ryskin *et al*, 1960; Ryskin and Stavitskaya, 1960).

The two sharp intense bands, $\delta = 930$ cm^{-1} and $\delta = 1030$ cm^{-1}, are likely due to ZnO–H vibrations, and the 1150 cm^{-1} band to AsO–H bond vibrations. When deformation vibrations of OH^- groups occur, the hydrogen atoms vibrate in a plane perpendicular to the direction of the O–H bond. The frequencies of the deformation vibrations of the OH^- groups depend basically on the degree of covalence of the X–O bond (where X = metal). In crystals where the X–O bond has ionic character, as occurs if X is an alkali metal, the
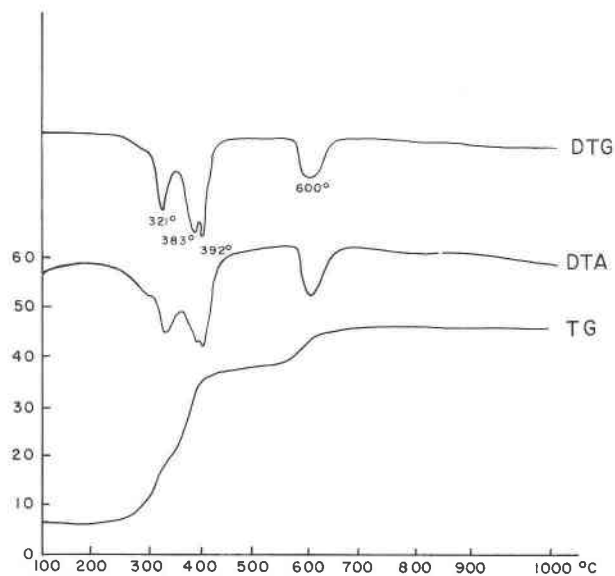
FIG. 2. Differential thermal analysis and dehydration curve of legrandite. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal (DTA) curves of legrandite. Rate of heating is 5°C/min.

frequency of these deformation vibrations lies lower than 400 cm⁻¹. In crystals of the $Zn(OH)_2$ or $Al(OH)_3$ type that have Zn–O and Al–O bonds of partially covalent nature, the deformation vibration bands lie at 1090 cm⁻¹ and 915 cm⁻¹, and 960 cm⁻¹ and 1020 cm⁻¹ respectively (Kolesova and Ryskin, 1959). The frequencies of deformation vibrations are also affected by the strength of H bonds, whose presence shifts the bands to higher frequencies. The two bands at 930 cm⁻¹ and 1030 cm⁻¹ in the legrandite IR spectra indicate that there are differences in the degree of covalence of the Zn–OH bonds, probably due to Zn atoms in two different positions, coordinated with hydroxyl groups. This is in agreement with crystallographic data (Pusharovskii et al, 1971, 1972).

The high frequency of the OH⁻ group deformation vibrations (1150 cm⁻¹) indicates that there is a high degree of covalence of the bonds between arsenic atoms and hydoxyl groups. Correlation of the 1150 cm⁻¹ band with Zn–OH bond vibrations is not possible because the strength of this bond is not sufficient to raise the frequency to this value. In the IR spectra of compounds with X–OH bonds (where
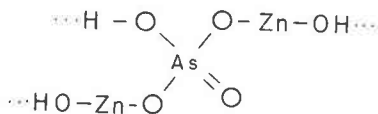

FIG. 3. Schematic structural formula for legrandite.

X = Zn, Cu, Al, and other metals), the bands representing X–OH deformation vibrations lie lower than 1050 cm⁻¹ (Glemser, 1961). Bands analogous to the 1150 cm⁻¹ band in legrandite have been observed in the natural acid arsenates, pharmacolite (Portilla et al, 1971) and picropharmacolite (Sumin de Portilla, 1974b), where As–OH bonds have a significant degree of covalence. Furthermore the correlation with As–OH bonds in these arsenates is not in question, because the Ca–OH bond is ionic and thus the band due to deformation vibrations lies lower than 400 cm⁻¹. The frequencies of the deformation vibration bands of the As–OH bond in different arsenates indicate the comparative degree of acidity of these compounds (in relation to a standard proton acceptor). The acidity of the arsenate anion decreases from legrandite to picropharmacolite; this is accompanied by a shift of the As–OH deformation vibration band from 1150 cm⁻¹ in legrandite to 1210 cm⁻¹ in pharmacolite and 1290 cm⁻¹ in picropharmacolite.

In the IR spectra of legrandite, there is a band in the region of deformation vibrations of water at 1650 cm⁻¹ which is not affected by deuteration. Thus the band is not due to deformation vibrations of water molecules. IR spectra of anhydrous arsenates like olivenite, adamine, austinite, mimetesite, and durangite also show this band (Sumin de Portilla, 1974b). In arsenates known to have water molecules in their structures, such as pharmacolite (Portilla et al, 1971), picropharmacolite (Sumin de Portilla, 1974a), euchroite, and liroconite (Sumin de Portilla, unpublished), the band due to deformation vibrations of water is more intense and always shifts after deuteration. Thus we conclude that the crystal structure of legrandite contains no water molecules. It is likely that any water molecule entering the legrandite structure is so deformed when one of its O–H bonds is stretched by the formation of a strong H bond with the arsenate anion that the hydrogen atom becomes strongly bonded with the arsenate anion and forms an acidic group $(HOAsO_3)^{2-}$. This leaves a virtually free hydroxyl group which then coordinates with a Zn atom (Fig. 3). The DTA curve for legrandite (Fig. 2) seems to support this hypothesis. It shows three maxima at $t_1 = 321°C$, $t_2 = 383–392°C$, and $t_3 = 600°C$. The first two maxima, taking into consideration our IR data, are probably due to release of two weakly bound hydroxyl groups in the vicinity of two non-equivalent Zn atoms, one in the bipyramid and the other in the deformed tetrahedron. The t_3 peak is probably due to release of the hydroxyl in the arsenate anion. If we consider the

formula $(ZnOH)_2(HOAsO_3)$ to be correct, then three distinct hydroxyls may be present (Fig. 3). These hydroxyls differ in the strength of the H bonds that they form. The strongly bound hydroxyl is the OH in As–OH and thus it is correlated with peak $t_3 = 600°C$ in the DTA curve.

The two OH^- groups coordinated to Zn atoms are capable of forming H bonds having slightly different energies, because the positions and surroundings of the two Zn atoms are not the same. The energy of the H bonds also depends on the nature of the acceptor for the hydrogen. One of the main differences could be the formation of inner H-bond bridges within the same arsenate anion or the formation of H bonds between adjacent arsenate anions.

Conclusions

The A, B, C, and D bands as well as the presence of the $\nu_1(A_1)$ band in the IR spectra of legrandite indicate the presence of an acid anion $(HOAsO_3)^{2-}$ in the structure of this mineral. The absence of H_2O bands in the IR spectra, demonstrated by deuteration of the samples, indicates that there are no water molecules in the crystal structure. The 3580 cm^{-1} and 3300 cm^{-1} bands result from hydroxyl groups coordinated to Zn atoms in different positions in the structure. The DTA confirms the presence of different types of hydroxyls and the absence of water molecules in the structure of legrandite.

The ν_3 and ν_4 bands in the spectra indicate that the site symmetry of the arsenate ion is C_{2v}. Comparison of the IR spectra of legrandite, adamine, and austinite permits correlation of frequencies in the spectra of these minerals with bond vibrations in their structures. The presence of acid anions and absence of water seems to be characteristic of arsenates that are reported to contain only one water molecule per formula unit in their structure.

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