NMR Measurements in the Paramagnetic State of Uranium-Phosphorus Compounds. I. Line Shifts of ^{31}P in UP and in $UP_{1-x}S_x$

F. Friedman and J. Grunzweig-Genossar
Department of Physics, Technion—Israel Institute of Technology, Haifa, Israel
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NMR line shifts ΔH of ^{31}P in the antiferromagnetic semimetal UP and in its solid solutions $UP_{1-x}S_x$ ($x \simeq 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$) in the paramagnetic state are proportional to the magnetization of the solid: $K = \Delta H/H = K_0 + \alpha\chi_M$, where the parameters are nearly independent of composition x and fall within a narrow range $K_0 = (-35 \pm 15) \times 10^{-4}$; $\alpha = 5.2 \pm 0.5$ (emu/mole)$^{-1}$. This line shift is interpreted as superhyperfine (shf) polarization transferred through U-P bonds, where the shf coupling constants are $A_s = -32.4 \pm 1.0$ MHz and $A_p = +3.6 \pm 0.6$ MHz. Although the U-U magnetic coupling is carried by conduction electrons (Ruderman-Kittel-Kasuya-Yosida interaction), the U-P magnetic coupling is through bonds of localized electrons. The results are compared with NMR line shifts in rare-earth monopnictides and with electron-nuclear double-resonance experiments on rare-earth ions.

I. INTRODUCTION

NMR studies in paramagnetic and magnetically ordered solids have provided important information about the magnetic interactions and electronic properties of these materials. In this and in the following papers, we deal with the line shifts observed in uranium-phosphorus compounds. Uranium and pnictogens (column V*A* elements: v = N, P, As, Sb, and Bi) form three types of compounds: Uv, U_3v_4, and Uv_2. All these compounds are good or fair conductors of electricity; Uv and Uv_2 order antiferromagnetically at low temperatures, while U_3v_4 become ferromagnetic.

It has been shown that, in a number of alloys and compounds of the lanthanides, the magnetic interaction between paramagnetic ions, which brings about magnetic ordering at low temperature, is primarily due to conduction electrons—the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[1] In some uranium compounds, although the actual details must be very complicated, surprisingly enough the simple RKKY model can also account satisfactorily for the main magnetic properties, e.g., types of ordered structure and ordering temperatures, observed in monocompounds of uranium with column-V*A* and column-VI*A* elements.[2] The model proposed assumes that the uranium ion present is U^{4+}_4, with the $f^2(^3H_4)$ ground multiplet, split by the crystal field. The nearest excited multiplet is ~5000 cm^{-1} higher. The column-V ions appear as v^{3-}, those of column VI*A* as vi^{2-} ions, while the Z surplus electrons contributed by each uranium ion presumably go into the conduction band. Thus, for example, because of the difference in the concentration of conduction electrons, uranium monopnictides Uv, which contain $Z \sim 1$ conduction electrons per uranium ion, order antiferromagnetically, while uranium monochalcogenides Uvi, with $Z \sim 2$, show ferromagnetic order. The Uv-Uvi compounds $UP_{1-x}S_x$, $UAs_{1-x}Se_x$ which form solid solutions are therefore of interest[2(b)]; their composition affects Z, the concentration of conduction electrons per uranium ion, and hence the magnetic properties of the alloys. As the content, e.g., of sulfur in $UP_{1-x}S_x$ solid solution increases, the concentration of conduction electrons increases from $Z \sim 1$ to $Z \sim 2$, and is approximately given by $Z \sim 1 + x$. As the conduction-electron concentration changes, the RKKY interaction between the paramagnetic ions changes rapidly, and the relative stability of the different magnetic structures varies appropriately. The magnetic phase diagram of the UP-US system has been studied in detail by Kuznietz, Lander, and Baskin,[3] who showed that there is a gradual change of ordered magnetic structures from UP antiferromagnetic type-I (AF1) via two intermediate more complicated structures, till the final ferromagnetic US, in fair agreement with theory.[2]

It was therefore expected that in these solids the Knight shifts observed in NMR experiments on the nuclei of the diamagnetic ions would also be due to a similar mechanism. The interactions between the spin of the paramagnetic ion and the observed nuclei of the diamagnetic ion were assumed to take place indirectly; that is, the spin on the paramagnetic ion polarized the surrounding conduction electrons; these in turn produced a local field at the observed nucleus, be it directly, by contact or dipole interaction, or by polarizing the core electrons there. This mechanism was proposed by Jaccarino *et al.*,[4] who assumed uniform polarization of conduction electrons. A more elaborate model was suggested by de Gennes[5] and has been confirmed in a number of intermetallic compounds.[4,6–8] In a series of very convincing experiments, Buschow, Diepen, and de Wijn[6] showed that the Knight shifts, e.g., of the Al nucleus in $LnAl_i$

(Ln is any lanthanide element; $i = 1, 2, 3$), depend on the concentration of free electrons. Additional complications were observed, since there is a mixing of other bands into the conduction-electron wave functions, which apparently affects the magnitude and even the sign of the $4f$-spin–conduction-electron interaction constant.[6(f)] For these reasons, it was expected that similar interaction mechanisms will determine the Knight shifts of the anion, in compounds of lanthanides and actinides with pnictides and chalcogenides. Jones[9] carried out an extensive series of measurements of Knight shifts in the paramagnetic state of a large number of lanthanide monopnictides (Lnv). He could not determine which mechanism was responsible for the shifts observed.

We report here on work on UP and on UP-US solid solutions, while line shifts observed in U_3P_4 and in UP_2 are dealt with in the following paper.

II. EXPERIMENTAL

We have studied the NMR line shifts of ^{31}P in the solid solutions $UP_{1-x}S_x$, where $x \cong 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$. A parallel study including T_1 measurements was performed by Kuznietz, Baskin, and Matzankin of the ANL, who have published their results in the meantime.[10] Our specimens were prepared by the AERE-Harwell group, and were kindly supplied by Dr. Dell. Dr. Baskin of ANL kindly supplies a specimen of UP. (See Table I.)

The solid solutions are all of NaCl ($B1$) structure. The uranium ions sit on the fcc lattice, the remaining sites being occupied at random by P or S ions. The lattice-unit constant varies continuously from $a(\mathrm{UP}) = 5.587$ Å to $a(\mathrm{US}) = 5.488$ Å, and shows a slight departure from Vigard's law. In order to determine the tensor components of the hyperfine interaction constant conclusively and accurately, it is preferable to work with a single crystal. In metals the work with single crystals is very difficult, as the penetration for the rf field is reduced to the skin depth, and the signal decreases. We were therefore forced to use powder samples. This causes several complications. One is the gross smearing out of all angular effects; secondly, the demagnetization fields of individual grains and of the whole sample must be taken into account, as well as fields generated by the neighboring grains, which are oriented at random.

Magnetic susceptibility measurements on pure uranium monophosphide have been published by Trzebiatowski and Troc[11] and by Allbutt, Dell, and co-workers.[12,13] For the $UP_{1-x}S_x$ solid solutions, magnetic susceptibility measurements were made by the Harwell group[12,14] and by Trzebiatowski and Palewski.[15] The Knight shift measurements described here were performed on samples taken from the same batches as used by the Harwell workers, in their recent measurements of susceptibility[13,14] and low-temperature specific heat.[16] (See Table II.)

The powder specimens were enclosed in glass containers under vacuum. The work was performed on a Varian V-60 variable frequency unit. The resonance line shifts were measured with respect to the proton (or ^7Li) reference line, using a marginal oscillator gaussmeter. All frequencies were determined by means of a BC-221 frequency meter. The measurements were carried out in the temperature range 180–400 °K. The NMR frequencies used were limited by the instrument to the range 2–16 MHz.

We define the line shift at constant rf frequency ω_0 as $K = (H_{\mathrm{ref}} - H_0)/H_0$, where $H_{\mathrm{ref}} = \omega_0/\gamma(^{31}P)$ and H_0 is the field corresponding to the center of gravity of the integrated line. Positive K denotes an induced field parallel to the applied field (paramagnetic shift). We write $K = K_0 + k/(T - \theta_K)$. The constants K_0, k, and θ_k were determined by minimizing the least-squares deviation of the experimental points from the above straight line. The Curie-Weiss constant θ_K so obtained agreed very closely with θ_M, as determined by Allbutt and co-workers on the same specimens; therefore, we do not distinguish between θ_K and θ_M and shall use their results for the magnetic susceptibility of the different samples. In Fig. 1, we plotted K against the magnetic molar susceptilibity. The straight lines so obtained, for the different solid solutions, very nearly overlap. The parameters obtained are included in Table II. Our results agreed well with Knight shift measurements on UP by Scott *et al.*[17] and on UP-US solid solutions by Kuznietz *et al.*,[10] though our values for α are slightly higher than those of the other two groups. The average for all compositions is

TABLE I. Analysis of samples (see Ref. 16).

Nominal composition	wt%U	wt%S	wt%P	wt%O	Total	Assumed composition
$UP_{3/4}S_{1/4}$	88.17	2.92	8.48	0.25	99.81	$UP_{0.754}S_{0.251} + 0.0207\,UO_2$
$UP_{1/2}S_{1/2}$	88.07	5.92	5.64	0.15	99.78	$UP_{0.498}S_{0.505} + 0.0128\,UO_2$
$UP_{1/4}S_{3/4}$	88.00	8.75	2.77	0.25	99.77	$UP_{0.247}S_{0.754} + 0.0216\,UO_2$

further complication as there is an additional phase transition at 22.9 °K, which involves no distortion and no change of magnetic order, but shows a sudden jump in the moment of the uranium ions, from $n_a = 1.72$ at high temperature to $n_a = 2.00$ at low temperature,[32,34] accompanied by a sharp peak in specific heat[35] and in susceptibility.[36]

For the ordered spin lattice arrangement we find that the field H_{AF} at the ^{31}P nucleus is given by

$$\alpha_{AF} = H_{AF}/Nn_a\mu_B = 2a_s - 8(a_\sigma - a_\pi) \ . \qquad (6)$$

In UP at 4 °K, the magnetic moments at the uranium sites are $n_a = (2.00 \pm 0.05)\mu_B$. The observed NMR of ^{31}P shows that the field at the P sites is $H_{AF} = 27.3$ kOe. If NMR results for the high-temperature phase ($T > 23$ °K) are used, at, e.g., 77 °K, where $H_{AF} = 23.5$ kOe and $n_a = 1.72 \pm 0.05$, the ratio H_{AF}/n_a is unchanged. Together with Eq. (5) we obtain

$$a_s = 0.78 \pm 0.02 \ \text{(emu/mole)}^{-1} \ ,$$

$$a_p = a_\sigma - a_\pi = -0.087 \pm 0.012 \ \text{(emu/mole)}^{-1} \ .$$

Assuming that the uranium ions are in a pure $^3H_4$ state, that is, that any breakdown of the Russell-Saunders coupling if present is negligible,[2] we obtain (for U^{4+}) $A_i = 41.538a_i$ and

$$A_s = -32.4 \pm 1.0 \ \text{MHz} \ ,$$

$$A_p = (A_\sigma - A_\pi) = +3.6 \pm 0.6 \ \text{MHz} \ .$$

The K_0 term in Eq. (1) obtained by extrapolation in Fig. 1 is usually related to that part of susceptibility that does not depend on the polarization of the 5*f* electrons. Therefore in the case of UP it should be identical with the line shift in ThP, which presumably differs from UP only by the absence of 5*f* electrons. However, this is the case neither in the phosphides, nor in other uranium and thorium monocompounds. In Table III we bring together the K_0 terms for U*X* compounds (*X* = N, P, C) and the (total) Knight shift for the analogous thorium compounds. In each case there is a difference in sign between the thorium and uranium compound. This is so even in the carbides, although there the sign of the Knight shifts has been reversed. Lewis *et al.*[26(b)] proposed that the negative Knight shift in ThC is due to the 2*p* character of the conduction electrons at the carbon site. In light atoms (e.g., Be), 2*p* electrons induce diamagnetic core polarization. However, in such a case, the same reasoning should apply to the Knight shift of ^{14}N in ThN; however, the latter is positive. One could try to analyze both the susceptibility and the Knight shift as sums of several terms: contributions dependent on the 5*f*, on conduction *s* (contact), on conduction orbital, on Van Vleck, etc. Scott *et al.*[17] attempted this approach for UP and assumed $\chi = \chi_0 + \chi_f(T)$, where the first term is orbital and temperature independent, while the second depends on 5*f* electrons. They further assumed $K = \alpha\chi_f(T)$. Thus, from the K-vs-χ graph they determined χ_0 as the value of susceptibility for which $K = 0$. However, χ_0 so obtained (400×10^{-6} emu/mole by Scott *et al.*[17] and 500×10^{-6} emu/mole from our Fig. 1) is very large compared with the temperature-independent term of susceptibility as determined directly by Allbutt *et al.*[13] Allbutt assumes $\chi = \chi_0 + C/(T - \theta)$ and obtains $\chi_0 = 36$ and 42×10^{-6} emu/mole from low- and high-temperature data, respectively, about ten times less than Scott's results. Thus, at present we cannot account for the value of K_0 found in Uv compounds.

TABLE III. K or K_0 for Th*X* and U*X* compounds. (The values in the table are in 10^4 K.) The magnetic susceptibility of UC and of all thorium compounds is independent of temperature, and entries show the total Knight shifts. For UN and UP the temperature-independent part of the Knight shift, K_0, is shown.

Compounds of	^{13}C	^{14}N	^{31}P
Thorium	−2.2[a]	+10.7 ± 1.5[b]	+4.4 ± 0.2[b]
Uranium	+18[a]	−32 ± 4[c]	−23 ± 2[d]
			−17 ± 0.8[e]

[a]Reference 26(b).
[b]M. Kuznietz, J. Chem. Phys. 49, 3731 (1968).
[c]Reference 22.
[d]This work.
[e]Reference 17.

V. DISCUSSION

Our results will now be compared with measurements on isomorphous lanthanide compounds. We expect that as the 4*f* wave functions in the lanthanides will be more contracted than the 5*f* in the actinides, the shf coupling there will be smaller. In Fig. 3 we plotted the results of line-shift measurements on lanthanide monopnictides Lnv[9,37] and on actinide monopnictides.[22,38] All these compounds have the NaCl structure. We plotted the (super)hyperfine field per unit spin on each of the six paramagnetic ion neighbors $H^{hf} = g_J N\alpha\mu_B/(g_J - 1) = (2\pi)6A_s/\gamma$ as functions of the number of electrons in the *f* shell. As expected, for a given pnictogen, as the number of *nf* electrons increases, H^{hf} decreases, because the *f* shell shrinks (lanthanide contraction). This shrinkage is faster than the shrinkage of the ionic radius of the lanthanide. Compared with the phosphides, the fields in the corresponding arsenides are about 2 times stronger, in the antimonides about 3–3.7 times larger, and in the bismuthides (as far as can be judged from the scant data available) about 4.7 times stronger. Fields in the nitrides are about 0.7 times weaker than in the corresponding phosphides. This is due both to the in-

TABLE IV. Superhyperfine coupling constants (A_i in units of MHz).

	$Ce^{3+}(f^1)$		$U^{4+}(f^2)$			$U^{3+}(f^3)$			$Nd^{3+}(f^3)$			$Yb^{3+}(f^{13})$			$Tm^{2+}(f^{13})$	
	Rep	A_s	A_p	Rep	A_s	A_p	Rep	A_s	A_p	Rep	A_s	A_p	Rep	A_s	A_p	Rep	A_s	A_p
A_i (X-P) from NMR on XP		−17[a]			−32[b]	−3.4[b]					−8.35[a]			−4.03[a]				
A_i (X-P) from ENDOR on ZnTe													Γ_7	±42.0[c]	0[c]			
A_i (X-F) from ENDOR on CaF_2:X																		
with interstitial F	Γ_8	−18.4[d]	−7.5[d]				Γ_8	−9.8[e]	−32.0[e]	Γ_8	−10.5[e]	−20[e]						
with nearest-neighbor F													Γ_7	−3.96[f]	−18.2[f]	Γ_7	+6.01[g]	+5.76[g]

[a] Reference 9.
[b] This work.
[c] Reference 39.
[d] D. Kiro, W. Low, and D. J. Schipper, Phys. Letters 29A, 586 (1969).
[e] B. Secenski, D. Kiro, W. Low, and D. J. Schipper, Phys. Letters 31A, 45 (1970).
[f] D. Kiro and W. Low, Phys. Rev. Letters 20, 1011 (1968).
[g] R. G. Bessent and W. Hayes, Proc. Roy. Soc. (London) A285, 430 (1965).

crease of covalency of the bond as the weight of the anion increases, and also to the increased hyperfine coupling of the heavy anions. It has been already pointed out by Jones[9] that the ratios of the Knight shifts are approximately equal to the ratio of the estimated hyperfine coupling constants of these anions. This would mean that the covalency of the bond on going from P to Bi does not change appreciably. However, the hyperfine interaction constants $A(ns)$ used by Jones[9] were those computed by Knight for column-IV elements using an extrapolation method, and it is not certain how reliable these approximate values are. In Fig. 3, in the lanthanides, there is a peculiar break in the otherwise smooth curves between europium and gadolinium. This coincides with the dip in the coupling constant A, observed in Knight shifts of ^{17}O in aqueous solutions of lanthanide salts.[26(a)]

The hyperfine fields in actinide phosphides are about 2.5 times larger than in the corresponding lanthanide phosphides. However, the valency of the actinide ions present has not been yet definitely established. Again there are probably two effects present: increased covalency of bond and stronger coupling of $5f$ electrons into the ligand wave functions, due to their larger radius as compared with lanthanides $4f$ functions.

The most complete information about transferred hyperfine (superhyperfine) interactions is obtained from ESR experiments (Table IV). The most popular ligands used are fluorine and hydrogen, and meager data are available on interaction between rare-earth ions and pnictogen ions. The only experiments reported are those of Title,[39] who used as matrix ZnTe, a II–VI semiconductor (which crystallizes in the ZnS lattice). He replaced Zn^{2+} by a Yb^{3+} ion, and to compensate the charges, exchanged an adjoining Te^{2-} ion for a P^{3-} ion. The site symmetry was approximately tetragonal, trigonally distorted. The nearest-neighbor distance in ZnTe is 2.64 Å, while in YbP the distance (in the NaCl lattice) is 2.77 Å. Thus, in Title's experiment there is probably appreciable lattice distortion present. Attempts to determine the shf coupling between ^{31}P and Y^{3+} and Er^{3+} in CdTe were unsuccessful.[39(b)] As the meager electron-nuclear double-resonance (ENDOR) data on ^{31}P prevent us from fully discussing the problem, we also included in Table IV the ENDOR results on the shf coupling between lanthanides and fluorine ^{19}F. These were obtained in a matrix of CaF_2, where the lanthanide ion sits on a site of cubic coordination. The data for Ce^{3+}, Nd^{3+}, U^{3+} were obtained for the F^- ion placed on the interstitial site at the center of the adjoining cube ("No. 9 neighbor"), 2.73 Å away. The data for Yb^{3+} and Tn^{2+} are for the nearest-neighbor fluorine on one of the vertices of the cube surrounding the lanthanide ion ("shell 1" neighbor),

2.37 Å away. We found it rather frustrating that physicists working in the field of NMR, while discussing transferred hyperfine interaction, employ $\vec{S}$, the actual electron-spin operator operating on the paramagnetic ion wave functions, while workers in the ENDOR field frequently use the same Hamiltonian $\vec{I} \cdot \overleftrightarrow{A} \cdot \vec{S}$ as in Eq. (3), but without stating explicitly each time that, in some cases, the spin $\vec{S}$ is the fictitious spin operator as introduced by Abragam and Pryce, in the "spin Hamiltonian." Such duplication and confusion in two closely related fields is very annoying, as it affects both the magnitude and sign of A. We specify in Table IV the representation of the ground state in the ENDOR experiments. Table IV contains Ln-P and U^{4+}-P hyperfine coupling constants obtained from Knight shift measurements on phosphides. Here the site coordination is octahedral.

The magnitudes of the interaction constants cannot be compared directly, as coordination and bonding functions are different in the ENDOR and NMR cases. As far as uranium is concerned, there is also a difference in the ionization state. Thus, we must limit ourselves to stating the following:

(i) The coupling constants derived from ENDOR and NMR measurements are of a similar order of magnitude, and the A_s terms are of the same sign (negative) (using the "real" spin operator), as is the case in all lanthanide compounds.[26(b)] The only exception reported up to now is the case of Tm^{2+} ions in CaF_2 crystals.[40]

(ii) For a given lanthanide the isotropic coupling constant A_s(Ln-F), as obtained from ENDOR experiments, is very nearly equal to A_s(Ln-P) obtained from NMR. This implies that on substituting phosphorus for fluorine, the effective magnetic field at the ligand nucleus is increased by a factor of about 2.3 (the ratio of their gyromagnetic constants), due probably both to increased covalency of bonds and larger hyperfine coupling constants. However, the site symmetry, as pointed out above, is different in the two cases.

(iii) Replacing a Nd^{3+} ion by the isoelectric U^{3+} does not affect $A_s(X\text{-F})$, but increases A_p by about 60%. This is surprising, as one would naively expect a large increase, due both to increased bond covalency and a larger overlap caused by the increased radius of the $5f$ electron shell in U.

(iv) ENDOR[39] measurements of isotropic hyperfine constants between Yb^{3+} and P^{3-} (in the ZnTe matrix) give results for A_s about 10 times larger than those obtained for A_s(Yb-F) or A_s(Yb-P) from Knight shift in Lnv. However, the ENDOR experiment showed that the interaction is isotropic, that is, $A_p = 0$, which is rather surprising. Note that $A_{\parallel}$(Yb-F) (when $A_{\parallel} = A_s + 2A_p$, $A_{\perp} = A_s - A_p$) equals approximately $A_{\parallel}$(Yb-P) but the $A_{\perp}$ differ in the two cases. It should be stressed that A_s(Yb-P) obtained from NMR measurements refers to octahedral coordination around both Yb and P, while A_s(Yb-P) obtained from ENDOR refers to (approximately) tetrahedral coordination.

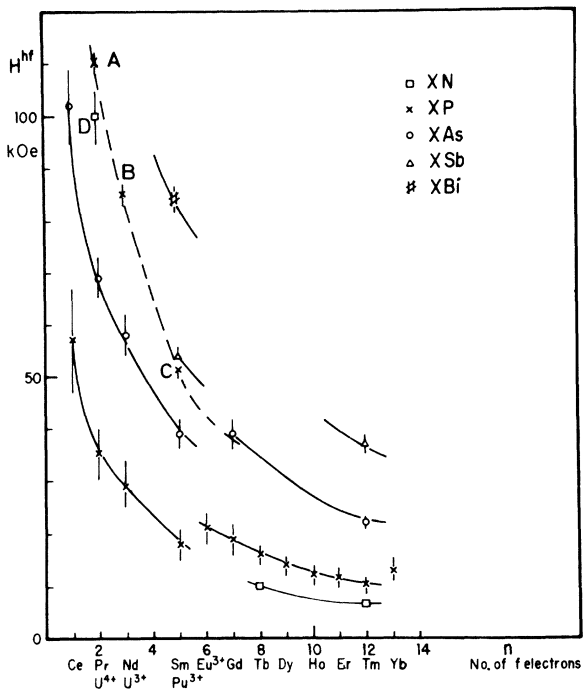

FIG. 3. Superhyperfine field H^{hf} at the anion due to unit spin at each of its six paramagnetic neighbors (in a $B1$ lattice) as function of the number of electrons in the f shell. Data for LnN from Ref. 37, for LnP, LnAs, LnSb, and LnBi from Ref. 9. Point A is for $U^{4+}P$ ($g_J = 0.8$ assuming Russell-Saunders coupling), point B for $U^{3+}P$ (as assumed in Ref. 38 and using their value of $g_J = 0.766$ for the case of intermediate coupling). We used for both A and B our value of $\alpha = 4.7 \pm 0.1$ (emu/mole)$^{-1}$. Point C is for $Pu^{3+}P$ from Ref. 38. Point D is for $U^{4+}N$ ($g_J = 0.8$) from Ref. 22.

The available Knight shift measurements on ^{19}F in lanthanide trifluorides[41-43] are difficult to interpret, since the exact site symmetry and coordination of the fluorine are not quite certain. From some NMR measurements it seems that there are two, perhaps four,[41] or even five or six nonequivalent fluorine sites,[43,44] but x-ray work so far has not confirmed this. However, it seems that the general trend (decrease) of the coupling constant with the number of f electrons is similar to that observed in NMR measurements on lanthanide monopnictides and in ENDOR results, but the reported Knight shifts[42] are about 3 times smaller than those computed from ENDOR hyperfine interaction constants in CaF_2 matrix.

From the hyperfine coupling constants available,[45] and the values obtained for A_s and for A_p for phosphorus, we calculated that the fractional s or p

character of the covalent bond is given by

$$f_s = 2SA_s/A_{3s}(0) = -3.0\times10^{-3}\ , \tag{7a}$$

$$f_p = 2SA_p/A_{3p}(0) = +4.6\times10^{-3}\ . \tag{7b}$$

A_s (and f_s) are negative, as in all other cases of transferred hyperfine interaction with $4f$ and $5f$ ions.[26(b)] The exact mechanism which gives rise to the negative sign is not clear. Several different mechanisms have been proposed by Freeman and Watson,[25,46] by Lewis,[26(a)] by Clogston,[47] and by Shulman.[28] Also the magnitude of f_s is in keeping with other results on uranium salts.[26(b)] The value of f_p seems to be very large indeed and is of the order reported in transition-ion compounds (see Ref. 24, Appendix 3, p. 724).

Since the differences in electronegativity between the elements of column V from P to Bi are very small, probably the overlap of the outer electron shells does not vary appreciably as one goes along the row from phosphides to arsenides to antimonides to bismuthides. Extrapolating, therefore, from the rather scanty Knight shift measurements on Lnv compounds, we expect that in the uranium monopnictides in the paramagnetic state the line shift of the anions will be

$$\alpha(U^{75}As) = 5.4 \quad \text{(emu/mole)}^{-1}\ ,$$

$$\alpha(U^{121}Sb) = 14-17 \quad \text{(emu/mole)}^{-1}\ ,$$

$$\alpha(U^{204}Bi) = 22 \quad \text{(emu/mole)}^{-1}\ .$$

So far no line-shift measurements have been reported for the above compounds in the paramagnetic states. However, Ruby *et al.* reported Mössbauer measurements on USb in the ordered state.[48] At 4 °K they found that the field at the ^{121}Sb nucleus was $H_{AF}(U^{121}Sb) = 160\pm5$ kOe, while the neutron diffraction measurements show that, at that temperature, the U sites are occupied by ions with magnetic moments of $n_a = 2.85\mu_B$.[49,50] Assuming

$$\alpha(U^{121}Sb)/\alpha(U^{31}P) = 3.1-3.7\ ,$$

we obtain $H_{AF}(U^{121}Sb) = 120-144$ kOe, in reasonable agreement with experiment. The discrepancy is probably due to the even greater increase of the A_p term as the atomic number of the anion increases.

VI. CONCLUSIONS

We analyzed the line-shift measurements of ^{31}P in $UP_{1-x}S_x$ solid solutions. The crystals presumably contain metallic and ligand ions and a high density of conduction electrons. Although the magnetic interactions leading to the observed low-temperature ordering are due to interactions of localized moments through conduction electrons, the line shifts observed are due primarily to shf interactions, through exchange by the strong covalent bonds between the neighboring cations and anions. In such a case, one would expect that the exchange interactions, which give rise to the observed polarization of the ligand wave functions, will also bring about superexchange interactions between the paramagnetic ions and hence affect the magnetic order at low temperature and θ, the Curie-Weiss parameter, as is the case in transition-metal compounds. We assumed originally that in uranium monopnictides and monochalcogenides RKKY interactions dominate and that superexchange interaction mechanism via covalent bonds is only of secondary importance. However, in some lanthanide compounds where the RKKY interactions are much weaker than those of their actinides analogs, the superexchange interaction can become important.[2(b)] The present paucity of available data does not allow us to determine the relative strength of the two coupling mechanisms in the materials discussed here. It is unfortunate that in $B1$ lattices in the paramagnetic state the shf field at ligand nucleus is determined by the A_s term alone, while the superexchange interactions between the paramagnetic ions are determined by A_π and A_σ terms at the ligands.[24] Thus, although similar exchange mechanism through bonds give rise to both effects, different terms enter in each of the two interactions; the Knight shift in the paramagnetic state cannot provide a direct measure of the superexchange interactions between the paramagnetic ions. The full data are required for this purpose.

The mechanism proposed for the line shift is confirmed by the fact that the interaction parameters of shf coupling obtained from NMR experiments agree, in sign and in order of magnitude, with those derived by ENDOR methods. The coupling terms between P and different lanthanides vary with the number of f electrons in the same manner as those determined by ENDOR for the (Ln-F) interaction in CaF_2 matrix.

The presence of strong covalent bonds in uranium pnictides is also corroborated by their narrow homogeneity ranges, high melting points, and brittleness.

The line shift of ^{31}P in UP is due to covalent interactions, while the line shift of ^{27}Al in Ln-Al intermetallics, of ^{115}Sn in LnSn intermetallics, and presumably of ^{1}H in β-UH_3 are dominated by conduction-electron interactions. This difference is due to the difference in the density of conduction electrons at the Fermi surface at the site of the investigated nucleus: In UP the phosphorus is occupied by a negative ion P^{3-}, which repulses conduction electrons, so that $|\psi_c(0)|^2$, the electron density at the P nucleus, is probably very small compared to the average charge density in the crystal. In the intermetallic compounds, e.g., $LnAl_2$,

the aluminum site is occupied by a positive metal ion, thus there $|\psi_c(0)|^2$ is appreciable, so that RKKY-type interaction can be significant. The conditions are similar at the hydrogen site in β-UH_3.[20]

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PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

s-d Exchange Integrals Obtained from Experiment in Cu:Mn, Ag:Mn, and Au:Mn

D. A. Smith and G. B. Smith*
Department of Physics, Monash University, Clayton, Victoria, Australia
(Received 18 September 1970)

s-d exchange integrals are estimated (i) from the energies of virtual bound states appearing in the optical absorption and (ii) from susceptibility, specific-heat, and resistivity measurements above T_K, using the high-temperature results of the *s-d* exchange model. The resistivity gives values which are much too low; it is suggested that this arises from neglecting nonlogarithmic terms especially important in the theory of transport properties.

I. INTRODUCTION

There are two parts to this paper. First, we wish to point out that the validity of the *s-d* exchange model of dilute alloys is proscribed by optical absorption and photoemission experiments, and the *s-d* exchange integral can be estimated. The second part is a quantitative test of the available predictions of the *s-d* exchange model at high temperatures, where perturbation theory *à la* Abrikosov[1] might be expected to hold good. That the current theories are not quantitatively successful even at 100 times the Kondo temperature is due, we believe, to neglecting nonleading logarithmic terms. Nevertheless, values for the *s-d* exchange integral J can be obtained by force fitting the available experimental data, which we do for Mn impurities in the noble metals. J values from susceptibility and specific-heat measurements are similar and also compare favorably with $J = -0.45$ eV derived from optical data on Ag:Mn. But the resistivity yields J's which are much too low, and it is suggested that this is again due to the omitted nonleading logarithmic terms.

II. *s-d* EXCHANGE INTEGRALS FROM OPTICAL DATA

Recent optical absorption[2] and photoemission[3] experiments on Ag:Mn reveal the presence of two widely separated virtual bound states, one above and one below the Fermi level. This is strong evidence for large intra-atomic Coulomb interactions and hence a well-defined localized spin (presumably $S = \frac{5}{2}$) at each Mn impurity. This is precisely the situation where one ought to be able to do perturbation theory starting from the "atomic limit," or, more specifically, the canonical transformation first given by Schrieffer and Wolff[4] which leads to the *s-d* exchange model.

For Mn which is assumed to be an S-state ion ($3d^5$ or $3d^5 4s^2$) the passage from Anderson's model to the *s-d* exchange model is straightforward and is given by Schrieffer.[5] One finds an impurity Hamiltonian with potential and exchange scattering terms

$$H_{\text{imp}} = \frac{5}{N} \sum_{\vec{k}\vec{k}'\sigma\sigma'} P_2(\cos\theta_{\vec{k}\vec{k}'}) \{V\delta_{\sigma\sigma'} - J\vec{s}\cdot\vec{s}_{\sigma\sigma'}\} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}'\sigma'}, \tag{2.1}$$

where the fivefold degeneracy of the impurity d orbitals is responsible for the $\vec{k}$-space form factor P_2. Here $\vec{s}_{\sigma\sigma'}$ are matrix elements of half the Pauli matrices and V and J are fixed by the energies of the two virtual bound states measured from the Fermi level. Let T_+ and $-T_-$ be the energy changes on adding an electron and a hole, respectively, at the Fermi level to the Mn impurity in its ground state; for stability, both must be positive. Then T_+ and T_- are the one-electron energy levels of the virtual bound states from the Fermi level. One finds that

$$V = -\tfrac{1}{2} v^2 (T_-^{-1} + T_+^{-1}), \qquad J = \tfrac{2}{5} v^2 (T_-^{-1} - T_+^{-1}), \tag{2.2}$$

where

$$v = (4\pi N)^{1/2} \int_0^\infty r^2 dr\ \phi(r)\, V(r)\, j_2(k_F r) \tag{2.3}$$

is the covalent admixture matrix element and its energy dependence is suppressed by putting $k = k' = k_F$. For Mn, J is necessarily negative leading to the Kondo-Suhl instability, but since J is really energy dependent and changes sign for energies below T_- or above T_+, the cutoff energy D in the usual theories is not the Fermi energy but more nearly $|T_+ T_-|^{1/2}$. Contrary to general expectation, exchange scattering dominates potential scattering here; V is small because the two resonances contribute with opposite signs and this is borne out by a very small residual thermopower.[6]

Now Meyers, Wallden, and Karllson[2] found impurity absorption in Ag:Mn below the d-band edge at 1.6 and 3.25 eV which they attribute to virtual