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Nuclear Magnetic Resonance and Relaxation of ^{31}P in the Paramagnetic State of the UP-US Solid Solutions*

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Measurements by continuous wave and pulsed NMR were made on ^{31}P in the paramagnetic state of the UP-US solid solutions. All the $UP_{1-x}S_x$ compositions used have a NaCl-type structure, are good conductors of electricity, and show systematic changes in the paramagnetic Curie temperature θ and in the magnetic ordering, from type-I antiferromagnetic in UP to ferromagnetic in the US-rich compositions. Measurements were made of the Knight shift K, the linewidth ΔH, the Bloch decay time constant T_2^*, the echo decay time constant T_2, and the spin-lattice relaxation time T_1, as functions of temperature T and sulfur concentration x. K is linear in the molar susceptibility, $K=K_0+(4.0\pm0.5)\chi_M$, with $|K_0|\ll K$, and with a slope independent of x and similar to the slopes of K versus χ_M for other U compounds with magnetic ordering. The changes in θ and in magnetic ordering along the $UP_{1-x}S_x$ system that could be accounted for by RKKY-type (Rudermann-Kittel-Kasuya-Yosida) interactions are not reflected in K, thereby disqualifying the RKKY model for the Knight shift. The broad NMR lines are due to inhomogeneous effects in the powder samples (demagnetization and composition variation), and both ΔH and T_2^* are dominated by inhomogeneous magnetic fields. The spin-spin relaxation time T_2', deduced from T_2, is due mainly to homogeneous internuclear dipolar interactions. T_1 increases with temperature for all compositions, regardless of the magnetic ordering. T_1T is empirically related to K differently in the antiferromagnetic compositions ($T_1TK^2\cong$const) and in the ferromagnetic compositions ($T_1TK\cong$const). The T_1 results are analyzed in terms of recently proposed models for nuclear relaxation due to indirect interactions with localized magnetic moments via the conduction electrons.

I. INTRODUCTION

MEASUREMENTS of the Knight shift of the NMR of nuclei of nonmagnetic atoms in the paramagnetic state of metallic materials with localized moments have been made for some years.[1–5] Investigations of such materials with either ferromagnetic or antiferromagnetic orderings have furnished information on hyperfine interactions and fields, on coupling constants between conduction electrons and nuclei or localized moments, and on other important quantities in metallic magnetic materials. The conduction electrons are polarized by the localized magnetic moments, thus giving rise to the Knight shift K in the paramagnetic state. Information about the conduction-electron polarization has been obtained from the Knight shifts, using either the uniform-polarization[2–4] or the Ruderman-Kittel-Kasuya-Yosida (RKKY)[5] model. When the Knight shift in the paramagnetic state was compared to the Knight shift K_e in the isostructural nonmagnetic material, an enhancement effect due to the polarization of the conduction electrons by the localized magnetic moments was observed.[6]

A feature common to all the above measurements[1–6] is the linear dependence of K on the temperature-dependent molar susceptibility χ_M, which arises from the localized moments:

$$K=K_0+\alpha\chi_M. \quad (1)$$

The slope α in Eq. (1) is a function of the localized moment properties and of the coupling of these moments to the conduction electrons. K_0 is equal, in many reported cases, to K_e. The enhancement factor α' is introduced by writing

$$\alpha=K_e\alpha'. \quad (2)$$

Full discussion of the validity and use of Eq. (1) in the lanthanide compounds, and of various features of the Knight shift, can be found in a paper by Jones.[4]

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References to most of the published results on continuous-wave (cw) NMR in lanthanide compounds are compiled in that paper.

In contrast with the large number of Knight-shift measurements, only few measurements have been made of the spin-lattice relaxation time T_1 in the paramagnetic state of metallic materials with magnetic ordering. The first report of such measurements was made[7] for protons in β-UH$_3$ above the Curie temperature (~182°K). The important feature of T_1 in the paramagnetic state of metallic materials that was found in β-UH$_3$, and in all other later measurements,[8–11] was the increase of T_1 with increasing temperature. This contrasts with the simple behavior of metals, in which T_1T (T is the absolute temperature) is constant, and T_1 consequently decreases with increasing temperature. In the case of β-UH$_3$, which has a ferromagnetic ordering, the T_1 data obey the *empirical* relation

$$T_1T = A(T-\theta), \tag{3}$$

where θ is the paramagnetic Curie temperature and A is a constant. The behavior described by Eq. (3) has been explained[7] as due to direct interactions of the investigated proton with the localized moments of the ferromagnetically coupled uranium ions.

Later, relaxation measurements were made[8] on ^{31}P in the paramagnetic state of uranium monophosphide (UP), which orders antiferromagnetically below ~125°K. Again T_1 increases with increasing temperature, but in this case T_1 obeys the *empirical* relation

$$T_1TK^2 = p = \text{const}, \tag{4}$$

which is a generalized Korringa-type relation. The relaxation mechanism used to explain the results in β-UH$_3$ was shown to be inapplicable for UP, but indirect interactions of the investigated ^{31}P nucleus with the localized uranium moments via the conduction electrons were shown to account for relation (4), as well as for the observed magnitude of T_1.

For ^{27}Al in CeAl$_2$, PrAl$_2$, and NdAl$_2$ in the paramagnetic state, Silbernagel *et al.*[9] constructed a theory based on pair correlations that predicts that with increasing temperature, $T_{1f}T$, where T_{1f} is the contribution to T_1 of the localized f electrons, should *increase* for ferromagnets and *decrease* for antiferromagnets (in the paramagnetic state). The theory has some inaccuracies and does not account for their experimental results in that although $T_{1f}T$ was found to increase with temperature in all three compounds, one of them, CeAl$_2$, was later found[12] to be antiferromagnetic. Discussions have also been presented[8] that the theory of Silbernagel *et al.*[9] is not adequate for UP.

Recently, Shen *et al.*[10] have found that for protons in the lanthanide hydrides CeH$_x$, PrH$_x$, NdH$_x$, and SmH$_x$ ($2<x<3$), T_1 and K are empirically related by a Korringa-type relation of the same form as Eq. (4).

In the case of ^{31}P in PuP (ferromagnetic below 126°K), Fradin[11] observed the *empirical* relation

$$T_1TK = p' = \text{const} \tag{5}$$

and explained the results theoretically. Equation (5), which is similar to Eq. (3), shows definitely that the relation between T_1 and K in the paramagnetic state has a different form in ferromagnetic materials than in antiferromagnetic materials.

Measurements on a series of metallic materials exhibiting a systematic change from antiferromagnetic to ferromagnetic ordering would be useful for investigation of the different relations between T_1 and K.

We report continuous-wave (cw) and pulsed NMR studies of ^{31}P in the paramagnetic state of the UP-US solid solutions UP$_{1-x}$S$_x$, which have the desirable systematic change in magnetic ordering (Sec. II). Experimental details are given in Sec. III. Measurements of the Knight shift K, the linewidth ΔH, the Bloch decay time constant T_2^*, the echo decay time constant T_2, and the spin-lattice relaxation time T_1 for ^{31}P in the UP$_{1-x}$S$_x$ system are given and discussed in Sec. IV.

II. UP-US SOLID SOLUTIONS

UP, uranium monosulfide (US), and their solid solutions UP$_{1-x}$S$_x$ ($0<x<1$) have a NaCl-type structure, with a lattice parameter that varies from 5.589 Å in UP to 5.489 Å in US with a slight positive deviation from linearity.[13] UP, US, and the UP$_{1-x}$S$_x$ compositions are good conductors of electricity; their resistivities are less than one order of magnitude higher than the resistivity of metallic uranium (~30 $\mu\Omega$ cm).[14]

UP has a type-I antiferromagnetic structure[15] and a Néel temperature of ~125°K. UP is ferromagnetic[16]

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TABLE I. Properties of the $UP_{1-x}S_x$ samples of the present study.

	UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
Actual x (%)[a]	···	5.50	10.27	14.78	23.47	34.17	48.62
Lattice constant (Å) (±0.001 Å)[a]	5.589	5.584	5.579	5.571	5.567	5.561	5.543
Magnetic properties, ordering[b] below T_N or T_C	AF-I	AF-I	AF-IA	AF-IA	F	F	F
Néel temperature T_N (°K)[c]	125±2	122±3	102±3	95±2	···	···	···
Curie temperature T_C (°K)[c]	···	···	···	···	102±2	118±2	150±3
Paramagnetic Curie temperature θ (°K)[d]	32	51	73	91	102	···	146
Paramagnetic moment (μ_B)[d]	3.19	3.21	3.10	3.03	2.83	···	2.75

[a] The chemical analyses and lattice constants of the UP-US solid solutions will be summarized in a paper by M. Kuznietz, G. H. Lander, and Y. Baskin (to be published).

[b] Reference 20 (AF denotes antiferromagnetic, type I or IA; F denotes ferromagnetic).

[c] Reference 20.

[d] Reference 17.

and has a Curie temperature of ~180°K. Magnetic susceptibility measurements[17] above 100°K on various $UP_{1-x}S_x$ compositions have shown that the paramagnetic Curie temperature increases monotonically from ~30°K in UP to ~180°K in US. All these magnetic properties were accounted for in a simple model proposed[18] for the NaCl-type compounds of U with elements of group VA (N, P, As, Sb, and Bi, denoted by v) and group VIA (S, Se, and Te, denoted by vi). According to this model, both UP and US are composed of U^{4+} cations; UP has P^{3-} anions and one conduction electron per U atom ($Z=1$), and US has S^{2-} anions and two conduction electrons per U atom ($Z=2$). The model treats the U ions by crystal field theory, and considers the magnetic interactions between the U ions (assumed to have $J=4$ as a good quantum number) to be via the conduction electrons, in an RKKY[19] mechanism. The model accounts for the type-I antiferromagnetic structure of UP, for the ferromagnetic structure of US, and for the smooth change of θ in the UP-US solid solutions. The model also accounts for the ordered and the paramagnetic moments.

The proposed model predicted the existence of intermediate magnetic structures, mainly in the UP-rich UP-US solid solutions. These structures are more complicated than those of UP or US. A neutron diffraction study[20] of the UP-US solid solutions showed that the transition from the type-I antiferromagnetic structure to the ferromagnetic proceeds through more complicated structures. In the $UP_{1-x}S_x$ system a new antiferromagnetic structure (type IA, Ref. 21) was found for low temperatures in the $0.05<x<0.10$ range, and for the compositions in the $0.10<x<0.20$ range, up to their Néel temperatures. Around $x=0.25$ another structure[22] occurred between the high-temperature ferromagnetic and the low-temperature type-IA antiferromagnetic structure. For $x \gtrsim 0.28$ the system became ferromagnetic. The various structures were summarized[20] in the magnetic phase diagram of the $UP_{1-x}S_x$ system. Both the type-IA structure, which is essentially a doubled type-I structure with layers stacked $++--$ (instead of $+-+-$ as in type I), and the new antiphase structure (five layers plus and four layers minus: $+++++----$, etc.) in $UP_{0.75}S_{0.25}$ are long-range magnetic structures, and confirm the assumption of the long-range RKKY-type interactions in the $UP_{1-x}S_x$ system.

The well-defined magnetic phase diagram of the UP-US solid solutions makes the $UP_{1-x}S_x$ system appropriate for investigation of the effects of magnetic ordering on various NMR properties in the paramagnetic state, such as the Knight shift and the spin-lattice relaxation time for the "good" spin-$\frac{1}{2}$ ^{31}P nucleus.

III. SAMPLES AND EXPERIMENTAL DETAILS

The preparation of the UP-US solid solutions is described in detail elsewhere.[13,21,23] Required amounts of UP and US were mixed and pelletized, and then heated in vacuum for 3 h at 1800°C. The products were crushed into fine powders (−400 mesh) in order to obtain randomness in the present NMR study as in the neutron diffraction study.[20] The particle size was well below the "skin depth" of these materials. Nevertheless, the samples were not completely homogenized,[23] although only the fcc phase was found by x-ray diffraction; the inhomogeneity ranges of the $UP_{1-x}S_x$ powders were about $x=x_0\pm 0.05x_0$,[23] where x_0 is the mean sulfur concentration.

The samples for our NMR study had the nominal compositions $x_0=0$, 0.05, 0.10, 0.15, 0.25, 0.33, and 0.50. The actual compositions of these samples, their lattice parameters, and their magnetic properties are

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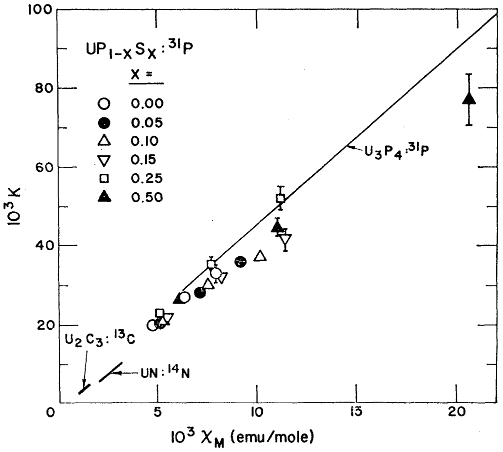

FIG. 1. Knight shift of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system as a function of the molar susceptibility, with the temperature as an implicit parameter. Also, K versus χ_M for ^{31}P in the paramagnetic state of U_3P_4 (Ref. 26), for ^{14}N in the paramagnetic state of UN (Ref. 29), and for ^{13}C in the paramagnetic state of U_2C_3 (Ref. 30).

summarized in Table I. Amounts of about 1 g of each composition were used for both the cw and pulsed NMR studies of these materials.

Continuous-wave and pulsed NMR measurements of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ compositions were made at room temperature (300°K) and at the bath temperatures of liquid freon-22 (232°K) and dry ice in liquid freon-22 (192°K). The use of bath temperatures was dictated by the pulse system.

The cw measurements were carried out with a Varian variable-frequency spectrometer (model V-4210A), generally at 15.3 MHz. The field sweep (over a range of 50 or 100 Oe) was controlled by a Varian Field Dial Mark II. Suitable field modulations (at 40 Hz), of amplitudes less than one-third of the linewidths, were used for recording the first derivatives of absorption lines by means of a lock-in detector with a suitable response time. The lines did not saturate even at the highest rf fields available (~0.3 Oe). The Knight shifts of ^{31}P in the UP-US solid solutions were measured with respect to the NMR line of ^{31}P in H_3PO_4. Although cw lines could be recorded for all compositions at room temperature, the lines could not be recorded for high sulfur compositions at lower temperatures because of the excessive line broadening due to inhomogeneity.[23] In these cases, the Knight shifts were obtained from pulsed measurements only. The lower temperatures were obtained by means of a special Dewar, which fitted into the NMR probe and was filled with the bath liquid so that the sample was immersed in the coolant.

The pulsed measurements were carried out using a phase-coherent, crossed-coil pulsed NMR spectrometer. The free-induction decay time constant T_2^* was determined from the shape of the Bloch decay following a 90° pulse. The decays were exponential. T_2^* could not be measured at the high sulfur concentrations at low temperatures because of the extremely short Bloch decays ($T_2^* < 2$ μsec). The echo decay time constant T_2 was found from the amplitude of the echo following a 90°-t-180° pulse sequence. The echo amplitude varied exponentially with the separation time t. Measurements of the spin-lattice relaxation time T_1 were generally made from the amplitude of the Bloch decay following a 180°-t-90° pulse sequence. The Bloch-decay recovery was exponential. In those cases in which T_2^* was very short, the echo-amplitude recovery following a three-pulse 180°-t-90°-τ-180° (τ = const) sequence was used for the measurement of T_1. No effects due to spectral diffusion were observed, and the change of the echo amplitude was exponential; the rf fields used (at least 50 Oe) were sufficiently large to achieve complete saturation of the lines. Knight shifts obtained by the pulsed method were taken with respect to aluminum metal (for which $K_e = 0.161\%$).

Most of the pulsed measurements were made at 12 MHz. Measurements at 8 MHz yielded different values of T_2^*, as in the case of UP.[8] T_2 and T_1 were, however, independent of frequency. All the experimental values in Sec. IV were measured at 12 MHz. For the measurements of T_2^*, T_2, and T_1, data were taken by the signal-averaging technique using a Fabritek 952 high-speed digitizer (1 μsec per channel) and 1052 signal averager.

IV. RESULTS AND DISCUSSION

The studies of cw and pulsed NMR of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system are extensions of the cw[24,25] and pulsed[8] NMR studies of ^{31}P in the paramagnetic state of UP. Continuous-wave measurements have also been made on ^{31}P in the paramagnetic state of the other uranium phosphides, U_3P_4 (ferromagnetic)[26] and UP_2 (antiferromagnetic),[27,28] on ^{14}N in the paramagnetic state of UN (antiferromagnetic),[29] and on ^{13}C in uranium carbides (antiferromagnetic U_2C_3 in its paramagnetic state, and nonmagnetic UC and UC_2).[30] The present measurements of K, ΔH, T_2^*, T_2, and T_1 for ^{31}P in the $UP_{1-x}S_x$ system are compared below with the previous measurements on U compounds that have an ordered magnetic state. The cw data are also compared to the various results for lanthanide compounds summarized by Jones.[4]

A. Knight Shift

The Knight-shift measurements for ^{31}P in the paramagnetic state of the UP-US solid solutions were

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reported previously.[31] K increases with increasing sulfur concentration x and with decreasing temperature. Figure 1 shows K as a function of χ_M values[17] in the temperature range 192–300°K for all the $UP_{1-x}S_x$ compositions studied (except $UP_{0.67}S_{0.33}$, for which χ_M data are not available from Ref. 17). The plot yields a linear dependence similar to Eq. (1) with

$$|K_0| \ll K$$

and

$$\alpha = 4.0 \pm 0.5 \text{ mole/emu}.$$

The slope α is practically the same for all $UP_{1-x}S_x$ compositions. As indicated previously,[31] α is also the same for other U compounds with an ordered magnetic state: U_3P_4,[26] UN,[29] and U_2C_3.[30] These results are also indicated in Fig. 1. The plots of K versus χ_M for ^{14}N in UN and for ^{13}C in U_2C_3 fall in regions where data for ^{31}P in $UP_{1-x}S_x$ and U_3P_4 are not available, yet all the data appear to lie near a line with a slope of about 4 mole/emu. So far only positive slopes have been reported for actinide compounds. Besides the above results, a slope α of 0.4 mole/emu was obtained for ^{1}H in β-UH_3,[32] and a slope α of 16.7 mole/emu was obtained for ^{31}P in PuP.[11,33] The positive slopes in the actinides with less-than-half-filled $5f$ shells reproduce the behavior of the slopes for the lanthanides,[1,2,4] which are positive for less-than-half-filled $4f$ shell and negative for more-than-half-filled $4f$ shells. This was initially found in $LnAl_2$ (Ln denotes a lanthanide),[1] and later in the Lnv compounds[2] and in other lanthanide compounds.[5] (Negative slopes have been reported[3] for ^{31}P in MnP and the CoP-MnP solid solutions.)

The Knight shift in metallic magnetic materials is caused primarily by polarization of the conduction electrons by the localized moments ($5f$ in our case), which brings about the term $\alpha\chi_M$ in K [Eq. (1)]. This term arises from the effective hyperfine interaction, which can be written[4]

$$A\mathbf{I}\cdot\langle\mathbf{S}\rangle = \gamma\hbar H^{\text{hf}}\mathbf{I}\cdot\langle\mathbf{S}\rangle. \tag{6}$$

In Eq. (6), A is the hyperfine interaction constant, $\mathbf{I}$ is the nuclear spin, $\langle\mathbf{S}\rangle$ is the time-averaged value of the localized spin component of the angular momentum $\mathbf{J}$, γ is the nuclear gyromagnetic ratio, and H^{hf} is the hyperfine field per *unit spin S*. For the hyperfine interaction of the form of Eq. (6), the $\alpha\chi_M$ term of K [(Eq. (1)] is given by[4]

$$\alpha\chi_M = H^{\text{hf}}(g_J - 1)\chi_M / N_A g_J \mu_B , \tag{7}$$

where g_J is the Landé factor for the localized moment, N_A is Avogadro's number, and μ_B is the Bohr magneton. Under the assumption of U^{4+} ions ($5f^2$ configuration[18]; $J=4$ and $g_J=0.8$), the value

$$H^{\text{hf}} = -90 \pm 15 \text{ kOe}$$

is obtained. H^{hf} depends on the configuration assumed, and for $5f^3$ it is -60 ± 10 kOe. The hyperfine field is negative as in the lanthanide compounds, but the magnitude is somewhat higher. Jones[4] quotes an average value of -50 kOe in the lanthanide compounds.

The slope α (or the coupling constant A) is usually[4,5,29] analyzed by the following methods.

1. *Uniform Conduction-Electron Spin Polarization*

In this model[1,2,4] the conduction-electron spins are uniformly polarized. Under the assumption of s conduction electrons and f localized moments, the s-f exchange constant J_{sf} is given by

$$\alpha = (g_J - 1) K_e J_{sf} / 2 g_J \mu_B^2 N_A , \tag{8}$$

where K_e is the Knight shift due to unpolarized conduction electrons as found, e.g., in the isostructural nonmagnetic compounds. For ^{31}P in the $UP_{1-x}S_x$ system we use the K_e of ^{31}P in ThP,[34] i.e., $+(4.4\pm0.2)\times10^{-4}$. The value

$$J_{sf} = -2.4 \pm 0.4 \text{ eV}$$

is obtained, which is similar to the value given by Jones[26] for U_3P_4. The value of J_{sf} depends strongly on the choice of K_e. However, it seems reasonable that using the value of K_e in ThP will yield at least the correct order of magnitude for J_{sf}. J_{sf} is negative, as in the lanthanide compounds[4]; this means that the uniform conduction-electron spin is antiferromagnetically coupled to the localized U moments. A representative value for J_{sf} in the lanthanide compounds[4] is -0.3 eV; the higher value for U compounds is probably a result of the greater extent of the $5f$ electronic functions.

2. *RKKY Model*

The simple form of the RKKY model,[5,19] used for analysis of K,[5] is slightly more realistic than the uniform-polarization model. The RKKY model predicts oscillatory polarization of the conduction electrons and seems to account for some features of the Knight shift in lanthanide aluminides.[5] However, difficulties in applying RKKY model to U compounds have been pointed out in the case of UN.[29] In the RKKY treatment of K, J_{sf} in Eq. (8) is replaced[29] by an expression that includes the s-f coupling constant Γ and a summation of the Ruderman-Kittel function of the distances R_{in} over all the magnetic ions i interacting with the investigated nucleus n. The value of Γ for UN obtained[29] from the analysis of the Knight shift is at least eight times higher than that obtained by Rocher's procedure[35]

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[32] J. Grunzweig and M. Kuznietz, in *Magnetic Resonance and Relaxation, Proceedings of the Fourteenth Colloque Ampère: Ljubljana, 1966* (North-Holland Publishing Co., Amsterdam, 1967), p. 1224.

[33] D. J. Lam, F. Y. Fradin, and O. L. Kruger, Bull. Am. Phys. Soc. **14**, 387 (1969); Phys. Rev. **187**, 606 (1969).

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[35] Y. A. Rocher, Advan. Phys. **11**, 233 (1962).

TABLE II. Linewidth ΔH (at 15.3 MHz) and Bloch (free-induction) decay time constant T_2^* (at 12 MHz) for ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system. The product ΔHT_2^* is given for comparison.

NMR properties		UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
$T=300$°K	ΔH (Oe)	5.8± 0.5	8.2± 0.8	9.8± 1.0	13.2± 2.0	15.5± 2.0	18.0± 2.0	22.5± 2.5
	T_2^* (μsec)	33 ± 3	24 ± 1	18.5± 0.8	13.7± 0.8	15.0± 1.5	10.4± 0.6	9.0± 0.5
	ΔHT_2^* (Oe μsec)	191 ±34	197 ±27	181 ±26	181 ±38	232 ±53	187 ±35	202 ±29
$T=232$°K	ΔH (Oe)	9.0± 0.6	14.0± 1.5	22.0± 2.0	32 ± 4	39 ± 5	...	...
	T_2^* (μsec)	18 ± 2	10.7± 0.5	7.0± 0.6	4.5± 1.0	3.2± 0.8	2.0± 0.8	<2
	ΔHT_2^* (Oe μsec)	162 ±32	150 ±23	154 ±27	144 ±50	125 ±47	...	...
$T=192$°K	ΔH (Oe)	11.5± 1.5	25 ± 3	35 ± 3	...	...	...	...
	T_2^* (μsec)	12.2± 1.2	6.2± 0.4	3.4± 1.0	<2	<2	$\ll 2$	$\ll 2$
	ΔHT_2^* (Oe μsec)	140 ±32	155 ±29	119 ±45	...	...	...	...

from the paramagnetic Curie temperature θ and the magnetic resistivity ρ_m. In the $UP_{1-x}S_x$ system the problem with the RKKY model is even more serious. Although the changes in θ on going from UP to US,[17] and in the various magnetic structures in the UP-US solid solutions,[20] are understood on the basis of the variation in the appropriate Ruderman-Kittel sum over interuranium distances,[18] the corresponding change in the sum over R_{in} distances[36] is not reflected in α or in the Knight shift. We find that in the UP-US solid solutions there is no correlation between θ and K when the simple RKKY model is used. It is therefore concluded that a simple RKKY model cannot account for the features of K in the $UP_{1-x}S_x$ system. The same conclusion was drawn by Jones[4] for the Knight shift in lanthanide compounds.

More complicated RKKY models have not been used for the analysis of the Knight shift, but they are unlikely to explain the constant value of the slope α throughout the $UP_{1-x}S_x$ system.

The intercept K_0 is of small magnitude for all the $UP_{1-x}S_x$ compositions. Since our measurements were taken at only three temperatures for each composition, the error in determining K_0 is quite large. However, from the analysis of K_0 in UP[24,25,29] it follows that the difference between K_0 and the K_e of ^{31}P in ThP is due to some temperature-independent susceptibility χ_{M0}, which is discussed also by Jones.[4]

B. Linewidth

The linewidth ΔH of each cw NMR absorption line was determined from the separation between the maximum and the minimum of the recorded first derivatives. The linewidth of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system was measured for all compositions at room temperature, for compositions up to $x=0.25$ at 232°K, and for UP, $UP_{0.95}S_{0.05}$, and $UP_{0.90}S_{0.10}$ at 192°K. The data obtained at 15.3 MHz are given in Table II. Measurements at other frequencies show that ΔH is proportional to the applied magnetic field H_0, as long as H_0 is not too small (above ~1000 Oe). From Table II it is evident that ΔH increases with increasing x and also with decreasing temperature.

In the case of UP, Friedman[25] obtained the relation

$$\Delta H \simeq bH_0/(T-\theta)\,, \tag{9}$$

with the constant $b=0.2$°K. This relation also fits our UP results (Table II). The magnetic part of the linewidth in UN[29] is also proportional to $H_0/(T-\theta)$ or $\chi_M H_0$ or the magnetization. The linewidths in the Lnv compounds were also found[4] to obey Eq. (9). However, for the UP-US solid solutions one cannot fit the linewidth with a formula similar to Eq. (9), and ΔH changes strongly with x and T. Such changes are related to the inhomogeneity of the solid solutions.[23]

For spin-$\frac{1}{2}$ nuclei (such as ^{31}P) in powdered paramagnetic materials, the contributions to the NMR linewidths and to the second moments are caused by internuclear dipolar interactions and by magnetic interactions. The magnetic interactions include both direct dipolar interactions with the localized moments and demagnetization effects.[4,32] The various linewidth contributions add through their squares and therefore through the second moments. The internuclear dipolar contribution to the second moment M_V of ^{31}P in UP is 0.22 Oe^2, and is less for the higher $UP_{1-x}S_x$ compositions. The magnetic-interaction contributions are proportional to the magnetization or $\chi_M H_0$. For applied magnetic fields that are not too small, the internuclear contribution can be neglected, and ΔH is then proportional to $\chi_M H_0$ or $H_0/(T-\theta)$, as found empirically in UP [Eq. (9)].

In UP and the UP-US solid solutions the ^{31}P nuclei are located in highly symmetric (octahedral) sites, and the dipolar field due to the localized uranium moments vanishes.[4] However, demagnetization effects due to the powdered nature of the sample do exist, and their contribution to the linewidth is proportional to the magnetization or $\chi_M H_0$.[37] We therefore expect the linewidths in the UP-US solid solutions to be propor-

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TABLE III. Measured values of the echo decay time constant T_2 of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system at 12 MHz and the computed static T_2' values.

T (°K)	UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
Measured T_2 (μsec)							
300	88±11	85±10	95±8	94±9	113±8	112±8	129±12
232	92±10	89±4	95±4	99±4	99±6	104±8	115±7
192	78±8	81±6	81±4	87±7	82±6	91±6	86±7
T_2' (μsec) from $1/T_2=1/T_2'+1/2T_1$							
300	101±17	98±16	112±22	109±22	134±19	131±23	159±27
232	112±23	111±12	118±12	125±14	122±18	128±19	148±21
192	101±15	102±15	104±14	111±18	103±18	119±20	118±28
Average T_2'	105±15	104±12	111±12	115±14	120±18	126±19	142±21

tional to χ_M when comparing measurements for the same applied magnetic field.

If all the compositions are assumed to contain particles of similar shapes and sizes, and, therefore, to have similar demagnetization effects, and if the change in χ_M in going from UP to the UP-US solid solutions is known, then the linewidth for UP can be extrapolated to yield the linewidths for the ideal homogeneous UP-US solid solutions $UP_{1-x_0}S_{x_0}$. This has been done in Fig. 2 for measurements at room temperature and $H_0\sim 8700$ Oe. The measured linewidth ΔH exceeds the extrapolated linewidth ΔH_0. The excessive linewidth $\Delta H-\Delta H_0$ is caused by the inhomogeneous nature of the UP-US solid solutions; the inhomogeneity also causes broadening of the x-ray diffraction lines and changes in the magnetic properties.[23] The inhomogeneity range δx, defined by $x=x_0\pm\frac{1}{2}\delta x$, was found to be $\sim 0.1x_0$. A second homogenization treatment of the $UP_{0.72}S_{0.28}$ solid solution has been reported[23] to reduce the linewidth of ^{31}P at room temperature from 20±1 to 15±1 Oe, which is closer to the value of ΔH_0 ($\sim$9 Oe).

The broadening of NMR lines by inhomogeneity is due to the strong dependence of K on x. Since each sample contains particles $UP_{1-x}S_x$ with x varying within the inhomogeneity range δx around x_0, the Knight shifts vary and bring about broadening of the lines. However, the centers of the lines are still a good measure of the Knight shift at the x_0 sulfur concentration. The inhomogeneity broadening is expected to affect the Bloch decay time constants T_2^*, but to have no effect on T_2 or T_1.

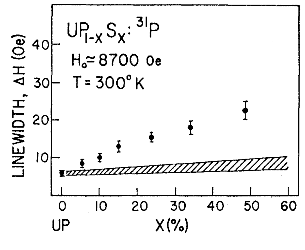

FIG. 2. Linewidth of ^{31}P in the $UP_{1-x}S_x$ system (at $T=300$°K, $H_0\simeq 8700$ Oe) as a function of the sulfur concentration x. The shaded region indicates the linewidth extrapolated from UP to completely homogeneous $UP_{1-x}S_x$ compositions.

In spite of the inhomogeneity broadening, the NMR lines were symmetric and very close to Gaussian.

C. Bloch Decay Time Constant

The Bloch (free-induction) decays following 90° pulses were exponential. T_2^* was determined from the shape of the Bloch decay by observing the time at which the decay reached $1/e$ of the "maximum" initial amplitude. The Bloch decay could not be determined for high sulfur compositions at low temperatures, since it was well below the response time (2 μsec) of the pulse system.

The T_2^* values obtained at 12 MHz are given in Table II along with the ΔH values obtained at 15.3 MHz. The variation of T_2^* at 8 MHz was in agreement with the variation of linewidth as indicated in the case of UP.[8]

Although ΔH and T_2^* were obtained at different frequencies (15.3 and 12 MHz, respectively), the proportionality expected between ΔH and H_0 permits the consideration of products $\Delta H T_2^*$, as given in Table II.

The practically constant value of $\Delta H T_2^*$ throughout the $UP_{1-x}S_x$ compositions at each temperature indicates the close relation between ΔH and T_2^* and also the similarity of line shapes (approximately Gaussian) in all the compositions. The slight change of $\Delta H T_2^*$ with temperature is not too significant, but it might be due to some change in the line shape with temperature.

D. Echo Decay Time Constant

Since most of the linewidth of ^{31}P in the $UP_{1-x}S_x$ system consists of magnetic and inhomogeneity broadenings, one expects to observe a spin echo following a 90°-t-180° pulse sequence. The center of the echo is expected to appear at a time t after the 180° pulse. The echo decay time constant T_2 is obtained from the variation of the echo amplitude with t. The results at 12 MHz are given in Table III; measurements at 8 MHz yield the same T_2 values. T_2 is independent of temperature, and increases slightly with increasing x. All the T_2 values are much higher than the T_2^* values

TABLE IV. Static spin-spin relaxation time T_2', calculated internuclear dipolar second moment M_V and linewidth ΔH_V, and $\Delta H_V T_2'$ for ^{31}P in ThP and the $UP_{1-x}S_x$ system.

NMR properties	$ThP_{0.95}$	UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
T_2' (μsec)	140±5[a]	105±15	104±12	111±12	115±14	120±18	126±19	142±21
$M_{V\,\mathrm{calc}}$ (Oe^2)	0.1640	0.2226	0.2126	0.2025	0.1918	0.1709	0.1537	0.1169
$\Delta H_{V\,\mathrm{calc}}$ (Oe)	0.810[b]	0.944	0.922	0.900	0.876	0.827	0.784	0.684
$\Delta H_V T_2'$ (Oe μsec)	113±4	99±14[c]	96±11	100±11	101±12	99±15	99±15	97±14

[a] $T_2' = T_2^*$ as determined from the Bloch decay.
[b] Measured $\Delta H = 0.85 \pm 0.10$ Oe leads to $\Delta H T_2^* = 119 \pm 18$ Oe μsec.
[c] Average value of $\Delta H_V T_2' = 99 \pm 8$ Oe μsec.

(Table II), thus indicating inhomogeneous broadening of the NMR lines.

The echo decay time constant T_2 is actually the spin-spin relaxation time, which is related to the homogeneous broadening of the NMR lines. In the present case, this broadening is due mainly to internuclear dipolar interactions, and is therefore temperature-independent. Such interactions give rise to the static value T_2' of the spin-spin relaxation time. Since the spin-lattice relaxation times T_1 (see the discussion of spin-lattice relaxation time below) are very close to T_2, the measured (dynamic) T_2 values are given by[38]

$$1/T_2 = 1/T_2' + 1/2T_1, \qquad (10)$$

where an additional spin-spin relaxation mechanism is provided by the coupling to the lattice.

The values of T_2', which are slightly longer than T_2, are also given in Table III. We find no temperature dependence, and the average T_2' values vary from ~105 μsec in UP to ~142 μsec is $UP_{0.50}S_{0.50}$.

No echo is observed in the nonmagnetic isostructural compound ThP, and the spin-spin relaxation time T_2' $(=T_2)$ is equal to the Bloch decay time constant $T_2^* = 140 \pm 5$ μsec.[8] Table IV lists values of T_2' and calculated values of the internuclear dipolar second moment M_V for ThP and for the $UP_{1-x}S_x$ system. For interactions between identical nuclei (having spin I and gyromagnetic ratio γ), M_V is given by the Van Vleck expression[39]

$$M_V = \tfrac{3}{5}\gamma^2\hbar^2 I(I+1) \sum_{n\neq 0} \frac{1}{(r_{0n})^6}, \qquad (11)$$

where the summation is over all the nuclei (n) interacting with the investigated nucleus 0. Summations for cubic lattices were given by McGarvey and Gutowsky.[40] For ^{31}P in ThP and UP, the M_V values are 0.1640 and 0.2226 Oe^2, respectively. The values for $UP_{1-x}S_x$ are computed from the UP value. The linewidths ΔH_V, related to M_V by

$$\Delta H_V = 2(M_V)^{1/2}, \qquad (12)$$

are also given in Table IV. In forming the products $\Delta H_V T_2'$ in Table IV, a constant value of about 99 Oe μsec is obtained for the UP-US solid solutions. The constant value of $\Delta H_V T_2'$ throughout the $UP_{1-x}S_x$ series and its proximity to the value of $\Delta H T_2$ ($\simeq 1/\gamma \simeq 92$ Oe μsec) for a symmetric, Gaussian-like line show the direct relation between ΔH_V and T_2' and indicate that the spin-spin relaxation takes place by internuclear dipolar interaction. The value of $\Delta H_V T_2'$ in ThP is slightly higher, probably because of a slight change in the line shape or in the homogeneous broadening.

E. Spin-Lattice Relaxation Time

Perhaps the most important results obtained in the present NMR study of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system are those for the nuclear spin-lattice relaxation time T_1. The T_1 results were independent of frequency or appplied magnetic field (as in UP[8]). Values of T_1 obtained at 12 MHz and the products T_1T are listed in Table V for different temperatures T.

Several important features can be seen for Table V:

(i) The T_1 values (150–400 μsec) are three orders of magnitude shorter than the T_1 values in the nonmagnetic isostructural compound ThP (50–200 msec).[8]

(ii) The T_1 values *increase* with temperature for all compositions, regardless of the magnetic ordering. This is in contrast with ThP, in which T_1 decreases with increasing temperature and $T_1T = 16.2 \pm 0.8$ sec °K.[8] A Korringa relation

$$T_1 T K_e^2 = (3.13 \pm 0.42) \times 10^{-6} \text{ sec °K} \qquad (13)$$

represents the results for ThP, which are similar to the behavior of most metals. The increase of T_1 in the $UP_{1-x}S_x$ system between 192 and 300°K is a factor of ~2 for all compositions.

(iii) The T_1 values are relatively constant within the experimental error throughout the UP-US system, except for $UP_{0.75}S_{0.25}$ and $UP_{0.67}S_{0.33}$, for which they are slightly higher.

(iv) The product T_1T increases rapidly with increasing temperature for all compositions, regardless of the magnetic ordering. Such a behavior contradicts the theory proposed by Silbernagel *et al.*[9] for the temperature dependence of T_1T. When T_1T is plotted as function of T, a linear dependence

$$T_1 T \cong D(T - \theta_1) \qquad (14)$$

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[38] D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

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[40] B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **20**, 1472 (1952).

TABLE V. Spin-lattice relaxation time T_1 of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system (at 12 MHz).

T (°K)	UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
			T_1 (μsec)				
300	340±15	330±17	310±30	335±35	360±25	395±40	340±25
232	250±25	227±15	248±16	236±16	265±25[a]	280±20[a]	255±20[a]
192	172±12	195±15	185±15	202±17[a]	200±25[a]	195±20[a]	160±25[a]
			T_1T (msec −°K)				
300	102±5	99±5	93±9	100±10	108±8	118±12	102±8
232	58±6	53±3	58±4	55±4	62±6	65±5	59±5
192	33±2	37±3	36±3	39±3	38±5	37±4	31±5
			θ_1 (°K) from $T_1T=D(T-\theta_1)$				
···	140±8	(134)[b]	124±18	(100)[b]	130±20	141±15	143±15

[a] T_1 determined from the three-pulse echo amplitude.
[b] A straight-line fit is only approximate.

is observed for all the compositions, except $UP_{0.95}S_{0.05}$ and $UP_{0.85}S_{0.15}$. In Eq. (14), θ_1 is the temperature at which the line T_1T versus T cuts the T axis, and D is a constant. The θ_1 values are summarized in Table V, and are equal to the Curie temperature T_C or to θ for the compositions with ferromagnetic ordering, but exceed the Néel temperature T_N for the antiferromagnetic compositions (and T_N exceeds the paramagnetic Curie temperature θ for the antiferromagnetic compositions). For the $UP_{0.95}S_{0.05}$ and $UP_{0.85}S_{0.15}$ compositions the θ_1 values are those obtained by an approximate straight-line fit to the experimental points.

Because of their appearance in Eqs. (4) and (5), the products T_1TK^2 and T_1TK are listed in Table VI. Although T_1TK^2 was constant in the antiferromagnetic compositions (as was the case in UP [8]), T_1TK was constant in the ferromagnetic compositions (as was also found by Fradin for ^{31}P in the paramagnetic state of ferromagnetic PuP [11]). However, the scatter involved in the product T_1TK^2 and T_1TK are quite appreciable, and this admits the possibility of other relations between T_1 and K.

Spin-lattice relaxation due to direct interactions of the ^{31}P nucleus with the uranium moments was shown to be inefficient in the case of UP.[8] Since the T_1 values are about the same throughout the $UP_{1-x}S_x$ system, such a mechanism is also inefficient in this case.

The relaxation mechanism in ThP is of the Korringa type, i.e., by direct interaction between the nucleus and the conduction electrons. The constant in Eq. (13) is 1.95±0.25 times the theoretical Korringa value (1.6×10^{-6} sec °K) for ^{31}P. Such a mechanism also exists in UP, but it is inefficient, as indicated above. The relaxation rate $1/T_1$ in UP is composed of the Korringa relaxation rate and another rate, which predominates. As discussed in the case of UP,[8] the efficient relaxation mechanism that gives rise to the observed order of magnitude of T_1 is due to indirect interactions, via the conduction electrons, between the ^{31}P nucleus and the localized f electrons of the U ions. Therefore, in the cases of UP and of the $UP_{1-x}S_x$ system,

$$1/T_1=1/(T_1)_{\text{Korringa}}+1/T_{1f}. \qquad (15)$$

If $(T_1)_{\text{Korringa}}$ in UP and the UP-US solid solutions is assumed to be about equal to T_1 in ThP, then

$$T_1 \simeq T_{1f}. \qquad (16)$$

We may therefore say that the relaxation mechanism in UP and the UP-US solid solutions, and in other metallic paramagnetic materials that have magnetic ordering,

TABLE VI. Temperature dependence of T_1TK^2 and T_1TK for ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system.

		Antiferromagnetic				Ferromagnetic	
T (°K)	UP	$UP_{0.95}S_{0.05}$	$UP_{0.90}S_{0.10}$	$UP_{0.85}S_{0.15}$	$UP_{0.75}S_{0.25}$	$UP_{0.67}S_{0.33}$	$UP_{0.50}S_{0.50}$
			T_1TK^2 (10^{-6} sec °K)				
300	41±3	42±3	42±6	49±8	58±7	71±11	72±9
232	42±5	41±4	52±5	57±6	77±11	94±16	117±20
192	36±5	48±7	49±7	65±11	104±24	139±37	182±59
const	39±5	45±6	47±7	57±14	···	···	···
			T_1TK (10^{-5} sec °K)				
300	204±13	203±13	197±24	220±28	251±25	289±36	271±27
232	157±15	148±10	175±15	177±16	220±26	247±32	263±34
192	109±10	133±15	134±15	160±20	198±37	226±43	238±59
const	···	···	···	···	225±45	257±45	255±35

proceeds via interactions of the investigated nucleus with the conduction electrons, which, in turn, interact with the localized moments. As the temperature is lowered to near the Curie or the Néel temperature, the magnetic interactions between the localized moments and the conduction electrons become stronger, and one therefore expects a shorter T_1 (due to a more efficient relaxation mechanism). Such behavior is indeed observed in all metallic paramagnetic materials,[8–11] and in the $UP_{1-x}S_x$ system as well.

The correct treatment of the nuclear spin-lattice relaxation in the presence of dilute localized moments in metallic materials was first given by Giovannini and Heeger[41] and later, independently, by Fradin[11] for the case of paramagnetic materials with a lattice of localized moments. The treatment of Fradin[11] introduces the generalized susceptibility $\chi(\mathbf{q})$ of the conduction electrons, which determines the ordering of the localized moments, and shows how it determines the dependence of T_1 on T in the paramagnetic state. The expression derived by Fradin is[11]

$$\frac{1}{T_{1f}T} \simeq C \sum_q [\Gamma(\mathbf{q})]^2 \chi_f(\mathbf{q}), \tag{17}$$

where $\mathbf{q}$ is the change in the conduction-electron wave vector $\mathbf{k}$, $\Gamma(\mathbf{q})$ is the s-f interaction parameter appropriately averaged over the conduction-electron states, $\chi_f(\mathbf{q})$ is the generalized susceptibility of the interacting localized f-electron moments, and C is a constant that depends on the models of the localized moments and of the conduction electrons used in the calculation.

For materials with ferromagnetic ordering, $\chi(\mathbf{q})$ has a maximum at $\mathbf{q}=0$, and, as a first approximation, the static value χ_f (which is χ_M discussed in the previous Knight-shift consideration) is used in Eq. (17). Using χ_f, one obtains the relation

$$1/T_{1f}T \cong C^f \chi_f \cong C^{ff} 1/(T-\theta), \tag{18}$$

which explains the temperature dependence of T_1 in the paramagnetic state of ferromagnetic materials by the constant value of T_1TK as mentioned in connection with Eq. (5) (C^f and C^{ff} are constants). The temperature dependence of T_1 in the ferromagnetic $UP_{1-x}S_x$ compositions (Tables V and VI) are therefore understood by the same method used by Fradin for PuP.[11] The constants θ_1 for the ferromagnetic compositions in Table V are close to θ or T_C (especially for $UP_{0.50}S_{0.50}$).

The situation is not as simple for materials with antiferromagnetic ordering, since $\chi(\mathbf{q})$ peaks around some critical wave vector $\mathbf{q}_c$, which depends on the yet unknown band structure of the electrons. One would hope to express T_{1f} in a form similar to Eq. (18):

$$1/T_{1f}T \cong C^a (T-\theta_1)^{-1}, \tag{19}$$

where θ_1 is the same constant defined in the empirical relation of Eq. (14), and should be related to T_N (C^a is a constant). The values of θ_1 cited in Table V tend to support Eq. (19); however, in the $UP_{0.95}S_{0.05}$ and $UP_{0.85}S_{0.15}$ compositions, Eq. (19) does not hold.

Since both Eqs. (18) and (19) employ the assumption that $\chi(\mathbf{q})$ is proportional to a δ function at $\mathbf{q}_c$, a good fit to the experimental results is not *a priori* certain. However, the difference expressed in Table VI between the $UP_{1-x}S_x$ compositions with ferromagnetic and with antiferromagnetic orderings is clear, though a Korringa-type relation [as given in Eq. (4)], which was expressed previously by us[8,42] and by Shen *et al.*,[10] is not necessarily the best description of the relation between T_1 and K in the antiferromagnetic case.

V. CONCLUDING REMARKS

The magnetic properties of the $UP_{1-x}S_x$ system as found by susceptibility measurements[17] and by neutron diffraction[20–22] can be accounted for by the simple model proposed for the Uv and Uvi compounds.[18] This model treats the magnetic interactions in the UP-US solid solutions, which are good conductors of electricity, by means of the RKKY mechanism.[19]

The magnetically well-characterized $UP_{1-x}S_x$ system was used for further investigation of NMR properties (of ^{31}P) in the paramagnetic state of materials with various magnetic orderings. The following conclusions can be drawn from the cw and pulsed measurements reported in this paper:

(i) The plots of K versus χ_M have a constant slope for all the compositions, despite the changes in θ and in magnetic structure throughout the $UP_{1-x}S_x$ system. Thus, a simple RKKY model cannot account for the features of the Knight shift. The same conclusion was drawn by Jones[4] for his measurements in the Lnv compounds.

(ii) The linewidth of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system has a small internuclear dipolar contribution and another contribution due to the powdered structure of the sample (demagnetization effects). However, a large portion of the linewidth is due to the sample inhomogeneity, since the Knight shift depends strongly on x. The inhomogeneity also affects the x-ray diffraction lines and the magnetic properties.[23]

(iii) The linewidth is correlated with the Bloch (free-induction) decay time constant, and the product $\Delta H T_2^*$ is constant for all compositions, with a slight temperature dependence. This indicates the dominance of inhomogeneous fields (demagnetization, composition variation) on ΔH and T_2^*.

(iv) The echo decay time constant is correlated with the internuclear dipolar linewidth, and the product $\Delta H_V T_2'$ is constant in the $UP_{1-x}S_x$ system and is close

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to the value in the nonmagnetic isostructural compound ThP. T_2' is determined by homogeneous internuclear dipolar interactions.

(v) The spin-lattice relaxation time of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system is three orders of magnitude shorter than T_1 in ThP, does not have the simple temperature dependence that occurs in metals ($T_1T=$const), and *increases* with temperature for all compositions, regardless of the magnetic ordering. The product T_1T *strongly increases* with temperature for all compositions, thus contradicting the previously proposed theory of Silbernagel *et al.*[9] The present results support the treatment given recently by Fradin.[11] For the ferromagnetic compositions a relation T_1TK $=$const is obtained, similar to Fradin's result[11] in PuP and also to the result in β-UH_3,[7] although the latter involves larger experimental errors. For the antiferromagnetic compositions a different relation is obtained, but it cannot be formulated in a simple formula as in the case of ferromagnetic compositions. Relations such as $T_1TK^2=$const or $T_1T=D(T-\theta_1)$ can be used to approximately characterize the temperature behavior of T_1 in the antiferromagnetic compositions, with the latter [Eq. (14)] having some basis in the treatment of Fradin.[11]

The NMR results of ^{31}P in the paramagnetic state of the $UP_{1-x}S_x$ system make use of the special magnetic properties of this system. The extension of the NMR work to the ordered state would provide a direct relationship with the magnetization and neutron diffraction studies of the $UP_{1-x}S_x$ system.

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Mössbauer Study of Several Ferrimagnetic Spinels*

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The ferrimagnetic spinels Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$, and $MgFe_2O_4$ have been prepared and studied with the Mössbauer-effect technique over a wide temperature range both with and without large applied magnetic fields. The cation distributions have been determined and compared with magnetization measurements. For $CoFe_2O_4$ and $MgFe_2O_4$, this distribution depends on the heat treatment; two extremes—quenched and slowly cooled samples—have been investigated. The hyperfine magnetic fields at Fe^{57} nuclei in A and B sites have been obtained as a function of temperature. A number of hyperfine fields are identified with the B sites of $CoFe_2O_4$, $MnFe_2O_4$, and $MgFe_2O_4$ and attributed to the kind and distributions of cations in the nearest-neighbor A sites. From the data, the ratio of the Co(A)-Fe(B) and Mn(A)-Fe(B) to the Fe(A)-Fe(B) superexchange interactions is found to be 0.68 and 0.66, respectively. Since the Mössbauer spectra provides no evidence for Fe^{2+} ions in $MnFe_2O_4$, a canted spin arrangement for the Mn ions in A and B sites is proposed to account for the small observed magnetization.

I. INTRODUCTION

A FERRIMAGNETIC spinel can be represented by the formula (M)[M_2']O_4, in which the round and square brackets refer to metal ions situated in an oxygen tetrahedron or octahedron, respectively. If the tetrahedral (A) and octahedral (B) sites are occupied by metal ions possessing a magnetic dipole moment, cooperative phenomena known as ferrimagnetism may be observed below a particular temperature. The properties of these materials depend on what kinds of metal ions are present in the different sites and how these are distributed. Spinels with only divalent ions in tetrahedral or in octahedral sites are called "normal" or "inverse," respectively. The main cause for a cooperative behavior of the magnetic dipoles in a spinel is the antiferromagnetic A-B superexchange interaction.

Ferrimagnetism was discovered in materials with a spinel structure. Consequently, these materials have been investigated very often.[1–3] Also the Mössbauer-effect (ME) technique has been used to investigate

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