# Lattice dynamics of layered $MPX_3$ (M = Mn, Fe, Ni, Zn; X = S, Se) compounds

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An experimental and theoretical study of the lattice dynamics of  $MPX_3$  layered compounds (M = Mn, Fe, Ni, Zn; X = S, Se) has been carried out. We present room-temperature infrared and Raman spectra and the phonon dispersion curves calculated in the framework of an axially symmetric force-constant model. The parameters of the dynamical model have been fitted on the Raman and ir data, consistently with the conditions of static equilibrium and of vanishing stress. A satisfactory assignment of the vibrational bands and a qualitative explanation of the dynamical differences among the materials are obtained. Moreover, the theoretical results support the hypothesis of phonon branches' folding effects in the antiferromagnetic phase of FePS<sub>3</sub> and provide the basis for an interpretive scheme of the vibrational spectra of lithium intercalated phases.

### I. INTRODUCTION

Layered materials such as transition-metal dichalcogenides are particularly attractive for their unusual physicochemical properties.<sup>1</sup> They exhibit a strong anisotropy in transport and magnetic properties and, due to the weak interlayer forces and the presence of acceptor centers, they can be intercalated with positive ions and molecules in a redox process. This feature has been exploited to fabricate primary and secondary batteries based on cathode materials which can be intercalated with lithium ions.<sup>2</sup>

More recently, another class of layered compounds, the transition-metal phosphorous trichalcogenides  $MPX_3$  (*M* denotes transition metal; X = S or Se),<sup>3</sup> have attracted an increasing interest, both for their basic properties and for the promising performances of NiPS<sub>3</sub> as cathode material in electrochemical generators.<sup>4,5</sup>  $MPX_3$  compounds can be intercalated with a variety of ions and molecules,<sup>4-11</sup> either with the reduction of the host compound or the substitution of the metal cation. The magnetic,<sup>12-15</sup> optical,<sup>16-18</sup> and structural<sup>19-24</sup> properties of both pure and intercalated phases have been investigated only very recently.

Visible and infrared-absorption data as well as Raman spectra have been interpreted under the assumption of strong phosphorous-chalcogen interactions and weak metal-chalcogen interactions, i.e., on the basis of a molecular picture of these compounds. Recent band-structure calculations, however, have shown that the covalent contribution to the M—S bond in trisulfides is not negligible.<sup>25–27</sup> In particular, it has been pointed out that the M-S interaction plays an important role in determining the electronic structure around the Fermi level. Electronic bands arising from the overlap of metal 3d and sulfur 3p orbitals very likely act as acceptor levels in the lithium intercalation process.<sup>25</sup>

Recently, we have performed a systematic study of the

lattice dynamics of pure  $MPX_3$  crystals by Raman and infrared spectroscopies and studied the magnetic ordering effects on the Raman spectrum of iron phosphorus trichalcogenides.<sup>28-30</sup> The vibrational bands have been assigned in the framework of a molecular approach. This is a fairly good approximation in the high-frequency region (300-600 cm<sup>-1</sup>), but it does not work in the lowfrequency region where the internal normal modes of the P<sub>2</sub>S<sub>6</sub> group cannot be separated from the dynamics of metal ions. Moreover, the lack of information on the phonon dispersion does not allow for a satisfactory interpretation of the magnetic ordering effects observed in the phonon Raman spectrum of FePS<sub>3</sub>.<sup>28</sup>

Therefore, we have undertaken a lattice-dynamics calculation using an axially symmetric force-constant model. This model allows us to correct some misleading attributions of the molecular model, supports the hypothesis of phonon branches folding effects in the antiferromagnetic phase ( $T < T_N = 118$  K) of FePS<sub>3</sub> as suggested in a previous paper,<sup>28</sup> and finally provides an interpretative scheme for the vibrational spectra of intercalated phases. The effects of lithium intercalation on the MPX<sub>3</sub> normal modes have been studied and the lithium-ion vibrational frequencies calculated.

In this paper we present and discuss the calculated phonon dispersion curves for a set of significant materials in the pure phase and a set of Raman and infrared measurements. A satisfactory attribution of the experimental peaks is achieved, and a qualitative explanation of the dynamical differences among the materials is obtained. The lattice dynamics of the Li-intercalated  $MPX_3$  crystals will be discussed in the subsequent paper,<sup>31</sup> hereafter referred to as II.

## **II. CRYSTAL STRUCTURE**

 $MPS_3$  compounds (M = Mn, Fe, Ni, Zn) are layered crystals whose structure can be derived from that of AlCl<sub>3</sub>

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(Ref. 32) with the empty intralayer anion octahedra filled by phosphorus dimers and the transition-metal ions occupying the Al positions. Hexagonal sulfur sheets are arranged along the *c* axis in an *ABCABC* stacking and the corresponding space group is  $C_{2/m}(C_{2h}^3)$  (Refs. 19-22) [Fig. 1(a)].

MPSe<sub>3</sub> descend from the rhombohedral FeCl<sub>3</sub> structure with phosphorus dimers filling the empty intralayer octahedra and transition-metal ions occupying Fe positions. The selenium planes are stacked along the c axis in an ABAB sequence, and the corresponding space group is  $R\overline{3}$ . The metallic sheets are shifted so that every phosphorus dimer has a metal atom in the corresponding octahedra above and below in the adjacent layers. The layer structure is the same as in trisulfides. In FePSe<sub>3</sub> a little distortion probably reduces the symmetry from  $R\overline{3}$  to R3space group.<sup>20</sup> However, these little distortions are negligible in the lattice dynamics in the harmonic approximation, so that for the sake of simplicity the more symmetric  $R\overline{3}$  space group is considered here. The crystallographic cell of the triselenides, containing three layers and six FePSe<sub>3</sub> units, is shown in Fig. 1(b).

The crystallographic parameters of some trichalcogenides<sup>22,33</sup> are reported in Table I. It is worthwhile to point out that, despite the different space groups, the unit cell is the same in all compounds and contains a group  $M_2P_2X_6$  [Fig. 1(c)].

# III. RAMAN SCATTERING AND INFRARED-ABSORPTION STUDIES

### A. Experiment

Raman measurements were carried out on crystals of iron phosphorus triselenide and of manganese, iron, nickel, and zinc phosphorus trisulfide. The infrared studies are not completed for all these compounds, definitive results are available for iron phosphorus trisulfide and for iron phosphorus triselenide, while the measurements on the other crystals are in progress. Flat monocrystals, a few mm large, were grown by sublimation in a two-zone furnace, as described in detail in Refs. 33 and 34. The samples used in Raman measurements were cleaved to obtain good-optical quality surfaces and then minimize the elastic light scattering, whereas in infrared-absorption experiments the thin slices were scraped to avoid interference fringes.

Raman experiments were carried out in a quasibackscattering geometry by using the visible wavelengths of  $Ar^+$  and  $Kr^+$  lasers, a Coderg PH1 spectrometer, and a conventional photon-counting detection system connected to a microcomputer for data processing.

Infrared spectra were recorded by means of a Brucker Fourier-transform (FT) interferometer model IFS 113. The flat crystal samples were illuminated with an incident beam perpendicular to the surface, so that only phonons with a dipole moment in the plane of the layers are expected to be observed.

### B. Raman and infrared spectra

Here we present the room-temperature vibrational spectra of transition-metal phosphorus trichalcogenides.



FIG. 1. (a) Monoclinic crystallographic cell of  $MPS_3$  compounds, (b) rhombohedral crystallographic cell of  $MPSe_3$  compounds, and (c) unit cell of  $MPX_3$  compounds.

 TABLE I. Lattice parameters of some transition-metal phosphorus trichalcogenides.

	a (Å)	b (Å)	c (Å)	$\beta$ (deg)
MnPS <sub>3</sub>	6.077	10.524	6.796	107.35
FePS <sub>3</sub>	5.947	10.300	6.722	107.16
NiPS <sub>3</sub>	5.812	10.070	6.632	106.98
ZnPS <sub>3</sub>	5.972	10.342	6.756	107.14
FePSe <sub>3</sub>	6.260		19.82	

In Fig. 2 we show the first-order Raman and infrared transmission spectra of iron phosphorus trisulfide and of iron phosphorus triselenide. In Fig. 3 we show the first-order Raman spectra of MnPS<sub>3</sub>, NiPS<sub>3</sub>, and ZnPS<sub>3</sub>. The frequencies of observed Raman- and infrared-active modes are compared with the calculated frequencies in Table II. The ir data of MnPS<sub>3</sub>, NiPS<sub>3</sub>, and ZnPS<sub>3</sub> reported in Table II are taken from the measurements performed by Mathey *et al.*<sup>24</sup> and by Sourisseau *et al.*<sup>23</sup> In these works the spectra are carried out on polycrystalline samples dispersed in Nujol. The trends observed in Raman and infrared spectra and the sensitivity of the different vibrational modes to the metal cation and chal-

FePS<sub>3</sub>

cogen anion substitution are apparent.

In the trisulfides a doublet is observed in the Raman spectrum in the frequency range  $560-590 \text{ cm}^{-1}$ . The peak around 585 cm<sup>-1</sup> is polarized, the other one is depolarized. They only exhibit a slight dependence on the metal cation, but they shift to lower frequencies when selenium substitutes sulfur. The polarized peak around 580 cm<sup>-1</sup> in the phosphorus trisulfides corresponds to the weak band observed around 500 cm<sup>-1</sup> in iron phosphorus triselenide, while the depolarized peak corresponds to the band around 450 cm<sup>-1</sup>. The weak band around 435 cm<sup>-1</sup> is due to an overtone of the intense band around 218 cm<sup>-1</sup>.

The most intense Raman peak in trisulfides and in iron phosphorus triselenide is found around 380 and 218 cm<sup>-1</sup>, respectively. It is completely polarized with scattered-light polarization parallel to that of the laser beam. In FePs<sub>3</sub> its intensity grows as the incident photon energy increases in the range 1.92-2.71 eV.<sup>29</sup>

The peak around 278 cm<sup>-1</sup> is depolarized in trisulfides, and at low temperature it splits in two components, which are active in two orthogonal scattering geometries.<sup>28</sup> The Raman peak around 250 cm<sup>-1</sup> is po-





FIG. 2. Raman-scattering and infrared transmission spectra of  $FePS_3$  and  $FePSe_3$  recorded at room temperature. Raman spectra of the trisulfide and of the triselenide were obtained by using the 488.0- and 514.5-nm lines of an  $Ar^+$  laser, respectively.

FIG. 3. Raman-scattering spectra of manganese, nickel, and zinc phosphorus trisulfides recorded at room temperature. The spectra were obtained by using the 488.0-nm line of an  $Ar^+$  laser.

	MnP	S <sub>3</sub>		FePS <sub>3</sub>			ZnPS			NiPS	3		FePe3	
щ	Expt.	Theor.		Expt.	Theor.	щ	Expt.	Theor.		Expt.	Theor.		Expt.	Theor.
ir <sup>a</sup>	Raman		.ir	Raman		ir <sup>a</sup>	Raman		ir <sup>b</sup>	Raman		Ŀ.	Raman	
	117	$114 A_g, B_g$		101 (dp)	107 $A_g, B_g$		83	93 $A_g, B_g$ 140 $R$		131	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		74 (dp)	$\begin{array}{c} 87 \ E_g \\ 108 \ B_g \end{array}$
152		$154 A_{}B_{}$	151		$150 \ A_{}B_{}$	140		$141 A_{\mu}, B_{\mu}$	156		$162 A_{\mu}, B_{\mu}$	108		$102 E_u$
•	155	$157 A_{g}, B_{g}$		153 (dp)	$153 A_{g}, B_{g}$		132	133 $A_{g}, B_{g}$		176	$160 \ A_{g}, B_{g}$		117 (dp)	$106 E_g$
		165 B <sub>u</sub>		x	158 B <sup>°</sup>			170 B <sup>°</sup>			178 B			143 B <sub>u</sub>
194		222 $A_u, B_u$	185		221 $A_u, B_u$	182		225 $A_u, B_u$	187		221 $A_u, B_u$	126		$137 E_u$
	225	$205 A_g, B_g$		220 (dp)	204 $A_{_R}, B_{_R}$		226	205 $A_g, B_g$		236	$204 A_g, B_g$		159 (dp)	$136 E_g$
		252 A <sup>"</sup>			252 A <sub>u</sub>			$261 A_u$			$250 A_u$			$147 A_u$
	247	245 $A_{g}$		244 (p)	$242 A_g$		260	$252 A_g$		253	$250 A_g$		150 (p)	$150 A_g$
255		$262 A_u, B_u$	258		258 $A_{u}, B_{u}$	259		$262 A_u, B_u$	265		$267 A_u, B_u$	159		164 E <sub>u</sub>
	276	$279 A_{o}, B_{o}$		277 (dp)	278 $A_{e}, B_{e}$		279	279 $A_{e}, B_{e}$		280	$280 A_{g}, B_{g}$		172 (dp)	$167 E_g$
316		$271 B_u$	295 <sup>b</sup>		262 B <sub>u</sub>	312		$268 B_u$	289		$270 B_u$			154 B <sub>u</sub>
		295 B <sub>e</sub>			295 $B_{g}$			$301 B_g$			291 $B_{_R}$			164 $B_g$
	385	$394 \ A_{e}$		378 (p)	$394 \ A_{s}$		388	394 A <sup>°</sup>		384	395 A <sub>R</sub>		218 (p)	231 $A_g$
450		440 $B_{u}^{\circ}$	445 <sup>b</sup>	I	437 B <sub>u</sub>	451		436 $B_{u}$	440		434 B <sub>u</sub>	305		292 B <sub>u</sub>
572		571 $A_u, B_u$	578		570 $A_u, B_u$	571		$567 A_u, B_u$	575		575 $A_u, B_u$	442		430 $E_u$
	568	555 $A_{g}, B_{g}$		573 (dp)	555 $A_{g}, B_{g}$		568	553 $A_{g}, B_{g}$		560	559 $A_{g}, B_{g}$		450 (dp)	414 $E_g$
	581	582 A <sub>g</sub>			573 Ag		578	584 A <sub>g</sub>		588	594 A <sub>g</sub>		506 (p)	$510 A_g$

larized in trisulfides. Its frequency slightly grows from manganese to zinc phosphorus trisulfides, while it is lowered down to  $150 \text{ cm}^{-1}$  in iron phosphorus triselenide. Weak Raman peaks are observed in trisulfides around 225 cm<sup>-1</sup>. At low temperatures this structure, which is depolarized, is split in two components in iron, manganese, and zinc phosphorus trisulfides.<sup>29,30</sup> The corresponding mode in the triselenide is found around 160 cm<sup>-1</sup>. It is very weak and can hardly be detected due to the width of the more intense bands around 150 and 170 cm<sup>-1</sup>.

Around  $180 \text{ cm}^{-1}$  a strong infrared band is observed in iron phosphorus trisulfides, which is resolved into a doublet at low temperatures. In the triselenide it is found around  $120-130 \text{ cm}^{-1}$ .

A depolarized Raman peak is found at  $150 \text{ cm}^{-1}$  in trisulfides and at  $115 \text{ cm}^{-1}$  in triselenide. In mixed iron and zinc phosphorus trisulfides this peak shows a marked dependence on the concentration of the cations, its frequency decreasing by about 14% from pure iron to pure zinc phosphorus trisulfide.<sup>35</sup> In FePS<sub>3</sub> a strong infrared band is found around 150 cm<sup>-1</sup>, right at the same frequency of the Raman band. The infrared spectrum of NiPS<sub>3</sub> crystals<sup>23</sup> is quite different with respect to the FePS<sub>3</sub> spectrum (Fig. 2). No strong band is observed around 150 cm<sup>-1</sup>, but only a shoulder around 160 cm<sup>-1</sup>.

At lower frequency it is difficult to establish any peak correspondence among the different compounds. In mixed iron and zinc phosphorus trisulfides a one-mode behavior is found for the Raman peak which occurs at 100 cm<sup>-1</sup> in FePS<sub>3</sub> and at 82 cm<sup>-1</sup> in pure ZnPS<sub>3</sub>.<sup>35</sup> A weak band around 50  $cm^{-1}$  in iron phosphorus trisulfide and two bands at 27 and 54  $cm^{-1}$  in the iron phosphorus triselenide are observed in the infrared transmission spectra (Fig. 2). However, due to their low-frequency position and to their minor intensities, they have not been attributed to the one-phonon processes at zone center, which are the unique processes considered in the fitting of our theoretical model. As a concluding remark we observe that the Raman spectrum of NiPS<sub>3</sub> exhibits some peculiarities.<sup>30</sup> A broad continuum is observed up to 600  $cm^{-1}$  and the relative intensities of the peaks are different with respect to the other trisulfides.

#### **IV. THEORY**

# A. Dynamical model

The lattice dynamics of layered  $MPX_3$  has been approached in the framework of an axially symmetric force-constant model generated by short-range two-body potentials.

The choice of such a simple model is imposed by the lack of experimental data. Only information about zonecenter modes from ir-absorption and Raman spectra is available. Therefore, the number of parameters of the phenomenological model has to be as small as possible.

By considering the appreciable covalent contribution to P—X and M—X bonds, proposed in recent electronic band-structure calculations,  $2^{5-27}$  and the absence of neutron data and ir reflectivity measurements necessary to check the longitudinal-optical-transverse-optical (LO-TO) splittings, no Coulomb interaction has been included in the model.

The force constant between the atom  $\kappa$  in the *l* cell and the atom  $\kappa'$  in the *l'* cell takes the usual central-potential form:

$$\Phi_{\alpha\beta}(l\kappa;l'\kappa') = \frac{r_{\alpha}r_{\beta}}{r^2} \left[ \frac{\phi_{\kappa\kappa'}'(r)}{r} - \phi_{\kappa\kappa'}''(r) \right] - \frac{\delta_{\alpha\beta}}{r} \phi_{\kappa\kappa'}'(r)$$
(1)

where

 $\mathbf{r} = \mathbf{x}(l\kappa) - \mathbf{x}(l'\kappa') ,$ 

and  $\phi'$  and  $\phi''$  are first and second derivatives of the twobody potentials between the atoms  $l\kappa$  and  $l'\kappa'$ .<sup>36</sup>

 $\phi'/r$  is a tangential force constant, while  $\phi''$  is a radial force constant. We did not impose an analytical expression for the two-body potentials, as done in a previous work on triselenides,<sup>37</sup> because we realized that the many-body effects prevent us from considering the inplane and interplane X-X interactions as scaled with the distance. Thus, the radial and tangential force constants have been used directly as fitting parameters.

Eight different interactions have been considered: intraplane and interplane X-X in the same layer, X-X interlayer, P-P, P-X first and second neighbor, M-X first neighbor, and M-P first neighbor. Interactions between different metallic planes have been neglected, so that the stacking of metallic sheets does not affect the phonon spectrum.

The number of independent parameters can be reduced by imposing equilibrium and vanishing stress conditions. The force acting on a single atom produced by the interactions with the other atoms in the crystal can be calculated in a two-body potential model. The equilibrium condition yields

$$F_{\alpha}(x) = -\sum_{l',\kappa'} \frac{r_{\alpha}}{r} \phi_{\kappa\kappa'}'(r) = 0 . \qquad (2)$$

In an infinite crystal the conditions of vanishing stress are not implicit in Eq. (2). Neglecting finite-temperature contributions to the equation of state, these conditions can be written in the present case as follows:<sup>38</sup>

$$S_{\alpha\beta} = \sum_{l',\kappa',\kappa} \frac{r_{\alpha}r_{\beta}}{2rv_{A}} \phi'_{\kappa\kappa'}(r) = 0$$
(3)

 $v_A$  is the volume of the unit cell.

The crystal symmetry reduces the constraints (2) and (3) to five independent linear equations in the first derivatives:

$$F_z(\mathbf{P})=0, \ F_z(\mathbf{S})=0, \ F_y(\mathbf{S})=0, \ S_{zz}=0, \ S_{yy}=0$$
,

and then the number of the independent disposable parameter is reduced to 11.

#### **B.** Results

A preliminary fitting of the model parameters onto the Raman and infrared data has been performed by a leastsquares procedure [the MINUIT program of the Organisation Européenne pour la Recherche Nucléaire (CERN) library]. The results have been taken as starting values for a subsequent manual fitting, in order to take account of the experimental trend between different transition-metal phosphorus trichalcogenides. The calculated frequencies of the Raman and infrared-active modes are compared in Table II with the experimental data. The infrared frequencies obtained on powders<sup>23</sup> are reported too, since some modes cannot be observed in experiments on single crystals with the light beam normal to the sample surface. The best values of the parameters, including the static equilibrium condition (2) and (3), are reported in Table III.

The displacements patterns of the atoms in the unit cell are shown for FePS<sub>3</sub> for all the zone-center normal modes in Table IV. Since the pairs of quasidegenerate A and Bmodes have symmetry properties very similar to an Emode, we report the displacements pattern of only one mode of the pair. Similar patterns have been found in the other trisulfides, whereas the sulfur-to-selenium substitution induces more significant changes in the low-energy modes ( <230 cm<sup>-1</sup> in MPS<sub>3</sub>).

The phonon dispersion curves of trisulfides have been calculated in the Brillouin zone (BZ) with  $C_{2h}$  symmetry shown in Fig. 4(a), while for the triselenides the BZ with  $D_{3d}$  symmetry shown in Fig. 4(b) has been taken, corresponding to the ideal stacking of the metal planes.

The phonon dispersion curves for the compounds studied in the present work are reported in Figs. 5-9.

At higher wave numbers (> 380 cm<sup>-1</sup> in the sulfides and > 200 cm<sup>-1</sup> in the selenides) a few, quite dispersionless, phonon branches are found. They are intramolecular vibrations of the  $P_2X_6$  group, involving P—S and P— P bond stretchings. These modes depend on the most intense force constants, i.e., the P—S and P—P radial force constants. The phase difference between adjacent cells influences the normal modes only through *M-X*, *X-X*, and M-P interactions (much weaker than P-S and P-P radial force constants) and therefore high-energy branches are quite dispersionless.

Different layers are coupled by the X-X interlayer radial force constant, which is much weaker than intralayer interactions (cf. Table III). The effects of such anisotropy show up in the dispersion curves as an upward curvature of the transverse-acoustic (TA) branch with polarization perpendicular to the sheets along in-plane directions. Another manifestation is seen in the small dispersion of the optical modes along the  $\Gamma A$  direction. These features are typical of layered compounds. Since a single layer has  $D_{3d}$  symmetry in the virtual structure with ideal stacking of sandwiches, the zone-center modes may be classified according to the irreducible representations of  $D_{3d}$  point group as follows:

$$\Gamma = 3A_{1g} + 2A_{2g} + A_{1u} + 4A_{2u} + 5E_g + 5E_u$$

The actual stacking of layers in trisulfides breaks the essential degeneracy of E modes, but it has poor influence on zone-center modes due to the weak interlayer coupling. As a matter of fact, the *E*-mode splitting never exceeds 2 cm<sup>-1</sup>. The stacking is more important at the K point of the BZ, where the symmetry reduction in trisulfides breaks the essential degeneracies occurring in the triselenide dispersion curves (Fig. 9).

Along the  $\Gamma K$  direction an anticrossing between the longitudinal-acoustic (LA) branch and the lowest optical branch occurs. The corresponding gap is bigger in trisulfides than in triselenide because the two branches are coupled through the *M*-X interaction, and this is weaker in triselenide.

#### V. DISCUSSION

The first studies of vibrational properties of  $MPX_3$  compounds data back to the works of Mathey<sup>24</sup> and Sourisseau,<sup>23</sup> who interpreted the Raman and infrared spectra

		and a set the put			
	MnPs <sub>3</sub>	FePS <sub>3</sub>	NiPS <sub>3</sub>	ZnPS <sub>3</sub>	FePSe <sub>3</sub>
$\phi_t$ X-X intraplane	-0.136	-0.090	-0.197	-0.263	-0.53
$\phi_r$ X-X intraplane	1.5	1.5	1.45	1.8	1.65
$\phi_t$ X-X interplane	0.037	0.102	0.011	0.040	0.0
$\phi_r$ X-X interplane	0.89	0.89	1.0	1.0	1.5
$\phi_t$ X-X interlayer	0.0	0.0	0.0	0.0	0.0
$\phi_r$ X-X interlayer	0.3	0.3	0.3	0.3	0.26
$\phi_t$ P-X NN	-0.096	-0.259	-0.03	-0.103	-0.019
$\phi$ , P-X NN	22.6	22.6	22.6	22.6	16.0
$\phi_t P-X NNN$	0.0	0.0	0.0	0.0	0.02
$\phi$ , P-X NNN	2.0	2.0	2.0	1.2	2.0
$\phi_t M-X$	-0.096	-0.260	-0.028	-0.102	-0.01
φ, <i>M</i> -X	5.6	5.6	5.7	6.1	2.0
$\phi_t P-P$	-0.80	-0.90	-0.93	-1.42	-1.54
<i>φ</i> , P-P	25.0	24.5	26.5	25.5	19.0
$\phi_t M-P$	0.242	0.239	0.309	0.446	0.84
<i>φ</i> , <i>M</i> -P	0.96	0.96	1.30	0.70	1.2

TABLE III. Best values of the parameters in  $10^{-12}$  erg/Å<sup>2</sup>.

			TABL	E IV. D	isplacen	nents pat	terns in	arbitrary	units of	f the zon	e-center	normal	modes o	f FePS, i	ndicatec	l in cm			
									Wa	ve numt	ber (cm	-1)							
vton	IS	106	125	150	152	158	203	222	242	252	258	262	278	294	394	437	554	570	573
_	×		-	38	09	0	15	30	0		0	0	18	0	0	0	74 2	75 2	0
	y v	00	0 0	00	00	r 77	00	0 0	0 ო	0 0	- 0	0 18	00	0 0	0 23	0 — 39	0 0	00	0 95
5	x	- 0	- 1-0	38 0	09	0 ٢	-15 0	30	0 0	- 0	0	00	-18	0 0	0 0	0 0	- 74 0	75 0	0 0
	N N	0	0	0	0	LT.	0	0	- <del>.</del> –	0	0	18	0	0	-23	- 39	0	0	- 95
_	xvs	- 6 8 40	-15 -31 -3	15 - 14 50	47 - 12 13	17 - 12 - 13		16 - 38 - 38	9 4 - 54	25 43 0	-15 -39 -12	+ 4 - 37	7 - 22 - 36	21 39 3	45 26 11	43 - 25 7	37 23 8	-36 23 -11	-11 - 6 - 6 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0
2	XVS	21 0 0	31 0 0	-13 0	24 0 0	0 28 1	$-62 \\ 0 \\ 0$	-41 0 0	0 10 -55	<b>6</b> 4 0 0	0 - 12 27	0 4 -35	$-39 \\ 0 \\ 0$	42 0	0 53 9	0 8 8	3 0 0	400	$\begin{array}{c} 0 \\ -13 \\ 0 \end{array}$
ŝ	xvs	6 8 40	-15 31 3	15 14 -50	47 12 -13			16 38 38	- 9 - 4 - 54	-25 43 0	15 - 39 - 12	- 4 - 3 - 37	7 22 36	-21 39 3	45 26 11	43 25 7	37 23 8	36 23 11	11 6 0
**	xvz	6 8 6 40	15 31 3	15 14 - 50	47 12 13		13 - 28 37	16 38 38	9 4 5 54 4	-25 43 0	15 39 12	- <b>4</b> - 3 - 37	7 22 36	21 39 3	45 26 -11	43 25 7	37 23 -8	-36 - 23 - 23 - 11	-11 - 6 - 6 - 0
\$	xvs	6 - 8 - 40	15 31 3	15 - 14 50	-47 12 -13	17 - 12 - 13	13 28 -37	16 38 38	- 9 4 54	25 43 0		+ + - 37	7 22 36	21 39 3	-45 26 -11	43 25 7	37 23 8	$-36 \\ 23 \\ -11$	$\frac{11}{-6}$
<b>2</b>	x n z	$-21 \\ 0 \\ 0 \\ 0$	31 0 0	-13 0 0	-24 0 0	0 28 1	62 0 0	-41 0 0	$\begin{array}{c} 0 \\ -10 \\ 55 \end{array}$	<b>6</b> 6 0 0	0 	0 4 35	39 0 0	-4200	0 53 9	0 8 8	$\begin{array}{c} -3\\ 0\\ 0\end{array}$	400	0 13 0
el	x n	0 54 6	0 7 57	$-31 \\ 0 \\ 0$	0 - 6 1	0 6 28	0 - 14 1	-11 - 0 0 0	000	7 7 0 0	0 51 -1	0 1 53	0 45 - 3	0 2 4	000	00%	$\begin{array}{c} 0 \\ - 2 \\ 0 \end{array}$	$-2 \\ 0 \\ 0 \\ 0$	000
e2	xvs	- 54 6	0 7 57	$-31 \\ 0 \\ 0 \\ 0$	0   0	0 - 6 - 28	0 <b>1</b>   1	- 11 0 0	000	7- 0 0	0 51 1	0 1 53	0 -45 3	0 2 + 44	000	00%	0 7 0	0 0	000

in the framework of a molecular model for the  $P_2S_6$ group.<sup>39,40</sup> The zone-center normal modes were separated in high-energy internal molecular vibrations of the group  $P_2S_6$  and in low-energy librations of the  $P_2S_6$  group and in rigid vibrations of the metal cations. This interpretation was suggested by the similarity in the energy range 300-600 cm<sup>-1</sup> between the spectra of MPS<sub>3</sub> phases and of Na<sub>4</sub>P<sub>2</sub>S<sub>6</sub>·6H<sub>2</sub>O (Ref. 39) and Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> (Ref. 40) which contain P<sub>2</sub>S<sub>6</sub> groups.

Such a model requires internal  $P_2S_6$ -group force constants much stronger than the force constants of the metal-cation- $P_2S_6$ -group interactions. These conditions are not completely fulfilled in  $MPX_3$  phases, as shown by the results of our calculations (Table III). The metalchalcogen radial force constant is weaker than



FIG. 4. (a) Brillouin zone of transition-metal phosphorus trisulfides. The high-symmetry points have the following coordinates:  $A = (0,0,\pi/d)$ ,  $M = (2\pi/3a,0,0)$ ,  $K = [0, -\pi\sqrt{3}(4/9a + a/9d^2),0]$ ; and  $M' = (0, -2\pi/a\sqrt{3}, 2\pi/3d)$ , where  $d = c \sin\beta$  and  $a,c,\beta$  are the lattice parameters reported in Table I. (b) Brillouin zone of transition-metal phosphorus triselenides. The high-symmetry points have the following coordinates:  $A = (0,0,\pi/d)$ ,  $M = (2\pi/3a,0,0)$ ,  $K = (0,4\pi\sqrt{3}/9a,0)$ , and  $M' = (0,2\pi\sqrt{3}/3a,0)$ , where d = c/3 and  $a,c,\beta$  are the lattice parameters reported in Table I.

phosphorus-chalcogen and phosphorus-phosphorus force constants, but stronger than chalcogen-chalcogen radial force constant. This hierarchy implies that only modes with energy above  $300 \text{ cm}^{-1}$  are molecular vibrations of the  $P_2S_6$  group. These modes are dominated by P—S and P-P bond stretching and independent of the metal cation substitution, whereas the lower-energy modes all depend on the metal-chalcogen interaction. In particular, the M-S radial force constant, which controls the M-Xbond stretching, is more important for the modes in the range 220–280 cm<sup>-1</sup>, whereas the *M*-S tangential force constant influences the modes below 220 cm<sup>-1</sup>, which are dominated by M-S, S-S, S-P, M-P, and P-P bond bendings. The spectral pattern changes induced in the trisulfides by the metal-cation substitution in the energy range 70-220 cm<sup>-1</sup> are reproduced by modifying the tangential force constants. With regard to the chalcogen substitution, we remark that in our model the mass change without force-constant modifications produces frequency shifts smaller than the shift expected from the inverse square-root mass ratio. The experimental fre-



## WAVE VECTOR

FIG. 5. Phonon dispersion curves of MnPS<sub>3</sub> along the symmetry direction of the BZ. The dispersionless branches with energy above 300 cm<sup>-1</sup> are produced by molecular vibrations of  $P_2S_6$  group. The poor dispersion of phonon branches along  $\Gamma A$  direction and the upward curvature of the in-plane TA branches are typical features of layered compounds.

quencies are reproduced in the triselenides by reducing the P-Se, P-P, and M-Se radial force constants with respect to the trisulfides (Table III). The P-X and M-X force-constant decrease in the triselenides partly reflects the larger polarizability of selenium.

Let us now discuss in detail the main features of the  $MPX_3$  vibrational spectra. The high-energy modes are essentially dominated by the P-X radial force constant, except for the P-P stretching mode, which is controlled by the P-P radial force constant. It very likely corresponds to the polarized Raman peak observed in MnPS<sub>3</sub> at 581 cm<sup>-1</sup>. It is worthwhile to remark that this mode could be shifted even by about 200 cm<sup>-1</sup> by changing only the P-P radial force constant without any appreciable modification in the other normal modes. In FePSe<sub>3</sub> the P-P stretching has been associated to the Raman band around 500 cm<sup>-1</sup>.

The Raman mode around  $280 \text{ cm}^{-1}$  in trisulfides is characterized by a strong contribution of the metalcation motion. As shown in Table II its frequency is, however, almost completely independent of the metalcation substitution in the trisulfides. As a matter of fact, the isotopic shift is compensated by the *M-X* radial force-constant increase, which is also necessary to account for the trends observed in trisulfides for the Raman peak around 250 cm<sup>-1</sup> and for the ir band around 260 cm<sup>-1</sup>. In the Raman-active mode around  $250 \text{ cm}^{-1}$  the chalcogen planes move rigidly one against the other while metal and phosphorus ions are at rest. This mode gives rise to the largest modulation of the van der Waals gap. As a consequence, it is the most sensitive mode to the X-X interlayer interaction and exhibits the largest dispersion along the  $\Gamma A$  direction of the BZ. Moreover, it is expected to be the most sensitive to the lithium concentration in the van der Waals gap of the intercalated phases (see paper II).

X-X interlayer radial force constants are actually quite weak. In our model this interaction controls the splitting of the *E* modes induced in the trisulfides by the actual stacking of layers and observed at low temperature in FePS<sub>3</sub>, MnPS<sub>3</sub>, and ZnPS<sub>3</sub> around 220 and 280 cm<sup>-1</sup>. To reproduce the observed splitting of about 3 cm<sup>-1</sup> the X-X interlayer radial force constant cannot exceed  $1.5 \times 10^{-12}$ erg/Å<sup>2</sup>.

The ir band at  $257 \text{ cm}^{-1}$  in FePS<sub>3</sub> involves the in-phase vibration of the metal cations in the layer plane, whereas the ir band around 295 cm<sup>-1</sup> in the same compound may correspond to the in-phase vibration of the metal cations perpendicular to the planes. The two calculated frequencies are 258 and 262 cm<sup>-1</sup>, respectively. This small difference is an accidental degeneracy: as a matter of fact, the chalcogen cage has a strong trigonal anisotropy and a larger gap between in-plane and out-of-plane rigid











FIG. 8. The same as Fig. 5 for ZnPS<sub>3</sub>.

vibrations of the metal is expected in such a cage.

The mode with calculated frequency of  $252 \text{ cm}^{-1}$  in FePS<sub>3</sub> is an  $A_{1u}$  mode in the  $D_{3d}$  symmetry, but the reduction of symmetry related to the actual *ABCABC* stacking of the sulfur planes induces a nonvanishing dipole moment which activates a weak infrared-absorption structure around 230 cm<sup>-1</sup> in FePS<sub>3</sub>.

In conclusion, the results of our lattice-dynamics calculation are in satisfactory agreement with the available Raman-scattering and infrared-absorption data, and provide an interpretive scheme of the vibrational properties of pure transition-metal phosphorus trichalcogenides. This permits us to approach the lattice dynamics of the intercalated phases. Moreover, the present results support the hypothesis that the phonon lines activated below 200 cm<sup>-1</sup> in the Raman spectrum of FePS<sub>3</sub> below the Néel temperature<sup>28,29</sup> originate from the folding of phonon branches.<sup>29</sup> In the antiferromagnetic phase the unit cell is no longer that shown in Fig. 1(c). It is doubled both along the z axis and in the ab plane, and therefore the BZ is reduced to one-fourth. A and M points are folded in  $\Gamma$ , and some new Raman lines can be activated. In particular, the inversion center in the antiferromagnetic phase is in the middle of the van der Waals gap, and



FIG. 9. Phonon dispersion curves of FePSe<sub>3</sub>. The frequency decrease with respect to the trisulfides is mainly due to the chalcogen mass substitution.

the *u* modes in *A* and *M* become *g* modes. In *M* we found four modes with *u* character in the (80-150)-cm<sup>-1</sup> region: two degenerate TA phonons at 76 cm<sup>-1</sup>, the LA phonon at 98 cm<sup>-1</sup>, and the doublet at 128 and 135 cm<sup>-1</sup>. In *A*, besides the acoustic zone-boundary phonons, whose frequency is too low, an *u* mode is found around 150 cm<sup>-1</sup>. The two strong lines observed in the Raman spectrum of FePS<sub>3</sub> at low temperature at 88 and 95 cm<sup>-1</sup> may originate from the TA and LA phonons in *M*, while the strongly intensified line at 150 cm<sup>-1</sup> may be due to the folding along the  $A\Gamma$  direction of the quite dispersionless phonon branch around 150 cm<sup>-1</sup>.

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