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A Comparative Vibrational Study of $Cr^{III}_{0.5}M^{I}_{0.5}PS_3$ and $Mn^{II}_{1-x}M^{I}_{2x}PS_3$ Layer-Type Compounds with M^I = Cu (x = 0.13) and Ag (x = 0.5)

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The infrared (absorption and reflection) and Raman spectra (700–10 cm^{-1}) of the $Cr_{0.5}Cu_{0.5}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ compounds have been recorded and compared with those of copper- or silver-substituted $MnPS_3$ layer-type systems. A great analogy between the spectra of $Cr_{0.5}Cu_{0.5}PS_3$ and those of $Mn_{0.87}Cu_{0.26}PS_3$ and of the metal deficient $In_{2/3}\square_{1/3}PS_3$ compound, strongly suggests the existence of (S_3Cu . . . CuS_3) bimetallic entities and of metal vacancies. We propose to describe this compound by the approximate formula $Cr_{0.5}(Cu_2)_{0.25}\square_{0.25}PS_3$, a result in agreement with recent EXAFS data, but in opposition to published X-ray crystallographic results. Quite distinct spectra are obtained for the $Cr_{0.5}Ag_{0.5}PS_3$ and $Mn_{0.5}Ag_{1.0}PS_3$ compounds. Strong distortions on the PS_3 groups are evidenced in the former case: these data are in agreement with X-ray data showing that silver ions are stabilized in (AgS_6) environments in the puckered lamellar structure of $Cr_{0.5}Ag_{0.5}PS_3$. Thus, this vibrational study provides direct evidence that the structural properties of both chromium phases are different.

1. Introduction

The MPS_3 phases, where M is a bivalent transition metal, were first prepared by Hahn and Klingen (*1*) and by Nitsche and Wild (*2*). Klingen (*3*) has described the structure of $FePS_3$ in which the stacking of the two-dimensional $S(M_{2/3}(P_2)_{1/3})S$ slabs gives rise to van der Waals' gaps where molecules and cations can be easily intercalated (*4, 5*). The ability of this structural type to accept metal substitution is illustrated by the existence of the metal-deficient compound $In_{2/3}\square_{1/3}PS_3$ (*6, 7*) (where □ stands for a metal vacancy) and also by the possibility of replacing M^{II} by the couples ($Cr^{III}_{1/2}$ + $Cu^{I}_{1/2}$) and ($Cr^{III}_{1/2}$ + $Ag^{I}_{1/2}$).

The structural aspects and magnetic properties of the two lamellar systems $Cr_{0.5}Cu_{0.5}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ have been recently reported by Colombet *et al.* (*8–12*). In the first case, chromium, copper, and P_2 pairs share the octahedral voids between two sulfur layers but the copper is not located at the center of its octahedral sites; a complex distribution has been simulated attributing to copper two crystallographic general positions (in the space group $C_{2/c}$) with important thermal factors (*8–10*). In the second case, chromium, silver, and P_2

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pairs are orderly distributed among the octahedral sites so that homogeneous chains are formed with Cr^{III} and Ag^{I} zigzagging along the *a* axis of the monoclinic structure ($P_{2/a}$); magnetic susceptibility data consistent with a one-dimensional behavior in the high-temperature range were thus observed (*8, 11, 12*). The crystal structures and main interatomic interactions in both systems appear to be significantly different.

As a part of a general vibrational study on several MPS_3 host lattices and on some intercalated or substituted derivatives (*13–16*), we have investigated the infrared and Raman spectra of these chromium compounds. Moreover, in the course of this study, we were aware of recent EXAFS measurements performed on the $Mn_{0.87}Cu_{0.26}PS_3$ (*17*) and $Cr_{0.5}Cu_{0.5}PS_3$ (*18*) compounds showing the presence of (S_3Cu . . . CuS_3) bimetallic entities in both systems. These results, in partial disagreement with X-ray data, suggest the existence in the second case of metal vacancies. Therefore, one can expect vibrational spectra quite analogous to the substituted manganese lamellar compounds $Mn_{1-x}M^{I}_{2x}PS_3$ (M^I = Cu, $x = 0.13$; Ag, $x = 0.5$) which we have recently analyzed in detail (*16*).

As far as we know, no previous vibrational studies on the $Cr^{III}_{0.5}M^{I}_{0.5}PS_3$ compounds have been published, excluding an incomplete infrared absorption spectrum of $Cr^{III}_{0.5}Cu^{I}_{0.5}PS_3$ reported by Kliche (*19*). We therefore present a comparative vibrational study of these substituted systems in order to get a better insight into their structural properties and more precisely into the particular distributions of the copper and silver ions.

2. Experimental

$Cr_{0.5}Cu_{0.5}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ powder samples were kindly provided by Dr. Colombet (University of Nantes) and by Dr. Mathey (University Paris-Sud, Orsay). The purity of samples were checked by chemical analysis and X-ray diffraction methods. Some monocrystalline platelets of the copper derivative obtained from vapor-phase transport were also used.

Synthesis of $Mn_{0.87}Cu_{0.26}PS_3$ and $Mn_{0.5}Ag_{1.0}PS_3$ samples have already been described elsewhere (*16, 17*).

The infrared absorption spectra of polycrystalline samples (Nujol mulls) were recorded either on a Perkin–Elmer 983 spectrometer or on a Bruker IFS 113V interferometer. Infrared reflection spectra were also obtained at near-normal incidence from powder-pressed pellets and from oriented platelets (with 3 × 3 × 1-mm dimensions developed along *a* × *b* × *c* directions).

Raman spectra were recorded on a triple-monochromator Dilor RTI 30 instrument, equipped with argon (514.5 and 488.0 nm) and krypton (647.1 nm), Spectra Physics, Model 164, ion lasers. Detection was carried out by conventional dc technique using a cooled RCA C31034 photomultiplier tube and the microcomputer-controlled spectrometer allowed rapid and repeated scan accumulations. $Cr_{0.5}Cu_{0.5}PS_3$ appears to be a very poor scattering system despite its very weak absorption in the visible region (*8*); laser powers up to 800 mW were focused on the samples without damage. By contrast, much care must be taken with $Cr_{0.5}Ag_{0.5}PS_3$ in order to avoid any thermal and photochemical effects. Low concentrations in KBr (ca. 5%), rotating-disk techniques, and low laser power intensities (1–5 mW) were always used.

3. The $Cr_{0.5}Cu_{0.5}PS_3$ System

3.1. *Structural Considerations*

According to X-ray results (*8–10*), the crystal structure of $Cr_{0.5}Cu_{0.5}PS_3$ is described by the monoclinic space group $C_{2/c}$ ($Z = 8$) and, despite a complex distribution of copper ions, all the P_2 pairs contained in distorted octahedra form equivalent $P_2S_6^{4-}$ groups with P–S distances similar to those found in $FePS_3$ (2.03 Å). In fact, P_2 pairs are alternatively surrounded by smaller CrS_6 and by bigger CuS_6 octahedra. Under these conditions, one expects relatively simple vibrational spectra similar to those observed for most MPS$_3$ systems; the factor group analysis results in $\Gamma^{C_{2h}}_{\text{vib.}} = 14\,Ag + 16\,Bg + 13\,Au + 14\,Bu$ but only a small part of the allowed Raman and infrared modes are generally observed (*13–15*). However, following EXAFS data (*18*), bimetallic copper units may exist as in the $Mn_{0.87}Cu_{0.26}PS_3$ structure and some intralayer octahedra should be vacant if one neglects the possible existence of simple CuS_6 entities. One can thus assume the existence of two kinds of $P_2S_6^{4-}$ groups: in the former, one P_2 pair is surrounded by three (CrS_6) octahedra, two bimetallic (S_3Cu . . . CuS_3) entities plus one vacancy. In the latter, an inverse distribution of one (S_3Cu . . . CuS_3) octahedron and of two metal vacancies must occur (Fig. 1). Different perturbations on the P_2S_6 groups are expected with P–S bond lengths spread over a wide range of values. The crystal structure obtained from X-ray measurements probably results in an average combination of those different distributions and the precise arrangement of the four types of octahedra (Cr, P_2, Cu, □) is not known. As a consequence, it is difficult to establish the complete factor group analysis describing the real crystal disposition. However, when the Cu ions are situated in any general position, one expects the unit cell to be increased fourfold with respect to $FePS_3$. A higher multiplicity and a more complex vibrational pattern are thus expected as has been previously noted for the metal-deficient $In_{2/3}\square_{1/3}PS_3$ compound (*15*).

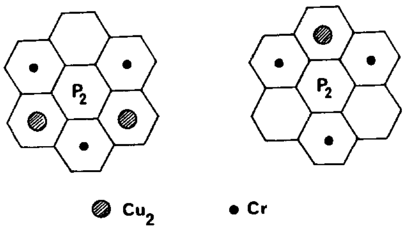

FIG. 1. Schematic representation of the different octahedra surrounding the P_2 groups in the structure of $Cr_{0.5}Cu_{0.5}PS_3$ under the assumption of bimetallic (Cu_2) pairs and metal vacancies.

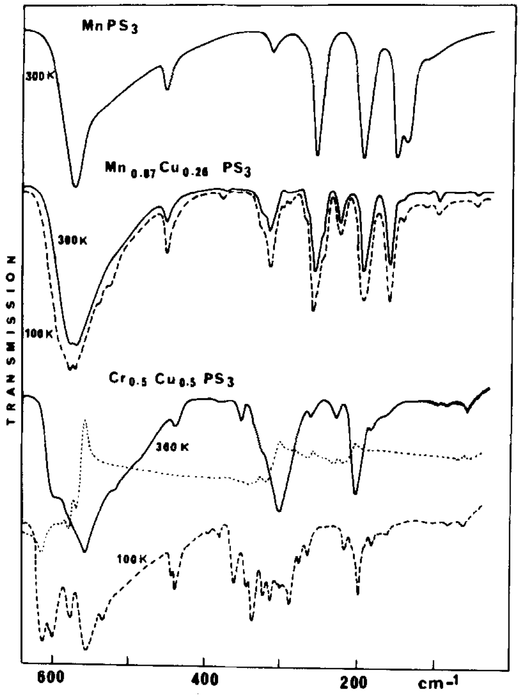

FIG. 2. Infrared spectra (640–30 cm^{-1}) of the Mn PS_3, $Mn_{0.87}Cu_{0.26}PS_3$, and $Cr_{0.5}Cu_{0.5}PS_3$ compounds. Full line, absorption spectra at 300 K; dashed line, absorption spectra at 100 K; dotted line, reflection spectra at 300 K.

3.2. Vibrational Results

The infrared transmission spectra (640–30 cm^{-1}) of $MnPS_3$ (at 300 K), $Mn_{0.87}Cu_{0.26}PS_3$ (at 300 and 100 K), and of $Cr_{0.5}Cu_{0.5}PS_3$ (at 300 and 100 K) are shown on Fig. 2. The infrared reflection spectrum of $Cr_{0.5}Cu_{0.5}PS_3$ (at 300 K) obtained from a monocrystalline platelet is also included. Similarly, the Raman spectra (600–10 cm^{-1}) of polycrystalline samples and of single crystals (in the α_{zz} configuration) for $Mn_{0.87}Cu_{0.26}PS_3$ and

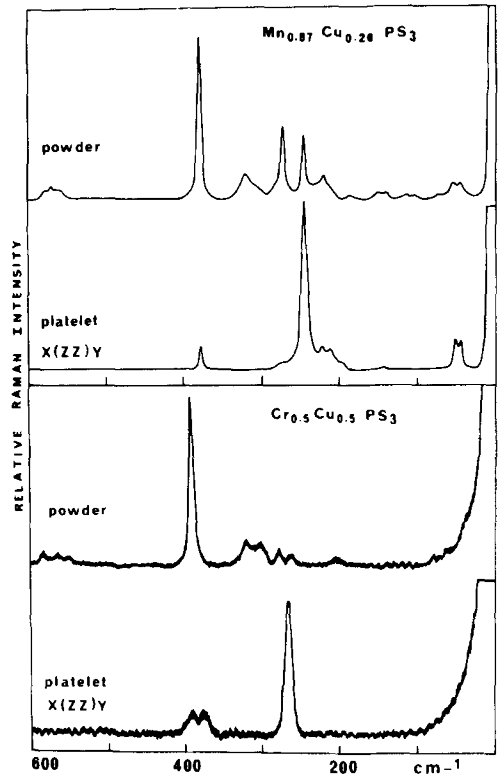

FIG. 3. Raman spectra (600–10 cm^{-1}) of powder samples and single crystal ((*ZZ*) configuration, perpendicular to the layer planes) for the $Mn_{0.87}Cu_{0.26}PS_3$ (λ_0 = 5145 Å) and $Cr_{0.5}Cu_{0.5}PS_3$ (λ_0 = 4880 Å) compounds.

$Cr_{0.5}Cu_{0.5}PS_3$ are compared in Fig. 3. The corresponding band wavenumbers and proposed assignments are reported in Table I.

First of all, it must be mentioned that the previously published (*19*) infrared spectrum of $Cr_{05}Cu_{0.5}PS_3$ is different and exhibits intense bands at 517, 408, 357, and 322 cm^{-1}. We believe that these bands were obtained as a result of a sample decomposition under high-pressure grinding or by use of pressed disks. We have observed the same behavior when using pressed pellets for the rotating-disk Raman technique; many difficulties were encountered in getting satisfactory Raman signals. Therefore, preresonance enhanced Raman spectra were recorded with the 488.0-nm exciting laser line.

A good match between the infrared and Raman band wavenumbers and intensities is evidenced by the vibrational spectra of $Mn_{0.87}Cu_{0.26}PS_3$ and $Cr_{0.5}Cu_{0.5}PS_3$; most of the bands, due to internal modes of P_2S_6 groups, are easily recognized (Table I). We also note in both cases the presence of new weak infrared components in the region 400–200 cm^{-1}, some characteristic Raman peaks in the range 350–300 cm^{-1}, and similar polarization effects on the α_{zz} polarized Raman spectra. In addition, bands assigned to deformation modes of the PS_3 groups are shifted toward higher frequencies in $Cr_{0.5}$ $Cu_{0.5}PS_3$ with respect to their values in $MnPS_3$, a result previously observed with $Mn_{0.87}Cu_{0.26}PS_3$ (*16*). All these vibrational results emphasize the structural analogy within these lamellar compounds and they strongly suggest the existence of (S_3Cu . . . CuS_3) units in the $Cr_{0.5}Cu_{0.5}PS_3$ compound.

Nevertheless, the spectra of this chromium/copper system are much more complex and the low-temperature (100 K) infrared spectrum (Fig. 2) exhibits many band splittings: seven infrared components are observed for the $\nu_d PS_3$ vibrations (620–500 cm^{-1}), a doublet corresponds to the infrared active ν P–P mode (425–436 cm^{-1}), and many bands appear in the region of the PS_3 deformations (320–250 cm^{-1}). Such Davydov splittings have previously been observed in all spectral regions with $In_{2/3}\square_{1/3}$ PS_3 (*15, 19*) which is known to contain three different sets of PS_3 groups per primitive cell (*6, 7*). This shows that the lower symmetry of the P_2S_6 units and of the lattice itself are conspicuous and that the cell doubling ($c' = 2c$) in the structure of $Cr_{0.5}Cu_{0.5}$ PS_3 probably derives from an ordering of the metal vacancies within the (*ab*) planes. We thus propose to describe this compound by the formula $Cr_{0.5}(Cu_2)_{0.25}\square_{0.25}PS_3$, a result which is in better agreement with the

TABLE I

INFRARED (IR) AND RAMAN (R) BAND WAVENUMBERS ($\mathrm{cm^{-1}}$) AND ASSIGNMENTS OF THE $\mathrm{Mn_{0.87}Cu_{0.26}PS_3}$, $\mathrm{Cr_{0.5}Cu_{0.5}PS_3}$, $\mathrm{Mn_{0.5}Ag_{1.0}PS_3}$, AND $\mathrm{Cr_{0.5}Ag_{0.5}PS_3}$ COMPOUNDS AT 300 K

		$\mathrm{Cr_{0.5}Cu_{0.5}PS_3}$							
$\mathrm{Mn_{0.87}Cu_{0.26}PS_3}$		IR[a]			$\mathrm{Mn_{0.5}Ag_{1.0}PS_3}$			$\mathrm{Cr_{0.5}Ag_{0.5}PS_3}$	
IR	R	Abs.	Refl.	R	IR	R	Assignments	IR	R
580 sh	577 w	598 vs	595 582	600 w 588 sh	575 sh	—	ν_d $\mathrm{PS_3}$	638 m 623 s	655 s —
573 vs	571 m	570 sh	570	565 vw	568 vs	567 m		575 vw	570 w
564 vs	562 w	553 vs	555	555 vw	558 vs	560 m		537 s	—
—	—	530 sh	—	—	—	—		515 m	512 m
—	—	516 sh	—	—	—	—		485 sh	—
449 m	—	475 sh 436 m	—	—	447 m	—	ν P–P	438 w 422 w	— —
375 w	382 vs	375 vw		391 s 378 sh	—	372 vs	ν_s $\mathrm{PS_3}$	374 w 358 w	376 w —
315 m	307 w	351 m 317 sh	—	—	311 m	—	δ_s $\mathrm{PS_3}$	325 sh 317 s	— 312 w
323 m	319 m	329 sh	324	321 w	—	319 w	δ SPS δ_d $\mathrm{PS_3}$	306 sh	—
289 w	281 w	—	—	—	—	—		285 m	289 w
266 w	271 vs	298 vs	297	304 w	—	306 s		274 w	268 vs
254 s		274 sh		282 w	292 s	294 m		260 sh	—
—	243 vs	260 w	255	265 w	—	246 m	$\mathrm{T'_{xy}}$ $\mathrm{PS_3}$	232 m	—
225 m	222 m	225 w	225	—	—	200 m		220 m	220 sh
—	211 sh	—	—	—	—	—		215 m	—
193 s	192 w	202 s	205	200 vw	211 s	211 m	R′ $\mathrm{PS_3}$	192 m	200 m
156 s	154 w	184 m	—	—	182 s	184 w		163 m	158 w
140 w	142 m	160 sh	—	—	—	160 w	T′ $\mathrm{Mn^{II}}$, $\mathrm{Cr^{III}}$	125 vw	—
110 vw	115 w	—	—	—	132 m	133 m		78 m	—
98 m	104 vw	84 vw	—	83 vw	95 m	97 m			
—	75 w	—	—	—	—	—	T′ $\mathrm{Cu^{I}}$, $\mathrm{Ag^{I}}$		
52 vw	57 w	58 w	60	66 w	48 m	51 w		—	59 m
45 w	46 s	—	—	44 w	32 s	31 vs		41 m	—
—	37 m	—	—	—	—	23 s			

[a] Abs., absorption; Refl., reflection.

EXAFS data (*18*). Finally, it must be pointed out that an averaged combination of the two structural models shown in Fig. 1 leads to a crystal structure as drawn from X-ray measurements with identical mean values of all the P–S bond lengths (*9, 10*). Unfortunately, due to the poor scattering efficiency of this system in the low-frequency Raman region we were unable to study the translational motions of copper ions and their dynamical behavior as previously carried out on the $\mathrm{Mn_{0.87}Cu_{0.26}PS_3}$ compound (*16*). As a consequence, we cannot exclude the possible existence of a different kind of copper site (*10, 18*).

4. The $\mathrm{Cr_{0.5}Ag_{0.5}PS_3}$ System

4.1. Structural Considerations

$\mathrm{Cr_{0.5}Ag_{0.5}PS_3}$ crystallizes in the monoclinic system, space group $P_{2/a}$ ($Z = 4$); the $\mathrm{P_2}$ pairs occupy one third of the octahedral voids between the sulfur sheets in the same manner as in $FePS_3$ (*11, 12*). Chromium and silver are ordered among the remaining sites so that all the P_2S_6 groups are equivalent and P_2 pairs are surrounded by three small (CrS_6) octahedra and three very large (AgS_6) octahedra (Fig. 4). A large distortion within the puckered layers takes place and three distinct P–S bond lengths are found in each PS_3 unit (P–S_a = 2.103 Å, P–S_b = 2.029 Å, and P–S_c = 1.964 Å). Therefore, we are probably dealing with a new, strongly perturbed MPS_3-type structure: large splittings due to a lowering of symmetry are expected for all the internal vibrations deriving from those of the PS_3 groups.

4.2. Vibrational Results

The infrared and Raman spectra (650–10 cm^{-1}) of $Mn_{0.5}Ag_{1.0}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ compounds at 300 K can be compared in Fig. 5. The corresponding band wavenumbers and tentative assignments are reported on the right part of Table I.

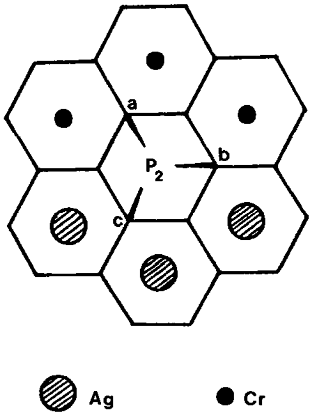

FIG. 4. Ordered distribution of Cr and Ag ions surrounding a P_2 pair in $Cr_{0.5}Ag_{0.5}PS_3$ according to X-ray data (*12*). (a, b, and c refer to the three sulfur atoms bonded to a phosphorus with distances PS_a = 2.105 Å, PS_b = 2.029 Å, and PS_c = 1.964 Å.)

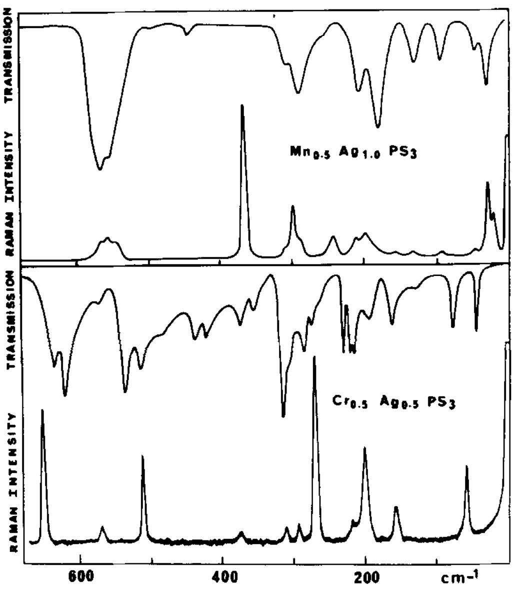

FIG. 5. Infrared and Raman spectra (675–10 cm^{-1}) of $Mn_{0.5}Ag_{1.0}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ compounds at 300 K.

Drastic frequency and intensity changes are noted on the vibrational spectra of both compounds so that the existence of (S_3Ag . . . AgS_3) bimetallic entities in the $Cr_{0.5}Ag_{0.5}PS_3$ derivatives can be definitely ruled out. At first glance, one cannot identify the vibrational pattern of a MPS_3-type structure in this chromium compound. Nevertheless, most of the infrared and Raman bands can be assigned to vibrations due to a distorted P_2S_6 framework: many bands attributed to ν P–S modes are observed in the ranges 650–500 and 380–360 cm^{-1}, an infrared doublet at 438–422 cm^{-1} is derived from the ν P–P vibration, and several bands arising from deformation modes appear in the region 320–160 cm^{-1}. More conspicuous effects are noted for the ν_d PS_3-type vibrations, which are split into three groups of bands at about 630, 570, and 520 cm^{-1} and for the bending δ SPS modes which give rise to a complex spectrum in the range 330–250 cm^{-1}. Quite similar vibrational perturbations were first identified in the infrared spectra of several MPS_3 compounds intercalated with large organometallic cations such as the cobaltocenium, $Co(C_5H_5)_2^+$, or the dibenzene chromium, $Cr(C_6H_6)_2^+$

(*13–15*); they were interpreted as due to a distortion of the PS_3 units upon electrostatic and packing forces.

Finally, in the low-frequency region, the infrared bands at 125 and 78 cm^{-1} probably correspond to translational motions of chromium ions and the intense signals at 59 cm^{-1} (Raman) and at 41 cm^{-1} (infrared) are assigned to silver motions. Unfortunately, neither polarization data nor temperature effects could be obtained on these signals but their frequency values confirm that Ag^I ions are firmly trapped inside (AgS_6) octahedra. In other ionic environments such as "AgS_3" in $Mn_{0.5}Ag_{1.0}PS_3$ (*16*) and "AgS_2" in Ag_3SbS_3 or Ag_3AsS_3 (*20, 21*) the corresponding translational Raman modes were always observed near 30–40 cm^{-1} and in the former case, a more complex low-frequency spectrum consistent with the existence of (S_3Ag . . . AgS_3) units was observed.

All these spectroscopic results are thus in agreement with X-ray and magnetic measurements (*11, 12*); we conclude that silver cations are stabilized in AgS_6 environments in the crystal structure of the lamellar $Cr_{0.5}Ag_{0.5}PS_3$ compound.

Curiously, one notes some similarities between the room-temperature infrared spectrum of $Cr_{0.5}Ag_{0.5}PS_3$ and the low-temperature spectrum of $Cr_{0.5}Cu_{0.5}PS_3$ (Fig. 2) in the ν_d (PS_3) frequency range (500–650 cm^{-1}). Such analogy might suggest the existence at low temperature of an ordered structure of $Cr_{0.5}Cu_{0.5}PS_3$ close to the silver derivative structure. However, the frequency splitting of the ν_d (PS_3) components is weaker in $Cr_{0.5}Cu_{0.5}PS_3$ than in $Cr_{0.5}Ag_{0.5}PS_3$ and the spectra of these compounds are completely different in the region 250–350 cm^{-1}, whose vibrational features have been shown to be very characteristic of the structural arrangement in such compounds (*16*). Moreover, we have taken the Raman spectra of $Cr_{0.5}Cu_{0.5}PS_3$ at 100 and at 10 K. These spectra are very close to those obtained at room temperature and differ drastically from those of the silver derivatives. For these reasons, we believe that, even at low temperature, the $Cr_{0.5}Cu_{0.5}PS_3$ compound maintains a structure specified by the formula $Cr_{0.5}(Cu_2)_{0.25}\square_{0.25}PS_3$.

5. Conclusions

From this vibrational study it is obvious that the $Cr_{0.5}Cu_{0.5}PS_3$ and $Cr_{0.5}Ag_{0.5}PS_3$ structures are quite different while the copper- and silver-substituted $MnPS_3$ phases form structural analogs (*16, 17*). A direct connection can be established between the vibrational spectra and the crystal structures of $Cr_{0.5}Cu_{0.5}PS_3$, $Mn_{0.87}Cu_{0.26}PS_3$ and $In_{2/3}\square_{1/3}PS_3$ compounds. Furthermore, the distinct spectra of $Cr_{0.5}Ag_{0.5}PS_3$ can only be accounted for in terms of a new structural distribution; more precisely, the presence of two kinds of chains formed with Cr^{III} and Ag^I ions induces strong perturbations on the vibrational modes of the PS_3 groups.

Finally, the versatility of these MPS_3 phases in accommodating peculiar distributions of ions in the octahedral voids of the sulfur layers, is again clearly demonstrated. Additional EXAFS and high-resolution electron microscopy measurements should provide new information about the short-range and long-range interactions in these systems.

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