Raman Spectra of Cinnabar (HgS), Realgar (As_4S_4) and Orpiment (As_2S_3)

W. SCHEUERMANN and G. J. RITTER

National Physical Research Laboratory, P.O. Box 395, Pretoria, South Africa

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The Raman shifts in naturally occurring cinnabar (HgS), realgar (As_4S_4) and orpiment (As_2S_3) have been measured at room temperature using a photoelectrically recording Raman spectrometer with He-Ne laser excitation at 6328 Å. By using the infra-red spectra of these compounds it was possible to make a partial assignment of these shifts. The number and symmetries of the Raman active phonons were calculated for the covalently bonded "sub-units". Most of the theoretically predicted vibrations were observed. The theory that realgar and orpiment are built from the same structural units could be supported.

The phonon spectra of the crystals cinnabar (HgS), realgar (As_4S_4) and orpiment (As_2S_3) have not been reported before. Only the infra-red spectrum of HgS was known [1]. Excitation with a mercury arc would most probably not yield any Raman result since cinnaber is dark-red opaque, realgar red transparent and orpiment yellow transparent. With the He-Ne laser radiation at 6328 Å as exciting line, however, high quality Raman spectra could be obtained.

These crystals are interesting because two types of bonds are active, namely covalently bonded spirals (in the case of HgS), molecules (in the case of As_4S_4), and layers (in As_2S_3), which are then held together by Van der Waals forces. These different bonds have to be taken into consideration when one attempts to assign the observed Raman spectra.

Experimental

The main components of the photoelectrically recording Raman spectrometer used in this investigation were as follows: laboratory-built He-Ne laser ($\lambda =$ 6328 Å, $P = 70$ mW); polarisation rotator; plasma line rejection filter; scattered light collecting lens ($f = 16$ mm, $A = 1 : 1.8$); secondary interference filter; imaging lens ($f = 140$ mm) producing an approximately 8.5-fold magnified picture of the scattering area on the entrance slit; Czerny Turner 1 meter scanning spectrometer (with grating 590 grooves/mm blazed for 5500 Å in first order); cooled photomultiplier (EMI 9558 A) of which the effective cathode area is decreased by means of a magnetic lens [2]. A dark current of only 0.004 nA at an overall sensitivity of 200 A/lumen is achieved in this manner. The light chopper is operated synchronously from the internal reference mode of the Princeton Applied Research JB5 lock-in amplifier. This ensures an adjustment free performance of the lock-in system. For further details of Raman spectrometers see for example [3] and references cited therein.

The infra-red data were obtained with a Perkin Elmer Model 621 using nujol mulls in the case of HgS and CsI mulls in the case of As_4S_4 and As_2S_3.

Results and Discussion

The results obtained are summarized in Table 1: the second column gives the I.R. data used in assigning the Raman bands given in the third column.

1. Cinnabar (HgS)

Mercury sulphide occurs in two modifications, namely metacinnabarite, which has the zincblende structure, and the more common phase cinnabar [4]. The latter has a hexagonal structure and can be considered as a distortion of the NaCl structure. The trimolecular hexagonal unit cell has D_3 symmetry. This is a structure composed of HgS chains running along the c axis. In the chain the interatomic distance Hg – S = 2.36 Å and between the chains it is ca. 3.2 Å. Within the chain each atom is strongly bound, mainly by homopolar forces, to its two immediate neighbours, but between the chains the forces are much weaker and the interatomic distances are correspondingly considerably greater than within the chain.

[1] F. A. MILLER, G. L. CARLSON, F. F. BENTLEY, and W. H. JONES, Spectrochim. Acta **16**, 135 [1960].
[2] G. FARKAS and P. VARGA, Magyar Pudomanyos Acad. Kozponti Fiz. Kutato Intezetnek Kozlemenyei **7**, 248 [1959].
[3] J. BRANDMÜLLER, K. BURCHARDI, H. HACKER, and H. W. SCHRÖTTER, Z. Angew. Phys. **22**, 177 [1967] and references cited therein.
[4] K. L. AURIVILLIUS, Acta Chem. Scand. **4**, 1413 [1950].

Sample	Infra-red ± 5 cm^{-1}	Raman ± 3 cm^{-1}	Assignment
HgS		254	A_1
	265		
	285	281.5	E
	348 (349[1])	344	E
	375		
	400		
As_4S_4		116	
		148	
		160 w	
		177	
		184.5	
		194.3	
	220	221	
		234	
		246 w	
		263 w	
		276 w	
		290 w	
		304 w	
		322 w	
	340	341	
	355	353	A_1
	370	368 w	
		403 w	(221+184.5)
As_2S_3		161	
		206	
		289.2	
		303.2	
	305	305.6	
	315		
		324 w	2×161
		350.9	
	355	353.5	A′
		363.1	
	370		
		382.1	
	384		

Table 1. Wave numbers [cm^{-1}] of the infra-red and Raman active modes in cinnabar (HgS), realgar (As_4S_4) and orpiment (As_2S_3).

Our samples were thin opaque plates of dark red colour, cut from a chunk of naturally occurring polycrystalline cinnabar. The laser beam was focussed onto the samples at an angle of approximately 50° and the scattered light was observed perpendicular to the incident beam. Fig. 1 shows the Raman spectrum of cinabar (HgS). The spectrum consists simply of three bands. The weak one at 281.5 cm^{-1} comes out clearly when the spectrum is taken with five-fold increased sensitivity. A high resolution test taken with 1 cm^{-1} spectral slit width did not reveal any fine structure with respect to the spectrum taken with a spectral slit width of 8 cm^{-1}.

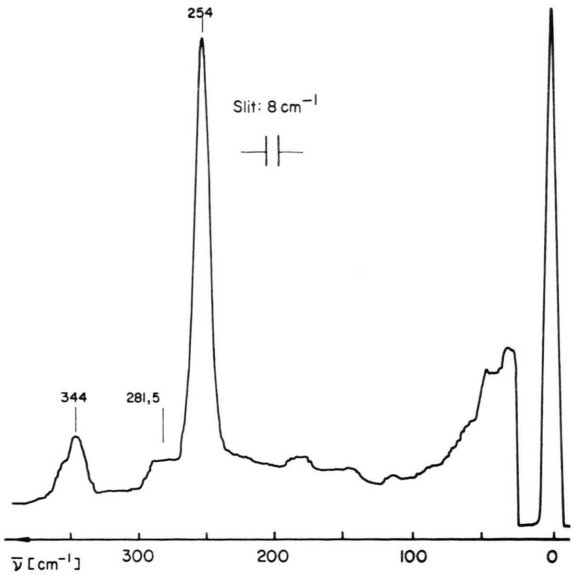

Fig. 1. Perpendicular scattering in cinnabar (HgS) with 6328 Å excitation. $s=8$ cm^{-1}; $T=1$ sec; $v=25$ cm^{-1}/min.

The phonons allowed by group theory in a crystal of D_3 symmetry are of the A_1 (R), the double degenerate E (R + IR) and the A_2 (IR) species [5]. The strong band at 254 cm^{-1} does not occur in the infra-red absorption spectrum. It must therefore be due to a totally symmetric A_1 vibration. The bands at 281.5 and 344 cm^{-1} do occur in the infra-red and are asigned as degenerate E vibrations.

2. *Realgar (As_4S_4)*

This compound has a surprisingly complicated structure. It is monoclinic with a tetramolecular unit of C_{2h} symmetry. The crystal is built up of As_4S_4 molecules, held together by Van der Waals forces [6]. The four sulphur and four arsenic atoms in the molecule are bound together by covalent bonds to form a square and a tetrahedron, respectively. The sulphur square cuts through the arsenic tetrahedron in the middle.

The sample was a small red transparent crystal of poor optical quality, about 3 mm average size and not oriented. The laser beam was focussed into the crystal and scattered light observed at right angles.

[5] G. Herzberg, Infra-Red and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, Inc., New York 1945.

[6] T. Ito, N. Morimoto, and R. Sadanaga, Acta Cryst. **5**, 775 [1952].

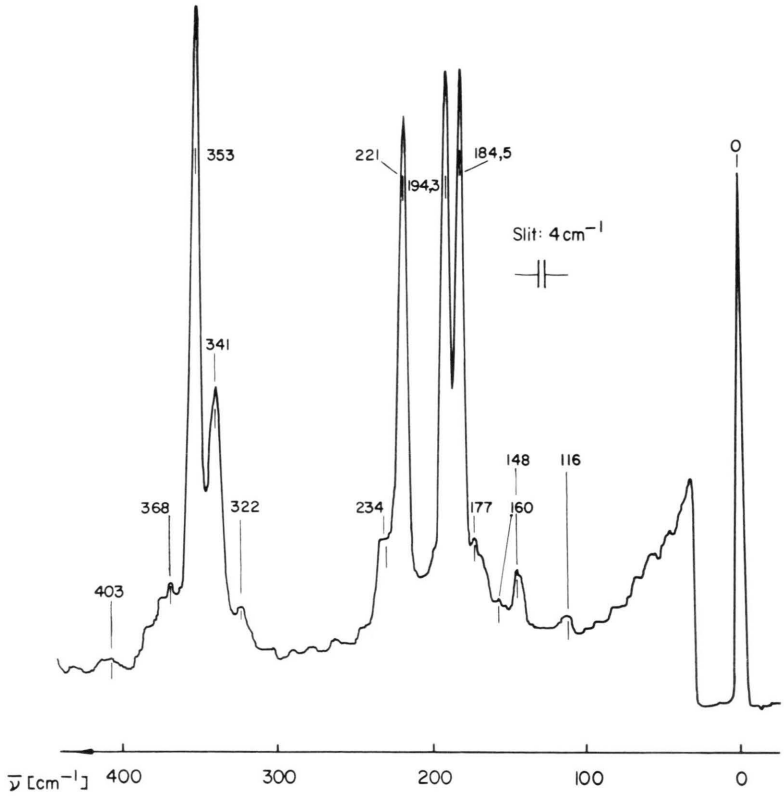

Fig. 2.
Perpendicular scattering in realgar (As_4S_4) with 6328 Å excitation.
$s=4\ cm^{-1}$;
$T=1$ sec;
$v=25\ cm^{-1}/min$.

Fig. 2 shows the Raman spectrum of realgar (As_4S_4). The peaks at 116 and 148 cm^{-1} occur weakened because of the spectral response of the secondary filter. A number of weak bands show up clearly when the spectrum is taken with ten-fold increased sensitivity. All of them except the band at 403 cm^{-1} have a half width equal to that of the stronger bands. This suggests that they belong to the first order spectrum. No fine structure is revealed when the spectrum is taken with a spectral slit width of 1 cm^{-1}. The 403 cm^{-1} band is assigned to be summation band of the $221+184.5\ cm^{-1}$ fundamentals.

An attempt was made to determine the symmetry character of the observed phonons by means of polarisation studies. No useful information could be obtained, mainly because there are four As_4S_4 molecules in the unit cell with their two-fold axes pointing in four different directions. Thus even with an oriented single crystal, polarisation measurements will most probably not lead to an unambiguous determination of the symmetry character of the observed phonons.

To explain the spectrum one cannot use the crystallographic unit cell since the Van der Waals forces holding the four As_4S_4 molecules together cannot be made responsible for the Raman spectrum. Thus one has to consider the symmetry properties of the As_4S_4 molecule itself. It belongs to the C_{2v} point group. A group theoretical calculation according to [5] then leads to the following phonon representation

$$\Gamma = 6\,A_1(R+IR) + 4\,A_2(R) + 4\,B_1(R+IR) + 4\,B_2(R+IR).$$

As explained in Section 4 the only phonon which could be assigned with certainty is the 353 cm^{-1} band with A_1 symmetry. From the calculated 18 Raman active phonons 17 have been observed. The missing one can be expected in the low frequency region, not observable in the present investigation due to the cut-off of the secondary filter.

3. Orpiment (As_2S_3)

This compound has a tetramolecular monoclinic unit cell of C_{2h} symmetry. The structure consists of As_2S_3 layers, in which spiral chains of AsS are running parallel to the c axis. The layers are parallel to the (010) plane and are held together by Van der Waals forces. Each arsenic atom has three

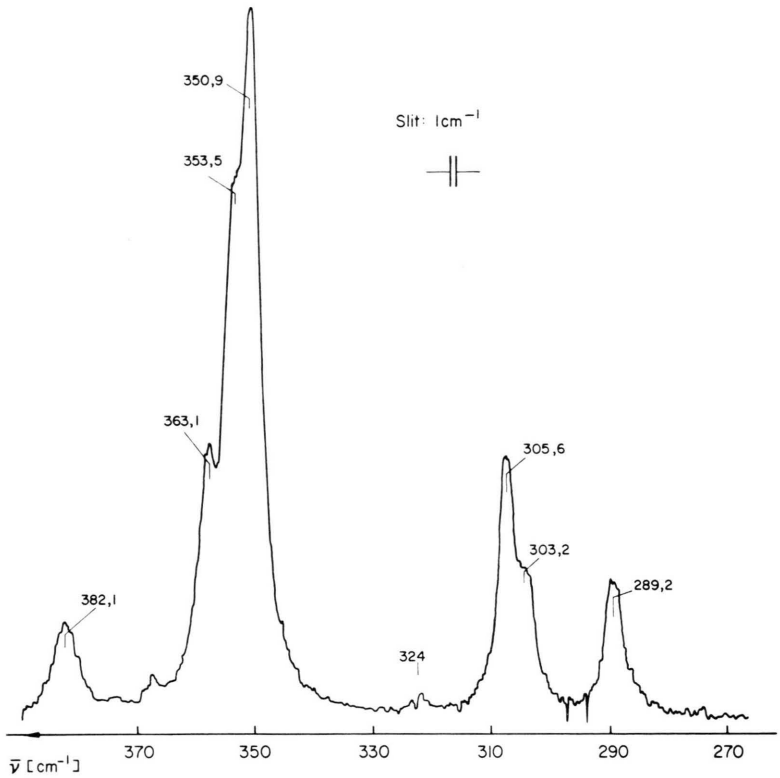

Fig. 3.
Perpendicular scattering in orpiment (As_2S_3) with 6328 Å excitation.
$s=1\ cm^{-1}$;
$T=1$ sec;
$v=6\ cm^{-1}$/min.

sulphur neighbours at distances between 2.21 and 2.28 Å, while each sulphur atom is closely bound to two arsenic atoms. The layers are far apart in the b direction. Within the layers the atoms are bound by covalent forces [7].

Our sample was a yellow transparent crystal of 10 mm average size and not oriented.

Fig. 3 shows part of the Raman spectrum of orpiment (As_2S_3) which was taken with 1 cm^{-1} spectral slit width. There are two more bands at 161 and 206 cm^{-1} not shown in this figure. The weak band at 324 cm^{-1} is assigned to be an overtone of the 161 cm^{-1} fundamental.

To explain the spectrum one again cannot, as in the case of As_4S_4, use the point group C_{2h} of the unit, because there are two layers of As_2S_3 in the cell held together by Van der Waals forces.

The unit cell in one layer contains one As_2S_3 molecule and belongs to the C_s point group. A similar calculation as in Section 2 leads to

$$\Gamma = 5\,A'(R+IR) + 4\,A''(R+IR).$$

A total number of nine phonons has been observed but an assignment seems impossible without careful polarization studies, which are at present not possible due to the lack of an oriented single crystal.

[7] N. MORIMOTO, Mineral. J. **1**, 160 [1954].

4. *Relationship between As_4S_4 and As_2S_3*

ITO et al. [6] stated that As_4S_4 and As_2S_3 were built from the same structural units upon different principles. These units consist of S – As – S – As spirals. There is one phonon occurring in the Raman as well as in the infra-red spectrum of both crystals at 353 cm^{-1}. This supports the above conclusions. The 353 cm^{-1} band is thus due to the totally symmetric vibration of the covalently bonded S – As – S – As spiral.

It was mentioned, e. g. reference [6], that realgar changes very easily to orpiment on exposure to light. We did not observe any change in the Raman spectrum of realgar even after a twelve hour exposure to the focussed 6328 Å radiation at a power of 60 mW, though a slight powdering at the point of incidence of the laser light was indeed observed.

Acknowledgement

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