

Vibrational studies of silicates and germanates—V. I.R. and Raman spectra of pyrosilicates and pyrogermanates with a linear bridge

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Abstract—The i.r. and Raman spectra of the pyro-silicates and -germanates of the type $A_2Pb_2Si_2O_7$ ($A = K, Rb, Cs$) have been investigated and compared with the spectrum deduced from a group theoretical analysis. The results are fully consistent with a true D_{3d} symmetry of the Si_2O_7 or Ge_2O_7 group.

The stretching frequencies of the Si_2O_7 and Ge_2O_7 groups have been assigned with the help of isotopic data on Si and Ge: these results, together with the comparison of i.r. and Raman spectra, show that the highest i.r. frequency must be assigned to the antisymmetric stretch of the Si–O–Si (or Ge–O–Ge) bridge, and not of the terminal SiO_3 (or GeO_3) group. The extension of these assignments to thortveitite $Sc_2Si_2O_7$ and other pyro compounds with a linear bridge is briefly discussed. Reasonable assignments can also be proposed for the bending modes, but unexpected values of isotopic shifts suggest that some of them at least are strongly coupled with torsional and/or external modes. Finally, some of the external modes have been identified as arising from a translation of either the alkali cation, or of the lead atom.

INTRODUCTION

THE EXISTENCE of “pyro” compounds (e.g. pyro-silicates, -phosphates, -vanadates, etc. . . .) characterized by the presence of a so-called linear anion $(X_2O_7)^{n-}$ offers 2 types of interesting problems: (1) a structural problem: it is not evident from the existing X-ray diffraction data that the $X-O-X$ bridge is really linear, since the bridge oxygen generally shows an abnormally large thermal motion, and it is thus possible that the $X-O-X$ bond angle is linear only as a result of thermal averaging. (2) a spectroscopic problem: a X_2O_7 anion with a linear $X-O-X$ bridge may have the rather high D_{3d} symmetry, but it does not seem that the experimental aspects of this problem have been fully investigated. Recent papers have been devoted to the spectrum of thortveitite $Sc_2Si_2O_7$ or thortveitite-like compounds [1–3]; but in this type of structure, the site symmetry is reduced to C_{2h} or even less (there seems to be some violation of the rule of mutual exclusion after [1]). Likewise, the i.r. spectrum of ZrP_2O_7 has been recently re-investigated [3]: this paper brings out a very interesting contribution to the problem of the P_2O_7 configuration as a function of temperature, but does not discuss the vibrational spectrum of a X_2O_7 group with D_{3d} symmetry. Finally, the most favourable case for a spectroscopic investigation is certainly offered by the silicates of the type $X_2Pb_2Si_2O_7$ ($X = K, Rb, Cs$) and the corresponding germanates.

[1] S. D. ROSS, *Spectrochim. Acta* **27A**, 1837 (1971).

[2] A. N. LAZAREV and A. P. MIRGORODSKII, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **7**, 1224 (1971).

[3] R. PASCARD, M. CHAUNAC and E. GRISON, *Bull. Soc. Chim. France* 429 (1971).

Their structure was determined by NARAY-SZABO [4], and by LAJZEROWICZ-BONNETEAU [5], who also investigated a part of their i.r. spectrum and pointed out the following advantages for a spectroscopic study: (1) the Si_2O_7 (or Ge_2O_7) group retains its full D_{3d} symmetry in the crystal lattice; (2) there is only one molecular formula in the unit cell; (3) the cation-oxygen vibrational frequencies should be rather low, and the separation of the vibrations into internal and external modes should be a good approximation.

To these, we may add the following points: (4) these compounds should give convenient Raman spectra, in connection with the presence of the highly polarizable lead atom. The simultaneous knowledge of both Raman and i.r. spectra is rather important in view of the centrosymmetric structure of the X_2O_7 anion and of the crystallographic cell; (5) the possibility of investigating isotopic mass effects on silicon and germanium should improve some at least of the assignments of the internal frequencies; (6) the comparison of the corresponding K, Rb and Cs compounds should give some information about the assignment of the external modes.

These considerations lead us to a complete re-investigation of the vibrational spectrum of this family of compounds.

EXPERIMENTAL

Synthesis of the compounds

The stoichiometric amounts of SiO_2 (or GeO_2), PbCO_3 and alkali (K, Rb or Cs) nitrate are thoroughly ground and mixed, and very slowly heated up to 680°C [5]. This final temperature is maintained for 7 or even 15 days. The purity of the compounds has been checked by X-ray diffractometry; but rather unexpectedly, the Raman spectrum proved to be more sensitive than the X-ray powder diffraction to the presence of non-combined PbO . This results from the great sharpness and the high intensity of the strongest Raman peak of PbO .

Spectra

Powder samples only were available. The Raman spectra were registered with a Coderg PHO double monochromator equipped with a 50 mW He-Ne laser (Spectra-Physics). The classical disc technique was used for the i.r. spectra (KI discs, Beckman IR 12 spectrometer for the $1400\text{--}200\text{ cm}^{-1}$ region; polythene discs, Cameca SI 36 spectrometer for the $200\text{--}50\text{ cm}^{-1}$ region), but some control spectra were also run as nujol mulls.

CRYSTAL STRUCTURE AND NORMAL MODES OF VIBRATION

The application of group theory to an isolated X_2O_7 anion with D_{3d} symmetry leads to the irreducible representation [5, 6]:

$$\Gamma_i = 3A_{1g} + 1A_{1u} + 3A_{2u} + 3E_g + 4E_u.$$

There are 6 Raman ($3A_{1g}$ and $3E_g$) and 7 i.r. ($3A_{2u} + 4E_u$) active internal modes. The A_{1u} mode is inactive.

[4] I. NARAY-SZABO, *Silika Techn.* **12**, 316 (1962).

[5] J. LAJZEROWICZ-BONNETEAU, Thèse de Doctorat, Grenoble (1964).

[6] R. W. MOONEY, S. Z. TOMA and J. BRUNVOLL, *Spectrochim. Acta* **23A**, 1541 (1967).

If we now consider the whole unit cell, with space group $P\bar{3} (C_{3i}^1)$ and $Z = 1$ [5], all the cations (Si or Ge, A and Pb) are located on 3-fold axes; the bridge oxygen is on the centre of symmetry, the remaining oxygens being in general positions. Since $Z = 1$, there are 13 atoms and hence 39 degrees of freedom for a unit cell. The character table associated to the $S 6$ group, and the application of the group theory, lead to the irreducible representation:

$$\Gamma_i = 6A_g + 6E_g + 7A_u + 7E_u.$$

These may be distributed into acoustical, translational, rotational and internal modes by classical methods [7] and the results are given in Table 1.

It will be noticed that there are now 8 internal, i.r. active modes (against 7 for the "free" X_2O_7 group). This is due to the fact that, when passing from the D_{3d} to the $S 6$ symmetry the formerly A_{1u} , i.r. inactive mode, becomes A_u , i.r. active.

Table 1. Raman and i.r. active modes for the $K_2Pb_2Si_2O_7$ unit cell

Symmetry classes Type	Raman active		I.r. active	
	$6A_g$	$6E_g$	$7A_u$	$7E_u$
Acoustical	—	—	1	1
Translational	2	2	2	2
Rotational	1	1	—	—
Internal	3	3	4	4

Approximate description of the internal modes

This description is necessarily an approximate one, since it neglects the interactions between vibrations of the same class of symmetry; moreover, the values of the force constants and the relative amplitudes of motion are unknown.

Nevertheless, this description (Table 2) will be helpful for a tentative assignment of the observed frequencies. Moreover, some of the modes (essentially the bridge antisymmetric modes) do not involve an important displacement of the X cation and thus may be identified if isotopic species of X are investigated.

Table 2. Approximate description of the internal modes

Raman active	I.r. active
Stretching modes	
A_g : Bridge symmetric stretch	A_u : Bridge antisymmetric stretch
A_g : In-phase XO_3 symmetric stretch	A_u : Out of phase XO_3 symmetric stretch
E_g : In-phase XO_3 antisymmetric stretch	E_u : Out of phase XO_3 antisymmetric stretch
Bending modes	
A_g : In-phase XO_3 symmetric bend	A_u : Out of phase XO_3 symmetric bend
E_g : In-phase XO_3 antisymmetric bend	E_u : Out of phase XO_3 antisymmetric bend
E_g : Bending of the whole X_2O_7 group with bridge oxygen at rest	E_u : Bridge bending
	E_u : Torsion
	A_u : Torsion

[7] S. S. MITTRA, *Solid State Phys.* **13**, 2 (1962).

EXPERIMENTAL RESULTS AND ASSIGNMENTS

All the experimental results, including isotopic data (^{28}Si - ^{30}Si ; ^{70}Ge - ^{76}Ge), are collected in Tables 3 and 4. Representative spectra are given in Figs. 1 and 2.

Since powder data only are available, there is no straightforward distinction between *A*-type and *E*-type modes. The tentative assignments proposed in Table 3 have been deduced in the following way.

Table 3. I.r. and Raman frequencies, and assignments

	$A_2\text{Pb}_2\text{Si}_2\text{O}_7$			$A_2\text{Pb}_2\text{Ge}_2\text{O}_7$			Assignments
	<i>A</i> = K	Rb	Cs	<i>A</i> = K	Rb	Cs	
i.r.	1014	1026	1014	896	903	913	A_u bridge stretch
	922	913	897	738	735	720	$A_u + E_u$ XO_3 stretch
	565	562	562	475	470	468	A_u and E_u XO_3 bend
	478	476	471	395	378	360	
	415	407	393	323	325		E_u bridge bending
	258	263	258	200	200	200	Torsion
	215			160			Torsion?
	162	115	92	112			Translation of the <i>A</i> cation
	127						
	Raman	902	889	890	798	798	786
			880	728	722	706	E_u XO_3 stretch
669		668	666	520	514	505	A_g bridge stretch
455		452	446	373	360	348	Bending notes
399		396	393	294	296	291	
367		360	348	270 ± 10	270 ± 10	$270 \pm 10^*$	
218		223	222	170	173	173	
134		89	74	133	84	70	External mode; see text
100		104	97	90	95	88	Translation of the <i>A</i> cation
			95				Pb translation? (See text)
56.5		53.5	49.5	45.5	44	41	Pb translation

* See text.

Table 4. Isotopic data

	$\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$			$\text{K}_2\text{Pb}_2\text{Ge}_2\text{O}_7$		
	^{28}Si	^{30}Si	$\Delta\nu$	^{70}Ge	^{76}Ge	$\Delta\nu$
i.r.	1014	1011	-3	897	895	-2
	922	903	-19*	740	735	-5*
	565	561	-4	477	472	-5*
	478	474	-4	397	395	-2
	415	414	-1	321	320	-1
	258	255	-3	201	201	0
	215	210	-5			
Raman	902	896	-6*	798	797	-1
	902	888	-14	729	725	-4
	669	659	-10	520	516	-4
	455	448	-7	373	373	0*
	399	394	-5	294	287	-7
	367	365	-2	270 ± 10		?
	218	216	-2	170	169	-1
	134	133.5	-0.5	133	133	0
	100.5	100.5	0	90	90	0
	56.5	56.5	0	45.5	45.5	0

* Relatively large uncertainty on the isotopic shift due to the broadness of the band.

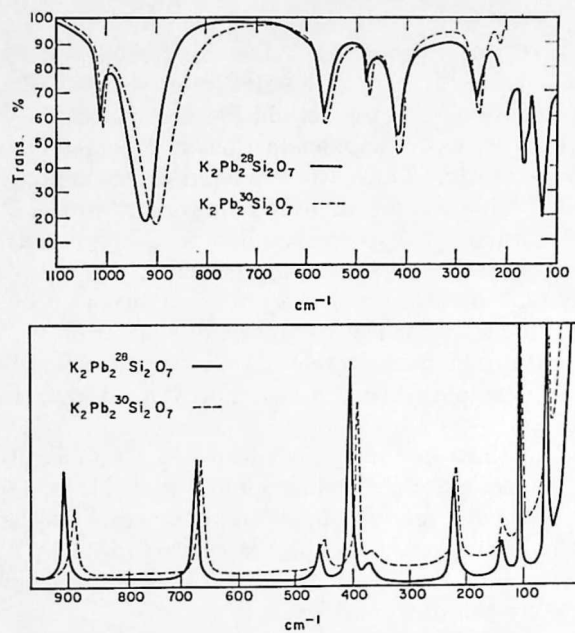


Fig. 1. Infrared and Raman spectrum of $K_2Pb_2Si_2O_7$ showing the ^{28}Si - ^{30}Si isotopic shifts.

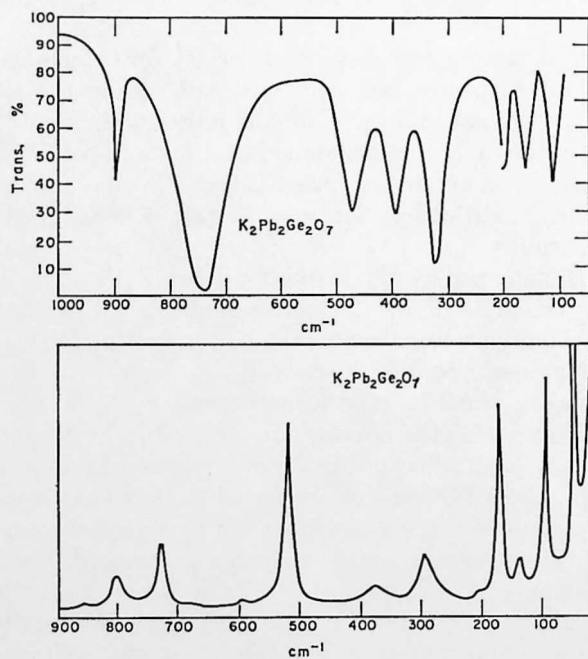


Fig. 2. Infrared and Raman spectrum of $K_2Pb_2Ge_2O_7$.

Stretching modes

It is expected that the various XO_3 stretching modes ($1A_g + 1E_g$, Raman; $1A_u + 1E_u$, i.r.—see Table 2) should exhibit more or less similar frequencies, whereas the 2 types of bridge stretch should be characterized by widely different frequencies, depending on their symmetric (lowest frequency) or antisymmetric (highest frequency) character. Thus, the i.r. band corresponding to the antisymmetric stretch of the bridge should have no counterpart in the Raman spectrum; and conversely, the Raman peak corresponding to the symmetric stretch of the bridge should have no counterpart in the i.r. spectrum.

Moreover, the symmetric stretch of the bridge involves an important displacement, and thus a significant mass isotope effect, of the cation X ; on the contrary, the corresponding antisymmetric stretch may be approximately described as a motion of the bridge oxygen against the terminal XO_3 groups: the mass influence of X should be weak.

Taking these points into account, the various types of stretching modes are easily identified by inspection of the values quoted in Tables 3 and 4. The highest i.r. frequency (near 1020 cm^{-1} for the silicates and 900 cm^{-1} for the germanates) has no counterpart in the Raman spectrum and is characterized by a rather moderate isotopic shift on either Si or Ge. Thus, this band may be assigned with confidence to the antisymmetric stretch of the bridge.

Likewise, the Raman peak observed near 668 cm^{-1} in the Raman spectrum of the silicates has no equivalent in the i.r. spectrum, and exhibits a fairly large ^{28}Si – ^{30}Si isotopic shift: it is thus assigned to the symmetric stretching motion of the bridge. The corresponding peak is observed near 520 – 510 cm^{-1} in the spectrum of the germanates.

The remaining high-frequency bands are observed, for the silicates, near 900 cm^{-1} in both i.r. and Raman spectra, and thus are assigned to the various stretching motions of the SiO_3 terminal groups. There is only one i.r. band in the 900 cm^{-1} region, but it is fairly broad, and it is assumed that it corresponds to the overlapping of the A_u and E_u modes. A similar situation is found in the i.r. spectrum of the germanates: the strong, broad absorption near 730 cm^{-1} is assigned to the $A_u + E_u$ modes of the GeO_3 groups.

Likewise, one Raman peak only is observed for $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$ in the frequency range expected for the A_g and E_g stretching modes of the SiO_3 terminal groups. But this peak is decidedly asymmetric for the corresponding Rb compound, and has 2 components for the Cs compound. Moreover, the single peak observed for $\text{K}_2\text{Pb}_2\text{-}^{28}\text{Si}_2\text{O}_7$ exhibits a weak shoulder in the spectrum of the heavy isotopic species $\text{K}_2\text{Pb}_2\text{-}^{30}\text{Si}_2\text{O}_7$, thus confirming the overlapping of 2 vibrational modes characterized by somewhat different mass effects. As a consequence of this different sensitivity to the cationic mass, these frequencies are found to be widely separated (by about 80 cm^{-1}) in the spectrum of the corresponding pyrogermanates, with a "high"-frequency and a "low"-frequency peak, the latter being considerably more sensitive than the former to the mass of germanium (Table 4 and Fig. 3). As far as their assignment to the A_g and E_g modes is concerned, the E_g , locally antisymmetric mode, is expected to be more sensitive than the A_g mode to the mass of the cation (either Si or Ge).

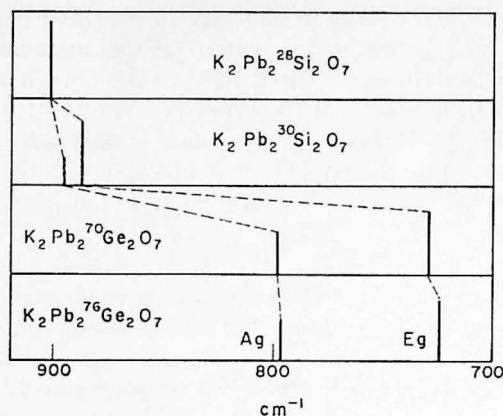


Fig. 3. Mass effects on the A_g and E_g stretching modes of the terminal XO_3 group.

The high- and low-frequency peaks are accordingly assigned to the A_g and E_g modes respectively.

It should be made quite clear that these descriptive assignments are only an approximation. The so-called "bridge symmetric stretch" and "in-phase XO_3 symmetric stretch" belong to the same A_g symmetry class and thus must interact. This is true also for the two A_u modes, namely the "bridge antisymmetric stretch" and the "out of phase XO_3 symmetric stretch."

Nevertheless, the combined i.r. and Raman data (with the very large difference between the frequency values assigned to the bridge symmetric and antisymmetric stretch), and the isotopic data suggest that these assignments are still of practical value.

Bending and torsional modes

These types of motions should be represented by 5 i.r. active, and 3 Raman active bands. The 2 i.r. bands near 560 and 470 cm^{-1} in the spectrum of the silicates exhibit a significant ^{28}Si - ^{30}Si isotopic shift (Table 4) and are thus assigned to the bending motions of the SiO_3 terminal groups. The former may be tentatively assigned to the E_u , and the latter to the A_u mode on the basis of their relative frequencies, intensities, and shapes, but it is clear that this assignment is simply a reasonable, but not a proved one. The next i.r. band in the silicate spectra, near 410–400 cm^{-1} , exhibits a very small (and possibly non-significant) ^{28}Si - ^{30}Si isotopic shift: it is thus assigned to the bridge bending motion. The corresponding bands are observed near 470, 390 and 320 cm^{-1} for the germanates.

The identification of the torsional frequencies is a matter of difficulty, since even their order of magnitude is unknown. We just know that such frequencies must be very low for the free X_2O_7 group. But in the crystal, the cation–oxygen bonding must introduce a supplementary restoring force which, owing to the covalent character of the Pb–O bond, is certainly far from being negligible. On the other hand, this type of motion must be more or less strongly coupled with external modes.

The 258 cm^{-1} band of the silicates is tentatively assigned to one of the torsional modes for the following reasons: (1) this frequency cannot be assigned to a translation of the alkali cation, since it is insensitive to the nature of this cation; (2) the frequency is too high to be assigned to a translation of either the Pb atom, or the Si_2O_7 group as a whole; (3) if the assignment to a translation is discarded, and since there is no i.r. active rotational mode, there just remains the assignment to an internal, torsional mode. The corresponding band is observed near 200 cm^{-1} in the spectrum of the germanates.

Finally, the weak 215 cm^{-1} band in the spectrum of $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$ is possibly due to the remaining torsional mode, but the available information about this band in other compounds is too scarce to justify the discussion of this assignment.

In the Raman spectrum of the silicates, 3 peaks are observed near 450 , 400 and 360 cm^{-1} , and are likely to be due to the 3 Raman active bending modes. However, their detailed assignment is a matter of difficulty since the (supposed) corresponding peaks exhibit, for the germanates, isotopic shifts which are non-consistent with those observed for the silicates: thus, the weak, moderately broad peak near 450 cm^{-1} in the spectrum of the silicate exhibits a ^{28}Si - ^{30}Si isotopic shift of 7 cm^{-1} ; but there is no significant shift for the corresponding peak of the germanate near 373 cm^{-1} . On the other hand, the isotopic shift of the strong, sharp peak near 390 (silicate) or 290 cm^{-1} (germanate) is *smaller* for the silicate than for the germanate. We have no detailed explanation for these facts; but it is expected that these bending motions are more or less severely mixed up with other modes of the same symmetry, with as a consequence a very poor knowledge of the relative amplitudes of the atomic displacements.

Finally, very little information is available for the third peak, since it is weak and broad in the spectrum of the silicates, and it is apparently missing in the spectrum of the germanates. However, all the spectra of the germanates exhibit a very broad hump, whose maximum is overlapped by the strong 290 cm^{-1} peak: this is probably the third bending mode.

External modes

I.R. data are rather scarce since 2 bands (against a total of 4 i.r. active modes) are observed for $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$, and one strong band only can be traced in the series of K, Rb and Cs compounds, where it is found to be shifted from 162 to 115 and finally 92 cm^{-1} . This points to a large influence of the mass of the alkali cation. Out of a total of 6 predicted, Raman-active modes (2 rotations, 4 translations: Table 1), 4 are effectively observed. For $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$, we find, in the order of decreasing frequencies (Tables 3 and 4; Fig. 2):

(1) A moderately strong peak at 218 cm^{-1} , with a small ^{28}Si - ^{30}Si mass effect, but no mass influence of the alkali ion. It is certainly related to a motion of the pyro X_2O_7 group, either a rotation, or a mixed translation-rotation.

(2) A weak band at 134 cm^{-1} , with no isotopic effect on silicon. There is a strong influence of the alkali cation, and the frequencies are nearly the same for the corresponding silicates and germanates. This frequency is thus assigned to a translation of the alkali cation.

(3) A strong, sharp peak at 100 cm^{-1} with no isotopic shift, and no mass influence of the alkali cation. This leads to 2 types of assignments, either a rotation of the X_2O_7 group around the $X-O-X$ axis, or a translation of the lead atom. This latter assignment may be preferred in view of the high intensity of the band.

(4) A very strong, very sharp peak at 56 cm^{-1} . Here again, the very high intensity, together with the low frequency, strongly suggest a lead translation with, possibly, some contribution from the alkali cation.

VIBRATIONAL BEHAVIOUR OF PYROSILICATE-PYROGERMANATE SOLID SOLUTIONS

The i.r. spectrum of solid solutions of the type $K_2Pb_2Si_{2-x}Ge_xO_7$ have already been investigated [5]. These spectra essentially appear as the sum of the spectra of the pyrosilicate and of the pyrogermanate and it was inferred that the solid solutions essentially consist of Si_2O_7 and Ge_2O_7 groups, with practically no mixed $SiGeO_7$ groups [5].

Our own results are not in agreement with these data: some peaks observed in the vibrational (either Raman or i.r.) spectrum of solid solutions are new and have no counterpart in the spectrum of the pure compounds, thus suggesting a lowering of the symmetry of the pyro group. Moreover, one frequency at least (which was missing in the spectra of the pure compounds) is simultaneously observed in both Raman and i.r. spectra, a result which implies the suppression of the centre of symmetry (Table 5). These data point to the simultaneous occurrence of Si_2O_7 , Ge_2O_7 and $SiGeO_7$ groups in the solid solutions. Our results are not significantly modified by changing the synthesis conditions (temperature, duration, tempering or quenching conditions), and the discrepancies with respect to LAJZEROWICZ's results [5] remain unexplained.

DISCUSSION AND CONCLUSIONS

One of the most interesting, and most disputed, points about the "pyro" groups with a linear bridge, is certainly the frequency values of the so-called bridge vibrations. Two problems in fact may be considered, namely the frequency difference between the symmetric and the antisymmetric bridge stretch, and the absolute frequency values corresponding to these 2 modes. Some aspects of these problems have been recently discussed [1-3], but without bringing sufficient experimental facts and convincing arguments.

In the case of thortveitite $Sc_2Si_2O_7$, the antisymmetric bridge stretch is assigned by Ross to an i.r. band located at 794 cm^{-1} , whereas the symmetric stretch is assigned to a strong 420 cm^{-1} Raman peak. After Ross, this assignment is substantiated by the good agreement between observed and calculated frequencies [1]. In our opinion, the value of these conclusions is considerably reduced by an *a priori* choice of the value of the antisymmetric stretching frequency; moreover, the agreement between observed* and calculated frequencies is a very weak argument since, in such a complicated case, it is *always* possible to adjust the force constants so as to fit the experimental data. As a matter of fact, a completely different assignment is

* Our own experimental data on synthetic and natural thortveitite are not always in agreement with the results published by Ross. These discrepancies will not be discussed here.

Table. 5. I.R. and Raman frequencies of $K_2Pb_2Si_{2-x}Ge_xO_7$ solid solutions

	$K_2Pb_2Si_2O_7$	$x = 0.5$	$x = 1$	$x = 1.5$	$K_2Pb_2Ge_2O_7$
Infrared	1014	1010	1008	1008	
		~960	~955	956	
			~927	927	
	922	907	897	895	896
			~770	767	
		759	747	741	737
		599	599	598	
	565	555	553	550	
	478	475	476	475	475
	415	410	403	397	395
		322	325	323	320
		310	~315		
	258	253	252	240	
Raman				~925	
	902	900	900	900	
		~875	~875	~875	
			~800	~802	798
		757	738	733	728
	669	663	655	648	
		~609	~609	~607	
		~600	~600	~600	
		492	502	510	520
	455	456	462	~468	
	399	387	374	~376	~373
	367	344	341	340	
			~290	291	294
	218	216	~220		
		186	178	174	170
134	133	133	133	133	
100.5	98	96	94	90	
56.5	54	50.5	48	45.5	

proposed by LAZAREV [2] for the same compound: the antisymmetric bridge stretch is assigned to the highest i.r. frequency, near 1170 cm^{-1} .

Our actual results on $K_2Pb_2Si_2O_7$ -type compounds strongly support this latter type of assignment.

For these compounds, the rather reduced isotopic shift (either ^{28}Si - ^{30}Si or ^{70}Ge - ^{76}Ge) on the high-frequency i.r. band provides the first *proof* that this frequency is essentially related to an oxygen displacement. The assignment to the bridge antisymmetric stretch is also supported by the absence of a corresponding Raman peak. Conversely, several arguments support the assignment of the bridge symmetric stretch to a comparatively low frequency (about 670 cm^{-1} for the silicates and 520 cm^{-1} for the germanates). These arguments are the fairly important isotopic shift, the absence of an equivalent i.r. frequency, and the large difference between the frequencies of the antisymmetric and the symmetric modes, such a large difference being expected for a linear $X-O-X$ bridge from simple kinematic considerations.

Since, in addition, the remaining bands are found in the frequency region expected for the terminal XO_3 group, we feel that our assignments give a coherent scheme for the stretching frequencies of the investigated compounds.

This type of assignment may be extended to thortveitite $Sc_2Si_2O_7$ and the corresponding germanate $Sc_2Ge_2O_7$, although the situation is much less favourable here because of the reduced symmetry (C_{2h}). We have no isotopic data for these compounds, but the following assignments can be made by analogy (Fig. 4); the bridge antisymmetric stretch is assigned to the high-frequency i.r. band (1170 cm^{-1} for

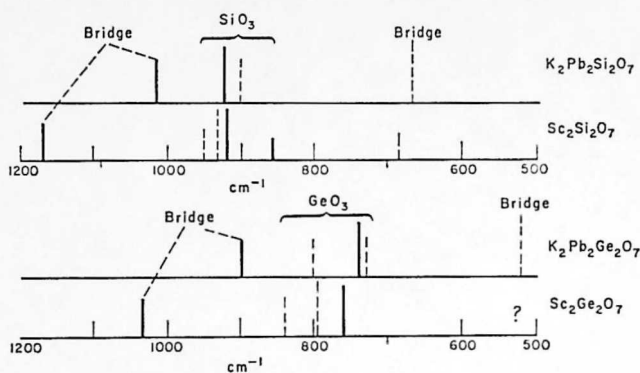


Fig. 4. Analogies between the stretching frequencies of $K_2Pb_2Si_2O_7$ -type and thortveitite-type compounds. Full lines: i.r. frequencies. Dotted lines: Raman frequencies.

the silicate; 1034 cm^{-1} for the germanate) with no equivalent Raman frequency; the various XO_3 stretching modes are found in the usual region for both i.r. and Raman spectra ($950\text{--}850\text{ cm}^{-1}$ for the silicate; $850\text{--}700\text{ cm}^{-1}$ for the germanate); the bridge symmetric stretch is assigned to a weak band observed at about 685 cm^{-1} in the Raman spectrum of the silicate, with no equivalent in the i.r. spectrum; the corresponding frequency cannot be immediately identified in the Raman spectrum of the germanate, since there are several peaks in the expected frequency region (near 500 cm^{-1}).

Extension to pyro-phosphates, -arsenates and -vanadates

A similar interpretation problem is met with various pyrophosphates such as ZrP_2O_7 . Here again, 2 types of assignments have been proposed for the i.r. active bridge antisymmetric stretch: either a high frequency in the $1200\text{--}1100\text{ cm}^{-1}$ region [3, 6, 8], or a rather low value of about 750 cm^{-1} [9]. But until very recently, no convincing proof or disproof was given about these 2 types of assignments. It has been shown recently, however, that the weak 750 cm^{-1} band completely disappears from the i.r. spectrum of ZrP_2O_7 and other pyrophosphates when these compounds are heated at a temperature such as the P–O–P bridge is really linear [3]. Such results show that the assignment of this band to the bridge *antisymmetric* stretch is definitely wrong, and strongly suggests that the 750 cm^{-1} band must be assigned to the bridge *symmetric* stretch, whose i.r. activity is related to the bent configuration of the P–O–P bridge at room temperature. Much work remains to be done on these compounds, and on the corresponding arsenates and vanadates. Progress in the assignment problem is strongly hindered by the lack of isotopic species (there is only *one* stable isotope of P, As and V), and also by the lack of convenient Raman data. Further work in this direction is actually carried out in this laboratory.

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