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Vibrational studies of molybdates, tungstates and related compounds—II. New Raman data and assignments for the scheelite-type compounds

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Abstract—New experimental data on pure compounds, isotopic species and solid solutions lead to more detailed and, in some cases, to revised assignments for the Raman spectrum of scheelite-type molybdates and tungstates. The ^{92}Mo–^{100}Mo isotopic shifts allow a more reliable assignment of the 2 types of internal bending modes, namely ν_4 and ν_2; it is found that $\nu_4 > \nu_2$; this is the reverse of the i.r. active modes, for which isotopic data show that $\nu_2 > \nu_4$. Thus, such assignments cannot be made by comparison. Likewise, the investigation of isotopic species and solid solutions leads to an easy discrimination between the rotational and the translational modes. Moreover, it appears that, for the lighter cations Ca and Sr at least, the 2 lowest-lying translational modes are essentially related to Mo–Mo (or W–W) motions, whereas the 2 highest-lying frequencies are related to a cation–cation (Ca–Ca or Sr–Sr) translation. This separation of the translations has only a practical significance, since it is not imposed by symmetry considerations; it is no longer really significant for the compounds of the heavy cations Ba and Pb. Some aspects of the relations between the internal frequencies and the nature of the cations are also discussed.

Introduction

In a previous paper [1], we have shown that, for scheelite-type compounds, the assignments for some i.r. active frequencies should be revised, this revision being particularly needed for the low-frequency, external modes. The same is true for the Raman-active modes, but the situation is much more complicated here, since they are 13 Raman-active fundamentals, including 6 external modes.

We show in this paper how reliable assignments may be obtained by combining some of the existing single crystal data, and new Raman data on powders resulting from the systematic investigation of pure compounds, isotopic species and solid solutions.

Experimental

The Raman spectra of powders have been registered with a Coderg PHO monochromator equipped with a 50 mW Spectra-Physics He–Ne laser. The powder is placed into a glass capillary of small diameter (1–2 mm) and formed into a cone.

The cone is illuminated along its axis by the laser beam, and the scattered light is collected into the spectrometer at a 90° angle. With substances which are good scatterers, it is possible to obtain good Raman spectra with very small samples (5–10 milligrams). This point is important for the investigation of isotopic compounds. Spectral slit widths of 4 cm^{-1} were used for exploratory work, but some regions of the spectrum were re-investigated with 2, 1 or even 0·5 cm^{-1} spectral slit widths.

[1] P. Tarte and M. Liegeois-Duyckaerts, *Spectrochim. Acta* **28A**, 2029 (1972).

THE EXISTING DATA AND ASSIGNMENTS

For the Raman active modes, the group theory [2] leads to the representation:

$$\Gamma_i = 3A_g + 5B_g + 5E_g.$$

They may be described as follows:

7 internal modes: stretching—$\nu_1(A_g)$; $\nu_3(B_g)$ and $\nu_3(E_g)$; bending—$\nu_2(A_g)$ and $\nu_2(B_g)$; $\nu_4(B_g)$ and $\nu_4(E_g)$;

6 external modes: 2 rotations A_g and E_g; 4 translations $2B_g$ and $2E_g$.

In some cases at least, the number of observed Raman bands corresponds to the number of expected fundamentals [2]. Moreover, the agreement between the experimental data obtained by different authors may be considered as fairly good (although some weak bands are observed by certain authors, but not by others). But rather controversial assignments have been proposed, chiefly for the low-frequency region.

The following points must be considered:

(1) The 3 high-frequency stretching modes belong to 3 different symmetry classes and thus are easily distinguished, provided single crystal data are available. Moreover, the assignments deduced from single crystal studies are easily extended to further compounds for which powder data only are available.

(2) Rather serious difficulties arise in the medium-frequency (internal, bending modes) and low-frequency (external modes: 2 rotations and 4 translations) regions. Even if good polarization data on monocrystals are available, some uncertainty remains about the proper assignment of the 2 medium-frequency B_g modes to either ν_2 or ν_4, and of the 3 low-frequency E_g modes to either a rotation or a translation.

The situation is even worse if the polarization data are of poor quality, or if powder data only are available: for the external modes, the rotational and translational frequencies depend in a very different manner on the nature of the cation, and their assignment cannot be deduced by comparison.

This is the type of assignment problem already met with the i.r. spectra [1], but with an increased difficulty due to the higher number of Raman-active fundamentals. As a matter of fact, this problem could not be completely solved by the investigation of pure compounds and isotopic species, and further information had to be gained through the study of solid solutions.

ISOTOPIC DATA ON CALCIUM MOLYBDATE

The previous data and assignments on $CaMoO_4$ are collected in Table 1. As expected, the main points of disagreement are the assignment of the 2 bending B_g modes to ν_4 and ν_2 ,and the discrimination between the rotational and translational E_g modes.

Our isotopic data and the resulting assignments are collected in Table 2.*

* It should be made quite clear that these final assignments are not deduced from our spectral data alone; the assignments to a given symmetry class (A_g, B_g, E_g) are those already deduced by PORTO and SCOTT [2] from single crystal data.

[2] S. P. S. PORTO and J. F. SCOTT, *Phys. Rev.* **157**, 716 (1967).

Table 1. Previous assignments for the Raman spectrum of $CaMoO_4$

	Ref. [2]	[3]	[4]	[5]	[6]	This work*
$\nu_1(A_g)$	878	878	878	880		879
$\nu_3(B_g)$	844	844	844	847		848
$\nu_3(E_g)$	797	797	794	796		794
$\nu_2(A_g)$	333	333	322	326		323
$\nu_2(B_g)$	339	393	322	394		323
$\nu_4(B_g)$	393	339	390	326		392
$\nu_4(E_g)$	401	401	404	394		403
$R(A_g)$	205	205	204	208	205	205
$R(E_g)$	263	263	189	270	189	268
$T(B_g)$	219	219				
$T(B_g)$	110	110	111	115	110	112
$T(E_g)$	189	189	111	192	263	191
$T(E_g)$	145	145	140	150	145	144

* After the isotopic data.

Table 2. Raman frequencies of the isotopic species of $CaMoO_4$

		$\Delta\nu$				$\Delta\nu$		
$^{40}CaMoO_4$	$^{44}CaMoO_4$	cm^{-1}	%	$Ca^{92}MoO_4$	$Ca^{100}MoO_4$	cm^{-1}	%	Assignment
879	879	0		879	879	0		$\nu_1(A_g)$
848	848	0		852	844·5	−7·5	0·88	$\nu_3(B_g)$
794·5	794	(−0·5)		797·5	791	−6·5	0·81	$\nu_3(E_g)$
403·5	403	(−0·5)		403	401	−2	0·50	$\nu_4(E_g)$
392	392·5	(+0·5)		393	390·5	−2·5	0·64	$\nu_4(B_g)$
323·5	323·5	0		323	323	0		$\nu_2(A_g)$ and/or $\nu_2(B_g)$
~269	~268	(−1)*		~267	267	(0)*		$R(E_g)$
205	205	0		205	205	0		$R(A_g)$
191·5	183·5	−8	4·2	190·5	190·5	0		$T(E_g)$ Ca/Ca
144	143	(−1)		145·5	142	−3·5	2·5	$T(E_g)$ Mo/Mo
112	111·5	(−0·5)		113·5	109·5	−4	3·6	$T(B_g)$ Mo/Mo

* Weak band.

For the internal vibrations, the ^{92}Mo–^{100}Mo isotopic shifts are of the same order of magnitude that those already observed for spinel molybdates [7]: about 7 cm^{-1} for ν_3, and 2–3 cm^{-1} for ν_4.

It should be pointed out that the shift is the same (within the experimental error) for the 403 and 393 cm^{-1} Raman bands. Now, the 403 cm^{-1} band (E_g) is certainly one of the ν_4 components (there is no ν_2 component of the E_g type); this leads us to assign the 393 cm^{-1} band (with the same isotopic behaviour) to the other component of ν_4 (B_g), and not to ν_2 (for which there should be no isotopic shift), as

[3] J. F. Scott, *J. Chem. Phys.* **48**, 874 (1968); **49**, 98 (1968).
[4] R. K. Khanna, W. S. Brower, B. R. Guscott and E. R. Lippincott, *J. Res. Natl. Bur. Std.* **72A**, 81 (1968).
[5] R. G. Brown, J. Denning, A. Hallett and S. D. Ross, *Spectrochim. Acta* **26A**, 963 (1970).
[6] M. Nicol and J. F. Durana, *J. Chem. Phys.* **54**, 1436 (1971).
[7] J. Preudhomme and P. Tarte, *Spectrochim. Acta* **28A**, 69 (1972).

proposed by SCOTT [3] and by BROWN *et al.* [5]. One band only (323 cm^{-1}) is free from a ^{92}Mo–^{100}Mo mass effect and thus may be assigned to ν_2 (A_g and/or B_g).

The actual assignments for the bending modes are a bit surprising if they are compared with those arrived at for the i.r. active modes [1]: there is an inversion of the frequencies, with ν_2(i.r.) $> \nu_4$(i.r.), but ν_2(R) $< \nu_4$ (R), or, very roughly: ν_2(i.r.) $\approx \nu_4$(R) and ν_4(i.r.) $\approx \nu_2$(R).

Although unexpected, these assignments are fully supported by those already found for the spinel molybdates Na_2MoO_4 and Ag_2MoO_4 and tungstate Na_2WO_4 [7]: here again, ν_4(R) $> \nu_2$(R) and ν_4 (i.r.) $\approx \nu_2$(R) (Table 3).

Table 3. Opposite behaviour of the ν_2 and ν_4 bending vibrations in Raman and i.r. active modes

	$CaMoO_4$		Na_2MoO_4		Na_2WO_4		Ag_2MoO_4	
	i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.	Raman
ν_4	329 and 284	403 and 392	318	382	309	377	287	353
ν_2	431	323	inact.	304	inact.	313	inact.	277

This shows that the actual behaviour of ν_4 and ν_2 is not a consequence of the MoO_4 deformation in the scheelite structure, since the MoO_4 tetrahedron retains its full T_d symmetry in the spinel structure.

If we now consider the external frequencies, the rotational modes should be completely free from any cationic mass effect (provided they are not significantly mixed up with a translational mode). This is clearly the case of the 205 cm^{-1} band, whose assignment to a rotation was already unequivocal, since there is no translation of A_g symmetry. The next band free from a mass effect (268 cm^{-1}) is assigned to the second, E_g, rotational mode.

All the remaining low-frequency bands* must correspond to translations and are accordingly found to be mass sensitive. In addition, it is possible to distinguish between the translations which are predominantly related to either calcium or molybdenum.

It may be noticed that the 2 lowest-lying frequencies are essentially related to a Mo–Mo translation, and hence to displacements of the heaviest atoms.

The influence of the relative masses is also clearly appearing in the $PbMoO_4$ isotopic data (Table 4): here again, the 2 lowest-lying frequencies correspond predominantly to translations of the heaviest atoms, which are here Pb. This point is further discussed in the next part of this paper.

THE VIBRATIONAL BEHAVIOUR OF SOLID SOLUTIONS AND THE ASSIGNMENT OF THE EXTERNAL MODES

3 types of solid solutions have been investigated and will be discussed in turn: solid solutions resulting from the isomorphic replacement of the cation in either the

* One external mode is missing in the results quoted in Table 2. It has been observed at 219 cm^{-1} by Porto and Scott [2]. This peak is extremely weak in the spectrum of a monocrystal and thus its absence in our powder spectra is not too unexpected.

Table 4. Isotopic data for $PbMoO_4$

$PbMoO_4$	$Pb^{92}MoO_4$	$Pb^{100}MoO_4$	$\Delta\nu$
869	870	869	(−1)
766	770·5	763·5	−7
743	747·5	740·5	−7
~357	broad and weak		?
350	350	349·5	(−0·5)
317	318	318	0
192	~193	~192	(−1)
168	168	168·5	(+0·5)
102·5	104	101·5	−2·5
73	74·5	72·5	−2
66·5	~67	~66·5	(−0·5)
60·5	61	61	0

molybdates or the tungstates; and tungstate–molybdate solid solutions for a given cation.

Isomorphic replacement of the cation in the molybdates

The following solid solutions have been investigated: (Ca, Sr)MoO_4; (Sr, Ba)MoO_4; (Ba, Pb)MoO_4. A general account of the results is given in Fig. 1. In this figure, the

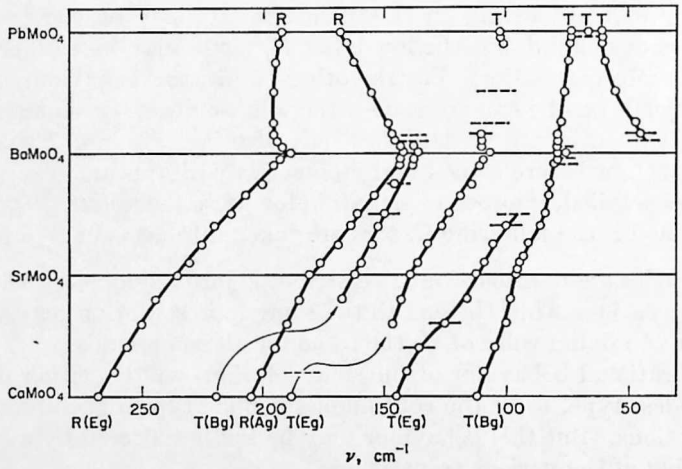

Fig. 1. Raman frequencies for the molybdate solid solutions. Full lines correspond to evident filiations.

assignments to the various symmetry classes for $CaMoO_4$ and $SrMoO_4$ are those given by PORTO and SCOTT [2]; the assignments to rotational and to the various types of translational motions for $CaMoO_4$ are those deduced from our isotopic data (Table 2). It is clear from this figure that 2 different types of vibrational behaviour are observed in the solid solutions: 3 bands only are observed throughout the various solid solutions, where they are displaced continuously, although not always regularly; the 3 others exhibit a much more complicated behaviour, since they seem to disappear or

to be split into 2 components for some types and some ranges of isomorphic substitutions.

Rotational modes. There is little point about the 2 rotational modes. They have been identified in $CaMoO_4$ through the lack of any isotopic mass effect (Table 2), and they are expected to be continuously displaced in the solid solutions. It is worth while to point to the very characteristic behaviour of the A_g rotational mode, whose frequency *increases* when passing from the barium to the lead compound: this reflects the lack of any mass effect, together with a significant decrease of the cation–oxygen distance. Things are not so clear-cut for the other rotational E_g, mode: it is possibly slightly coupled with another E_g translational mode, whereas such a coupling is impossible for the A_g mode, which is the only external mode of its class.

Translational modes. The situation is considerably more complicated here: one band only (the B_g mode observed at 112 cm^{-1} for $CaMoO_4$) can be traced without significant alteration throughout the various solid solutions, where it remains strong and sharp. In the spectrum of $CaMoO_4$, the relatively large ^{92}Mo–^{100}Mo isotopic shift (4 cm^{-1}), and the small, non-significant ^{40}Ca–^{44}Ca shift (0·5 cm^{-1}) show that it must be assigned to a Mo–Mo translation. In the case of $BaMoO_4$ and $PbMoO_4$, isotopic data are missing for the bivalent cation, but this frequency clearly depends on the mass of molybdenum (Table 4). Finally, the vibrational behaviour in the solid solutions (namely the continuous shift of this band, and the very small influence of the nature and of the mass of the bivalent cation) also points to a very reduced influence of the bivalent cation on this vibration. It may be concluded that, for the whole series of molybdates, the low-lying B_g mode may be assigned with confidence to a Mo–Mo translation. For the other bands, the behaviour is apparently erratic and depends on the composition of the solid solution: in some instances, the bands are shifted continuously; but they may also be split into 2 components (2-modes behaviour), or be broadened and momentarily disappear.

We have no detailed, rigorous explanation for these facts, but they may be tentatively explained if the following factors are taken into account:

(1) The 4 modes under discussion are distributed into 2 symmetry classes ($2E_g$ and $2B_g$). The translations which belong to the same representation may be mixed up, but the degree of mixing will not be the same for all compounds.

(2) The vibrational behaviour of the solid solutions will be, either of the discontinuous, 2-modes, type, or of the continuous, 1-mode type, depending on the mass ratio of the cations. But this behaviour may be further altered by a change of the degree of mixing of the various translations.

(3) The detailed isotopic data on $CaMoO_4$ will give a convenient starting basis to the discussion.

In $CaMoO_4$, the 2 high frequency translation modes are assigned to an essentially 'pure' Ca–Ca translation, the 3rd one (145 cm^{-1}) being (essentially) a Mo–Mo translation (the origin of the 4th mode at 112 cm^{-1} has already been discussed and needs no further comment). It should be pointed out that this separation of the translational modes into Ca–Ca and Mo–Mo motions is not imposed by symmetry considerations: indeed, both Ca and Mo atoms should be simultaneously displaced during these translations. Nevertheless, the isotopic data show that, in the case of

$CaMoO_4$, this separation has a *practical* significance. The participation of one type of cation only to a given translational mode is probably related to the large mass ratio of the 2 cations (Ca: 40; Mo: 96), but also to significant differences in the restoring forces, in relation with the different environment of Ca and Mo cations in the crystal (CaO_8 polyhedra have oxygen edges in common, whereas MoO_4 tetrahedra are 'isolated'). This explains, for the (Ca, Sr)MoO_4 solid solutions, the 2-modes behaviour of the high-frequency E_g mode (Sr/Ca mass ratio = 2·19) originating from the cation-cation translation, and the continuous shift of the low-frequency E_g mode (Mo–Mo translation).

Now, the rather different behaviour of the (Sr, Ba)MoO_4 solid solutions is reasonably explained as follows: the Ba/Sr mass ratio (= 1·56) is smaller than the Sr/Ca mass ratio, and this explains the one-mode behaviour of the 2 high frequency translations. Since, in addition, the bivalent cation (Ba) is now heavier than molybdenum, the separation of these modes in cation–cation and Mo–Mo translations is no longer a satisfactory approximation. As a consequence, the low-frequency E_g mode is no longer a 'pure' Mo–Mo translation, but a mixed cation-molybdenum translation, and this would explain its broadening, and non-continuous occurrence in (Sr, Ba)MoO_4 solid solutions.

Finally, the 3 bands under discussion exhibit a rather complicated, non-continuous behaviour in the (Ba, Pb)MoO_4 solid solutions, and it is impossible to propose a reasonable band-to-band correlation. This situation is certainly related to the fairly large Pb/Ba and Pb/Mo mass ratio. But whatever the band correlation, the final assignments for $PbMoO_4$ may be deduced from the ^{92}Mo–^{100}Mo isotopic shifts (Table 4): the lack of an isotopic shift for the 2 low-frequency bands points to a predominantly Pb–Pb translation, the Mo–Mo translations being assigned to the 2 high-frequency bands at 73 and 102·5 cm^{-1}. These assignments should be considered as a first approximation, since it is not certain that the Pb/Mo mass ratio is large enough to ensure a complete (or nearly so) separation of the translational modes into Pb–Pb and Mo–Mo translations. Moreover, the isotopic shifts are too small to be sensitive to a moderate mixing of the translations.

Isomorphic replacement of the cation in the tungstates

The investigation of (Sr, Ba)WO_4 and (Ba, Pb)WO_4 solid solutions gives results (Fig. 2) which are consistent with the previous assignments.

Isotopic data are lacking here, but for $CaWO_4$ and $SrWO_4$, the bands are immediately assigned by comparison with the spectrum of the corresponding molybdates: out of 5 Raman bands, 3 are observed at nearly the same frequency in the corresponding molybdates and tungstates, and should be given the same assignments: in the order of decreasing frequencies, we find the 2 rotational modes (one E_g and one A_g), and a Ca–Ca (or Sr–Sr) translation. The 2 remaining, low-frequency bands are strongly displaced towards lower frequencies in the tungstates and thus are assigned to a W–W translation.

In the solid solutions, the behaviour of the rotational modes is similar in all respects to that already observed for the molybdates: we find an upward shift of the A_g mode in the (Ba, Pb)WO_4 solid solutions.

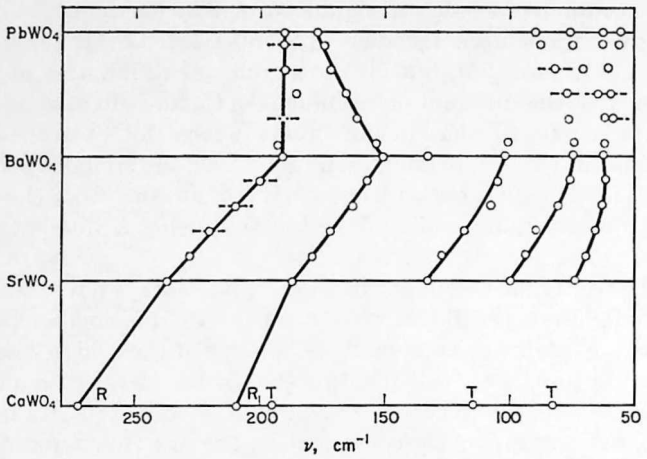

Fig. 2. Raman frequencies and correlations for the tungstate solid solutions.

Some differences, however, are observed for the translational modes: in (Sr, Ba)WO_4 solid solutions, the frequency changes remain of the continuous type, against some discontinuous changes in (Sr, Ba)MoO_4 solid solutions. In this latter case, the non-continuous type of some modes was assigned to the mixing of Mo and Ba translations, as a consequence of the similarity of the masses of molybdenum and barium. Since tungsten is much heavier than either strontium or barium, there is no mixing of the translations, which remain essentially pure cation-cation, or W–W motions. As a consequence, the translational frequencies remain of the continuous type in the (Sr, Ba)WO_4 solid solutions. Finally, the situation is again rather complicated for the $(Ba_{1-x}Pb_x)WO_4$ solid solutions, and there is no evident correlation between the spectra as a function of x. Two factors are probably responsible for this situation: (1) the large Pb/Ba mass ratio, which brings out a 2-modes behaviour, at least for some translations; and (2), the great similarity between the masses of lead and tungsten: the translational modes should involve a simultaneous displacement of both atoms (against nearly pure cation-cation and W–W motions in the Ca, Sr and even Ba tungstates). Unfortunately, we have no independent means to check this point.

The molybdate-tungstate solid solutions

All the previous assignments are again supported by the vibrational behaviour of molybdate-tungstate solid solutions (Fig. 3). We find:

(1) a continuous, very small shift for the rotational modes;

(2) in the Ca(Mo, W)O_4 and Sr(Mo, W)O_4 solid solutions, a continuous shift for the bands previously assigned to the Ca–Ca or Sr–Sr translations, but an evident 2-modes behaviour for the bands previously assigned to the Mo–Mo or W–W translations;

(3) in Ba(Mo, W)O_4 and Pb(Mo, W)O_4 solid solutions, a various, non simple behaviour of the low-frequency bands. This is not unexpected since some at least of these bands have been assigned to a mixed translation of both bivalent and hexavalent cations.

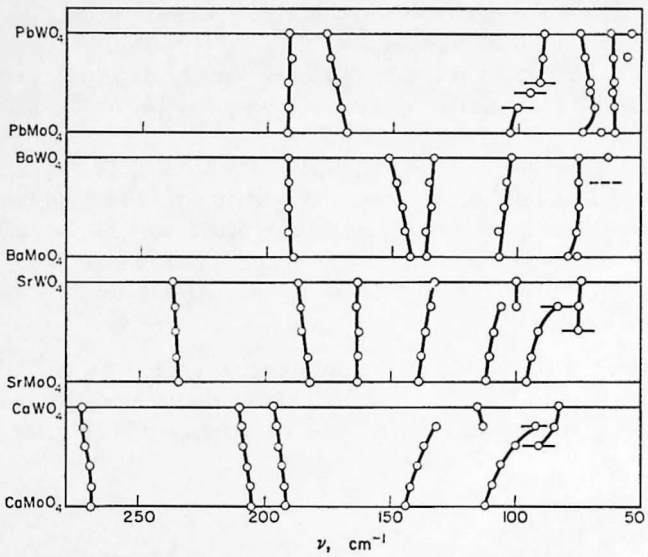

Fig. 3. Raman frequencies of molybdate–tungstate solid solutions.

Final Assignments and Discussion

The final assignments deduced from all available experimental data are collected in Table 5. The following points should be noticed:

Table 5. General assignments

	$CaMoO_4$	$CaWO_4$	$SrMoO_4$	$SrWO_4$	$BaMoO_4$	$BaWO_4$	$PbMoO_4$	$PbWO_4$
Internal modes								
ν_1 (A_g)	879	910	887	919	891	922	869	902
ν_3 (B_g)	848	836	845	836	838	831	766	764
ν_3 (E_g)	794·5	795	796	797	792	791	743	750
ν_4 (E_g)	403·5		382		360	353	357	
ν_4 (B_g)	392	399	367	370	346	346	350	356
ν_2	323·5	331	327	335	325	333	317	327
Rotational modes								
E_g	~269	273	234	237	189	~191	192	190·5
A_g	205	210	182	187	143	151	168	176
Translational modes								
X^{II}/X^{II}	219		163		* 136	~133	67	54·5
	191·5	196	139	133	107	102	61	62·5
Mo/Mo or	145	115	112	100	76	75	102·5	89·5
W/W	112	83	96	74	79	63	73	75

* The discrimination between X^{II}/X^{II} and Mo/Mo (or W/W) translations is significant only for the Ca and Sr compounds. It is doubtful for some modes of the Ba and Pb compounds, and certainly non-significant for $PbWO_4$ (see text).

Internal modes

The relationship between the frequency and the nature of the bivalent cation strongly depends on the mode under consideration; in the series Ca–Sr–Ba, we find an *increase* of the ν_1 frequency; a small, non systematic, variation for ν_2 and also for the E_g component of ν_3; a very small decrease for the B_g component of ν_3; a

rather significant frequency decrease for the 2 components of ν_4. These relations cannot be extended to the lead compounds.

Clearly, there is no simple relationship between the internal frequencies and either the ionic radius of the cation, or its electronegativity, or the unit cell parameters.

For tungstates of the scheelite type (Ca, Sr, Ba, but not Pb), Scott [3] has proposed an apparently interesting relation between the splitting of the vibrational levels, and dipole–dipole interactions between adjacent tungstate ions. This relation was used to predict band assignments for $ZnWO_4$, which was assumed to be structurally related to the scheelite. The validity of this relation seems actually very doubtful, for at least 2 major reasons:

(1) The data related to the lead compounds (either $PbMoO_4$ or $PbWO_4$) do not fit this relation: especially for the B_g and E_g components of ν_3, the points fall well outside the relation given by the Ca, Sr and Ba compounds (Fig. 4). It has been

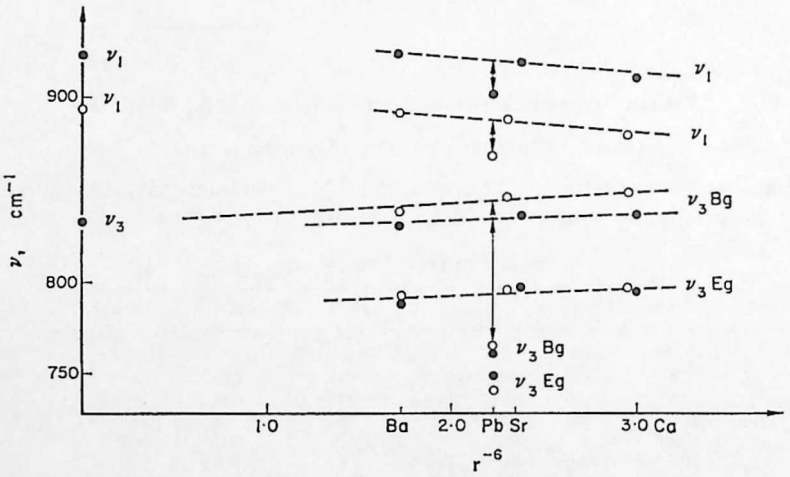

Fig. 4. Relation between the MoO_4 (open circles) or WO_4 (black circles) stretching frequencies for Ca, Sr, Ba and Pb scheelites, and the Mo–Mo or W–W distance (expressed as r^{-6} in cm^{-6} units). The left-hand values correspond to the 'free' ion in solution. The figure shows (1) the fairly large discrepancies for the lead compounds ($PbWO_4$ and $PbMoO_4$) and (2) the lack of convergence of the split ν_3 frequencies towards the unsplit level in solution.

suggested by Scott [3] that, for $PbWO_4$, the discrepancy is due to vibrational perturbations in relation with the mass similarity of Pb and W. This explanation is clearly meaningless if we consider the perfect similarity existing between the tungstates and the molybdates. If a mass similarity effect was into play, $PbMoO_4$ should exhibit a normal behaviour, but anomalies should be found for either $SrMoO_4$ or $BaMoO_4$. Since an abnormal behaviour is found for both $PbMoO_4$ and $PbWO_4$, and not for Sr or $BaMoO_4$, Scott's explanation is definitely ruled out.

(2) The extension of the relation to $ZnWO_4$ is most probably non-significant: such an extension would at least imply that the $ZnWO_4$ structure should be derived from the scheelite structure by some kind of a lattice distortion. But all recent structural and spectroscopic data on $ZnWO_4$ point to an *octahedral* co-ordination of tungsten in this compound. This co-ordination has been inferred from crystal structure determination for the tungstates of Mg [8], Ni and Zn [9], and Fe [10]; in this latter case, accurate values of the oxygen parameter were derived from neutron diffraction data. Likewise, i.r., Raman and X-ray powder diffraction work carried out in this laboratory strongly suggests that the tungstates $X^{II}WO_4$ with X^{II} = Mg, Ni, Fe, Mn, Zn and Cd are, either isomorphic, or at least very closely related from a structural point of view.

Thus, according to the wealth of information actually available, it may be considered with confidence that the co-ordination of tungsten is octahedral in $ZnWO_4$; this structure has really nothing to do with the scheelite structure, and any correlation between their spectra is meaningless. Finally, in SCOTT's Fig. 2 [3], the convergence of the split vibrational levels (in crystals) towards the unsplit levels corresponding to the free ion (in solution) is not convincing: the slope of some straight lines does not fit the regular trend observed for Ca, Sr and Ba compounds, and has been clearly chosen to include the points related to $ZnWO_4$. If the straight line is traced through the consistent values related to the Ca, Sr and Ba compounds, the convergence between the B_g and E_g components of the ν_3 mode is hardly detectable (Fig. 4). Thus, although attractive, the interaction model proposed by Scott does not fit the experimental results sufficiently well to be considered as realistic.

In our opinion, the relation between the nature of the bivalent cation and the values of the internal frequencies depends on factors which are too numerous to be properly handled within a single relationship. The peculiar behaviour of the lead compounds is most probably related to the different electronic structure and to the increased electronegativity of lead: the electron density on oxygen is certainly less in a Pb—O bond than in Ca—, Sr— or Ba—O bonds, and this must have an influence on the electron density along Mo—O or W—O bonds, and hence on the bonding force. But the relationship is certainly not a simple one and depends on the vibrational mode under consideration. We may consider, as an example, the relationship between the stretching frequencies of the anion and the second ionization potential of the cation (Fig. 5): we find a nearly linear relationship (*including the lead compounds*) for the totally symmetric mode ν_1: the frequency decreases with increasing values of the second ionization potential, and this result is consistent with an increased electron-withdrawing from the Mo—O (or W—O) bond to the cation–oxygen bond with increasing values of the cation ionization potential. But this apparently coherent explanation appears as completely wrong for the antisym-

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[8] O. S. FILIPENKO, E. A. POBEDIMSKAYA, V. I. PONOMAREV and N. V. BELOV, *Kristallografiya* **13**, 1073 (1968).
[9] R. O. KEELING, *Acta Cryst.* **10**, 209 (1957).
[10] D. ULKU, *Z. Krist.* **124**, 192 (1967).

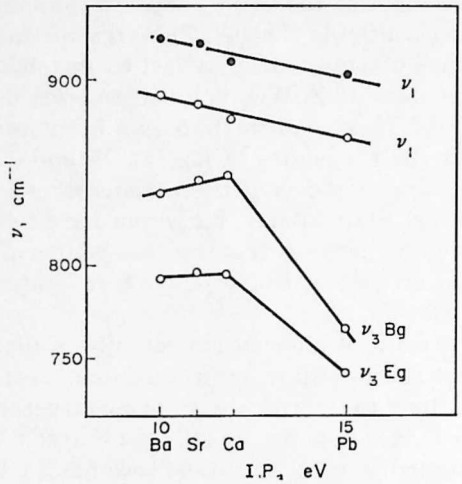

Fig. 5. Relation between the MoO_4 (open circles) or WO_4 (black circles) stretching frequencies of Ca, Sr, Ba and Pb scheelites, and the second ionization potential of the cation.

metric modes ν_3: the slope of the relationship for Ca, Sr and Ba compounds is reversed, with increasing frequencies for increasing values of the ionization potential; and the points related to the lead compounds are erratic.

Rotational modes

The very characteristic behaviour of the A_g rotational mode has already been mentioned: we find a linear relationship between its frequency and the ionic radius of the cation (Fig. 6). For the rotational E_g mode, the frequencies related to the lead compounds are well below the values expected from the ionic radius; this is most probably the consequence of a mass effect, resulting from a coupling with an E_g translational mode.

Translational modes

Whenever possible, the translational modes have been assigned to definite cation–cation, or Mo–Mo(W–W) motions, but this is clearly an approximation, which may be satisfactory, fairly rough, or even bad, depending on the relative masses of both types of cations.

This approximation is the best for the calcium compounds, in view of the large mass ratio of the bivalent and the hexavalent cations, and this is supported by our isotopic data; the resulting assignments are opposite to those presented by KHANNA *et al.*[4] On the contrary, the case of $PbWO_4$ is a particularly difficult one, with very similar masses of both atoms, and 4 fundamental frequencies within a 40 cm^{-1} spectral region: no definite assignment or correlation may be actually proposed. KHANNA *et al.* [4] give polarization data for this compound, but some of their

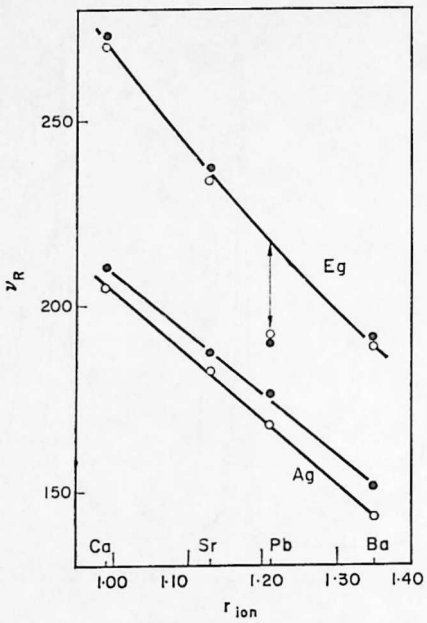

Fig. 6. Relation between the rotational frequencies and the ionic radius of the cation (Pauling scale) for the A_g and E_g modes.
Open circles: molybdates; black circles: tungstates.

experimental results are not convincing, and we feel that these polarization data should be checked before definite assignments could be made.

The Behaviour of the Internal Modes in the Solid Solutions

This behaviour has not been fully investigated so far, but it is worth while to mention some aspects of the actual results.

(Ca, Sr)MoO_4 *and* (Sr, Ba)MoO_4 *solid solutions.* The bands related to the MoO_4 internal modes are continuously shifted in the spectra of these solid solutions. Most of them are not significantly broadened; but there is a very noticeable exception, namely the totally symmetric stretch $\nu_1(A_g)$: this band is very sharp in the spectra of the pure compounds, but suffers an unexpectedly important broadening (by a factor of 5 or more) in the solid solutions of intermediate composition. This broadening appears for this mode only (Fig. 7), and we have no explanation for this peculiar behaviour being restricted to the A_g stretching mode.

(Ba, Pb)MoO_4 *and* (Ba, Pb)WO_4 *solid solutions.* Here again, we find an important broadening of ν_1 for the intermediate compositions; in addition, the band is slightly but decidedly asymmetric. But the most important difference with respect to the (Ca, Sr) and (Sr, Ba)MoO_4 solid solutions is the behaviour of the 2 components of the ν_3 mode: the B_g component exhibits a 2-modes behaviour, at least for the 50/50 composition; and the degenerate E_g component behaves in a very complicated manner, with shoulders appearing on a very broadened absorption band: this is probably resulting from the simultaneous influence of 3 factors,

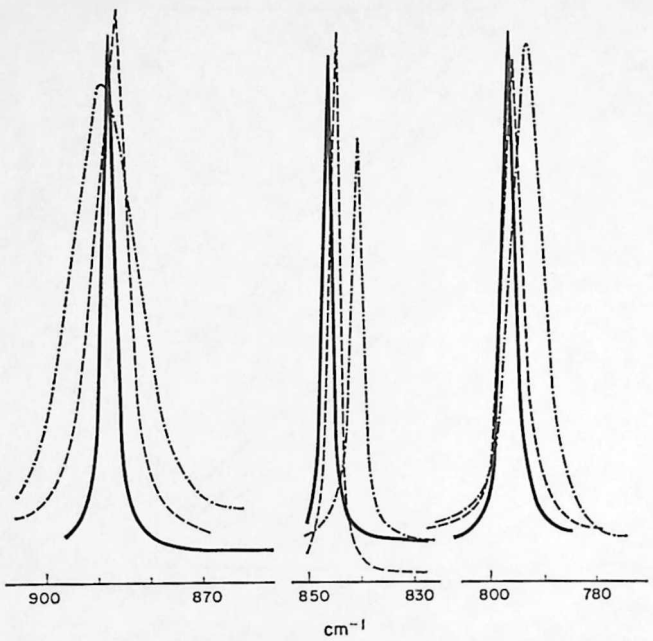

Fig. 7. Band width of ν_1, $\nu_3(B_g)$ and $\nu_3(E_g)$ for $(Sr_{1-x}Ba_x)MoO_4$ solid solutions.
————— $x = 0$, – – – – – $x = 0{\cdot}1$, –·–·–·–·– $x = 0{\cdot}4$.
The spectral slit width is 2 cm^{-1} for all spectra.

namely a 2-modes behaviour, the suppression of the degeneracy and some broadening of the bands.

Such results cannot be explained by the difference in the ionic radii of Ba and Pb, since this difference is greater for the (Sr, Ba) system; thus, they should be ascribed to the difference in the electronic structure of the 2 cations and to the resulting large difference between the ν_3 frequencies of the pure compounds $BaMoO_4$ and $PbMoO_4$.

Molybdate–tungstate solid solutions. So far, detailed spectra have been obtained for the $Ca(Mo, W)O_4$ solid solutions only. Since most of the internal frequencies of the corresponding tungstate and molybdate are nearly the same, we find a continuous frequency shift for the solid solutions. However, the A_g totally symmetric stretch ν_1 offers a very noticeable exception, with a full 2-modes behaviour, and a frequency *increase* for *each* tetrahedral group (either MoO_4 or WO_4) with the decrease of its amount in the solid solution (Fig. 8). This unexpected result cannot be related to a simple unit cell dimension effect: in this case, we should find a small increase of the frequency for the molybdate, but a small frequency decrease for the tungstate, since the unit cell volume is slightly larger for the molybdate than for the tungstate.

The vibrational behaviour of ν_1 is roughly the same (2-modes behaviour) for $Pb(Mo, W)O_4$ solid solutions, but the frequency variation is very small for WO_4 (maximum shift: 3 cm^{-1}) and negligible for MoO_4.

The observed shifts are possibly in relation with the importance of the MoO_4–MoO_4

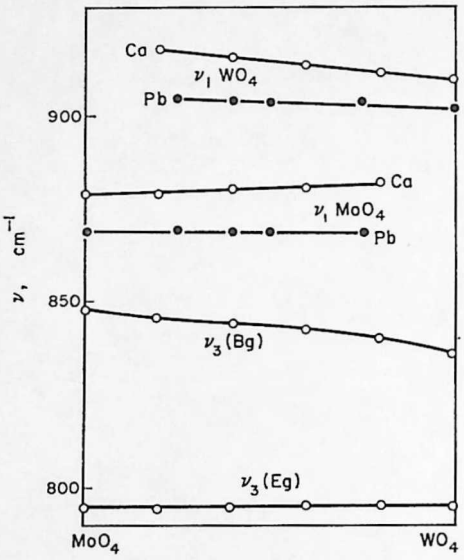

Fig. 8. Stretching frequencies of MoO_4 and WO_4 ions in Ca(Mo, W)O_4 (open circles) and Pb(Mo, W)O_4 (black circles) solid solutions.

or WO_4–WO_4 vibrational interactions, but further work will be necessary to check this point. A similar vibrational behaviour has been observed for other, non-scheelite, molybdate–tungstate solid solutions.

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