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Magnetic Susceptibility and Nuclear Magnetic Resonance in Transition-Metal Monophosphides*

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The magnetic susceptibilities of the monophosphides of V, Cr, Fe, and Co have been measured from 4.2°K to room temperature. They were all found to be weakly paramagnetic. The previously reported metamagnetic transition in the MnP was confirmed, whereas none of the other compounds exhibited a magnetic transition. The relative magnitudes of the susceptibilities are shown to be consistent with a band structure proposed by Goodenough in which Mott's suggestion of a critical distance for localized or itinerant electron states is used. The uniqueness of magnetism in MnP is shown to result from the intersection of the Fermi level with a localized electron state before exchange splitting occurs. The nuclear magnetic resonance frequencies of P^{31} and Co^{59} were also measured and indicated some overlapping of the *d* band with the conduction band.

I. INTRODUCTION

THE study of magnetism has been carried out principally with transition-metal ions occurring in metals and alloys or in insulating ionic compounds. In the case of the latter, the localization of the 3*d* electrons causes an intra-atomic exchange splitting in the ground state according to Hund's rule. In the metals, on the other hand, the 3*d* energy levels are broadened into a band and the electrons are itinerant. Part of the difficulty in understanding ferromagnetism in metals has been, first, to understand the mechanism of the splitting and, second, to see what role it plays in the *inter*-atomic spin coupling.

To throw some light on this question we thought it worthwhile to study the magnetic properties of the monophosphides of vanadium, chromium, manganese, iron, and cobalt, since they are intermediate between the metals and the insulators. Mott[1–3] has suggested that the metal-metal distance is an important factor in determining whether electrons are localized or itinerant. He asserts that there is a critical metal-metal distance R_c such that for $R<R_c$ itinerant behavior occurs, while $R>R_c$ localized behavior occurs. This is due to the fact that although a small number of electron-hole pairs exhibit a higher energy than none, for certain interatomic spacings shielding effects may allow the presence of many pairs to lower the energy relative to a state in which there are none. Thus the Heitler-London scheme, which ignores ionized states, may break down for $R<R_c$.

A theory for the electronic properties of these compounds has not yet been derived from first principles. By adopting a semiphenomenological approach, however, Goodenough[4] has met with considerable success in interpreting many experimental results concerning the transition metal oxides. In this approach Goodenough has extended Mott's theory of a sharp R_c and also introduced a covalent mixing parameter λ which relates to covalent mixing of the cation and anion orbitals. For $\lambda>\lambda_c$, the appropriate cationic state is banded. The electronic structure of the transition-metal monophosphides lies between the extremes of the pure metals and the ionic salts in that metal-metal distances exist which are both greater and smaller than R_c. Consequently, both itinerant and localized electrons may be present simultaneously in these compounds.

MnP has already been shown[5] to be magnetic below 292°C. We have confirmed this but have found that ***none*** of the other isomorphic transition metal compounds are magnetic down to 4°K. These results are interpreted within a band structure proposed by Goodenough,[6,7] and the implications for the occurrence of magnetism in metals are discussed. By the very nature of Goodenough's approach, its extension to the transition metal phosphides is done *ad hoc*, the question of justification residing in comparison with experiment.

We have also measured the shift in the nuclear magnetic resonance frequency of the P^{31} nucleus in VP, CrP, FeP, and CoP, as well as that of the Co^{59} nucleus in the latter. The results confirm the nonmagnetic character of these compounds and reveal the presence of a conduction band overlapping the *d* band.

All values of magnetic susceptibilities throughout the paper are in units of emu g^{-1} G^{-1}.

II. CRYSTAL STRUCTURE

VP crystallizes in the hexagonal *B*8 (NiAs) structure while CrP, MnP, FeP, and CoP crystallize in the ortho-

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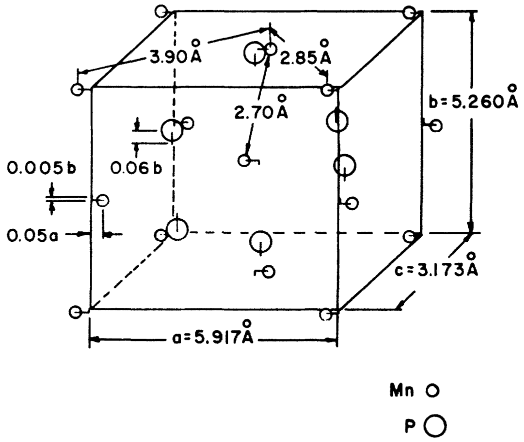

FIG. 1. *B*31 structure of MnP.

rhombic *B*31 (MnP) structure. The *B*31 structure is an orthorhombic distortion of the *B*8 structure and is shown in Fig. 1.

In the *B*8 structure there are eight atoms per unit cell, four metal and four phosphorus. The metal lattice is hexagonal, with each metal atom having six nearest metal neighbors in the basal plane and two next nearest metal neighbors along the orthorhombic *b* axis (hexagonal *c* axis). Each metal atom is surrounded by six P atoms in an octahedral configuration. Each P atom is surrounded by six nearest metal atoms and is at the center of a triangular prism formed by them. There are 12 P neighbors within 4 Å.

The *B*31 structure can be regarded as an orthorhombic distortion of the hexagonal *B*8 structure in which the metal atoms are displaced toward one another in the basal plane. The P atoms are displaced along the *b* axis. Each metal atom is surrounded by six P atoms in a highly distorted octahedron and is no longer at the center. Each P atom is surrounded by six metal atoms at the corners of a highly distorted triangular prism.[8,9]

III. SAMPLES

The CrP #1 sample was obtained from Semi-Elements Inc., Saxonburg, Penna. The rest of the samples, VP, CrP, #2 MnP, FeP #1 and #2, and CoP #1 and #2 were fabricated by one of us (B. S.) by direct mixing at high temperatures. There are two eutectic points in the Mn-P system, which is typical of these metal-phosphorus systems.[10] The first occurs at a lower temperature than the second, the first varying from a low of 960°C in Mn-P to 1370°C in Cr-P. Thus a solid-state diffusion reaction can occur if one keeps the temperature of the system below that of the lowest eutectic. The formation of an ingot of incorrect stoichiometry, which occurs if one passes through a liquid region, is avoided by this method.

Two methods were used in the preparation of these compounds. The first employed two furnaces maintained at approximately 400 and 950°C, respectively. It had the virtue of allowing the vapor pressure of the phosphorus to be maintained at a known, safe level. This method took between 4 and 7 days to prepare the samples. The second method involved use of a single furnace and took from 12 to 15 days.

Quantitative analyses were made by two commercial laboratories. One laboratory analyzed the metal and phosphorus content of CrP #1 and FeP #2. The other laboratory analyzed only the metal content in both samples of CrP, FeP, and CoP. The results are given in Table I. No quantitative analyses were made of VP or MnP. The total amount of material reported by Laboratory B was not 100%. This occurred since there was an over-all loss in material during the analyses. This is borne out by the higher metal content reported for the same compounds by the other laboratory. Nevertheless, the ratio of metal to phosphorus content was very close to the theoretical value. The ratios reported were 1.76 for FeP and 1.67 for CrP as compared to the stoichiometric values of 1.80 and 1.68, respectively.

The composition of each sample was confirmed by powder x-ray photographs. Sharp lines were obtained in all cases, and in no case was there evidence of the presence of other phases. Furthermore, the magnetic susceptibility results showed only minor variations from sample to sample of the same compound. Since these compounds are weakly paramagnetic, any strongly magnetic impurities could easily be detected. Therefore we believe the results are closely representative of the pure stoichiometric compounds.

IV. EXPERIMENTAL DETAILS

The magnetic susceptibility was measured by means of a Foner vibrating sample magnetometer.[11] The magnetization induced in the sample acts as a dipole and is directed along the external field. Pickup coils are fixed relative to the magnet and are connected in series opposition. The sample signal obtained from these coils is compared with that obtained from a reference magnet which is calibrated against a known standard. Narrow-band amplification and phase-sensitive detection of the

TABLE I. Sample analyses by two commercial laboratories, A and B (in percent).

Laboratory A		Laboratory B	
CrP #1	Cr 61.39	Cr 60.66	P 36.36
CrP #2	Cr 61.34		
FeP #1	Fe 62.37		
FeP #2	Fe 62.37	Fe 60.81	P 34.65
CoP #2	Co 63.58		
CoP #2	Co 63.14		

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[10] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

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difference signal were used to obtain maximum sensitivity. The apparatus could detect a magnetization of 1×10^{-4} emu g^{-1}, corresponding to $\Delta\chi=1\times10^{-8}$ for a one-gram sample in 10 000 Oe. A conventional double Dewar system was used with liquid nitrogen and liquid helium as the refrigerants.

The nuclear resonance measurements were made using a conventional Pound-Watkins spectrometer. The magnetic field was modulated at approximately 200 cps and the derivative of the absorption displayed on a Brown recorder. The magnet was a 12-in. Varian with a 3-in. gap, tapered pole pieces, and a field inhomogeneity over the sample volume of $\frac{1}{2}$ Oe. Measurements of the P^{31} resonance in pure red phosphorus relative to that of Al^{27} in 99.999% Al were made. Some aluminum powder was mixed into each of the phosphide samples so that the shifts in the P^{31} resonance frequency in the compounds could be determined directly from a measurement of the P^{31} resonance relative to that of Al^{27}. The Co^{59} resonance in CoP was measured relative to the reference compound potassium hexacyanocobaltate.[12] A conventional double Dewar system was used. The temperature was controlled in the range 77°K to room temperature. It could be controlled to $\pm\frac{1}{2}\%$ from 77 to 150°K, $\pm1\%$ from 150 to 200°K, and to $\pm2\%$ above 200°K.

V. EXPERIMENTAL RESULTS

A. Magnetic Susceptibility

The magnetic susceptibility of each compound was measured at 298, 77, and 4.2°K. On certain samples intermediate temperatures were studied. The range of magnetic fields used was from 250 to 7800 Oe. Measurements were made for both increasing and decreasing values of magnetic field to determine whether or not hysteresis was present. All results quoted for a given compound are averages of a number of separate measurements.

Except for MnP, the measured susceptibilities were small ($\sim5\times10^{-6}$). Differences in stoichiometry and small amounts of paramagnetic impurities may produce variations in the susceptibility of different samples of a given compound. It is difficult to separate the contributions due to these sources, but it is believed that the differences in the room temperature values are due to the differences in stoichiometry which are inherent in the method of preparation. Between 20 and 30°K a relatively rapid rise in susceptibility occurs which results in differences in χ from sample to sample as large as 25% at 4.2°K. This effect is attributed to paramagnetic impurities. Thus an extrapolation of $1/\chi$ versus T has been made to 4.2°K to obtain values of χ which include a minimal effect from impurities. Cold working was also found to influence the susceptibility, an effect which will be discussed in detail under the CrP results.

TABLE II. The magnetic susceptibility of vanadium phosphide.

T(°K)	χ (10^{-6} emu g^{-1} G^{-1})
298	1.96 ± 0.06
77	2.06 ± 0.06

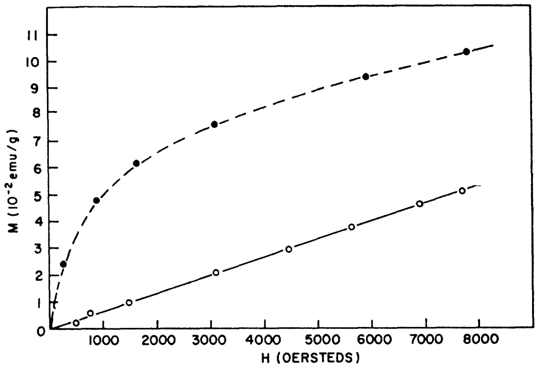

FIG. 2. M versus H for CrP. The dashed curve shows the results of a cold-worked sample.

The errors quoted in these results represent an upper bound and are greater than the mean square deviations which are obtained from an average of results in a single sample. Differences from sample to sample of a given compound are discussed in detail under the results for that compound.

1. *Vanadium Phosphide*

The susceptibility of VP was measured at 298 and 77°K on a single sample. The results are given in Table II.

2. *Chromium Phosphide*

The susceptibilities of both samples of CrP were found to be weakly temperature-dependent.

An important feature of the results is the effect of cold working on the samples. Samples which were ground to a fine powder in a porcelain mortar exhibited magnetizations from two to ten times larger than those of unground samples. A sample of $CuSO_4\cdot5H_2O$ ground in a similar mortar showed no change in magnetic properties. For the ground samples a saturation effect was observed as can be seen from the dashed curve in Fig. 2. If the slope of the high field points is used to determine χ, results are obtained which are about 20% greater than those obtained from unworked samples. This effect has been observed in other alloy systems by several workers and is probably due to the production of interstitial metal atoms.

The results quoted in this investigation are on samples for which gross cold working has been avoided. However some crushing must be done to bring the samples into a form suitable for measurement. Thus a small but un-

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[12] R. Freeman, E. R. Murray, and R. E. Richards, Proc. Roy. Soc. (London) **A242**, 455 (1957).

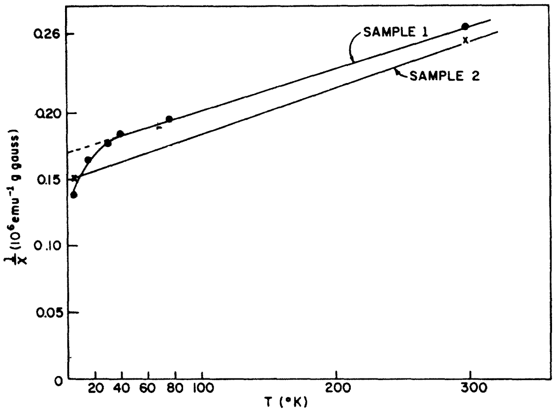

FIG. 3. $1/\chi$ versus T for CrP.

known portion of the variation from sample to sample may be due to this effect.

Figure 2 shows a typical M versus H curve. A graph of $1/\chi$ versus T is given in Fig. 3 and shows the extrapolation to 4.2°K.

3. *Manganese Phosphide*

The results obtained for MnP confirm the existence of a metamagnetic transition at 50°K which has been reported in a single crystal specimen.[5] MnP is ferromagnetic with a T_c of 291.5°K and a T_p of 312°K. Measurements at 298°K showed that MnP was in the transition region from ferromagnetic to paramagnetic behavior.

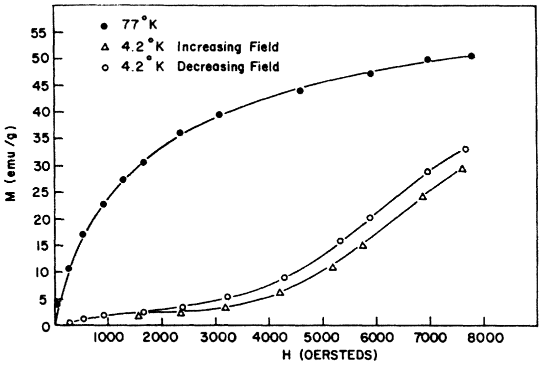

FIG. 4. M versus H for MnP.

The magnetization determined at 77°K in 7800 Oe was $\sigma = 51.0 \pm 0.5$ emu/g (see Fig. 4), which corresponds to a magnetic moment per metal ion of 0.79 ±0.01 Bohr magnetons. This result is considerably lower than the previously reported value of 1.29±0.04, but the difference in values is clearly due to the large anisotropy field in MnP. (At 90° to the easy axis the magnetization is about 15% of the easy axis magnetization.) A field-dependent ferromagnetic-antiferromagnetic transition occurs near 50°K, as may be seen from Fig. 4 and Fig. 5. The magnetic susceptibility in the antiferromagnetic region was found to be $5.18 \times 10^{-3} \pm 0.10 \times 10^{-3}$. This agrees well with the previously reported value of 5.20×10^{-3}.

4. *Iron Phosphide*

The magnetic susceptibility results for both samples of FeP are given in Fig. 6.

The lower phosphides, Fe_2P and Fe_3P, are ferromagnetic. It is possible for local areas of these compounds to exist in the sample and to act as paramagnetic impurities.

Figure 6 shows that strong paramagnetic behavior begins to occur between 20 and 30°K. Magnetization data showed marked curvature with field below 1000 Oe, indicating the presence of ferromagnetic impurities.

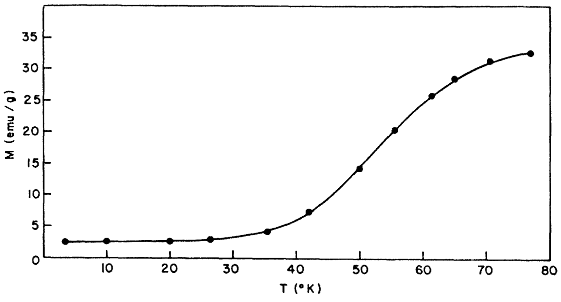

FIG. 5. M versus T for MnP at 2000 Oe.

Furthermore, measurements on samples taken from a slightly metal rich area of the original batch showed that their susceptibilities varied more strongly with temperature than did those of samples #1 or #2.

5. *Cobalt Phosphide*

Cold-worked samples of CoP showed the same effect as did the CrP and FeP samples. A saturation effect was observed in these samples, and the magnetization at 7800 Oe was about ten times as large as that of uncrushed samples. The uncrushed samples exhibited a very small susceptibility. The results are given in Fig. 7.

In order to assess the effect of excess Co in the samples, the susceptibility of Co_2P was measured. It

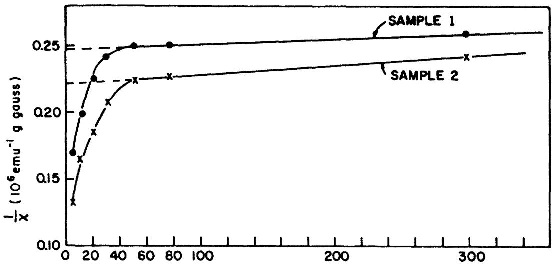

FIG. 6. $1/\chi$ versus T for FeP.

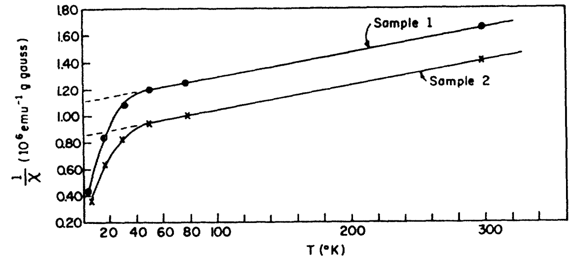

FIG. 7. $1/\chi$ versus T for CoP.

was found to be paramagnetic, having values of 3.54×10^{-6} at 298°K and 4.26×10^{-6} at 77°K.

B. Nuclear Magnetic Resonance

In contrast to the magnetic susceptibility results, which showed variations of up to 25% from sample to sample, the nuclear resonance results were the same from sample to sample of the same compound to within the experimental error. For VP, CrP, and CoP, the results presented are averages of measurements made on a number of different samples, including those whose susceptibility was measured. An attempt was made to measure the shift in paramagnetic MnP at 350°K which was unsuccessful due to the large value of the magnetization at that temperature.

1. P^{31} Resonance in VP, CrP, FeP, and CoP

The shifts of the P^{31} resonance in each compound are given in Table III at various temperatures. They were independent of magnetic field, and since the P^{31} nucleus is spin-$\frac{1}{2}$, no electric quadrupole effects were present.

In the cases of VP, CrP, and CoP, the line shapes were symmetrical and Gaussian with widths independent of magnetic field.

The case of FeP differed from the others in that the linewidth was both field- and temperature-dependent. Below 120°K the linewidth became too great for the line to be observed. This is thought to be due most likely to magnetic impurities. The lower phosphides of iron, Fe_2P and Fe_3P, are magnetic while the lower phosphides of the other compounds are not. It seems possible that local deviations from stoichiometry and metal interstitials cause small regions of the FeP samples to become magnetic. This explanation is supported by the indications of magnetic impurities in the susceptibility data of FeP alone.

2. Co^{59} Resonance in CoP

The resonance shift on the cobalt nucleus was measured relative to the reference compound $K_3Co(CN)_6$ at 4.2 and 2°K in a field of 10 000 Oe. Co^{59} has a spin of $\frac{7}{2}$ and a quadrupole moment of 0.5×10^{-24} cm^2. The values given for the shift are those obtained from the $I=-\frac{1}{2}\rightleftarrows+\frac{1}{2}$ transition. The shift was independent of temperature at the two temperatures studied. It was found to be $-(0.361\pm0.010)\%$. No line was found at either 298 or 77°K because of the weakness of the signal.

TABLE III. P^{31} resonance shifts (in percent).

	298°K	77°K	4.2°K
VP	0.023 ± 0.004		
CrP	-0.166 ± 0.010	-0.143 ± 0.010	-0.143 ± 0.010
FeP	0.034 ± 0.002		
CoP	0.360 ± 0.010	0.345 ± 0.010	0.345 ± 0.010

Quadrupole splitting of the Co^{59} resonance line was observed. The central line was asymmetrical with a width of 17.8 ± 2.0 Oe. Satellite lines corresponding to the $I=\pm\frac{1}{2}\rightleftarrows\pm\frac{3}{2}$ transitions were observed on each side of the central line. They were separated by 136 ± 6 Oe and were equidistant from the center of the $I=-\frac{1}{2}\rightleftarrows\frac{1}{2}$ line. The satellite lines were broad and their maximum nearer to the central line was attenuated because of interference with the central line. The other satellites were not observed owing to their weak intensity.

VI. SUMMARY OF GOODENOUGH'S THEORY

Goodenough's theory for the transition metal monophosphides assumes that a formal valence state of $M^{3+}P^{3-}$ is approximately correct and that the $3d$ metal states lie in a gap between the occupied phosphorus $3sp$ valence band and an empty conduction band. However, as will be mentioned later, the NMR results indicate some overlap from the conduction band. The cubic component of the crystal field splits the e_g states (which are directed toward the anions) and the t_{2g} states. The latter are involved in the metal-metal bonding. Those states for which the intermetallic distance R is less than a critical value R_c are considered banded and their electrons itinerant. On the other hand no banding occurs for states for which R is less than R_c, and their electrons remain localized. The value of R_c is determined semi-empirically. Goodenough finds a value of 3.05 ± 0.15 Å for MnP, from which the values for the other compounds may be predicted. These values together with the various known intermetallic distances are given in Table IV. These considerations then lead to the schematic band structures shown in Figs. 8, 9 and 10.

TABLE IV. Room-temperature metal-metal distances and critical distances for the transition-metal monophosphides.

	$R_{me,me}$(Å)	R_c(Å)
VP	3.12, 3.19	3.21
CoP	2.91, 3.12, $\cdots$	3.18
MnP	2.85, 3.17, 3.90	3.15
FeP	2.79, 3.10, 3.80	3.12
CoP	2.76, 3.28, 3.75	3.03

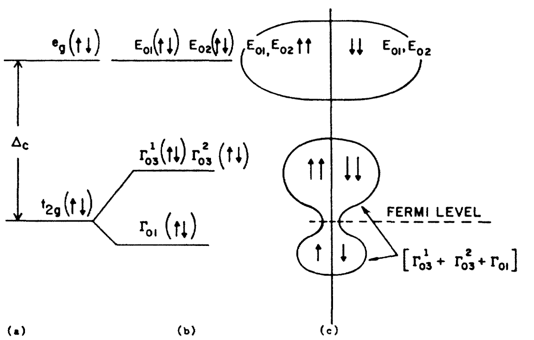

FIG. 8. Schematic density of states diagram for VP. (a) Cubic field splittings. (b) Total ligand field splittings including the effect of the trigonal distortion. (c) Energy-band diagram obtained by broadening into bands those states for which $R<R_c$ and $\lambda>\lambda_c$.

Vanadium phosphide has the hexagonal *B8* structure which gives the crystal field splittings shown in Fig. 8. Since both metal-metal distances in this structure are less than R_c, the Γ_{01}, Γ_{03}^1, and Γ_{03}^2 states are all banded, as depicted in Fig. 8c, and represent itinerant electrons.

The remaining phosphides have the *B*31 structure. In this case the orthorhombic distortion splits the remaining degeneracies. (See Figs. 9a, 9b, and 9c.) Because of the distortion, the metal-metal distances are altered such that $R<R_c$ and $R>R_c$ may be found. The wave functions corresponding to the Γ_{01} and Γ_{03}^1 levels are directed such that the interatomic separation is less than R_c. These levels are then broadened into overlapping bands. The wave function corresponding to the Γ_{03}^2 level is directed such that we have $R>R_c$ and the state is considered localized.

If the localized Γ_{03}^2 states are partially occupied, an intra-atomic exchange splitting is induced, since the exchange energy gained more than compensates for the increased Bloch kinetic energy. Depending on the magnitude of this splitting the compound may be in either a high- or a low-spin state. The saturation moment of MnP indicates that it is in a low-spin state, i.e. $\Delta_{ex}<\Delta_c$. This leads to the band structure shown in Fig. 10.

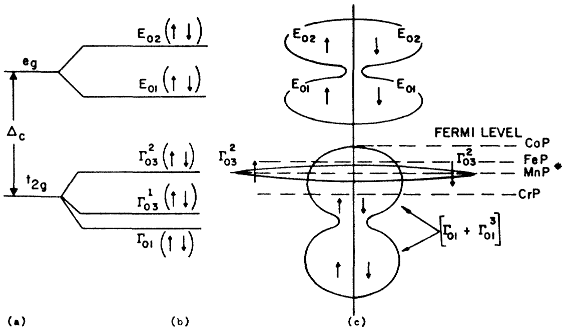

FIG. 9. Schematic density of states diagram for CrP, FeP, MnP*, and CoP. (a), (b), and (c) have the same significance as in Fig. 8. The intersection of the Fermi level with the Γ_{03}^2 state which leads to magnetic MnP is shown explicitly.

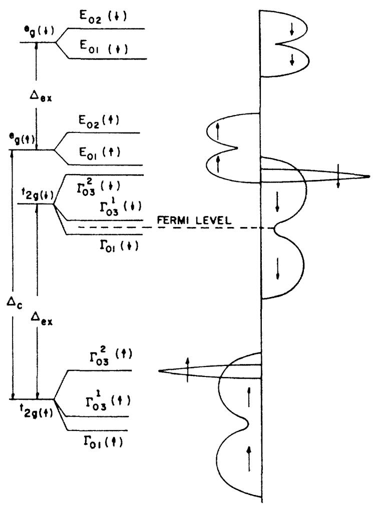

FIG. 10. Schematic density of states diagram for magnetic MnP.

VII. DISCUSSION

The magnetic susceptibility and nuclear magnetic resonance results reported in this paper present three basic features which must be explained by any comprehensive theory: (1) All the transition metal monophosphides are metals; (2) For all the compounds in the series, only MnP is magnetic. The rest exhibit no spontaneous magnetism down to 4.2°K. (3) CoP has a susceptibility which is from three to six times smaller than those of the other nonmagnetic compounds.

The only existing theory which can be tested is that due to Goodenough, which we have outlined briefly, and we will show in the following discussion that it is indeed consistent with these facts.

To interpret the magnetic susceptibility results within this model, we note the position of the Fermi level in each of the compounds. Any small overlap from the *s*-*p* conduction band would not affect the magnetic susceptibility results significantly, because of the low density of states in this band compared with that in the *d* band.

VP has a $3d^2$ configuration. Consequently the Fermi level lies at a minimum in the density of states, leading to a small, relatively temperature-independent susceptibility as observed.

CrP has a $3d^2$ configuration, and the Fermi level lies at a position of greater magnitude in the density of states than it does for VP. Experimentally, the value of the susceptibility of CrP, 3.80×10^{-6} at room temperature, is about three times the value for VP.

MnP, with a $3d^4$ configuration, presents a case in which the localized states are half occupied in the nonmagnetic state. Since the density of states at the Fermi level is very large, the nonmagnetic state is unstable. An intra-atomic exchange splitting then occurs and MnP is magnetic, as observed. If the splitting is greater than the width of the banded states, as shown in Fig. 10, a spin-only value of $2\mu_B$ per ion would result. On the other hand, if the splitting proceeds only so far as to spin polarize the localized Γ_{03}^2 state, the saturation moment would be $(1+\alpha)\mu_B$, where α is approximately the ratio of the width of the localized Γ_{03}^2 state to the width of the banded Γ_{03}^1 state. This latter alternative appears to be closer to the experimental value of $1.29\mu_B$. Of course, some intermediate degree of overlapping of the broad-band states is also possible.

In FeP, which has the $3d^5$ configuration, the Fermi level is above the localized states, lying near the maximum in the broadband states. Experimentally, FeP is found to be paramagnetic with a room-temperature susceptibility of 4.0×10^{-6}, slightly larger than that of CrP.

CoP has a $3d^6$ configuration and therefore illustrates the case of a nearly full $3d$ subband. It exhibited the smallest experimental susceptiblitiy, being 0.6×10^{-6} at room temperature.

The P^{31} resonance shifts show the decrease with increasing susceptibility usually observed in transition-metal binary alloys, but do not exhibit a strict linear relationship. This is not surprising, however, since the bands cannot be expected to be rigid in compounds of this type.

In the case of CoP there is a substantial positive shift, typical of a metal. This can be produced only by an s-wave amplitude on the phosphorus sites. Since this susceptibility indicates full d band, it would appear that some phosphorus s band is only partially filled in the ground state, and the most likely candidate is the conduction band. We suggest, then, that the d band does not lie in a gap, as first supposed, but rather is overlapped by the bottom of the conduction band.

VIII. SUMMARY AND CONCLUSIONS

The transition metal monophosphides were chosen for study because the interatomic spacings and the anion electronegativity lie in a range intermediate between the metals and the oxides. It was hoped that if the nature of the electronic d states in these compounds could be elucidated and correlated with their magnetic properties, we would obtain some insight into the relative importance of itinerant and localized states for the occurrence of ferromagnetism in the transition metals.

The magnetic susceptibility results indicate that Goodenough's proposal for the d-band structure is qualitatively satisfactory. Not only do its predictions concerning the relative magnitudes of magnetic susceptibilities agree with experiment, but it also explains why MnP is magnetic while FeP and CoP are not. As a result of the distorted $B31$ structure, some metal-metal distances are less than a critical distance for banding R_c and some are greater. In the nonmagnetic state, the Fermi level for MnP intersects the peak of the density of states corresponding to the localized Γ_{03}^2 state. A magnetic splitting of the ground state results since a relatively large intra-atomic exchange energy can be gained by such a splitting at little cost in Bloch kinetic energy. For FeP and CoP the Fermi level lies in the banded Γ_{03}^1-Γ_{01} states, and the nonmagnetic ground state is stable.

The NMR results show that the transition metal d states do not lie in a gap, as had been supposed originally. The 0.36% frequency shift of P^{31} in CoP, which has a nearly full d band, shows that the d band is overlapped by some state having a phosphorus s-wave component. Presumably this is from the bottom end of the conduction band. Additional weight is added to this assumption by recent results of Jones and Hesse[13] who have observed the NMR in MnP between 375 and 575°K. They find a negative shift which is temperature-dependent and proportional to the magnetization. A positive shift of approximately 0.6% is found from their K versus χ diagram by extrapolation to zero-d-band susceptibility. This is consistent with our result for CoP, which has a nearly full d band.

The critical role played by localized states in the precipitation of magnetism in these metallic compounds suggests a generalization to the transition metals themselves. The potential usefulness of this point of view is underscored by recent NMR studies of αMn which indicate the presence of both localized and itinerant electrons in that metal also.[14,15]

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