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Knight Shift and Spin-Lattice Relaxation Time Measurements in the Phosphides with the Ti_3P Structure Type*

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Knight shifts for ^{31}P have been measured for the compounds M_3P (M = Ti, Zr, Hf, V, Nb, and Ta) which have the Ti_3P structure type. These Knight shifts are small, temperature independent, and positive, ranging from 0.01% for Ti_3P and V_3P to 0.03% for Hf_3P and Ta_3P. Knight shifts for ^{51}V and ^{93}Nb in V_3P and Nb_3P have also been measured and are 0.59 and 0.34% for vanadium and 0.9% for niobium. The method of tone-burst modulation was used to obtain the ^{31}P spin-lattice relaxation times. Short (~0.1 sec) relaxation times were obtained and found to be inversely proportional to the absolute temperature. These results are suggestive of participation by phosphorus in the conduction process through the contribution of electronic configurations higher in energy than the ground state configuration, s^2p^3.

Introduction

The metal-rich (M_pX with $p > 1$) compounds of the transition metals with the Group V and VI nonmetals show marked similarities of both structures and qualitative physical properties. Other than structural data, little quantitative is known about the properties of the compounds with the Ti_3P[1] structure type. Most of the metal-rich phases are metallic or semimetallic, and all have structures very different from the pure metal. The above observations hold true for a large number of transition metal-rich compounds of sulfur, phosphorus, selenium, and arsenic. The involvement of the nonmetals in bonding in these compounds seems to be rather important. The importance of trigonal prismatic coordination of chalcogens has been pointed out in a discussion of the bonding in some transition metal monochalcogenides (*1*) in which the nonmetal bonding is interpreted using the model suggested by the early work of Rundle (*2*) and Pauling (*3*). In the present paper, this model is extended to the M_3P compounds, where M is a Group IV or V transition metal.

The monophosphides of most of the first row transition metals (*4–6*) and the Group III (*7*), IV and V (*4*) transition metals have been studied by NMR. Knight (paramagnetic) shift data show that the phosphorus atoms in these compounds have wavefunctions which contribute to the conduction band at the Fermi surface. It was suggested in one of these papers, discussing the phosphorus NMR in the monophosphides (*4*), that phosphorus 3*d*-atomic wavefunctions make appreciable contributions to the electronic wavefunctions in the band system. In this paper, Knight shift data, along with spin-lattice relaxation times, are used to further substantiate this suggestion.

Solid state NMR studies to yield Knight shifts and spin-lattice relaxation times have been used for a number of years to obtain information about the contributions of atomic wavefunctions to the conduction band (*8–10*). The Knight shift (K) arises from a paramagnetism, whereas the chemical shift (σ) is a diamagnetic effect. The Knight shift is a combination of effects as given by the following equation

$$K_{tot} = K_s + K_{p,d} + K_{orb}, \qquad (1)$$

where K_s is the shift arising from those conduction electrons with *s* wavefunctions, $K_{p,d}$ is the core-

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[1] Hereafter referred to as M_3P compounds.

polarization shift arising from the interaction of conduction electrons with *p*- or *d*-like wavefunctions with core *s* electrons, and K_{orb} is the shift arising from the field-induced orbital magnetic moment of the conduction electrons with *p* or *d* wavefunctions. Since $K_{p,d}$ has been found to be negative, arguments as to the breakdown of K_{tot} into its components are difficult unless $K_{\mathrm{tot}} < 0$ or other data are available. In previous studies of phosphides no attempt to measure spin-lattice relaxation times has been made. Knight shift studies together with spin-lattice relaxation measurements can be expected to yield useful information about the conduction band. For example, Narath et al. have used Knight shifts along with spin-lattice relaxation times and other data to evaluate the separate components to the Knight shift in W (*8*), Mo (*9*), and Ir (*10*). In the case of the phosphides with the Ti_3P-structure type spin-lattice relaxation data such as reported here are extremely useful in analyzing the observed Knight shift data.

The Ti_3P Structure

The Ti_3P structure can be viewed as an array of corner- and edge-sharing tricapped trigonal prisms, as shown in Fig. 1 taken from the comprehensive review article by S. Rundqvist (*11*). Some of the metal atoms have been deleted in Fig. 1 for clarity. The space group for the Ti_3P structure is $P4_2/n$. In this structure there are three structurally inequivalent metal atoms (labeled I, II, and III) but there is only one type of phosphorus atom. The phosphorus atom is located near the centre of a trigonal prism at the corners of which are metal atoms. There are additional atoms off each of the three rectangular faces of each prism, for instance M(I) and M(II). The phosphorus coordination is tricapped trigonal prismatic, a very common coordination for phosphorus, sulfur, and related nonmetals in metal-rich compounds.

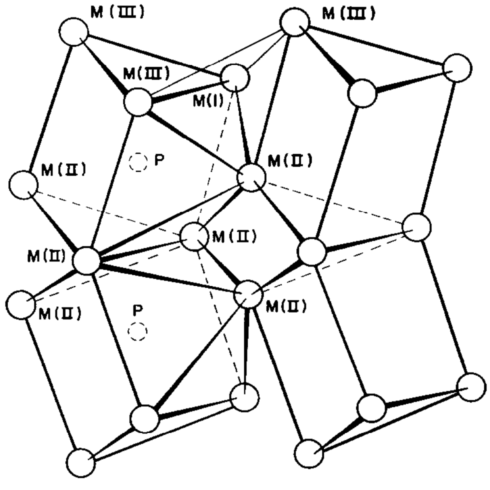

FIG. 1. The Ti_3P or ϵ_1(Fe–P–B) structure viewed down the *a* axis. M(I), M(II), M(III) are metal positions and P is the phosphorus position. Several atoms have been omitted for clarity.

Experimental

Compound Preparation

All compounds described were prepared in the same manner. Stoichiometric amounts of the elements were mixed in sealed Vycor tubes with residual pressures $<10^{-5}$ Torr. The purities of the starting materials were Ti (>99.95%), Zr (99.99%), Hf (99%, ~1% Zr), V (>99.99%), Nb (>99.92%), Ta (99.99%), and P (99.9%) (*12*). The sealed tubes were placed in a low-temperature furnace and the temperature raised to between 550 and 700°C, depending upon the sample. The tubes were removed from the furnace after all the phosphorus had reacted. Sample pellets were formed from the resulting mixture by pressing under vacuum in a tungsten carbide die, followed by isotatic pressing to 50 000 ψ. Sealed tungsten crucibles and induction heating were used to anneal the sample pellets to ~1500°C in a vacuum of $<10^{-6}$ Torr. In some cases (Ti_3P, Hf_3P, and Ta_3P), the high-temperature annealing was followed by arc-melting.

The phase identities of the resulting products were determined from Debye–Scherrer X-ray powder photographs and published structural parameters. A comparison of the intensities and $\sin^2\theta$ values from the powder patterns was made with those either published or calculated using "A FORTRAN IV Program for the Intensity Calculation of Powder Patterns", 1969 version, by Yvon, Jeitschko, and Parthé (*13*). In the case of Hf_3P an unknown phase persisted after many attempts to eliminate it. This phase represented less than 10% of the total sample. A weak and rather broad NMR peak was attributed to this impurity phase. The intensities and diffraction angles from all other samples agreed within experimental error with those calculated.

NMR Data Collection

Two spectrometers were used in the NMR data collection, a standard Varian Associates wide-line spectrometer and a spectrometer designed by D. R. Torgeson (*14*). Knight shift data were collected using the method of continuous averaging in conjunction with a 400-channel analyzer and frequencies up to 26 MHz. The spin-lattice relaxation times were measured using the method of Tone-Burst Modulation (*15*) and an apparatus designed by Torgeson and Smith (*16*). For low-temperature experiments, the samples were either immersed in liquid nitrogen, or cold gas from liquid nitrogen or liquid helium was passed over the sample. The latter method was used to attain temperatures down to 20°K for low-temperature Knight shift studies.

Phosphorus Knight shifts were determined using ^{31}P in H_3PO_4 as a reference, or by using ^7Li in LiCl solution and the ratio $\nu(P)/\nu(Li) = 1.0413$. Vanadium Knight shifts were measured with respect to the ^{51}V effective gyromagnetic ratio of 11.1927 MHz/10 kOe using ^{27}Al in $AlCl_3$ solution as an intermediate reference and the ratio, $\nu(V)/\nu(Al) = 1.0089$.

Magnetic Susceptibilities

Temperature dependence of magnetic susceptibility of all samples except Hf_3P was tested by the Faraday method. The range of temperature was 77 to 300°K. An isopentane bath was used from 113 to 273°K and an ice-water bath at 273°K. Five magnetic fields were used along with a Honda–Owen plot to extract ferromagnetic impurities (range, 1–10.8 ppm Fe).

Results

Magnetic Susceptibility

Figure 2 summarizes the results of the magnetic susceptibility measurements in a plot of $\chi(M)$ vs. T. Hf_3P was the only compound for which a susceptibility measurement was not made. However, it is estimated that the susceptibility of Hf_3P should not be much different than that of Ta_3P (note Zr_3P and Nb_3P). The susceptibilities are temperature independent or weakly temperature dependent and small indicating Pauli paramagnetism. In the case of V_3P, and perhaps Nb_3P, most of the temperature dependence at low temperatures is attributed to paramagnetic impurities such as iron phosphides which are known to have large moments (*17*, *18*). Further evidence for this conclusion is given by the temperature-independent Knight shifts. V_3P has also been described as normal and nonsuperconducting by Matthias et al. (*19*).

Knight Shift and Spin-Lattice Relaxation Times

The metal atoms in the Ti_3P structure occupy three different sets of 8*g* positions (the phosphorus atom occupies a fourth set). These positions have point symmetry one. Both the quadrupole and shift interactions may, therefore, be expected to exhibit less-than-axial symmetry.

The NMR results are summarized in Table I. All of the shift values are averages of up-field and down-field scans in order to eliminate any effects of magnet hysteresis. The ^{31}P shifts are all positive and small, with only the shifts in Zr_3P and Hf_3P showing any measurable anisotropy. The ^{31}P shifts were found not to vary with temperature down to the lowest temperature attained in each instance, i.e., 47°K (Ti_3P), 85°K (Zr_3P), 109°K (Hf_3P), 39°K (V_3P), 77°K (Nb_3P), and 103°K (Ta_3P) at a resonance frequency of 22 MHz.

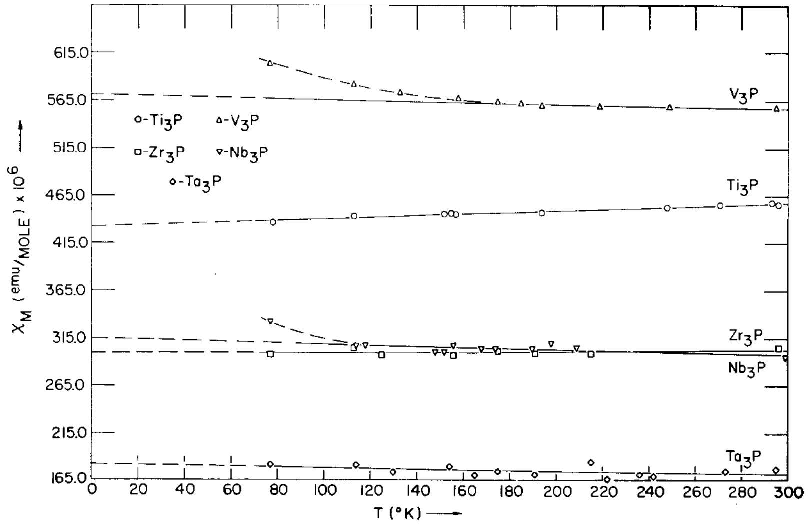

FIG. 2. A plot of magnetic susceptibility (χ_M, emu/mole) vs. the absolute temperature (T, °K) for the phosphides with the Ti_3P structure type.

TABLE I

SUMMARY OF NMR RESULTS

Compound[a]	K_{iso} (%)	K_{aniso} (%)	δH(Oe)[b]	T_1 (sec, 77°K)	T_1 (sec, 300°K)
Ti_3P	0.012(3)[c]	—	2.00(5)	0.62(5)	0.11(5)
Zr_3P	0.023(2)	−0.0064(1)	—	0.38(3)	0.13(6)
Hf_3P	0.030(1)	−0.0070(1)	—	0.57(3)	0.12(4)
V_3P	0.010(4)	—	9.1(2)	0.41(3)	0.11(1)
$^{51}V_3P$ (a)	0.59(5)[d]	—	—	—	—
(b)	0.34(5)				
Nb_3P	0.025(3)	—	8.4(1)	0.27(4)	0.09(3)
$^{93}Nb_3P$	0.9(1)[d]	—	—	—	—
Ta_3P	0.030(3)	—	4.5(1)	0.63(5)	0.15(1)

[a] ^{31}P nucleus unless otherwise noted.

[b] δH is the peak to peak width of the absorption derivative.

[c] Figure in parenthesis indicates uncertainty of the last place indicated.

[d] Estimated uncertainty.

Although the ^{31}P Knight shifts were small, the spin-lattice relaxation times were short. T_1 values are listed in Table I for both 77 and 300°K. Experimental problems were encountered in the T_1 determinations. Due to pick-up of the modulation signal, especially at large sweep widths, the base line from which the peak heights are measured became uncertain, so that within the limits of the method used the samples examined have constant values of $T_1 T$.

Knight shifts comparable to the metallic values were found for ^{51}V in V_3P and for ^{93}Nb in Nb_3P, and in the case of V_3P the ^{51}V shift did not vary with temperature down to 58°K. The ^{51}V spectrum in V_3P is rather complex and is shown in Fig. 3. The central region of this spectrum can be described as resulting from the overlap of two resonances having an intensity ratio of 2:1 and a separation of about 40 Oe at 26 MHz, the intensity ratio of 2:1 probably resulting from two of the sites having very similar shifts but different from the third site. The Knight shifts obtained in this way are $K = +0.59\%$ for two of the sites and $K = +0.34\%$ for the remaining site.

A large number of quadrupole satellite lines are also detected, as is evident in Fig. 2. However, no serious attempt was made to assign these lines, due to the complexities introduced by the nonaxially symmetric nature of the quadrupole interactions and by the presence of inequivalent sites. For the same reasons, no attempt was made to measure the ^{51}V spin-lattice relaxation time or shift anisotropy.

Similarly, in the case of the ^{93}Nb resonance in Nb_3P, the complex split central transition pattern due to the three inequivalent sites was never resolved. The stated Knight shift (Table I) is an average value

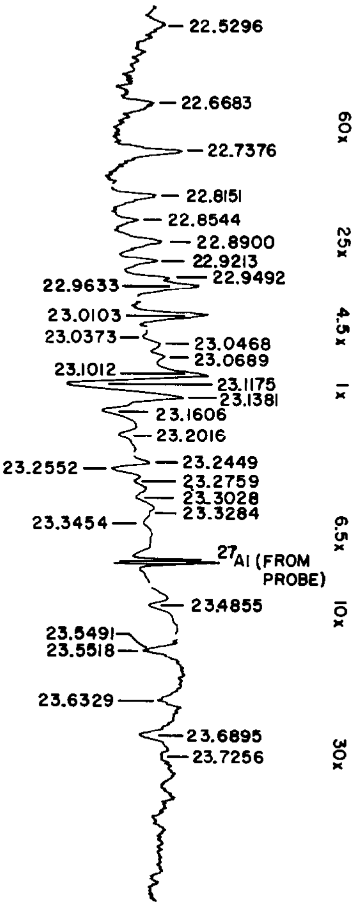

FIG. 3. The ^{51}V NMR spectrum in V_3P at 26 MHz. Approximate magnifications of the vertical axis shown above each section are relative to the central transition region (1X). Magnetic field is labeled above each peak.

for this spectrum. No attempt was made to determine T_1 in this case.

Conclusions

The magnetic susceptibility data are indicative of the metallic nature of these phosphides. In all cases, the susceptibilities behave very similarly to those of the metals themselves. No anomalies in the temperature dependence are observed, and it seems likely that the departure from straight-line behavior at lower temperatures for V_3P and Nb_3P is due to impurities. Table II presents a comparison of the susceptibilities (per g-atom) with those of the metals (*20*, *21*). For more direct comparison, the phosphide values are also given on a per metal atom basis. On this basis, the susceptibilities compare very closely in the cases of Ti and Zr, but the phosphide value falls below the metal value in the cases of V, Nb, and Ta by roughly the same magnitude in each case. The signs of the temperature dependence of χ are always the same in the phosphide and in the metal, showing the same (+) and (−) alternation as do the metals, and the magnitudes of the temperature dependences do not differ appreciably. In general terms, this comparison indicates that for Ti_3P and Zr_3P the orbital and *d*-spin contributions to the susceptibility are essentially unchanged from those of the metals. On the other hand, in the cases of V_3P, Nb_3P, and Ta_3P, there appears to be a significant reduction in the values of the orbital contribution, χ_{orb}, and/or *d*-spin contribution relative to those in the metals.

On the basis of the susceptibilities, comparing the case of V_3P with that of vanadium metal, we would anticipate an actual change in the ^{51}V Knight shift in V_3P of $\Delta K = +0.008\%$ between 77 and 300°K. Experimentally, we find that both the ^{31}P and ^{51}V shifts are constant within this temperature range, within the rather large limits of accuracy imposed by the complexity of the V_3P spectrum.

On the other hand, the ^{51}V Knight shift values in V_3P are essentially the same as that in vanadium metal (see Table I). This indicates that either the *d* spin and orbital contributions to the susceptibility are reduced proportionately so that the net contribution to the Knight shift remains constant, or that the effective hyperfine fields in the phosphides are sufficiently different from those in the metal that the final result again matches that found in the metal.

Phosphorus NMR shifts can be classified into two types. The first type is the relatively small chemical shift which arises from the diamagnetic interaction of the nucleus with the electrons in a completed valance shell. The second type of shift is the Knight shift which arises from the paramagnetic interaction of the nucleus with the conduction electrons. This type of shift can be large, as in MnP (*7*), or small, as observed here. In MnP the large temperature-dependent phosphorus shift is due to the interaction of the phosphorus nucleus with the spin-polarized conduction electrons. The spin polarization of conduction electrons comes about through conduction electron interaction with the local moment on manganese. In MnP the observed phosphorus Knight shift demonstrates that wavefunctions centered on the phosphorus nucleus contribute to the conduction band in this metallic compound.

A small NMR shift, as observed here for the M_3P compounds might be interpreted as an indication that phosphorus in these phosphides is present with a completed valence shell (e.g., chemical shift). However a small shift is expected due to the small hyperfine field of phosphorus (*6*, *22*), and similarities in structural and physical properties (excepting the local moment) of MnP and the M_3P compounds suggest that the small Knight shift interpretation is more reasonable.

When Knight shifts are small, the interpretation is facilitated by spin-lattice relaxation time (T_1) data. For phosphorus with fully satisfied valences, T_1's are expected to be on the order of tens of seconds (e.g.,

TABLE II

COMPARISON OF PARAMAGNETIC (*M*) SUSCEPTIBILITIES OF THE M_3P PHOSPHIDES AND THE TRANSITION METALS[a]

	Ti	Ti_3P	V	V_3P	Zr	Zr_3P	Nb	Nb_3P	Ta	Ta_3P
χ_M (at 300°K)	147	457	298	554	120	302	204	296	154	174
χ_M (per metal atom) (at 300°K)	—	152	—	185	—	101	—	99	—	58
$\chi^{-1}(d\chi/dT)$	+1.9	+1.9	−0.6	−0.9	+2.1	+0.6	−0.9	−1.9	−0.7	−2.0

[a] Units of χ_M are 10^{-6} emu/g-atom, and those of the temperature dependence, $\chi^{-1}(d\chi/dT)$, are $10^{-4}(°K)^{-1}$. Data for the metals are from Ref. (20) and (21). Diamagnetic corrections have not been included.

P_4O_6 (*l*, 294°K), $T_1 = 17$ sec; P_4O_6 (*s*, 294°K), $T_1 = 40$ sec (*23*); P (white, α), $T_1 = 28.7$ sec (*24*)) with no proportionality to $(T)^{-1}$. For nuclei in metals on which conduction electrons have some finite density T_1's are expected to be substantially shorter.

In the M_3P compounds T_1's are in the 0.1-sec range. These T_1's are consistent with substantial coupling of the phosphorus nuclei to the lattice via conduction electrons. Thus the phosphorus relaxation times show that the phosphorus NMR shift is a Knight shift, and that phosphorus wavefunctions are included in the states which appear at the Fermi surface.

Although an evaluation of the various components of the total Knight shift shown in Eq. (1) must await other experimental data, such as low-temperature heat capacities, and calculations, such as a good tight-binding band calculation, trends are observed which may give indications at least as to the important contributions. The similarities between the susceptibilities of the pure metals and the M_3P compounds have been noted above. The observed decrease in susceptibility in the metals is attributed to a decreasing density of states toward the heavier elements in a group. Increasing metal Knight shifts are observed for the same direction within a group. It has been shown that the increase in Knight shift with decreasing susceptibility is due to the relative increase in the orbital Knight shift (*8*, *9*, *25*, *26*). In the M_3P compounds the phosphorus Knight shift follows the same trend with susceptibility. It might be expected that the same relative contributions to K_{tot} from its components are found for phosphorus in M_3P compounds. Support for this conclusion is found in the T_1 results. Table III compares values of $T_1 T$ observed for phosphorus in M_3P compounds with the values calculated using the Korringa relation (*27*),

$$T_1 T = \frac{\Delta \mu_B{}^2}{\pi k h \gamma^2 K^2}, \qquad (2)$$

assuming that the shift arises solely from the contact interaction and $\Delta = 1$. For M_3P compounds of the first transition row, the calculated $T_1 T$ is much greater than the observed value, whereas the situation is reversed for the M_3P compounds of the second and third row. If the observed increase in K_{tot} is due to a relative increase in importance of K_s, then a better fit to Eq. (2) would be expected. Thus it is concluded that the observed trends in Knight shift, magnetic susceptibility and spin-lattice relaxation times are suggestive of importance of the orbital and core-polarization contributions to the phosphorus Knight shift. These contributions, together with the metallic nature of these solids, suggest that the phosphorus wavefunctions contributing to the binding and conduction contain configurations higher in energy than the ground state.

TABLE III

A COMPARISON OF THE OBSERVED AND CALCULATED (SEE TEXT) VALUES OF $T_1 T$

$T_1 T$ ($\Delta = 1$, sec −°K)

Compound	Obsd	Calcd
Ti_3P	34	70
Zr_3P	33	19
Hf_3P	35	11
V_3P	32	101
Nb_3P	28	16
Ta_3P	44	11

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