The MPS_3 Coloring Problem

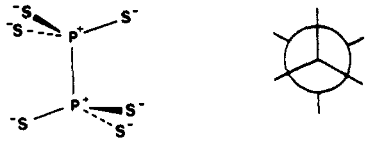
Stephen Lee*

Contribution from the Laboratoire de Chimie des Solides, U.A. CNRS No. 279, Universite de Nantes, 2 rue de la Houssiniere, 44072 Nantes Cedex, France.

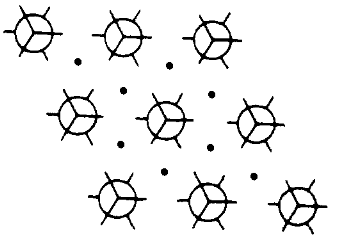
Received July 8, 1986

Abstract: The question of transition metal ordering in the $A_xB_{1-x}PS_3$ phases (A and B transition metals) is treated using extended Hückel band calculations. These theoretical results are interpreted using the moment method. It is found that the known orderings of these phases may be thusly accounted for. Prediction about new phases are made and the magnetic properties of these compounds are considered.

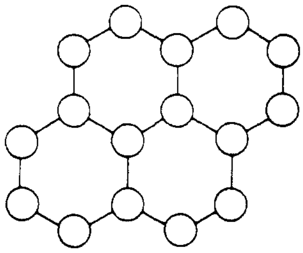
The transition metal phosphorus trisulfide M_xPS_3 ($x \leq 1$) phases form a large family of stable compounds. To date reported compounds are MPS_3 (M = Mn, Fe, Co, Zn, Cd), $V_{0.78}PS_3$, $AgVP_2S_6$, $AgCrP_2S_6$, and $AgInP_2S_6$.[1] All of these are isostructural.[2] Their structure may be thought to contain isolated $P_2S_6^{4-}$ ions which individually have the ethane structure **1**. These isolated $P_2S_6^{4-}$ units form a two-dimensional close-packed array. The metal counterions fill all the octahedral holes left within the sheet by this closed-packed array **2**. It may be seen that the metal atoms taken by themselves adopt a graphite-like configuration **3**.



1



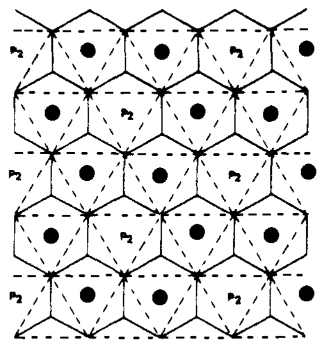
2



3

If one is interested in viewing the cation environment, the structure may alternately be seen as a variant of the $CdCl_2$ structure. In the $CdCl_2$ structure the anions (for us the S atoms) form a three-dimensional close-packed array with one out of two of the layers of octahedral holes filled. In this manner a layer of sulfur octahedra is produced in which two-thirds of the octahedra are occupied by metal cations and the remaining one-third by P_2 pairs, **4**.

In the case of the parent compound MPS_3, the above completes the description of the structure. But if there is more than one metal, as in $AgInP_2S_6$ or $AgCrP_2S_6$ (which hereafter we refer to as AgIn and AgCr, respectively), or if there are defects, as in $V_{0.78}PS_3$, the additional question of metal superstructure appears. The superstructures AgIn and AgCr are known and are shown in Figure 1.[1h,j] The natural question to ask is why AgIn adopts one structure while AgCr adopts another. One viewpoint adopted previously has been to consider the size of the constituent metallic cations.[1i,j] It has been argued that since Ag and Cr are quite different in size, the system wishes to minimize the number of edge sharing Ag and Cr octahedra. Therefore, the phase adopts the AgCr superstructure. In the AgIn case, it is further argued, the metal-containing octahedra are of nearly equal size. Such strain effects are no longer critical and the system is free to adopt the configuration which minimizes the Madelung energy, to wit, the AgIn superstructure. It must be pointed out that such an argument has not taken into account the differing number of d electrons in the two phases. After all, AgIn has filled d bands while AgCr does not. In this paper we turn to the question of what molecular orbital forces control the superstructures observed in the MPS_3 phases. Furthermore, we shall find that consideration of such molecular orbital forces will allow us to examine not only the question of metal order but that of the magnetic structure of these phases as well.



4

Coloring Problem and Moment Method

The problem of superstructure posed above is a well-known one in structural chemistry referred to by some as the coloring problem.[3] By the coloring problem these authors mean two separate problems. The first problem is to enumerate the types of colorings (i.e., superstructures) possible for a given stoichiometry, and the second is to evaluate which among the various enumerated colorings is lowest in energy and hence most stable. In this paper we will enumerate only the colorings which preserve

---

* NATO postdoctoral fellow. Current address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

(1) (a) Friedel, M. C. *Bull. Soc. Chim. Fr.* **1894**, *11*, 115. (b) Hahn, H.; Klingen, W. *Naturwissenshaften* **1965**, *52*, 494. (c) Hahn, H.; Klingen, W.; Eulenberger, G. *Ibid.* **1968**, *55*, 229. (d) Hahn, H.; Klingen, W.; Eulenberger, G. *Ibid.* **1970**, *57*, 88. (e) Soled, S.; Wold, A. *Mater. Res. Bull.* **1976**, *11*, 657. (f) Ouvrard, G.; Frēour, R.; Brec, R.; Rouxel, J. *Ibid.* **1985**, *20*, 1053. (g) Leblanc, A.; Rouxel, J. *C. R. Acad. Sci., Ser. C* **1980**, *291*, 263. (h) Colombet, P.; Leblanc, A.; Danot, M.; Rouxel, J. *Nouv. J. Chim.* **1983**, *7*, 333. (i) Lee, S.; Ouvrard, G.; Colombet, P., Brec, R. *Mater. Res. Bull.* **1986**, in press. (j) Ouili, Z.; Leblanc, A.; Colombet, P. *J. Solid State Chem.* **1986**, in press. (k) Ouvrard, G.; Brec, R.; Rouxel, J. *Mater. Res. Bull.* **1985**, *20*, 1181. (l) Colombet, P.; Leblanc, A.; Danot, M.; Rouxel, J. *J. Solid State Chem.* **1982**, *41*, 174. (m) Mathey, Y.; Mercier, H.; Michalowicz, A.; Leblanc, A. *J. Phys. Chem. Solids* **1985**, *46*, 1025.

(2) Another somewhat similar MPS_3 phase exists, $CuCrP_2S_6$.[1g,l,m] In this system Cu is trigonally coordinated to the sulfur. Because of this large difference in structure, we will not further consider this phase in the current work.

(3) Moore, P. B.; McLarnan, T. J. In *The Structures of Complex Solids*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981.

0002-7863/88/1510-8000$01.50/0

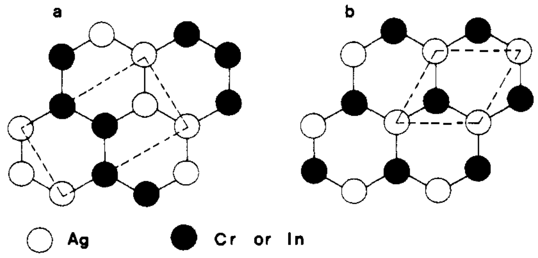


Figure 1. The $AgInP_2S_6$ and $AgCrP_2S_6$ superstructures. In this figure we show only metal atom positions: (a) AgCr ordering, (b) AgIn ordering. Dotted line indicates the unit cell.

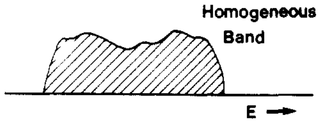
some translational symmetries and do not exceed a specified size in their unit cell.[3b] In evaluating these colorings, we will rely on extended Hückel, or tight-binding calculations.[4] We will lean heavily on moments method calculations for understanding our extended Hückel results.[5] Before proceeding with our analysis, we wish to recall several insights based on the moments method.

1. Let us suppose there is an electron band derived from a certain framework. We take for an example the graphite framework shown in **3**. The band in question may be the pπ orbitals located at each vertex of the graphite net. In examining this graphite net we see the following interesting property: there exists a coloring, the AgIn (shown in Figure 1) where no like atoms are bound to like atoms. Frameworks such as graphite for which this is possible are called bipartite or alternant. For them the following theorem is applicable.

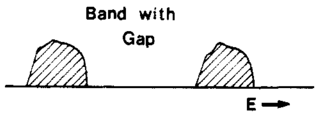
Theorem. When an electron band (such as the pπ band) is nearly filled with or nearly empty of electrons, colorings which maximize linkages between like atoms (as in the AgCr structure) are more stable. At the half-filled band the coloring (AgIn) with no linkages between like atoms is most stable. This is shown schematically in Figure 2.

The proof of this result is given in ref 5.

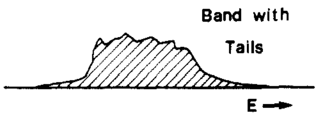
2. The crossover point between the regime of the AgCr and AgIn colorings is controlled by the general shape of the band. If the band in quesion is nearly homogeneous in shape (i.e., generally of even height throughout (**5**)), the crossover point occurs near the 1/3 and 2/3 filled band. But if the band is not of even shape, the crossover points may shift. This is especially true when a large range of energy states is covered by very few energy levels. This occurs when there is either a band gap, **6**, or a band tail, **7**. In the former case the crossover points collapse into the gap, while in the latter case they are brought near the band edge. This is shown schematically in Figure 3.



5



6



7

3. One general disadvantage in tight binding calculations is that structures with more overlap between orbitals are invariably favored over structures with less overlap. In terms of our earlier work this is called a second moment effect. Results due to second moments should in general be discounted.

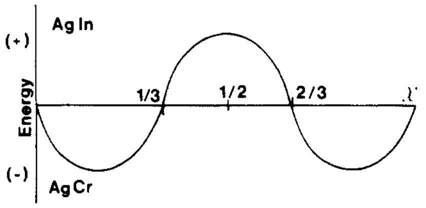


Figure 2. Difference in energy in the fourth moment on a simple homogeneous band. The curve plots as a function of band filling the difference in energy between two colorings which differ in their fourth moment. Band filling range from $x = 0$, the empty band, to $x = 1$, the full band. We have taken as examples the AgIn and AgCr colorings which respectively minimize and maximize the fourth moment. When the difference curve is positive, the coloring which minimizes the fourth moment (AgIn) is more stable, and when negative, AgCr is more stable. The curve shown is a schematic representation of the fourth moment effect. The true AgCr vs AgIn curve is given in Figure 7.

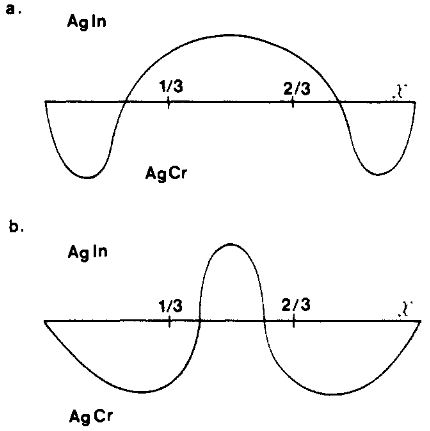


Figure 3. Action of band gaps and tails on the fourth moment effect: (a) effect for band **7**; (b) effect for band **6**. Conventions of curves are given in Figure 2.

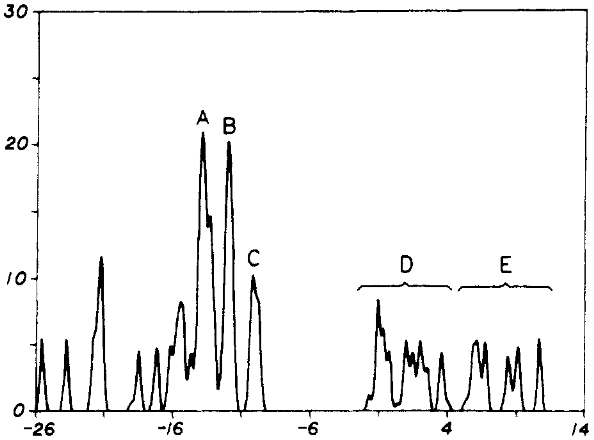


Figure 4. Total density of state in an MPS_3 system (provided by Brec and Ouvrard[6]). Peaks A and E represent anion bands, B and C are t_{2g} and e_g bands, respectively, while D shows metal s and p bands. Abscissa is in eV and ordinate in number of electrons per unit cell. It should be noted that B and C are slightly wider than the results of the present work.

MPS_3 Electronic Structure

The MPS_3 electronic structure has already been treated by Whangbo et al.[6] In this section we summarize some of their results. In Figure 4 we show the band structure of MPS_3, where M is a transition metal. We see in this figure that the $P_2S_6^{4-}$ unit is an extremely stable unit with a gigantic HOMO–LUMO gap. Sitting inside this gap are the transition metal d orbitals. Owing to the octahedral environment, the metal orbitals are split into t_{2g} and e_g blocks. The t_{2g} block is σ inert, contains very little anion

---

(4) (a) Burdett, J. K.; Haaland, P.; McLarnan, T. J. *J. Chem. Phys.* **1981**, *75*, 5774. (b) Hoffmann, R. *Ibid.* **1963**, *39*, 1397.

(5) Burdett, J. K.; Lee, S.; McLarnan, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3083.

(6) Whangbo, M. H.; Brec, R.; Ouvrard, G.; Rouxel, *Inorg. Chem.* **1985**, *24*, 2459.

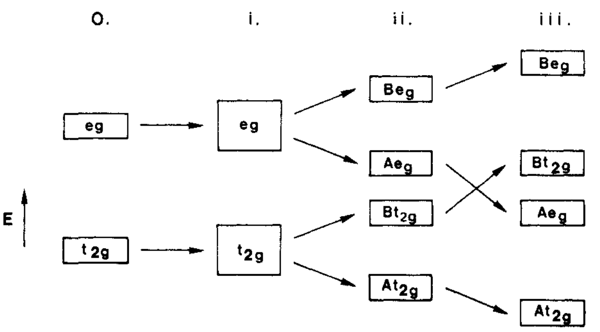


Figure 5. Schematic representation of effect of ΔH on metal d-band location. o represents the case where $\Delta H = 0$. In going to the right ΔH increases in magnitude. i, ii, and iii refer to regimes i, ii, and iii discussed in the text. Compare with actual results shown in Figure 8.

character, and lies near the d orbital Coulombic H_{ii} value. Futhermore, the metals are rather far apart, so the t_{2g} band remains quite narrow (see Appendix). The e_g band lies around 2 eV above the t_{2g} band. The upward shift is due to the expected sulfur lone pair–metal d interaction. The e_g band is also quite narrow, with bandwidths for both the t_{2g} and e_g blocks approximately 1 eV.

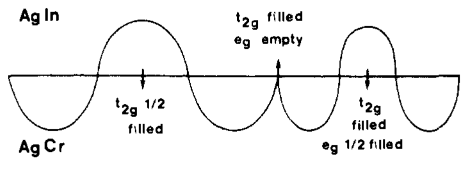
Let us now consider the effect of substituting two different metal atoms A and B onto the metal sites, thus creating the colorings of an $A_xB_{1-x}PS_3$ phase. We would expect the e_g and t_{2g} blocks to split apart into separate subblocks as shown in Figure 5. The driving force splitting the blocks apart is the difference in the Coulombic H_{ii} values (i.e., the electronegativity of the A and B atoms) of the A and B metal d orbitals. We may represent this difference as ΔH. As Figure 5 shows, three cases may be envisioned.

(i) The ΔH may be smaller than the half-band width of the e_g or t_{2g} blocks. There will then be no band gap in either of the original d blocks, or the band gap which occurs will be small in comparison to the overall band width (Figure 5).

(ii) ΔH may be sufficiently great to drive the d orbitals into four clearly separate blocks, the A e_g and t_{2g}, and the B e_g and t_{2g}. But the ΔH remains insufficient to bring the e_g block of the more electronegative atom beneath the t_{2g} of the more electropositive atom (see Figure 5).

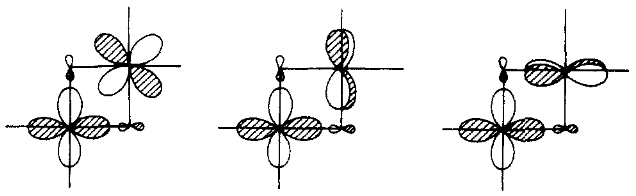
(iii) Finally, we may imagine the A and B atoms are so different that the more electronegative atom's e_g block lies beneath the other atom's t_{2g} block.

Now let us apply the moments results. We see that the system which is composed of two split metal d bands is more complicated than the simple band case discussed in the previous section. In order to understand this more difficult situation, let us first turn to case i discussed above where the t_{2g} and e_g still are nearly single blocks. For each individual t_{2g} and e_g block we can expect a curve as shown in Figure 2. To the extent that there is no interaction between e_g and t_{2g} blocks, we can expect a curve like **8**.



8

How important is the t_{2g}–e_g interaction? Recall that the metal atoms lie in edge-sharing octahedra. In **9** we show that no direct interaction exists between the e_g orbital x^2-y^2 and any t_{2g} orbital on a neighboring atom at k points of high symmetry.[7] Similarily, little interaction is possible between the other e_g orbital, z^2, and the t_{2g} block. Furthermore ignoring ligand orbital occupancy, the above statements are true throughout k space. Therefore, to a good extent e_g–t_{2g} interaction may be ignored, and hence the curve shown in **8** should be the appropriate curve for case i.



9

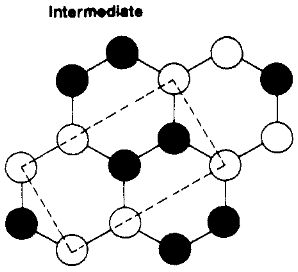
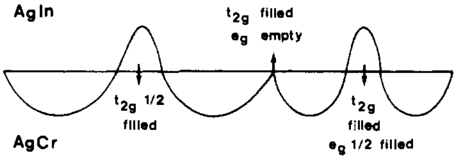
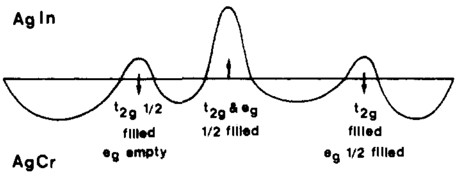


Figure 6. Intermediate ABP_2S_6 coloring. Compare with colorings given in Figure 1.

In going from the case i to ii regime, we note that qualitatively the same curve **8** should be found. In recalling though the rule concerning collapse of crossover points in the case where band gaps occur (point 2 in the discussion on the moment method), we may envision a changeover to **10**. Finally, in case iii we recognize the e_g and t_{2g} curves overlap and a reordered curve such as **11** is anticipated. Note this reordering not only effects the regions of stability of the colorings but actually produces a third zone of stability for AgIn coloring. We also note it is for the case iii that the point 3 of our moment section comes into play. In case iii we have two highly separated A and B blocks. Recalling our second-order perturbation theory, A and B interaction will therefore become quite weak. Thus there will be a second moment term which favors colorings with more linkages between like atoms. As mentioned earlier, we should try to sutract out such contributions.



10



11

ABP_2S_6 Systems

If we limit ourselves to four-atom unit cells for our graphite net, only three ABP_2S_6 colorings are possible. These are illustrated in Figures 6 and 1. Two of the colorings, AgIn and AgCr are found experimentally. The third structure, termed "intermediate" in Figure 6, can be seen to have a number of A–A and B–B linkages intermediate to those in AgCr and AgIn. It will therefore always have an energy between those of the other two structures. Only near the crossover points of Figures 2 and 3 will there be any chance of finding such a phase. In the discussion that follows we will therefore concentrate solely on the AgCr and AgIn structures. In Figure 7 we have calculated this relative stability

---

[7] We might choose as our basis orbitals the pure metal t_{2g} orbitals (see also though: Mercier, H.; Mathey, Y.; Canadell E. *Inorg. Chem.* **1987**, *26*, 963). For our basis e_g orbitals we incorporate a small amount of anion p character, antibonding with the metal. The interaction we refer to in the case of the e_g orbitals therefore includes both superexchange (through-bond) coupling as well as through-space coupling.

Table I. Crossover Points between AgIn and AgCr Colorings

	AgIn stability for t_{2g}[a]		AgIn stability for e_g[a]	
	beginning	end	beginning	end
homogeneous limit	4	8	14.7	17.3
ΔH = 0.4 eV	4.5	7	15.3	16.9
ΔH = 1.0 eV	5.5	6.4	15.4	16.6

[a] Values in d electrons.

for four different ΔH's, 0.4, 1, 2, and 4 eV which correspond to cases i, ii, iii, and iii, respectively. It may be seen that the results of Figure 7 accord well with the predictions of the previous section. The curve Figure 7i is identical with our predicted curve for case i. Near the half-filled t_{2g} and the half-filled e_g, the AgIn coloring is most stable. At the quarter-filled and the three-quarter filled t_{2g} and e_g bands, the AgCr coloring is most stable. The nodes are reasonably close to the anticipated location for homogeneous bands, **5**.

In going to the case ii regime (see Figure 7ii), we see there is, as anticipated, a collapse of both the t_{2g} crossover points as well as of both the e_g crossover points. As discussed above this is due to the evergrowing band gaps which separate half of the e_g and t_{2g} blocks from the other half. Table I tabulates this narrowing and compares the crossover points to the theoretical limit.

One unanticipated feature is the presence of a zone stability at the exactly filled and exactly empty bands. In fact, within the framework we have adopted of noninteracting single bands (i.e., noninteracting e_g and t_{2g} bands), the moments method which relies on Hückel rather than extended-Hückel ideas can never at the start or finish of a band give a preference for one coloring over another. Thus this observed deviation is a measure of the breakdown of both the use of Hückel, rather than extended-Hückel, ideas and of our noninteracting bands starting assumption. A moment explanation of this effect should therefore study the interaction of the metal d band with the anion bands. We leave this discussion for a subsequent publication. For now we should like to point out that these results for totally filled or totally empty bands parallel the prediction from Madelung energies. The coloring with the lower Madelung energy (AgIn) is found to be most stable in the absence of a partially filled d band. This seems like a very reasonable result.

Finally we may turn to our case iii. In a very satisfying manner the anticipated central region of AgIn stability at 10 d electrons appears (see Figure 7, iii and iv). The region of AgIn stability at 16 electrons remains unchanged. Two interesting effects may be observed in Figure 7iv. First, the second moment effect previously discussed has come into play, overemphasizing the AgCr stability. Second, the ΔH in Figure 7iv is now greater than the original t_{2g}–e_g band gap. Hence we no longer have the original double band picture. Figure 7iv may thus be seen to be intermediate between our double-band picture and the single-band picture of Figures 2 and 3.

Comparison with Experiment

There are at the moment only two known transition metal ABP_2S_6 phases, the $AgVP_2S_6$ and the $AgCrP_2S_6$ phases, though we shall also include the $AgInP_2S_6$ phase in our discussion. Before comparing these phases to our theoretical predictions we must decide which of the regimes in Figure 5 is applicable. In a case such as Ag vs Cr this is not hard. The metal d band in Ag is on the verge of having fallen into the core. Indeed in certain cases such as the Hume–Rothery rules they are completely ignored. Furthermore, we know from magnetic studies that the Ag is in the I oxidation state while the V or Cr is in the III state. The Ag e_g is therefore completely filled while the t_{2g} of Cr or V is about half-filled. Thus we are clearly in the regime iii, and Figures 7iii and 7iv are applicable. Were the two systems metallic, we could without further ado apply Figure 7, iii and iv. $AgVP_2S_6$ and $AgCrP_2S_6$ would correspond to 12 and 13 d electrons. Both would then be predicted to be of AgCr type. $AgVP_2S_6$ and $AgCrP_2S_6$ though are both strong antiferromagnets. They are not metals.[8] In another paper[9] we have reviewed this physical situation. We have shown that the Hubbard Hamiltonian is appropriate, and that (recalling that both systems are one-dimensional magnets) both Hückel and Heisenberg–Dirac (HD) Hamiltonians are appropriate zeroth-order starting points. We must therefore consider both the Hückel and HD ground states of $AgVP_2S_6$ and $AgCrP_2S_6$. The Hückel solution is that of the metal, which we have previously discussed. The HD solution may be obtained readily. The AgIn coloring eliminates all first nearest neighbor magnetic interactions. In the simplest approximation, it will have no HD stabilization energy in contrast to the AgCr coloring. Hence the AgCr coloring is predicted to be lower in energy by both Hückel and HD theories

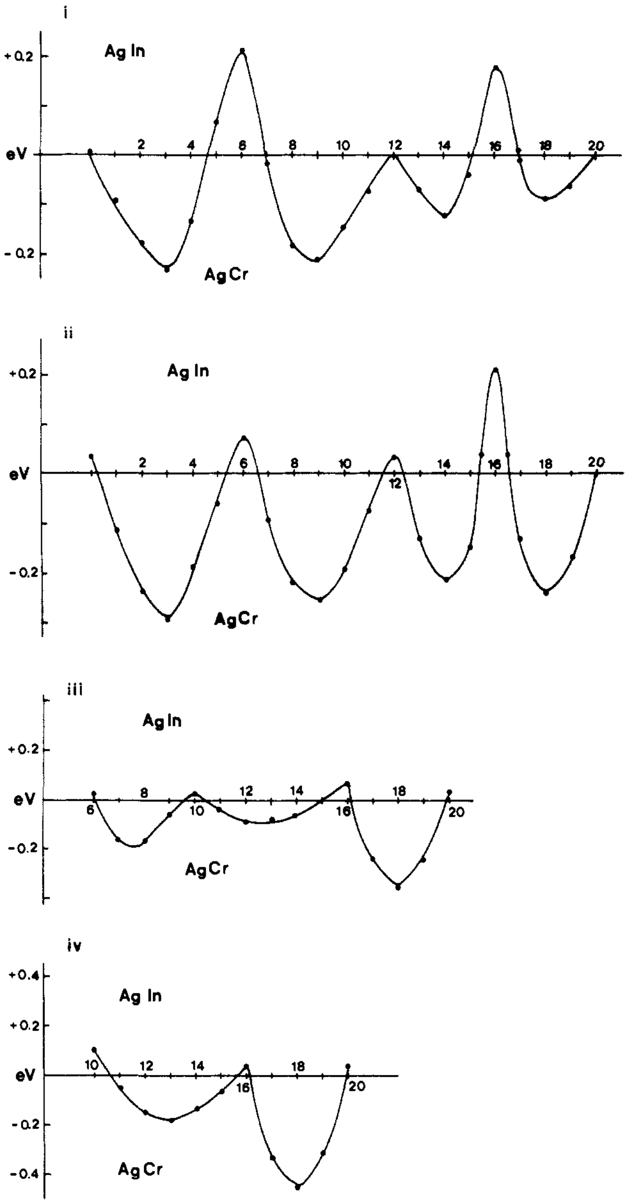


Figure 7. Relative stability of AgIn and AgCr colorings by d-orbital filling. Abscissa is in number of A + B d electrons per ABP_2S_6 unit; ordinate is in eV per four metal atom unit cell. i through iv correspond to ΔH = 0.4, 1, 2, and 4 eV, respectively. In iii and iv only d-band fillings corresponding to a d-band LUMO higher than the anion HOMO level are considered.

---

[8] Colombet, P.; Lee, S.; Ouvrard, G.; Brec, R., to be published. It is significant that the systems are strong antiferromagnets. $AgVP_2S_6$ has not reached its Neel temperature as of 500 °K, a temperature at which sulfur extrudes. Also, it should be noted that $AgVP_2S_6$ does not have a half-filled t_{2g} band. The theory developed in the previous paper is applicable only to half-filled bands. $AgVP_2S_6$, though, appears to undergo a Jahn–Teller distortion which places two of the t_{2g} orbitals below the third. Thus $AgVP_2S_6$ has half-filled the two orbitals stabilized by the Jahn–Teller distortion.

[9] Lee, S., *J. Chem. Phys.*, **1988**, accepted for publication.

Table II. Predictions for Regime iii Phases[a]

compound	B metal spin state	no. of B t_{2g} electrons	no. of B e_g electrons	prediction for coloring
$AgScP_2S_6$		0	0	AgIn
$AgTiP_2S_6$		1	0	AgCr
$AgVP_2S_6$		2	0	AgCr
$AgCrP_2S_6$		3	0	AgCr
$AgMnP_2S_6$	Mn hs	3	1	AgCr
$AgMnP_2S_6$	Mn ls	4	0	AgCr
$AgFeP_2S_6$	Fe hs	3	2	AgCr
$AgFeP_2S_6$	Fe ls	5	0	AgCr
$AgCoP_2S_6$	Co hs	4	2	AgCr
$AgCoP_2S_6$	Co ls	6	0	AgIn
$CdTiP_2S_6$		2	0	AgCr or biphased
$CdVP_2S_6$		3	0	AgCr or biphased
$CdCrP_2S_6$	Cr hs	3	1	AgCr or biphased
$CdCrP_2S_6$	Cr ls	4	0	AgCr or biphased
$CdMnP_2S_6$	Mn hs	3	2	AgCr or biphased
$CdMnP_2S_6$	Mn ls	5	0	AgCr or biphased
$CdFeP_2S_6$	Fe hs	4	2	AgCr or biphased
$CdFeP_2S_6$	Fe ls	6	0	AgIn
$CdCoP_2S_6$	Co hs	5	2	AgCr or biphased
$CdCoP_2S_6$	Co ls	6	1	AgCr or biphased

[a] In order to illustrate the type of results given by our calculations, we have considered "improbable" as well as probable oxidation states. Co(III) and Ti(III) are both difficult oxidation states. See discussion in text. [b] hs = high spin, ls = low spin.

for both $AgCrP_2S_6$ and $AgVP_2S_6$. We may infer that for the physically relevant intermediate region, this will also be true.

Finally we may consider the $AgInP_2S_6$ phase. The In is in the III oxidation state while the Ag is Ag(I). Both are therefore d^{10} configurations. The predicted AgIn coloring is therefore the observed one.

Experimental Predictions

As has been shown, our theoretical results agree quite nicely with our experimental ones. Of even greater interest is the making of new predictions where the experimental work has not yet been done. First let us turn to the case of highly different transition metals (case iii). For our very electronegative d-orbital metal we may choose Ag(I) or Cd(II). For our electroposition d-orbital metal we can take any of the first-row transition metals, especially those on the left-hand side. (We arbitrarily will draw the line at Co for our more electropositive element. It should be pointed out that for Fe and Co we may no longer be in regime iii.)

As may be seen in Table II, almost invariably the AgCr coloring is lower in energy. Exceptions to this are $AgScP_2S_6$, low-spin $CoAgP_2S_6$, and low-spin $FeCdP_2S_6$. Preparation of Co in the III oxidation state is quite difficult in a sulfide, while it should be pointed out there is little chance the Fe(II) will be low spin. (We know this as $FePS_3$ has high-spin Fe(II).) We may though anticipate that $RhAgP_2S_6$ or $IrAgP_2S_6$ will be low spin and hence of the AgIn type.

Finally we should like to note the following point: the predominance of the AgCr coloring forebodes badly for the stability of these phases. For if AgCr is the favored coloring, the biphase $APS_3 + BPS_3$ is by the same moments argument also favored. To see this, all we need to recall is that AgCr's stability is due to its minimization of Ag–Cr interaction. Of course, the biphases minimize such interaction to an even greater extent. Thus whenever the biphase is a possible alternative, i.e., whenever both metals are in the II oxidation state (as in all the Cd compounds), it may be hard to obtain the pure ABP_2S_6 phase. This problem, of course, cannot occur in the Ag phases of Table II, as by charge balance the compounds may not undergo disproportionation.

Another perhaps more interesting set of phases are those where the A and B atoms are close in d-orbital electronegativity. For such systems we may have charge transfer between the two t_{2g} blocks or the two e_g blocks. We may therefore have to leave our localized picture. In what follows we shall just briefly note what we might expect if charge transfer does take place and our t_{2g} and e_g blocks are occupied each from the bottom up. In any case we will fall into the regime of our cases i and ii. In Table III we tabulate some of the possible combinations. We consider here the first-row transition metals as to date they are the most widely studied MPS_3 phases. In making predictions for these families we must recall that the metals are generally high spin. Thus there will be partial occupations of both the t_{2g} and e_g bands. Hence there is the possibility that the t_{2g} occupation will favor one structure while the e_g will favor the other. This is shown in Table III in the $FeNiP_2S_6$ phase for instance. Also while, in general, regimes i and ii lead to the same prediction, this is not always the case, as can be seen in Table III. There is, therefore, an uncertainty in our results as we do not have exact figures for the ΔH of these potential phases. Finally, as in our previous discussion, we have assumed throughout Table III that the metal atoms couple antiferromagnetically and fill each band from the bottom up. In turning to Table III, we see that among the structures most likely to adopt the AgIn coloring are $CrMnP_2S_6$ and $MnFeP_2S_6$, while most likely to adopt the AgCr coloring is $CrFeP_2S_6$. Again as discussed above, the problem of disproportionation for the AgCr phases cannot be disregarded. Further, it may be seen that Cr(II) and, less importantly, Fe(II) are both Jahn–Teller unstable, and hence we must question the validity of our calculations. Finally, we should note that synthesis of Cr(II) under the conditions generally used in solid-state MPS_3 synthesis (preparation from the elements at 600 °C for several weeks) is a questionable proposition.

Synthesis of Possible One-Dimensional Ferromagnets and Ferrimagnets

The AgCr coloring mentioned above is composed of chains of Ag and Cr atoms. The atoms in these chains may magnetically couple. If as in AgCr one of the elements is magnetically inert, we may then isolate a single magnetic chain. This is indeed observed in $AgCrP_2S_6$ and $AgVP_2S_6$.

Of special interest would be finding such a magnetic chain structure where the metal atoms are coupled by ferromagnetic interactions. We pose the question: under what conditions is such a ferromagnetic coupling most likely to be favored? From the point of view of the band picture as discussed above, the answer would be that the Fermi level should be near a maxima so that there are many orbitals with good spatial proximity available to unpair the electrons.

In the case of one-dimensional systems such maxima generally occur at the Van Hove singularities at the band edge. Futhermore, such pseudo Van Hove singularities will be strongest when the system is most 1-D like. We know our AgCr coloring will be most 1-D like when there is a large ΔH gap which minimizes the non-1-D interaction between the two different metal types. This therefore corresponds to our case iii situation discussed above. In Figure 8 we show the development of these singularities with increasing ΔH. It may be seen that the largest maximum is found in the regime iii for the nearly filled t_{2g} band. Likely candidates are thus low-spin $Fe^{III}AgP_2S_6$ and high-spin $Co^{II}CdP_2S_6$.

One potential problem with the synthesis of these ferromagnetically coupled systems is the problem of Jahn–Teller or Peierls distortions which almost invariably come about when the Fermi level is near a maximum. We note for this reason that the $Co^{II}CdP_2S_6$ system is especially attractive. In this system the e_g band occupation may inhibit unwanted geometric distortions.

The problem of synthesizing one-dimensional ferrimagnets is also of interest. For a one-dimensional ferrimagnet we need to envision a system with three metal types. One of the metals will play the role of the Ag in $AgCrP_2S_6$ which isolates the magnetic chains. The other two metal types should alternate on the chain in an ordered fashion. Both these latter two metals should be magnetic. From this geometric prescription we can now see the electronic factors which might favor such a system. We should keep Ag as our neutral metal and we should have as the two magnetic ions atoms V(III) + low-spin Mn(III). These two ions would be in regime i or ii and would at their filling encourage

---

(10) Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

Table III. Predictions for Regime i and ii Phases[a]

	metal spin state[b]	no. of t_{2g} electrons	no. of e_g electrons	regime i coloring preference[c] t_{2g}	regime i coloring preference[c] e_g	regime ii coloring preference[c] t_{2g}	regime ii coloring preference[c] e_g
$VCrP_2S_6$	Cr ls	7	0	?		AgCr	
$VCrP_2S_6$	Cr hs	6	1	AgIn	AgCr	AgIn	AgCr
$VMnP_2S_6$	Mn ls	8	0	AgCr		AgCr	
$VMnP_2S_6$	Mn hs	6	2	AgIn	AgCr	AgIn	AgCr
$CrMnP_2S_6$	Cr ls, Mn ls	9	0	AgCr		AgCr	
$CrMnP_2S_6$	Cr hs, Mn hs	6	3	AgIn	?	AgIn	AgCr
$CrFeP_2S_6$	Cr ls, Fe ls	10	0	AgCr		AgCr	
$CrFeP_2S_6$	Cr hs, Fe hs	7	3	?	?	AgCr	AgCr
$FeCoP_2S_6$	Fe ls, Co ls	12	1		AgCr		AgCr
$FeCoP_2S_6$	Fe hs, Co hs	9	4	AgCr	AgIn	AgCr	AgIn
$FeNiP_2S_6$	Fe ls	12	2		AgCr		AgCr
$FeNiP_2S_6$	Fe hs	10	4	AgCr	AgIn	AgCr	AgIn
$CoNiP_2S_6$	Co ls	12	3		?		AgCr
$CoNiP_2S_6$	Co hs	11	4	AgCr	AgIn	AgCr	AgIn

[a] Caveat: see footnote *a* of Table II. [b] ls = low spin, hs = high spin. [c] AgCr represents biphased structure as well; see text.

Table IV. Relative Proportion of A–A, B–B, and A–B Linkages in $A_2BP_3S_9$ Colorings

coloring	relative proportion A–A	relative proportion B–B	relative proportion A–B
"double chain"	5	2	2
"ethylene"	4	1	4
"greek key"	4	1	4
"spur"	3	0	6
"intermediate"	3	0	0
"dimer + chain"	3	0	6

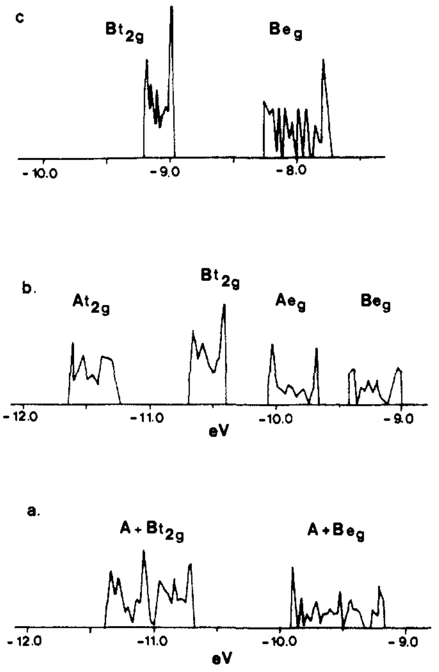


Figure 8. AgCr d bands with varying ΔH: (a) 0.4 eV, (b) 1 eV, (c) 4 eV. In (c) the more electronegative atom's d band has entered the anion manifold (see Figure 4) and hence is not shown.

an ABAB coloring within the chain. Thus $AgV_{0.5}Mn_{0.5}P_2O_6$ would have a good chance to be a ferrimagnet. But it should be noted that Mn(III) is of questionable stability under the standard high-temperature rection conditions.

$A_2BP_3S_9$ Systems

Restricting ourselves to a six-atom unit cell there are only six possible colorings. These are shown in Figure 9. It may be seen the major difference between these colorings and those previously considered in the ABP_2S_6 system is the absence of any coloring with no A–A and B–B linkages (see Table IV). Nevertheless, we may as in the ABP_2S_6 system choose two colorings, one which maximizes A–A and B–B linkages and the other which minimizes them. We shall choose for our two representative colorings the "double-chain" coloring (Figure 9a) and the "spur" coloring (Figure 9d). We shall consider only the regime iii where we choose the B atom to be the electropositive atom and A to be the elec-

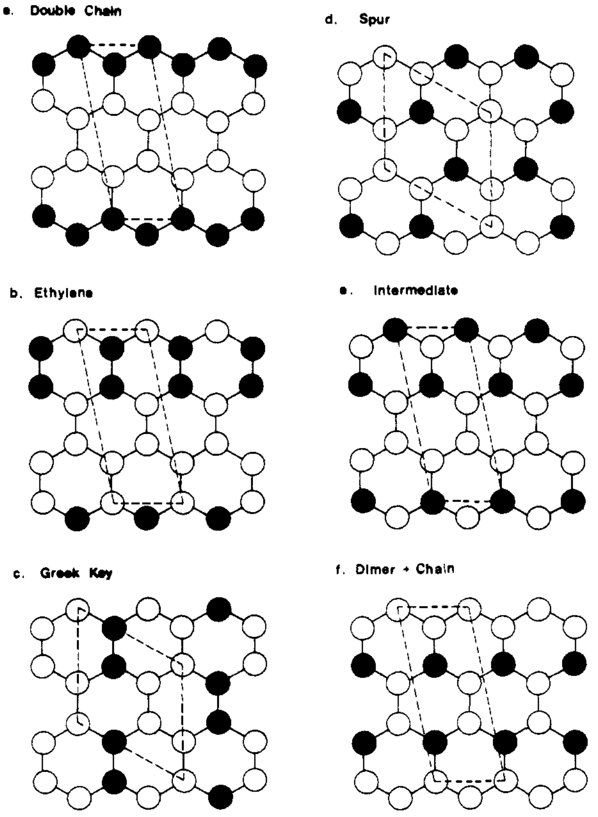


Figure 9. The six alternate $A_2BP_3S_9$ colorings. Dark and light circles represent B and A atoms, respectively. Unit cells are indicated with dotted lines. As in Figure 1, only metal atoms are shown.

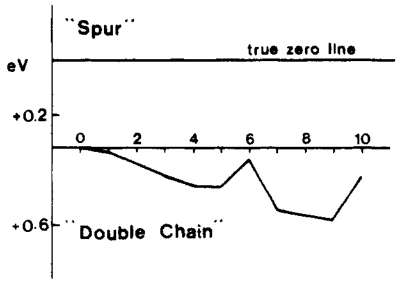


Figure 10. Relative stability of "spur" and "double chain" colorings. Abscissa is in number of B d electrons. Ordinate is in eV per $AB_{1/2}P_{3/2}S_{9/2}$ unit.

Table V. Extended-Hückel Parameters

	H_{ii} (eV)	Slater exponent	
		ζ_1	ζ_2
S 3s	−20.10	2.12	
S 3p	−13.30	1.83	
P 3s	−20.21	1.88	
P 3p	−12.57	1.63	
metal 4s		1.90	
metal 4p		1.90	
metal 3d		5.35 (0.5505)	2.0 (0.6260)

Table VI. Metal Coulombic Values[a]

ΔH	A 4s	A 4p	A 3d	B 4s	B 4p	B 3d
			ABP_2S_6			
0.4	−7.4	−4.3	−11.4	−7.0	−4.3	−11.0
1.0	−7.7	−5.0	−11.7	−6.7	−4.0	−10.7
2.0	−7.5	−5.5	−12.2	−5.5	−3.5	−10.2
4.0	−8.0	−6.0	−13.2	−5.0	−3.0	−9.2
			$A_2BP_3S_9$			
2.0	−8.2	−6.0	−12.2	−16.2	−6.0	−10.2

[a] All values in electron volts.

tronegative one. From our moments ideas we know the resultant curve will be not much different from the AgCr vs AgIn result. In Figure 10 we show the results of our calculation. One difference between these results and the previous ones is that the second moment effect predominates throughout the region of interest. The "double chain" coloring is seen to be preferred for all B d-electron counts. The second moment effect has swallowed up our regions of "spur" stability, and hence we are no longer able to predict the crossover points between the two colorings. Nevertheless, we know the local maxima and minima in Figure 10 correspond to potential regions of respectively the "spur" and "double chain" colorings. Thus while we can no longer conclude if the "spur" coloring is ever the preferred one, we do see the "double chain" coloring will certainly be preferred at 3 and 8 B d electrons.

Another difference is that where the AgIn structure was most favored previously, and the "spur" coloring might be preferred now, we now have many possible alternative structures (e.g., Figure 9e and 9f and Table IV). Disorder hence will be likely. On the other hand, the "double chain" is the only coloring with its number of A–B linkages (see Table IV) and hence may be viable. We can see that likely candidates for this coloring will be $Ag_2MP_3S_9$, where M is a metal in the IV oxidation state with d^2, d^3, or d^4 configuration. Turning this prescription into practice presents some difficulties. Promising metals would be those which take on the IV oxidation state in a sulfide where the metal coordination is octahedral. Unfortunately, the metals which exhibit the most unequivocal examples of such behavior, Ti, Zr, Hf, and Pt, have neither incomplete t_{2g} or e_g bands in the IV oxidation state. It is precisely for these metals that our theoretical results are inconclusive. Ta and Mo are among the best remaining alternatives. Unfortunately, in both these elements trigonal prismatic coordination of the metal is often observed.

d-Band vs Size Arguments

A previous publication has discussed the possibility that the controlling factor of coloring type was the size of the cation. It was suggested that the AgIn structure is found when the metal cation sizes are similar while the AgCr coloring is favored when metal cation size is disparate. In this article we have considered the coloring question from a molecular orbital viewpoint. We have seen that such a model can be used to account for the known ordered ABP_2S_6 systems. We have also seen that the energetic effect is small. There is so far insufficient experimental evidence to determine if it is the molecular orbital or the earlier steric argument that is the most useful. In order to determine this, it is necessary to study the prediction of the models in as yet uninvestigated systems. This has been the goal of the present paper. There are several compounds which if prepared could clearly evaluate the two alternate models. These include $AgIrP_2S_6$, $AgMoP_2S_6$, as well as ABP_2S_6 where A = Na, K, Li and B = Cr, V, Sc.

Acknowledgment. The author would like to thank the NATO postdoctoral program and the CNRS for providing financial support for this work. The calculations were performed using the extended Hückel program developed in its present state by M.-H. Whangbo, T. Hughbanks, S. Wijeyesekera, M. Kertesz, C.-N. Wilker, and C. Zheng. The author would also like to thank M. Evain for his introduction to the CIRCE computing system, and Dr. P. Colombet, Professor J. Rouxel, and K. Keery for helpful discussions.

Appendix

We adopted in our calculations a slightly idealized $FePS_3$ geometry in order to obtain threefold symmetry around the metal atoms. Fe–Fe distances were set at 3.44 Å while Fe–S distances were uniformly set at 2.54 Å. Both the normal Wolfsberg–Helmholtz and the modified Wolfsberg–Helmholtz[9] forms are used for off-diagonal terms. No major difference was observed between the two for these calculations. Throughout all calculations the Slater exponents were kept constant on all atoms. Atom positions were likewise invariant. Only the transition metal s, p, and d Coulombic values were altered. These are shown in Tables V and VI. Calculations for the ΔH = 4 eV case were performed using a nine k-point calculation. All other ABP_2S_6 calculations used four k-points always with reference to the same four-atom orthorhombic cell. The $A_2BP_3S_9$ calculations did not include metal p orbitals. Only a calculation at Γ was performed for this final case.