

Phosphorus Nuclear Magnetic Resonance in Transition-Metal Monophosphides: MnP, $\text{Co}_y\text{Mn}_{1-y}\text{P}$, RuP, and WP*

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The phosphorus NMR has been observed in the paramagnetic state of the metallic ferromagnet MnP. The phosphorus Knight shift was measured as a function of temperature and was found to be temperature-dependent and negative, varying from about -11% at 375°K to -2% at 575°K . Constructing a $K^{31}(T)$ -versus- $\chi(T)$ diagram for MnP yielded a straight line from which the total phosphorus hyperfine field was determined to be $H_{\text{hf}} = -37.4$ kOe per Bohr magneton. The effect of alloying cobalt into MnP upon the phosphorus Knight-shift data is presented. Additional phosphorus Knight-shift data in the nonmagnetic transition-metal monophosphides RuP and WP are also reported.

I. INTRODUCTION

A CONSIDERABLE amount of information concerning the electrical and magnetic properties of the transition-metal monophosphides can be found in the literature. Electrical-conductivity^{1,2} and magnetic-susceptibility measurements³⁻⁵ indicate that these compounds are basically metallic in nature. Interpretation of recent nuclear magnetic resonance (NMR) studies in the nonmagnetic transition-metal phosphides^{4,5} corroborate the concept of metallic conductivity in these compounds. A semi-empirical theory of metallic banding in some transition metal phosphides has been given by Goodenough,⁶ who used the Mott⁷⁻⁹ formalism of critical radii for the interatomic metal-metal distance as a criterion for the existence of d bands in these compounds. Using the Mott⁷⁻⁹ approach, Goodenough⁶ has proposed a series of density-of-states curves for the transition-metal monophosphides which have the $B8$, or the $B31$ crystal structure. Recently, Stein and Walmsley⁴ claim to have verified qualitatively Goodenough's predictions⁶ using the results of their magnetic and NMR measurements in the nonmagnetic transition-metal monophosphides.

Of current interest are the questions regarding the origins of magnetic coupling and nuclear hyperfine fields in transition metals and transition-metal intermetallic compounds. A convenient experimental method for obtaining information regarding the strength, sign, and temperature dependence of the nuclear hyperfine fields is afforded by NMR measurements. For example, with this type of information comparisons can be made

with the temperature dependence of the magnetization of the sample under study.

In current theories of nuclear hyperfine fields in metals, a knowledge of the signs of the various contributions to the total hyperfine field is a prerequisite in order to ascertain the sources of these hyperfine interactions. The purpose of this paper is to present and discuss the results of phosphorus NMR Knight-shift measurements in the paramagnetic state of MnP. Other phosphorus NMR data, such as the effect on the phosphorus NMR of alloying the nonmagnetic isomorph CoP in varying amounts with MnP and also the observation of the phosphorus NMR in WP and RuP will be presented.

Manganese phosphide crystallizes^{10,11} in the orthorhombic $B31$ structure, shown in Fig. 1, which can be considered as a small distortion from the hexagonal NiAs $B8$ structure. In the $B8$ crystal structure there are eight atoms per unit cell, four metal and four phosphorus. The metal lattice has hexagonal symmetry, 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 phosphorus atoms in an octahedral configuration. Each phosphorus atom has six nearest metal atoms and is located at the center of a triangular prism formed by them. Within 4 \AA there are twelve phosphorus neighbors around a given phosphorus atom.

The $B31$ crystal structure can be regarded as an orthorhombic distortion of the $B8$ structure in which the metal atoms are displaced toward each other in the basal plane. The phosphorus atoms are displaced along the b axis. Each metal atom is surrounded by six phosphorus atoms in a distorted octahedron and is no longer located at the center. Each phosphorus atom is surrounded by six metal atoms at the corners of a distorted triangular prism.

Huber and Ridgley⁸ have performed magnetic measurements on a single crystal of MnP and find a Curie temperature $T_c = 291.5^\circ\text{K}$ and a magnetic transition at 50°K , below which the crystal exhibited metamag-

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² T. Suzuki, Y. Matsumura, and E. Hirahara, *J. Phys. Soc. Japan* **21**, 1446 (1966).

³ E. E. Huber, Jr. and D. H. Ridgley, *Phys. Rev.* **135**, A1033 (1964).

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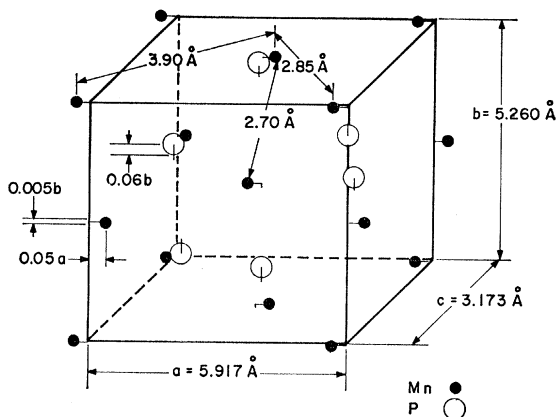


FIG. 1. The $B31$ crystal structure of MnP.

netic behavior. Neutron diffraction measurements^{12,13} in the metamagnetic temperature region of MnP revealed a modulated magnetic structure in which ferromagnetically coupled pairs of manganese spins are arranged in a spiral whose axis of propagation and rotation is $[100]$. From saturation magnetization measurements in the ferromagnetic phase of MnP, Huber and Ridgley³ deduce a value of 1.29 Bohr magnetons for the magnetic moment per manganese atom at $T=0^\circ\text{K}$. These authors also measured the temperature dependence of the paramagnetic susceptibility χ of MnP and found Curie-Weiss behavior, i.e., $\chi = C(T-\theta)^{-1}$ with $\theta=312^\circ\text{K}$ and the Curie-Weiss constant $C=1.06$ emu $^\circ\text{K}/\text{mole}$, corresponding to 2.9 effective Bohr magnetons per manganese atom. Huber and Ridgley³ also observed a small anisotropy in the paramagnetic susceptibility as a function of orientation between the applied magnetic field and the crystallographic axes.

Zero-field phosphorus and manganese NMR has been reported¹⁴ in the ferromagnetic state of MnP at 77°K . Two manganese NMR frequencies were observed having hyperfine fields of 136 and 111 kOe, and a single phosphorus NMR having a hyperfine field of 43 kOe. However, the signs of these respective hyperfine fields in the ferromagnetic state were not determined.

Section II describes the experimental apparatus used to observe the phosphorus NMR in the paramagnetic state of MnP and also the technique used to prepare the various samples. A discussion of the contributions to the magnetic susceptibility and phosphorus Knight shifts of MnP is presented in Sec. III. Sec. IV contains the experimental results and interpretation of the phosphorus Knight-shift measurements in MnP while the same type of data for the CoP-MnP alloys are presented in Sec. V. Miscellaneous phos-

phorous NMR Knight-shift data for nonmagnetic RuP and WP which have not been previously reported are discussed in Sec. VI.

II. EXPERIMENTAL

The phosphorus NMR was observed in powdered samples of the transition-metal monophosphides using a variable-frequency-induction spectrometer and a conventional laboratory electromagnet. The phosphorus Knight shifts were determined at a fixed frequency by measuring the magnetic field with respect to the phosphorus NMR in red phosphorus. Sample temperatures were controlled by the use of a calibrated variable temperature unit.

The samples were prepared by mixing correct proportions of phosphorus and transition metal in a quartz pressure bomb and heating to approximately 900°C for several days. Under these conditions a solid-state diffusion reaction occurs. When necessary, a small amount of excess phosphorus was added to the mixture in order to ensure sample stoichiometry. The samples were then pressed into a pellet and reheated in order to achieve uniformity. Standard x-ray powder pattern techniques were used to confirm that the samples had the correct crystal structure ($B31$) and lattice constants.

III. CONTRIBUTIONS TO THE SUSCEPTIBILITY AND PHOSPHORUS KNIGHT SHIFT IN MnP

A. Susceptibility

The partitioning of the various contributions to the magnetic susceptibility will be accomplished by writing an expression for the total susceptibility $\chi(T)$ in the paramagnetic state as

$$\chi(T) = \chi_0 + \chi_1(T), \quad (3.1)$$

where χ_0 and $\chi_1(T)$ are the respective temperature-independent and temperature-dependent contributions to the total susceptibility $\chi(T)$. The temperature-independent term χ_0 contains contributions from the Pauli paramagnetic susceptibility of any free-electron-like bands, the orbital susceptibility χ_{ov} (which for metals is the analog of Van Vleck orbital paramagnetism in insulators) and χ_{dia} the diamagnetic contribution from the ion cores and the filled portion of the d band. The temperature-dependent term $\chi_1(T)$ is the susceptibility associated with the magnetic properties of the d band.

The reason for not writing the customary explicit expression for χ_0 in terms of the various contributions is twofold: (1) Recent band-structure calculation for compounds¹⁵ suggest that pure s bands usually lie very high above the Fermi energy and thus are considered to be empty; (2) The total paramagnetic susceptibility $\chi(T)$ of MnP was found to obey³ a Curie-Weiss law and

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¹² J. B. Forsyth, S. J. Pickart, and P. J. Brown, Proc. Phys. Soc. (London) **88**, 333 (1966).

¹³ G. P. Felcher, J. Appl. Phys. **37**, 1056 (1966).

¹⁴ A. M. Portis and R. H. Lindquist, in *Magnetism*, edited by H. Suhl and G. Rado (Academic Press Inc., New York, 1964), Vol. 3A.

hence indicates that the contribution of χ_0 to $\chi(T)$ in the room-temperature region is negligibly small. Thus the distinctions between the various contributions to χ_0 are relatively unimportant in the analysis of the phosphorus Knight-shift data in MnP.

The temperature dependence of $\chi(T)$ is thus contained in the contribution from the d band susceptibility $\chi_1(T)$, and from the analysis of the phosphorus Knight-shift data in the paramagnetic state of MnP an estimate of the magnitude of χ_0 will be made.

B. Phosphorus Knight Shift

The phosphorus NMR frequency is shifted from the Larmor frequency by an amount $K^{31} \equiv (\delta H/H)$ by interactions between the conduction electrons and the phosphorus nuclear magnetic moment. The phosphorus Knight shift K^{31} consists of two terms: (1) A temperature-independent Knight shift K_0 arising from both the Fermi contact interaction of the phosphorus nuclear moment with s electrons and an interaction between the phosphorus nuclear moment and the magnetic-field-induced orbital magnetic moment; (2) a temperature-dependent Knight shift $K_1(T)$ resulting from a hyperfine interaction of the form $A\mathbf{I} \cdot \langle \mathbf{S} \rangle$ where $I = \frac{1}{2}$ is the phosphorus nuclear spin, A is the hyperfine coupling constant, and the temperature dependence of this interaction is contained in the time-averaged value of the manganese spin $\langle \mathbf{S} \rangle$. At the present time, the origins of the interaction between the phosphorus and manganese d spins are unknown. There are several mechanisms which can account for this interaction. However, the experimental results which will be presented in this paper are incapable of distinguishing between them.

Briefly, the various mechanisms which give rise to an interaction of the form $A\mathbf{I} \cdot \langle \mathbf{S} \rangle$ are as follows: The first to be considered is the Ruderman-Kittel-Kasuya-Yosida (RKKY)¹⁶⁻¹⁸ mechanism in which s -like conduction electrons are spin polarized by an s - d exchange interaction with localized d spins, thus producing a phosphorus Knight shift which will be proportional to the d -spin susceptibility. A second model, which was first proposed by Clogston and Jaccarino,¹⁹ involves an overlapping p - d band in which the p electrons are strongly admixed with the d electrons and the p electrons in turn produce a phosphorus Knight shift through core polarization of the inner phosphorus s -shell electrons. This mechanism also predicts a phosphorus Knight shift which would be proportional to the d -spin susceptibility. However, for both of these mechanisms, the resulting phosphorus Knight shift may be of either sign, i.e., positive or negative, depending on the details of the exchange polarization mecha-

nism. A third mechanism which predicts a phosphorus Knight shift proportional to the d -spin susceptibility, considers the possibility of a finite d wave-function overlap with the inner electron shells of the phosphorus atom which will cause core polarization of the phosphorus inner s shell electrons and hence, presumably a negative Knight shift. Another possible source of a phosphorus hyperfine interaction which would be proportional to the manganese d -spin susceptibility is the effect of a transferred hyperfine field through a covalent bond formed from localized manganese and phosphorus wave functions. This type of transferred hyperfine interaction is commonly observed in magnetic insulators, e.g., $\text{Se}^{77}:\text{MnSe}$.²⁰

The total temperature-dependent phosphorus Knight shift is thus written as

$$K^{31}(T) = K_0 + K_1(T), \quad (3.2)$$

where K_0 is the temperature-independent part of the conduction electron Knight shift and $K_1(T)$ is the temperature-dependent Knight-shift contribution proportional to the d -spin susceptibility. An expression for $K_1(T)$ can be written in the general form of

$$K_1(T) = (N\beta)^{-1} H_{\text{hf}} \chi_1(T), \quad (3.3)$$

where N is Avogadro's number, β is the Bohr magneton, H_{hf} is the total phosphorus hyperfine field per Bohr magneton, and $\chi_1(T)$ is the manganese spin susceptibility expressed in emu/mole. There is no diamagnetic-shift contribution included in Eq. (3.2) since the incremental-diamagnetic shift between MnP and the reference compound (red phosphorus) used to measure the Knight shift is negligible.

From Eqs. (3.2) and (3.3) it is evident that a graph of $K^{31}(T)$ versus $\chi(T)$, with temperature the implicit parameter, should be a straight line. The straight line will have a value K_0 at $\chi(T) = \chi_0$ and a slope α of

$$\alpha = \partial K^{31}(T) / \partial \chi(T) = (N\beta)^{-1} H_{\text{hf}}. \quad (3.4)$$

Thus the construction of a $K^{31}(T)$ versus $\chi(T)$ diagram will provide information regarding the sign and magnitude of the phosphorus nuclear hyperfine field H_{hf} per Bohr magneton.

IV. CONSTRUCTION OF THE $K(T)$ VERSUS $\chi(T)$ DIAGRAM: MnP

The phosphorus NMR was observed in powdered samples of MnP between 375 and 550°K. The phosphorus NMR linewidth was found to be dependent upon the magnetic susceptibility of the powder sample. For the lower-temperature range there was some evidence of an anisotropic phosphorus Knight shift even though the phosphorus NMR linewidth was approximately 150 Oe at 375°K and 16 Mc/sec. The measured temperature dependence of the phosphorus Knight shift $K^{31}(T)$ in MnP is shown in Fig. 2. It is to be noted

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¹⁷ T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).

¹⁸ K. Yosida, Phys. Rev. **106**, 893 (1957).

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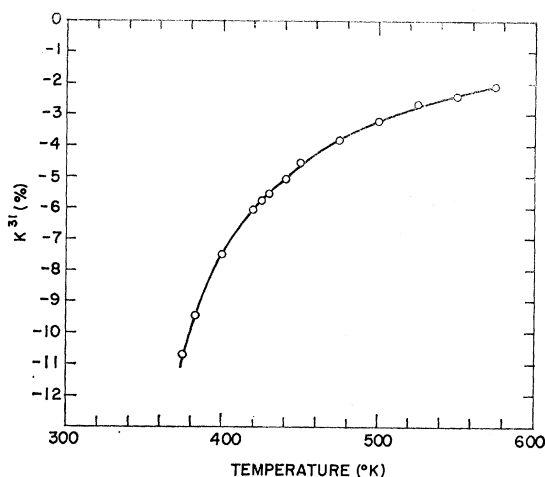


FIG. 2. The temperature dependence of the phosphorus Knight shift $K^{31}(T)$ in MnP. The solid line is a smooth curve drawn through the experimental data.

from Fig. 2 that the phosphorus Knight shift is strongly temperature-dependent and negative.

Figure 3 shows the results of plotting the phosphorus Knight-shift data shown in Fig. 2 as a function of the paramagnetic susceptibility χ as measured by Huber and Ridgley.³ It is evident from Fig. 3 that the plot of $K^{31}(T)$ versus χ does give a straight line as predicted by Eqs. (3.2) and (3.3). The slope α of the $K^{31}(T)$ versus $\chi(T)$ diagram is found from Fig. 3 to be $\alpha = -6.70$ (emu/mole)⁻¹ corresponding to a total phosphorus hyperfine field of $H_{hf} = -37.4$ kOe per Bohr magneton.

Since the magnitude and sign of the phosphorus hyperfine field H_{hf} has been determined from the paramagnetic state data, predictions for the phosphorus hyperfine field in the ferromagnetic state at $T = 77^\circ\text{K}$ can be made. Saturation-magnetization measurements⁸ in the ferromagnetic state of MnP indicate that the magnetization at 77°K is approximately 0.95 of the 0°K value of 1.29 Bohr magnetons per manganese atom. Thus the predicted phosphorus hyperfine field at 77°K is $|H(77^\circ\text{K})| = 0.95 \times 1.29 \times 37.4$ kOe = 45.8 kOe which is in good agreement with the observed value of 43 kOe.¹⁴ This small difference between the predicted and observed values of the phosphorus hyperfine field at 77°K possibly could be attributed to the fact that the experimentally observed value was probably obtained for phosphorus nuclei in domain walls and hence lack of dipolar fields, etc., need to be taken into account. Another source of error between the predicted and observed values of the phosphorus hyperfine field at 77°K in MnP could also be the value of the manganese magnetic moment used. For example, if the manganese moment were 0.90 of the 0°K value, the predicted magnitude of the phosphorus hyperfine field would be 43.4 kOe which is in better agreement

with experiment. However, the agreement between the two kinds of measurements is sufficiently good to say that the phosphorus hyperfine field in the ferromagnetic state of MnP in all probability is negative.

It is interesting to note that the phosphorus hyperfine field of $H_{hf} = -37.4$ kOe per Bohr magneton for MnP has essentially the same value found⁶ in the nonmagnetic isomorph CrP where $H_{hf} \approx -30$ kOe per Bohr magneton. This result suggests that the source of the phosphorus hyperfine field in magnetic MnP and nonmagnetic CrP have the same origins and hence the RKKY mechanism may not be appropriate for the phosphorus Knight shift in MnP.

Extrapolating the phosphorus Knight-shift data shown in Fig. 3 to zero susceptibility, yields a large value: $K_0 \approx +0.5\%$. Recent measurements⁴ in CoP find a small temperature-independent susceptibility $\chi \approx +0.36 \times 10^{-4}$ emu/mole and a phosphorus Knight shift $K^{31} \approx +0.36\%$. For the MnP data shown in Fig. 3 a phosphorus Knight shift $K_0 \approx +0.3\%$ also occurs for a susceptibility of $\chi \approx 0.36 \times 10^{-4}$ emu/mole. This result suggests that the origins of the temperature-independent susceptibility χ_0 and phosphorus Knight shift K_0 are the same in these two compounds. However, performing the same analysis in CrP,⁵ where the temperature-dependent phosphorus hyperfine field was found to have roughly the same value as observed for MnP, give an entirely different result for K_0 , i.e., for CrP, $K_0 \approx 0.0\%$.

The observed value $K_0 = +0.36\%$ for the phosphorus Knight shift in CoP⁴ and MnP is large when comparisons^{4,5} with other transition-metal phosphides are made. This large value of the phosphorus Knight shift K_0 may be evidence that there is a large orbital phosphorus hyperfine field in these two compounds, but not in the other transition-metal monophosphides. However, the situation regarding the origins of K_0 in MnP, CoP, and CrP is unclear.

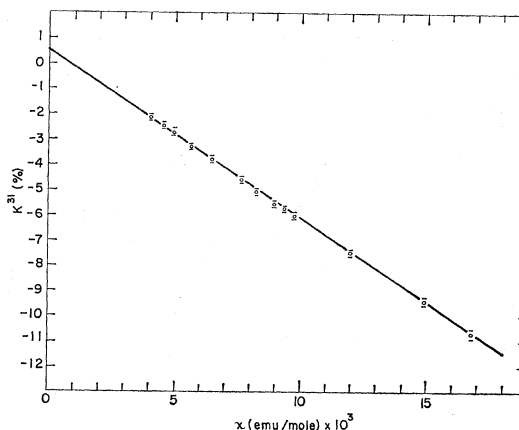


FIG. 3. A plot of $K^{31}(T)$ versus $\chi(T)$ with temperature the implicit parameter for MnP.

V. PHOSPHORUS NMR IN $\text{Co}_y\text{Mn}_{1-y}\text{P}$ INTERMETALLIC COMPOUNDS

In order to obtain further information regarding the origin of the negative temperature-dependent phosphorus Knight shift in MnP, phosphorus Knight-shift measurements were performed in the intermetallic compounds $\text{Co}_y\text{Mn}_{1-y}\text{P}$ in the range of $0 < y < 1$.

Experimentally, a single phosphorus NMR was observed for each compound and within experimental error, there was no evidence of a broadening of the phosphorus NMR linewidth that could be attributed to the effect of a random distribution of magnetic moments. In addition to the phosphorus NMR linewidth measurements, intensity measurements did not indicate any dependence on the cobalt or manganese concentration. The phosphorus NMR intensity measurements themselves, however, have an inherent uncertainty due to differences in particle size, sample volume, etc., which are difficult to estimate and therefore are not as reliable as the NMR linewidth measurements. Both of these results are contradistinctive to the results of other NMR measurements in nonmagnetic intermetallic hosts when a localized magnetic impurity is added.²¹ Under these conditions the resulting host NMR linewidth is found to be dependent upon the magnetic impurity concentration and can be interpreted in terms of the RKKY mechanism.

The cobalt NMR was observed in CoP at room temperature, however, upon an addition of 10% manganese to CoP, the cobalt NMR was unobservable. At this point it is worth mentioning that the manganese NMR in the paramagnetic state of MnP was also unobservable. An attempt to study the cobalt NMR linewidth in CoP containing 1% manganese was made. However, these samples were found to consist of two phases; this was verified by the observation of two phosphorus NMR. One of the phosphorus NMR was very weak in intensity and had a Knight shift equal to the one measured in CoP, while the other (strong-intensity) phosphorus Knight shift was found to be shifted slightly negative from CoP. However, in the 1% manganese in CoP compound, there was only one cobalt NMR observed having a very weak intensity and a Knight shift equal to the pure CoP sample. These data suggest that the cobalt NMR in $\text{Co}_y\text{Mn}_{1-y}\text{P}$ alloys disappears for a finite amount of manganese. There are several explanations which may account for the disappearance of the cobalt NMR and two of the most plausible are: (1) There is a quadrupolar broadening of the cobalt NMR linewidth due to the effect of a random distribution of electric field gradients; (2) The cobalt nucleus experiences a large hyperfine field, with the origins arising from the same interactions responsible for the manganese nuclear hyper-

²¹ A. C. Gossard, V. Jaccarino, and J. H. Wernick, J. Phys. Soc. Japan **17**, Suppl. B-1, 88 (1962).

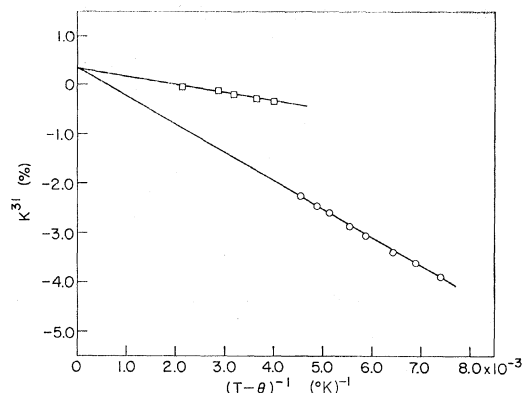


FIG. 4. A plot of the phosphorus Knight shifts $K^{31}(T)$ in $\text{Co}_y\text{Mn}_{1-y}\text{P}$ as a function of $(T-\theta)^{-1}$. The Curie-Weiss temperature θ has been adjusted to give a linear relationship between $K^{31}(T)$ and $(T-\theta)^{-1}$. The open circles are data for 10% Co and the squares are for 20% Co in MnP.

fine field, and hence resulting in a large cobalt NMR linewidth. Thus, for this case, the concept of a nonmagnetic cobalt atom is not valid. Therefore, it is tentatively concluded that for $\text{Co}_y\text{Mn}_{1-y}\text{P}$, the result of adding manganese to CoP is to deplete the number of electrons in the nearly full CoP d band or conversely, adding cobalt to MnP fills the d band. The magnetic properties of these compounds and hence the resulting phosphorus Knight shifts, are apparently determined by the number of electrons in the d band.

In the analysis of the phosphorus Knight-shift data in MnP, the observed linear relationship between the paramagnetic susceptibility $\chi(T)$ and the phosphorus Knight shift $K^{31}(T)$ was used to obtain the magnitude and sign of the phosphorus nuclear hyperfine field due to the d band. Unfortunately, at the present time, no paramagnetic susceptibility measurements are available for the $\text{Co}_y\text{Mn}_{1-y}\text{P}$ compounds for $0 < y < 1$. However some of the phosphorus Knight-shift data in $\text{Co}_y\text{Mn}_{1-y}\text{P}$ can be analyzed by noting that for MnP, the paramagnetic susceptibility obeyed a Curie-Weiss law.³ Thus the phosphorus Knight shift in MnP could have been written as

$$K^{31}(T) = K_0 + H_{\text{hf}}C[N\beta(T-\theta)]^{-1}, \quad (5.1)$$

with $C = 1.08$ (emu- $^\circ\text{K}/\text{mole}$) and $\theta = 312^\circ\text{K}$.³ It is not unreasonable to assume for the higher manganese concentrations of the $\text{Co}_y\text{Mn}_{1-y}\text{P}$ compounds that the paramagnetic susceptibility will also obey a Curie-Weiss law with different values for C and θ . Figure 4 shows the phosphorus Knight shifts in $\text{Co}_{0.1}\text{Mn}_{0.9}\text{P}$ and $\text{Co}_{0.2}\text{Mn}_{0.8}\text{P}$ plotted as a function of $(T-\theta)^{-1}$. The value of the Curie-Weiss constant θ has been adjusted for each compound in order to give a straight line. For the higher cobalt concentrations, the temperature dependence of the phosphorus Knight-shifts was negligible and no attempt was made to analyze the

TABLE I. Phosphorus Knight shifts at 300°K in $\text{Co}_y\text{Mn}_{1-y}\text{P}$ alloys.

Compound	K^{31} (%)
CoP	0.36
$\text{Co}_{0.9}\text{Mn}_{0.1}\text{P}$	0.26
$\text{Co}_{0.75}\text{Mn}_{0.25}\text{P}$	0.02
$\text{Co}_{0.2}\text{Mn}_{0.8}\text{P}$	-0.20
$\text{Co}_{0.1}\text{Mn}_{0.9}\text{P}$	^a
MnP	^a

^a The phosphorus NMR was not observable at 300°K in these intermetallic compounds.

data. It is to be noted in Fig. 4 that extrapolating the Knight-shift data to infinite temperature yields a value for K_0 consistent with that found for the case of CoP,⁴ i.e., the nearly filled d band. It is also evident that the addition of cobalt to MnP tends to reduce the magnitude of the negative phosphorus Knight shift contribution. Table I lists the phosphorus Knight shifts for CoP, $\text{Co}_{0.90}\text{Mn}_{0.10}\text{P}$, and $\text{Co}_{0.75}\text{Mn}_{0.25}\text{P}$ for $T=300^\circ\text{K}$. The temperature dependence of these phosphorus Knight shifts was negligible between 100 and 600°K.

Since the phosphorus hyperfine fields in MnP and CrP^5 were found to be essentially equal, it is not unreasonable to assume that for the $\text{Co}_y\text{Mn}_{1-y}\text{P}$ alloys, the total phosphorus hyperfine field has a constant value $H_{\text{hf}} \approx -37.5$ kOe per Bohr magneton. In this manner the Curie-Weiss constant and hence μ_{eff} , the effective number of Bohr magnetons per magnetic atoms, can be determined from Eq. (5.1). The slope of the straight lines of the K^{31} -versus- $(T-\theta)^{-1}$ graph shown in Fig. 4 is

$$\partial K^{31}/\partial(T-\theta)^{-1} = (N\beta)^{-1}H_{\text{hf}}C, \quad (5.2)$$

hence C (and μ_{eff}) are given from Eq. (5.2) and the experimentally observed slopes $\partial K^{31}/\partial(T-\theta)^{-1}$. Table II lists the values for C , θ and μ_{eff} for the data shown in Fig. 4. It must be emphasized at this point, that

TABLE II. Parameters used in the analysis of the phosphorus Knight-shift data in $\text{Co}_y\text{Mn}_{1-y}\text{P}$ alloys.

Compound	θ (°K)	C (emu°K/mole)	μ_{eff}
MnP	312	1.08	2.9
$\text{Co}_{0.1}\text{Mn}_{0.9}\text{P}$	330	0.8	2.52
$\text{Co}_{0.2}\text{Mn}_{0.8}\text{P}$	0	0.084	0.82

these values for C and μ_{eff} are derived from Eq. (5.2) on the assumption that for $\text{Co}_y\text{Mn}_{1-y}\text{P}$, $H_{\text{hf}} = -37.5$ kOe per Bohr magneton and is constant across the series of compounds listed in Table II. Only after susceptibility measurements are performed on these samples can an assessment of this assumption be made.

In summary, the phosphorus Knight-shift measurements in the $\text{Co}_y\text{Mn}_{1-y}\text{P}$ alloys strongly suggest that the number of electrons in the d band is the important magnetic parameter. However, the question regarding the origin of the interaction which is responsible for the temperature-dependent phosphorus Knight shift is still unresolved.

VI. PHOSPHORUS KNIGHT SHIFTS IN RuP AND WP

The intermetallic compounds RuP and WP, which have the $B31$ structure were studied in order to as-

TABLE III. Phosphorus Knight shifts in RuP and WP.

Compound	Temperature °K	K^{31} (%)
WP	300	0.015
RuP	300	0.09
	4.0	0.04

certain if there were any unusual magnetic properties associated with them. The measured temperature dependence of the phosphorus Knight shifts in RuP and WP are presented in Table III. Within the experimental error of $\pm 0.005\%$, the phosphorus Knight shift in WP was temperature-independent. The phosphorus Knight shift in RuP exhibited a small temperature-dependent Knight shift which decreased with decreasing temperature. The Knight shifts in RuP and WP are of the same order of magnitude as the phosphorus Knight shifts measured in the 3d non-magnetic compounds such as FeP.⁴

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