

## Far Infrared Spectra of Hexachalcogenohypodiphosphates

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The far infrared (fir) reflection spectra of the hexachalcogenohypodiphosphates  $M_2P_2X_6$  ( $M = \text{Mg, Cd, Mn, Fe, Co, Ni, Pb, Sn; } X = \text{S, Se}$ ) have been studied. TO/LO splittings are determined from Kramers-Kronig analyses, the splitting is large for the lattice vibration modes of ferroelectric  $\text{Sn}_2\text{P}_2\text{S}_6$  but very small for  $\text{Ni}_2\text{P}_2\text{S}_6$ . Measurements with polarized light permit an assignment of the  $A_{2u}$  and  $E_u$  modes of the ethane like  $\text{P}_2\text{S}_6$  units in  $\text{Mn}_2\text{P}_2\text{S}_6$ . Factor group analyses were performed for all hitherto described hexachalcogenohypodiphosphates. The fir absorption spectra of the less symmetric compounds  $\text{Hg}_2\text{P}_2\text{S}_6$ ,  $\text{Hg}_2\text{P}_2\text{Se}_6$ ,  $\text{Ca}_2\text{P}_2\text{S}_6$ ,  $\text{TiP}_2\text{S}_6$ ,  $\text{In}_{4/3}\text{P}_2\text{S}_6$ ,  $\text{In}_{4/3}\text{P}_2\text{Se}_6$ , and  $\text{CuCrP}_2\text{S}_6$  are given.

### 1. Introduction

Most of the hitherto known hexachalcogenohypodiphosphates  $M_2P_2X_6$  ( $M = \text{Mg, Ca, Zn, Cd, Hg, In}_{2/3}, \text{Sn, Pb, V, Cr, Mn, Fe, Co, Ni; } X = \text{S, Se; TiP}_2\text{S}_6$ ) were first prepared and characterized by Hahn and co-workers a decade ago (1, 2).

In this class of compounds a number of interesting chemical and physical properties recently were observed, e.g., the intercalation of lithium in the layered compound  $\text{Ni}_2\text{P}_2\text{S}_6$  (3), antiferromagnetic ordering in, e.g.,  $\text{Mn}_2\text{P}_2\text{S}_6$  or  $\text{Mn}_2\text{P}_2\text{Se}_6$  (4), photoelectrochemical response of  $\text{In}_{4/3}\text{P}_2\text{Se}_6$  (5), or the ferroelectric properties of  $\text{Sn}_2\text{P}_2\text{S}_6$  (6).

Here we want to report on the far infrared (fir) spectra of some hexachalcogenohypodiphosphates, especially on the fir reflection spectra, because only few such data are available from the literature: Audiere *et al.* (7) and Mathey *et al.* (8) give the fir absorption spectra of  $\text{Cd}_2\text{P}_2\text{S}_6$ ,  $\text{Zn}_2\text{P}_2\text{S}_6$ ,  $\text{Mn}_2\text{P}_2\text{S}_6$ , and  $\text{Mn}_2\text{P}_2\text{Se}_6$ ; Mercier *et al.* (9)

investigated the vibration spectrum of  $\text{Li}_4\text{P}_2\text{S}_6$ ; Bürger and Falius (10, 11) calculated force constants for the ethane like  $\text{P}_2\text{S}_6$  unit in  $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ ; Gurzan *et al.* (12) recorded the fir absorption spectrum of  $\text{Sn}_2\text{P}_2\text{S}_6$  at ambient temperatures.

### 2. Experimental

The hexachalcogenohypodiphosphates studied in this work were prepared by reacting stoichiometric mixtures of the pure elements (or the binary chalcogenides  $\text{MgS, CaS, ZnS, HgS, HgSe}$ ) in evacuated quartz tubes as described in the literature (1, 2, 13-17). In some cases single crystals in the form of yellow needles ( $\text{Hg}_2\text{P}_2\text{S}_6$ ), yellow-brown polyhedra ( $\text{Sn}_2\text{P}_2\text{S}_6$ ,  $\text{Pb}_2\text{P}_2\text{S}_6$ ), or thin plates (e.g., green  $\text{Mn}_2\text{P}_2\text{S}_6$  or black  $\text{Fe}_2\text{P}_2\text{S}_6$  and  $\text{Ni}_2\text{P}_2\text{S}_6$ ) were obtained by chlorine or iodine vapor transport. The samples were characterized by X-ray methods using a Huber-Guinier camera and  $\text{CuK}\alpha_1$  radiation.

The ir absorption spectra were recorded in the range from 4000 to 180  $\text{cm}^{-1}$  with a Perkin–Elmer model 580 grating spectrometer using CsI disks and in the range from 700 to 40  $\text{cm}^{-1}$  with a Bruker model IFS 114 Fourier spectrometer using Nujol mulls. Reflection spectra at near normal incidence were obtained from either single crystals or pellets pressed from polycrystalline samples.

A wire grid polarizer was used to separate the  $\mathbf{E} \perp \mathbf{c}'$  and  $\mathbf{E} \parallel \mathbf{c}'$  modes for studying a sample of layered  $\text{Mn}_2\text{P}_2\text{S}_6$  which was pressed to a 3-mm-thick pellet at 500°C under a pressure of  $10^8$  Pa in a piston–cylinder apparatus made of graphite.

Kramers–Kronig analyses of the reflection spectra were performed using the procedure described previously (18) in order to obtain the frequency dependence of the dielectric ( $\hat{\epsilon} = \epsilon' + i\epsilon''$ ) and optical ( $\hat{n} = n + ik$ ) constants. The transverse and longitudinal optical (TO and LO) phonon frequencies were determined from the positions of the maxima of the  $\text{Im}(\hat{\epsilon})$  and  $\text{Im}(-1/\hat{\epsilon})$  curves, respectively (19). The latter curve is denoted as  $\epsilon^*$  in the figures presented here.

### 3. Results and Discussion

#### (a) $\text{Fe}_2\text{P}_2\text{S}_6$ - and $\text{Fe}_2\text{P}_2\text{Se}_6$ -type Compounds

The crystal structures of the layered compounds  $\text{Fe}_2\text{P}_2\text{S}_6$  and  $\text{Fe}_2\text{P}_2\text{Se}_6$  are related to the  $\text{CdCl}_2$  and  $\text{CdI}_2$  structures, respectively. The metal atoms and  $\text{P}_2$  pairs occupy the octahedral sites of the slightly distorted cubic or hexagonal close packed arrangement of the chalcogen atoms. The P–P– bond of the resulting  $\text{P}_2\text{X}_6$  ( $X = \text{S}, \text{Se}$ ) units is parallel with the  $\mathbf{a} \times \mathbf{b}$  axis of the monoclinic  $\text{Fe}_2\text{P}_2\text{S}_6$  ( $C2/m$ ) and hexagonal  $\text{Fe}_2\text{P}_2\text{Se}_6$  ( $R3$ ). No significant differences of the P–X distances occur in the ethane like  $\text{P}_2\text{X}_6$  units (2).

Factor group analysis predicts

$$\Gamma_{\text{Fe}_2\text{P}_2\text{S}_6} = 6A_g + 9B_g + 7A_u + 5B_u$$

R            R            IR            IR

(space group:  $C2/m$ ; number of formulae units:  $Z = 2$ ; factor group:  $C_{2h}$ ; Ref. (2))

$$\Gamma_{\text{Fe}_2\text{P}_2\text{Se}_6} = 9A + 9E$$

R, IR        R, IR

( $R3$ ;  $Z = 3$ ;  $C_3$ ; (2))

i.e., a total of 12 and 18 infrared allowed modes (wavevector  $|\mathbf{q}| = 0$ ) for  $\text{Fe}_2\text{P}_2\text{S}_6$  and  $\text{Fe}_2\text{P}_2\text{Se}_6$ , respectively.

Figure 1 shows the fir reflection spectra of  $\text{Mn}_2\text{P}_2\text{S}_6$ ,  $\text{Fe}_2\text{P}_2\text{S}_6$ ,  $\text{Co}_2\text{P}_2\text{S}_6$ ,  $\text{Ni}_2\text{P}_2\text{S}_6$ ,  $\text{Mg}_2\text{P}_2\text{Se}_6$ ,  $\text{Mn}_2\text{P}_2\text{Se}_6$ ,  $\text{Fe}_2\text{P}_2\text{Se}_6$ , and  $\text{Ni}_2\text{P}_2\text{Se}_6$  which were obtained from pellets pressed from polycrystalline samples. The TO and LO frequencies of the main modes determined from Kramers–Kronig analyses are given in Table I.

The fir reflectivity of  $\text{Co}_2\text{P}_2\text{S}_6$  is low because no compact pellet was obtained from this material and surface defects prevent the formation of strong reststrahlen maxima. No Kramers–Kronig analysis was performed. Nevertheless one can conclude from the relatively high value of the high-frequency reflectivity that the high-frequency dielectric constant  $\epsilon_\infty$ , and therefore the electronic polarizability of  $\text{Co}_2\text{P}_2\text{S}_6$ , is also rather high. On the other hand, the frequency of the external lattice mode is relatively low, compared to, e.g.,  $\text{Fe}_2\text{P}_2\text{S}_6$  or  $\text{Ni}_2\text{P}_2\text{S}_6$ .  $\text{Co}_2\text{P}_2\text{S}_6$  was not so easy to prepare as compared to the other hexathiohypodiphosphates studied in this work because of its decomposition into CoPS and S at elevated temperatures. Further, all attempts to prepare  $\text{Co}_2\text{P}_2\text{Se}_6$  resulted in CoPSe and Se.

To demonstrate the typical behavior of the optical and dielectric constants of  $\text{Fe}_2\text{P}_2\text{S}_6$  and  $\text{Fe}_2\text{P}_2\text{Se}_6$  type compounds we give in Fig. 2 the results of Kramers–

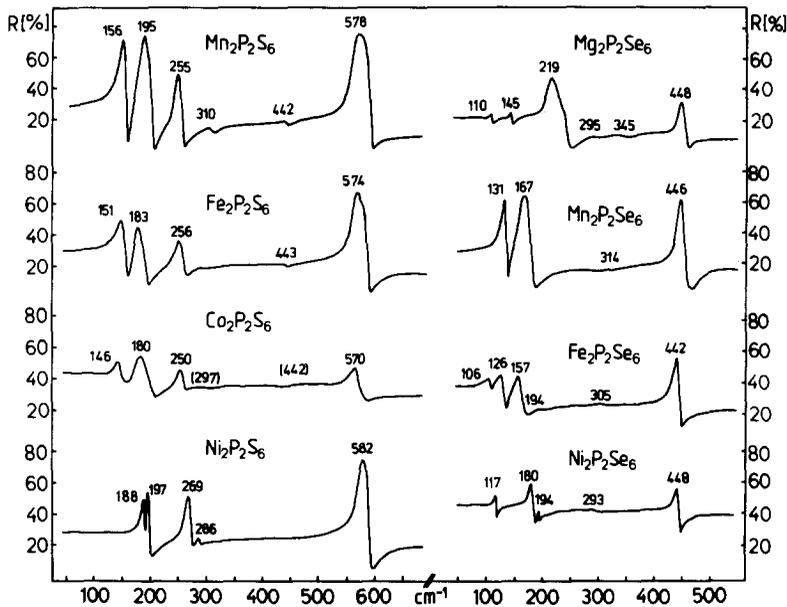


FIG. 1. Fir reflection spectra of layered hexachalcogenohypodiphosphates (pressed pellets, Bruker IFS 114).

Kronig analyses performed on  $\text{Cd}_2\text{P}_2\text{S}_6$  and  $\text{Cd}_2\text{P}_2\text{Se}_6$ .

From Figs. 1 and 2 it is seen that only a small amount of the infrared allowed modes can be observed in the spectra. The reststrahlen bands of  $\text{Cd}_2\text{P}_2\text{S}_6$ ,  $\text{Mn}_2\text{P}_2\text{S}_6$ , and  $\text{Mn}_2\text{P}_2\text{Se}_6$  correspond to the already known

ir-absorption data of Mathey *et al.* (8). Only one of the strong reststrahlen bands is sensitive to the metal atom. Splitting of these modes, as found by Mathey *et al.* in the absorption spectra, was not observed in the reflection spectra.

The frequencies of the other modes re-

TABLE I

TO AND LO PHONON FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE MAIN INFRARED REFLECTION MODES OF HEXACHALCOGENOHYPODIPHOSPHATES (KRAMERS-KRONIG ANALYSES) (THE COLUMN  $\Delta$  CORRESPONDS TO THE TO/LO SPLITTING OF THE METAL SENSITIVE MODE (FIRST TO/LO COLUMN))

	TO	LO	$\Delta$	TO	LO	TO	LO	TO	LO	TO	LO	TO	LO
$\text{Cd}_2\text{P}_2\text{S}_6$	109	133	24	194	203	254	258			567		593	
$\text{Mn}_2\text{P}_2\text{S}_6$	152	164	12	188	210	252	264			574		600	
$\text{Fe}_2\text{P}_2\text{S}_6$	151	163	12	183	199	257	266			572		595	
$\text{Ni}_2\text{P}_2\text{S}_6$	190	192	2	196	203	269	278	287	289	577		593	
$\text{Mg}_2\text{P}_2\text{Se}_6$	215	245	30	109	111	144	146			449		459	
$\text{Cd}_2\text{P}_2\text{Se}_6$	85	97	12	109	117	153	161			437		449	
$\text{Mn}_2\text{P}_2\text{Se}_6$	130	136	6			158	182			444		456	
$\text{Fe}_2\text{P}_2\text{Se}_6$	125	132	7	107	109	157	166			441		449	
$\text{Ni}_2\text{P}_2\text{Se}_6$			1(?)	117	118	181	186	195	196	442		448	
$\text{Sn}_2\text{P}_2\text{S}_6$	71	137	66	217	225	247	253	277	285	439	441	555, 571, 581	555, 573, 591 <sup>a</sup>
$\text{Pb}_2\text{P}_2\text{S}_6$	64	114, 136 <sup>a</sup>	$\approx 50$	224	228	242	246	276	286	438	440	568, 582	576, 590 <sup>a</sup>
$\text{Sn}_2\text{P}_2\text{Se}_6$	46, 60	56, 104 <sup>a</sup>	44	128	134	174	178			288	290	436, 444	454 <sup>a</sup>
$\text{Pb}_2\text{P}_2\text{Se}_6$	53	88	35	131	142	175	180			289	290	445	456

<sup>a</sup> Unresolved modes. No exact TO/LO splitting can be determined.

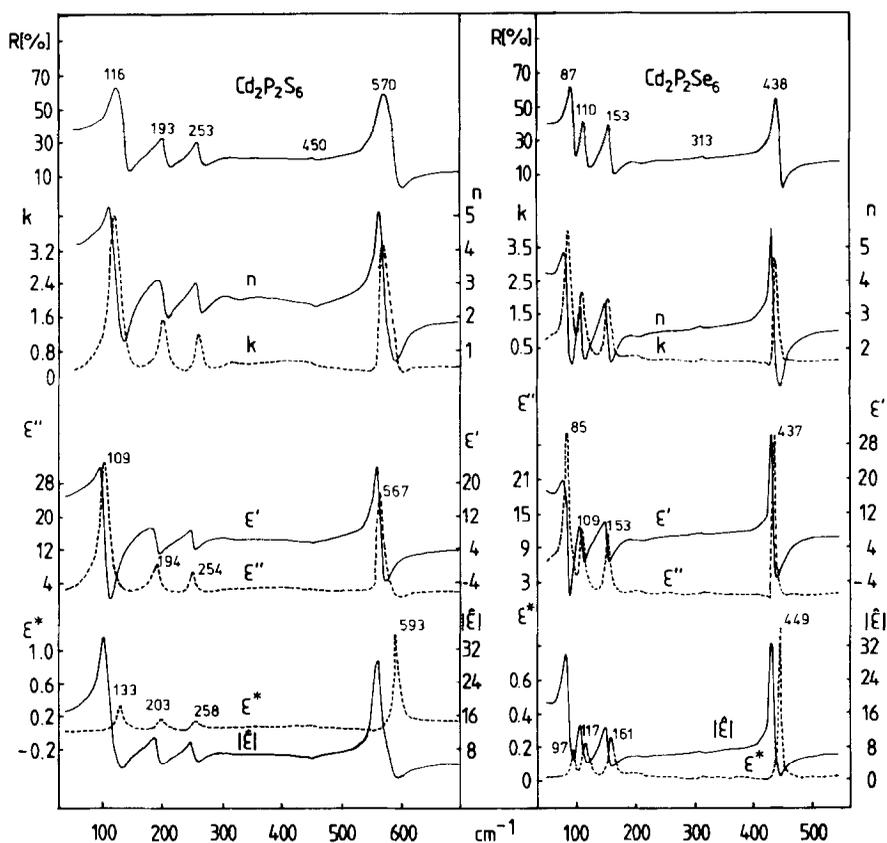


FIG. 2. Fir reflection spectra (pressed pellets, Bruker IFS 114) and optical and dielectric constants (Kramers-Kronig analyses) of  $\text{Cd}_2\text{P}_2\text{S}_6$  and  $\text{Cd}_2\text{P}_2\text{Se}_6$ .

main nearly constant by metal substitution. Mathey *et al.* discussed these modes in terms of the internal modes of  $\text{PS}_3$  units ( $C_{3v}$  symmetry) and assumed  $E$  symmetry for the 572 ( $\nu_d(\text{PS}_3)$ )-, 255 ( $T'_{xy}(\text{PS}_3)$ )-, and 194 ( $T'_{xy}(\text{PS}_3)$ )- $\text{cm}^{-1}$  modes and  $A_1$  symmetry for the 450 ( $T'_z(\text{PS}_3)$ )- and 316 ( $\delta_s(\text{PS}_3)$ )- $\text{cm}^{-1}$  modes (wavenumbers for  $\text{Mn}_2\text{P}_2\text{S}_6$ , absorption maxima, corresponding to the reststrahlen maxima at 578, 255, 195, 442, and 310  $\text{cm}^{-1}$ ). Contrary to Mathey *et al.* but in accordance with Bürger and Falus (10) and recent Raman investigations (20) we presume these modes to be the internal modes of  $\text{P}_2\text{S}_6$  units. Because of the ethane-like configuration of  $\text{P}_2\text{S}_6$  five infrared ac-

tive internal modes of species  $A_{2u}$  and  $E_u$  are expected ( $\Gamma_{\text{P}_2\text{S}_6} = 3A_{1g} + 3E_g + 2A_{2u} + 3E_u$ , point group  $D_{3d}$ ).

Fir reflection spectra of single crystal faces of  $\text{Mn}_2\text{P}_2\text{S}_6$  are restricted to the polarization  $\mathbf{E} \perp \mathbf{c}'$  because of the lamellar sample shape; the modes at 443 and 310  $\text{cm}^{-1}$  disappear (Fig. 3). These modes can be studied with light polarized  $\mathbf{E} \parallel \mathbf{c}'$ , but this approach is impossible because the single crystal plates are extremely thin. An approximate measurement with  $\mathbf{E} \approx \parallel \mathbf{c}'$  was possible after hot-pressing  $\text{Mn}_2\text{P}_2\text{S}_6$  and cutting the pellet in a direction parallel to the applied pressure. By means of pressing the layered sample one obtains a preferen-

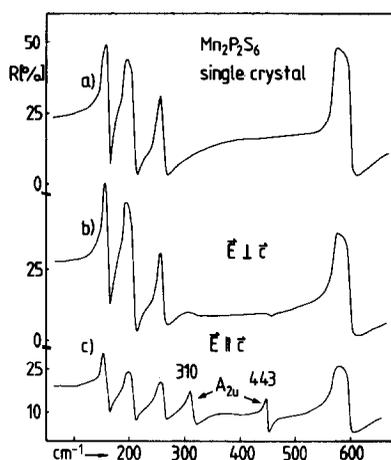


FIG. 3. FIR reflection spectra of  $\text{Mn}_2\text{P}_2\text{S}_6$ . (a) Single crystal, unpolarized light. (b) and (c) Same sample face of a hot-pressed pellet, cutted parallel to the applied pressure; polarized light (Bruker IFS 114).

tial (but not complete!) orientation of the  $001'$  plane perpendicular to the applied pressure.

Figure 3 shows that the 443- and 310- $\text{cm}^{-1}$  modes gain on relative intensity in the  $\mathbf{E} \parallel \mathbf{c}'$  spectrum, compared with the  $\mathbf{E} \perp \mathbf{c}'$  spectrum of the same surface. So the symmetry  $A_{2u}$  is evident for these two modes.

The frequency shift and the TO/LO splitting, i.e., the difference of corresponding TO and LO phonon frequencies, see Table I, of the metal sensitive intense mode deserves further attention. Differences in the frequencies of the metal sensitive modes can be explained in terms of an average optical mode frequency  $\bar{\nu} = [(1/3)(2 \text{TO}^2 + \text{LO}^2)]^{1/2}$ , (21). The ratios of the  $\bar{\nu}$  of the thio and seleno compounds are close to the square roots of the ratios of the corresponding reduced masses  $M\text{-S}(\text{Se})$ :  $\text{Cd}_2\text{P}_2\text{S}_6/\text{Cd}_2\text{P}_2\text{Se}_6$ : ratio of  $\bar{\nu}$ :  $117.5/89.18 = 1.32$ ; ratio of reduced masses:  $(\mu(\text{Cd}-\text{Se})/\mu(\text{Cd}-\text{S}))^{1/2} = 1.36$ ,  $\text{Fe}_2\text{P}_2\text{S}_6/\text{Fe}_2\text{P}_2\text{Se}_6$ : 1.22; 1.27,  $\text{Mn}_2\text{P}_2\text{S}_6/\text{Mn}_2\text{P}_2\text{Se}_6$ : 1.18; 1.26. The TO/LO splitting of the compounds, which is proportional to the ionicities, increases in the order  $\text{Ni} < \text{Fe} \approx \text{Mn} < \text{Cd}$ .  $\text{Ni}_2\text{P}_2\text{S}_6$ , the compound which is most

proper to lithium intercalation, is the most covalent thio compound and therefore just in this case delocalization of an additional electron can occur most easily.

The FIR spectra of the selenium compounds  $\text{Fe}_2\text{P}_2\text{Se}_6$  and  $\text{Cd}_2\text{P}_2\text{Se}_6$  are very similar to the spectra of the corresponding thio compounds. On the other hand, in  $\text{Mn}_2\text{P}_2\text{Se}_6$  and  $\text{Ni}_2\text{P}_2\text{Se}_6$  a strong reflection mode is lost what may be caused by an accidental degeneracy.  $\text{Mg}_2\text{P}_2\text{Se}_6$  surely is the most ionic of this series of compounds because of the magnitude of its TO/LO splitting. The frequency of the metal sensitive mode lies above the two lowest wavenumbered internal modes due to the small mass of magnesium. But in general the TO/LO splittings of the selenium compounds are smaller than those of the corresponding thio compounds and the high frequency dielectric constants, i.e., the electronic polarizabilities, are higher.

The vibration frequencies of the selenium compounds are shifted to lower wavenumbers compared to those of the thio compounds. Mathey *et al.* found a frequency ratio of  $\nu_d(\text{PS}_3)/\nu_d(\text{PSe}_3) = 1.29$  for  $\text{Mn}_2\text{P}_2\text{S}_6/\text{Mn}_2\text{P}_2\text{Se}_6$  and concluded a participation of phosphorus in this antisymmetric stretching mode (8).

A more detailed investigation of frequency shifts by metal or nonmetal atom substitution is possible by studying mixed crystals. We investigated the system  $\text{Ni}_2\text{P}_2\text{S}_6\text{-Ni}_2\text{P}_2\text{Se}_6$  (22) and found, besides an enhancement of the number of FIR modes caused by the formation of species like  $\text{P}_2\text{S}_5\text{Se}$ ,  $\text{P}_2\text{S}_4\text{Se}_2$ , . . . , a two mode behavior (23) of the internal and external modes of the end members  $\text{Ni}_2\text{P}_2\text{S}_6$  and  $\text{Ni}_2\text{P}_2\text{Se}_6$ , see Fig. 4. It is seen that  $\nu_d(\text{PS}_3)$  softens by the substitution of selenium in  $\text{Ni}_2\text{P}_2\text{S}_6$ , and  $\nu_d(\text{PSe}_3)$  hardens by the opposite substitution. An extrapolation of the data of Fig. 4 leads to the frequencies of the local mode of  $\text{P}_2\text{S}_6$  in  $\text{Ni}_2\text{P}_2\text{Se}_6$  ( $\nu_d(\text{PS}_3)_{\text{loc}} = 540 \text{ cm}^{-1}$ ) and of the resonant gap mode of  $\text{P}_2\text{Se}_6$  in

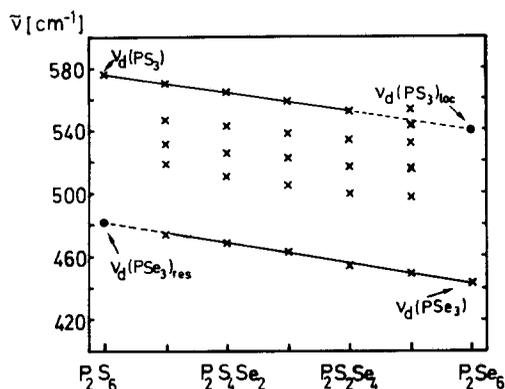


FIG. 4. Infrared absorption frequencies of mixed crystals  $\text{Ni}_2\text{P}_2(\text{S,Se})_6$ . Broken line: extrapolated. Only the frequencies of the  $\nu_d(\text{PX}_3)$  region are given (PE 580, CsI disks).

$\text{Ni}_2\text{P}_2\text{S}_6$  ( $\nu_d(\text{PSe}_3)_{\text{res}} = 480 \text{ cm}^{-1}$ ), the frequency ratios of the impurity modes to the corresponding modes of the host lattice are

$$\frac{\nu_d(\text{PS}_3)_{\text{loc}}}{\nu_d(\text{PSe}_3)} = \frac{540}{443} = 1.22 \quad \text{and} \quad \frac{\nu_d(\text{PS}_3)}{\nu_d(\text{PSe}_3)_{\text{res}}} = \frac{576}{480} = 1.20.$$

These values are in agreement with the square root of the ratio of the reduced masses of a P–X oscillator.

We calculated the force constant  $f_{\text{P-S}} = 3.0 \text{ N/cm}$  for the simple diatomic P–S oscillator. This value is slightly higher than  $f_{\text{P-S}}$  in  $\text{Li}_4\text{P}_2\text{S}_6$  or  $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$  ( $2.7 \text{ N/cm}$ , (9, 10)) obtained from normal coordinate calculations.

#### (b) $\text{Sn}_2\text{P}_2\text{S}_6$ - and $\text{Sn}_2\text{P}_2\text{Se}_6$ -type Compounds

The ferroelectric (6) compound  $\text{Sn}_2\text{P}_2\text{S}_6$  belongs to the acentric space group  $Pc$ .  $\text{Sn}_2\text{P}_2\text{Se}_6$ ,  $\text{Pb}_2\text{P}_2\text{S}_6$ , and  $\text{Pb}_2\text{P}_2\text{Se}_6$  crystallize in the centrosymmetric space group  $P2_1/c$ . As in  $\text{Fe}_2\text{P}_2\text{S}_6$  and  $\text{Fe}_2\text{P}_2\text{Se}_6$  there are still  $\text{P}_2\text{X}_6$  units present in the tin and lead compounds, but their symmetry is lower than  $D_{3d}$  and splittings of degenerate and activation of inactive modes are to be expected in the infrared spectra. The coordination of

the metal atoms by the chalcogens is no longer octahedral but ninefold, with two remarkable short  $M-X$  bonds in the coordination polyhedra (13). Factor group analysis predicts

$$\Gamma_{\text{Sn}_2\text{P}_2\text{S}_6} = 28A' + 29A'' \\ \text{IR, R} \quad \text{IR, R}$$

( $Pc$ ,  $Z = 2$ ,  $C_s$ , (17))

$$\Gamma_{\text{Sn}_2\text{P}_2\text{Se}_6} = 15A_g + 15B_g + 14A_u + 13B_u \\ \text{R} \quad \text{R} \quad \text{IR} \quad \text{IR}$$

( $P2_1/c$ ,  $Z = 2$ ,  $C_{2h}$ , (13))

i.e., 57 and 27 infrared allowed modes for  $\text{Sn}_2\text{P}_2\text{S}_6$  and  $\text{Sn}_2\text{P}_2\text{Se}_6$ , respectively.

Figure 5 shows the fir reflection spectra of  $\text{Sn}_2\text{P}_2\text{S}_6$ ,  $\text{Sn}_2\text{P}_2\text{Se}_6$ ,  $\text{Pb}_2\text{P}_2\text{S}_6$ , and  $\text{Pb}_2\text{P}_2\text{Se}_6$ . Optical and dielectric constants obtained from Kramers–Kronig analyses are given for the lead compounds. TO and LO frequencies are given in Table I. The spectra differ in three main points from the spectra of Figs. 1 and 2. (i) Mode splittings are observed, especially at low temperatures, i.e., site group effects are not negligible, see Sect. (c)). (ii) The intensity of the P–X stretching modes is relatively low. This fact may be due to the distribution of the vibrational energy among several oscillators and to the rather high value of the high frequency dielectric constant which screens the lattice modes. (iii) Very intense lattice modes (irrespective of mode splittings) appear at low wavenumbers. The TO/LO splittings of these modes are high; in analogy to other ferroelectric materials like  $\text{BaTiO}_3$  it is proposed that the strong anisotropy of the metal coordination, especially the formation of  $-M-X-M-X-$  chains, is responsible for this behavior. The ratios of the average mode frequencies  $\bar{\nu}$  correspond to the ratio of the reduced masses  $M-S(\text{Se})$  if the lowest TO and highest LO mode of the low wavenumber modes is considered:  $\text{Sn}_2\text{P}_2\text{S}_6/\text{Sn}_2\text{P}_2\text{Se}_6$ : ratio of  $\bar{\nu}$ :  $98.06/77.49 = 1.38$ ; ratio of reduced masses:  $(\mu(\text{Sn}-\text{Se})$

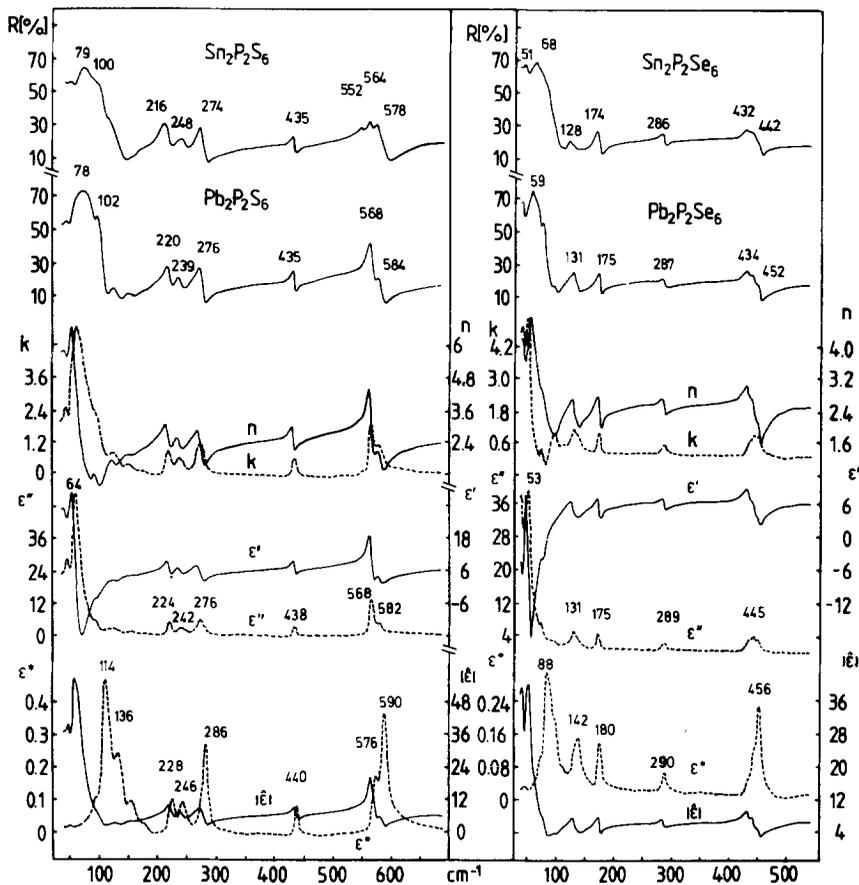


FIG. 5. Fir reflection spectra (Bruker IFS 114) of  $\text{Sn}_2\text{P}_2\text{S}_6$ ,  $\text{Pb}_2\text{P}_2\text{S}_6$ ,  $\text{Sn}_2\text{P}_2\text{Se}_6$ , and  $\text{Pb}_2\text{P}_2\text{Se}_6$  (pressed pellets) and optical and dielectric constants (Kramers-Kronig analyses) of the lead compounds.

$\mu(\text{Sn-S})^{1/2} = 1.37$ ,  $\text{Pb}_2\text{P}_2\text{S}_6/\text{Pb}_2\text{P}_2\text{Se}_6$ : 1.41; 1.44.

The ir absorption spectrum of  $\text{Pb}_2\text{P}_2\text{Se}_6$ -type  $\text{Ca}_2\text{P}_2\text{S}_6$  (I) is given in Fig. 6.

### (c) Further Structure Types

The hexachalcogenohypodiphosphates  $\text{Hg}_2\text{P}_2\text{S}_6$ ,  $\text{Hg}_2\text{P}_2\text{Se}_6$ ,  $\text{In}_{4/3}\text{P}_2\text{S}_6$ ,  $\text{In}_{4/3}\text{P}_2\text{Se}_6$ ,  $\text{TiP}_2\text{S}_6$ , and  $\text{CuCrP}_2\text{S}_6$  possess more complicated crystals structures (15, 16, 24, 25).

Factor group analysis results in

$$\Gamma_{\text{Hg}_2\text{P}_2\text{S}_6} = 15A_g + 12A_u$$

R            IR

$$(\bar{P}1, Z = 1, C_i, (15)),$$

$$\Gamma_{\text{Hg}_2\text{P}_2\text{Se}_6} = 15A_g + 15B_g + 14A_u + 13B_u$$

R            R            IR            IR

$$(C2/c, Z = 4, C_{2h}, (15)),$$

$$\Gamma_{\text{TiP}_2\text{S}_6} = 12A_1 + 13A_2 + 13B_1 + 13B_2$$

R, IR        R        R, IR        R, IR

$$(Fdd2, Z = 8, C_{2v}, (16)),$$

$$\Gamma_{\text{In}_4(\text{P}_2\text{S}_6)_3} = 42A_g + 42B_g + 41A_u + 40B_u$$

R            R            IR            IR

$$(P2_1/a, Z = 2, C_{2h}, (24)),$$

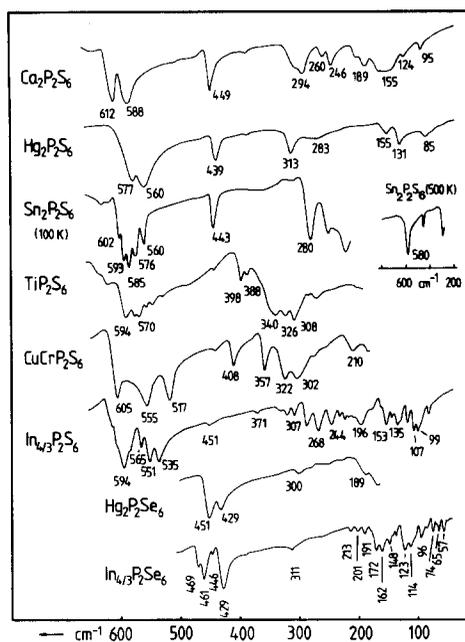


FIG. 6. FIR absorption spectra of less symmetric hexachalcogenohypodiphosphates (Bruker IFS 114, Nujol mulls, and PE 580, CsI disks).

$$\Gamma_{\text{In}_4(\text{P}_2\text{Se}_6)_3} = 125A_1 + 126A_2 + 125B_1 + 125B_2$$

R, IR            R            R, IR            R, IR

(*Pba*2, *Z* = 6, *C*<sub>2v</sub>, (24)),

$$\Gamma_{\text{CuCrP}_2\text{S}_6} = 14A_g + 16B_g + 13A_u + 14B_u$$

R            R            IR            IR

(*C*2/*c*, *Z* = 4, *C*<sub>2h</sub>, (25), the copper atom is assumed to occupy a 4(*e*) position).

It is seen from the far infrared absorption spectra of Fig. 6 that as in Sections (a) and (b) only a small part of the infrared allowed modes can be observed experimentally. Davydov splittings are observed in all spectral regions, i.e., the lowered symmetry of the  $\text{P}_2\text{X}_6$  units and of the lattice itself are conspicuous.

The liquid  $\text{N}_2$  absorption spectrum of  $\text{Sn}_2\text{P}_2\text{S}_6$  shows five to six modes in the  $\nu_d(\text{PS}_3)$  region according to the strongly distorted  $\text{P}_2\text{S}_6$  unit (P–S distances: 201.7,

202.0, 202.3, 202.4, 203.6, 203.7 pm (17)). At 500 K only one P–S mode is observed in  $\text{Sn}_2\text{P}_2\text{S}_6$ , confirming the already known phase transition of this material (6). In the case of  $\text{Hg}_2\text{P}_2\text{S}_6$  the number and relative intensities of the P–S modes correspond in a way similar to the P–S distances:  $r_{\text{P-S}} = 202.8$  pm,  $\nu_{\text{P-S}} = 577$   $\text{cm}^{-1}$ ;  $r_{\text{P-S}} = 203.6$  pm (2*x*),  $\nu_{\text{P-S}} = 560$   $\text{cm}^{-1}$ . But in general the fir spectra of these hexachalcogenohypodiphosphates are not so easy to explain.

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