PHYSICAL REVIEW VOLUME 137, NUMBER 3A 1 FEBRUARY 1965

Knight Shifts and Relaxation Times in the Group IIIb Metals and Metal-Hydrogen Systems*

D. S. SCHREIBER
Department of Physics, Northwestern University, Evanston, Illinois

(Received 2 September 1964)

The Knight shifts K of the Group IIIb metals Sc and Y alloyed with hydrogen, and T_1T of Sc in the Sc-H system, have been determined and are compared with K and T_1T of pure La, Y, and Sc and of La in the La-H system. It is found that K_{Sc} and T_1T_{Sc} (in $\mathrm{ScH_2}$) are 0.07% and 25 sec-°K, respectively while K_{Y} (in $\mathrm{YH_2}$) is 0.11%. The ratio $K_{Me\,\mathrm{H_2}}/K_{Me}=0.33\pm0.03$ for each metal $Me=$La, Y, or Sc while $T_1T_{Me\,\mathrm{H_2}}/T_1T_{Me}=2.2\times10^2$. The similarity in the ratio of K's and T_1T's is shown to suggest a similarity in the electronic band structure in the Group IIIb metals and their H alloys. The assumption of a large orbital contribution, dominating the s and d core polarization terms, to K and T_1 is shown to be consistent with the results. H alloying is interpreted in terms of hydrogen entering the metal interstitally as a bare proton, its electron being ionized and donated to the conduction band of the metal. A Korringa-like relation embodying s, d, and orbital effects is developed and shows a similarity in the band structure of La and Sc without considering H alloying. It is shown that $K^2T_1T=\rho^2(\hbar/4\pi k)(\gamma_e/\gamma_n)^2$, where ρ is explicitly given as a function of the s, d, and orbital contributions. For the pure metals, $\rho=0.37\pm.01$ while for the H alloys, $\rho=1.9\pm0.2$. T_1T for Y and for Y in $\mathrm{YH_2}$ is predicted.

INTRODUCTION

THE nuclear magnetic resonances (NMR) of Sc and Y in $\mathrm{ScH_2}$ and $\mathrm{YH_2}$ have been observed. A comparison of the Sc, Y, and La resonances in the pure metal with those in the metallic dihydrides, $Me\mathrm{H_2}$, $Me=$Sc, Y or La, suggests a strikingly similar band structure for these Group IIIb transition metals. The relative change in each Me Knight shift K and relaxation time T_1 (or more appropriately the product T_1T) when the metal is alloyed with hydrogen is found to be nearly the same in each case. A qualitative band structure analysis in terms of a filling of the metals' s and d bands (all three metals have the s^2d^1 atomic configuration) with electrons donated by the hydrogen is consistent with the results and is in agreement with the concept of a high density of states in the d band at the Fermi level for the pure metals.

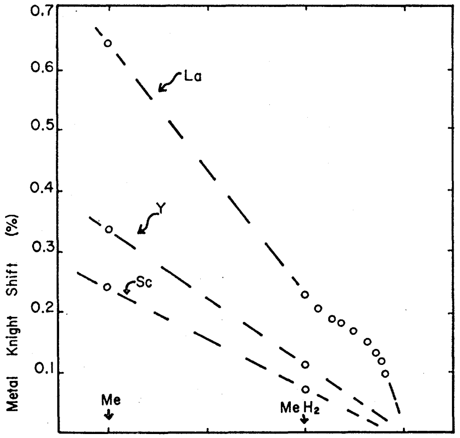

FIG. 1. The Knight shift of the metal nucleus expressed as a function of the ratio of number of hydrogen atoms to metal atoms, for the metals scandium, yttrium, and lanthanum.

EXPERIMENTAL

A Pound-Knight marginal oscillator and a high level marginal oscillator[1] were used in conjunction with a conventional lock-in amplifier in the determinations of the shifts and relaxation rates, the latter being made by the method of progressive saturation. The accuracy of

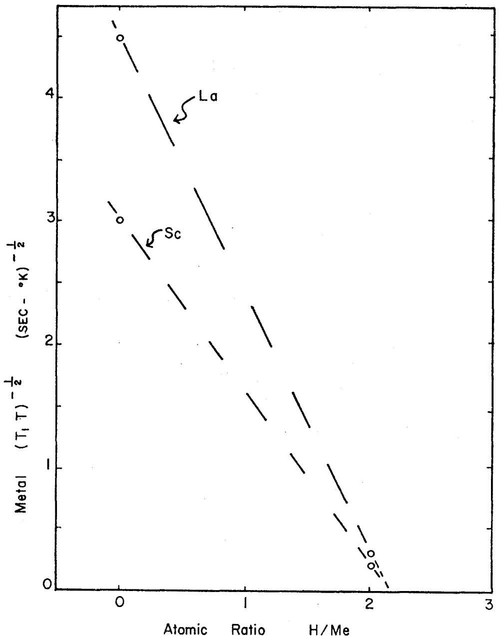

FIG. 2. The relaxation rate of the metal nucleus expressed as a function of the ratio of the number of hydrogen atoms to metal atoms, for the metals scandium, yttrium, and lanthanum.

---

* Work supported in part by the Advanced Research Projects Agency through the Northwestern Materials Research Center.

[1] W. D. Knight, Rev. Sci. Instr. 32, 95 (1961).

the absolute values of the T_1 determined by this method is perhaps only about 20%, but the relative accuracy for different temperatures is much better. T_1 measurement of Sc in ScH_2 made at 300 and 77°K clearly showed an expected $T_1 \propto 1/T$ relationship.

In order to obtain a favorable signal-to-noise ratio for the Knight shift measurement of Y in YH_2 (Y^{89} has a small magnetogyric ratio and spin), it was necessary to use the method of continuous averaging where the effective integrating time per sweep was about 4 h.

Hydrogen alloy samples having 2H/*Me* atom and possessing the CaF_2 structure were prepared by a direct union of H gas with the metal in a manner described elsewhere.[2]

RESULTS

Figures 1 and 2 and Table I show the results of the Sc and Y Knight shifts and relaxation rate measurements in ScH_2 and YH_2 determined in this investigation. Included for comparison are like data for the pure metals and LaH_x from other sources. The absolute values of the Knight shift and the relaxation rate for all three metals are seen to decrease with the addition of hydrogen. Noteworthy, however, is the fact that for a particular H alloy, the ratio of metal shift to that in the corresponding pure metal is about 0.33 in each of the 3 cases, and the corresponding ratio of the relaxation times are also about the same, being 2.2×10^2. This is illustrated in Fig. 3.

TABLE I. Knight shifts and spin lattice relaxation times for the metal nucleus in the group III*b* metals and their H alloys.

	K (%)	T_1T sec-°K	$\rho=\left[K^2T_1T\Big/\left(\frac{\hbar}{4\pi k}\right)\left(\frac{\gamma_e}{\gamma_n}\right)^2\right]^{1/2}$
Sc^{45}	0.24[a]	0.11[d]	0.37
Y^{89}	0.34[b]	(1.4)[e]	...
La^{139}	0.63[a]	0.05[d]	0.39
$Sc^{45}H_2$	0.07	25.0	1.7
$Y^{89}H_2$	0.11	(310.0)[e]	...
$La^{139}H_2$	0.23[c]	11.2[c]	2.1
V^{51}			2.5

[a] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters 5, 52 (1960).
[b] W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, Acta Met. 8, 663 (1960).
[c] D. S. Schreiber and R. M. Cotts, Phys. Rev. 131, 1118 (1963).
[d] Y. Masuda, J. Phys. Soc. Japan 19, 239 (1964).
[e] Predicted from K and the assumed constancy of ρ.

We can conclude then that the addition of hydrogen affects the resonance parameters of these three metals in much the same way. Since the Knight shift and relaxation rates are quite sensitive to various quantities which describe the electronic band structure, such as the density of states and the electron angular momentum character, *s* or *d*, it would appear that these band structure parameters are similarly affected.

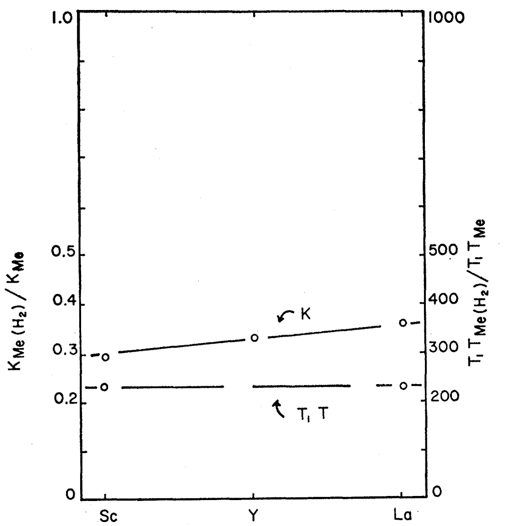

FIG. 3. The ratio of the Knight shifts and the ratio of the relaxation times of the metal nucleus in the hydrogen alloy to the pure metal proceeding from the low atomic number metal, Sc, to the highest, La.

If a simple linear extrapolation of the Knight shift to higher H concentration is made, we see that at about 3H/*Me* in each case, Sc, Y, and La, the Knight shift vanishes. In the case of LaH_x, there are additional experimental points above 2H/La or $2\leq x\lesssim 3$, so that this extrapolation procedure has some validity. A linear extrapolation of $(T_1T)^{-1/2}$ to higher H concentrations indicates a vanishing of the relaxation rate mechanism at about 2.2 H/*Me*.

The linewidths of the *Me* resonances were all about 6 G, while the proton linewidths were about 8 G at room temperature and below. Proton Knight shifts were zero to within the experimental error of 0.003%.

DISCUSSION

In analyzing the Knight shift and relaxation times observed in *d* band transition metals and alloys, the contributions from *d* electron orbital and core polarization effects as well as the usual *s* contact interaction, must be considered. Hence we write in a most general way:

$$K=K_s+K_d+K_o$$

$$\frac{1}{T_1}=\frac{1}{T_{1s}}+\frac{1}{T_{1d}}+\frac{1}{T_{1o}},$$

where *s* refers to the *s* contact hyperfine interaction, *d* is the *d* induced polarization of the *s* core electrons, and *o* refers to the Van Vleck or orbital interaction. We will take the approach of considering separate but overlapping *s* and *d* bands in these Group III*b* metals similar

---

[2] D. S. Schreiber and R. M. Cotts, Phys. Rev. 131, 1118 (1963); and M. R. Merriam and D. S. Schreiber, Phys. Chem. Solids 24, 1375 (1963).

to those used by Butterworth[3] in his analysis of the V-Cr system. The expressions for the components are

$$K_s=\frac{8\pi}{3}\langle|\psi(0)|^2\rangle\chi_s\Omega,\quad \chi_s=\beta^2N_s(\zeta) \tag{1}$$

$$K_d=\frac{8\pi}{3}\langle\rho(0)\rangle_d\chi_d\Omega,\quad \chi_d\cong\beta^2N_d(\zeta) \tag{2}$$

$$K_o=2\langle r^{-3}\rangle_D\chi_o\Omega,\quad \chi_o\cong\frac{\beta^2 4f(1-f)}{\Delta} \tag{3}$$

$$\frac{1}{T_{1s}}=\frac{\pi kT\hbar^3}{4}(\gamma_e\gamma_n)^2\left[\frac{8\pi}{3}\langle|\psi(0)|^2\rangle\right]^2\Omega^2N_s^2(\zeta) \tag{4}$$

$$\frac{1}{T_{1d}}=\frac{\pi kT\hbar^3}{4}(\gamma_e\gamma_n)^2\left[\frac{8\pi}{3}\langle\rho(0)\rangle_d\right]^2\Omega^2N_d^2(\zeta)\epsilon \tag{5}$$

$$\frac{1}{T_{1o}}=\pi kT\hbar^3(\gamma_e\gamma_n)^2\langle r^{-3}\rangle_d^2\Omega^2N_d^2(\zeta)a. \tag{6}$$

The usual s contact of the Knight shift[4] and T_1 [5] are well known, while the orbital contribution to the Knight shift has been considered only recently.[6] Obata has given an explicit expression for d orbital (and d dipolar, which is usually small, and we thus neglect it) relaxation.[7] The constant a, $(0\leq a\leq 10)$ measures the degree of admixture of Γ_3 and Γ_5 atomic functions at the Fermi level ζ. Kubo and Obata[8] have given a complete expression for χ_0 which we approximate crudely in terms of some average bandwidth Δ and the fraction of occupied states f in the band. The quantities $\langle r^{-3}\rangle_D$ and $\langle r^{-3}\rangle_d$ are averages over all contributing states and only those near the Fermi level, ζ, respectively. The d core contribution to the NMR shift and relaxation rate have been considered in some detail by several workers.[9] The constant ϵ of Eq. (5), $(0.2\leq\epsilon\leq 0.5)$ plays a role similar to that of the constant a in Eq. (6).

We see in all cases for the $1/T_1$ components and for the K_s component that a decrease in the density of states $N(\zeta)$, will decrease K and $1/T_1$. Hence from the T_1 data we strongly suspect that H alloying decreases the density of states. Since the sign of $\langle\rho(0)\rangle_d$ can be positive or negative (however it has always been observed to be negative in d band metals), a decrease in the state density would increase K. A net increase or decrease in K_0 will depend on the initial fractional population of occupied state in the d band and the number of states filled or depleted by hydrogen alloying. Since there is a net decrease in K upon H alloying, K_d (since K_d is probably negative) must be small or more than compensated for by K_s and K_o. There is strong evidence from the La and Sc Knight shift temperature dependence that K_o is much larger than K_d since the latter has the opposite dependence on temperature.[10] Theoretical considerations of Masuda[11] indicate that K_s and K_d are about equal in magnitude for La so that any density of state changes might leave their net contribution unchanged, and hence only changes in K_o affect the measured values of K. For Sc, Masuda finds that K_d is much smaller than K_s or K_o.

We begin by considering a parabolic-like rigid band model (which has been used with some success in the analysis of other alloy data, but which nevertheless is probably a gross approximation to the true state of affairs). The Fermi level is placed somewhere near the peak in the density of states in both the s and d bands of the pure metals. The d band is assumed to be split so that the lower energy sub band can contain at most four electrons per Me atom, so that a filled conduction band can hold nearly 6 electrons per metal atom. It is near the peak of this lower energy parabolic sub d band that we place the Fermi level. The concept of a split d band has been used previously and supporting arguments given earlier[2] in an analysis of the La-H system. It is reasonable to assume in these transition metals that the density of states in the s band is much smaller than in the d band so that it is not crucial to the analysis that the Fermi level be near the maximum in the s density of states.

The experimental results presented here are consistent with the concept that as H atoms are alloyed, their electrons are ionized and go into the Me conduction band. At concentrations of $3\text{H}/Me$ the bands are filled, the outer Me atomic configuration being s^2d^1. As the band fills, the Fermi level moves to a lower density of states, and thus K_s and K_d and $1/T_1$ decrease. Since $1/T_1$ appears to vanish at a lower H concentration than does K, it may be that the density of states decreases to quite a low value before the band is filled. This implies that the metal Knight shift in the alloys has its origin primarily in the orbital interaction.

The concept of filling rather than of depleting the d (and s) band(s) by the alloying of H is supported by the almost identical behavior in the variation of the Knight shift and T_1 of vanadium, whether it is alloyed with Cr [12,3] or H,[13,14] at concentrations of up to 0.6 H/V. Similarly for the Knight-shift variation of Nb

---

[3] J. Butterworth, Proc. Phys. Soc. (London) **83**, 71 (1964).

[4] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

[5] J. Korringa, Physica **16**, 601 (1950).

[6] See, for example, L. E. Orgel, Phys. Chem. Solids **21**, 123 (1961); and A. M. Clogston, A. G. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

[7] Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

[8] R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

[9] See, for example, M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959); and Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

[10] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

[11] Y. Masuda, J. Phys. Soc. Japan **19**, 239 (1964).

[12] L. E. Drain, J. Phys. Radium **23**, 745 (1962).

[13] H. Betsukayu, Y. Takagi, and Y. Betsukayu (to be published).

[14] D. Zamir (private communication).

when alloyed with Mo [15] or H.[16] We note that V and Nb are elements with 5 electrons per atom in the conduction band and that Cr and Mo are Group VI*b* elements with one more, or 6, electrons per atom. The observation that the conduction band may nominally have at most 6 electrons/*Me* atom (and presumably four of these are *d* electrons) or that there be at least a minimum in the states density near 6 electrons/atom, prevails throughout the Group III*b* through VI*b* elements when considered in terms of H alloying and the donating of the H electrons to the conduction band. Nominal maximum concentrations of 3, 2, 1, and 0 H/*Me* are found for the Group III*b*, IV*b*, V*b*, and VI*b* metals, respectively. Finally, for the III*b* metals we find that LaH_x becomes diamagnetic and semiconducting (or an insulator) as $x\rightarrow 3$. This is consistent with the observed vanishing of the Knight shift and a filled conduction band. To explicitly represent the modification of H alloying on the *s* and *d* electronic band structure we can express:

$$K'=c_sK_s+c_dK_d+c_oK_o \quad c_s=K_s'/K_s \text{ etc.}, \tag{7}$$

where the primed symbols refer to the H alloys and the unprimed to the pure metals. The H alloy Knight shift relative to that of the pure metal is then just:

$$\frac{K'}{K_i}=\sigma_i=\frac{c_{si}K_{si}}{K_i}+\frac{c_{di}K_{di}}{K_i}+\frac{c_{oi}K_{oi}}{K_i} \quad i,j=\text{La, Sc, or Y}. \tag{8}$$

From the near equality of the σ's ($\sigma\approx 0.33$) we have

$$K_i'/K_i=K_j/K_j. \tag{9}$$

Since we suspect that it is not accidental that the sums σ of the *s*, *d*, and *o* terms are the same for each metal, and since we do not expect the ratio of *s* terms, for example, of one metal to have any specific dependence on the *d* or *o* ratios in another metal, we may write as a solution of (9):

$$\frac{c_{oi}K_{oi}}{K_i}=c_{oj}\frac{K_{oj}}{K_j}, \quad \frac{c_{si}K_{si}}{K_i}=\frac{c_{sj}K_{sj}}{K_j}, \quad c_{di}\frac{K_{di}}{K_i}=\frac{c_{dj}K_{dj}}{K_j} \tag{10}$$

from which we may obtain, following the plausibility arguments given above and below:

$$c_{si}=c_{sj} \text{ etc. and } \frac{K_{si}}{K_i}=\frac{K_{sj}}{K_j} \text{ etc.} \tag{11}$$

Equations (11) imply that the changes from alloying on the *s* and *d* bands and on the number of occupied states are the same in each metal and the relative Knight shift contributions of *s*, *d*, or *o* origin are also the same. It may be that nature is such that the relative contributions to the Knight shift are different in each metal and that H alloying modifies each contribution just enough to satisfy Eq. (10) and to produce the same relative change in the net shift, but we would like to suggest that it would not be unreasonable to find the band structures of this group of metals similar.

A like argument again illustrating the similarity in the metal band structure can be carried out by relating the ratio of the T_1's. These arguments are certainly not rigorous, but perhaps reasonable, as we shall see in the section to follow when we exploit still another similarity in the NMR parameters, this time between the pure metals only.

In order to take the fullest advantage of the data at hand, we note that it would be desirable to have a Korringa relation which relates K and T_1T in the same metal and eliminates some not-very-well-known quantities which depend in a detailed way on the exact description of the bands and of the electronic wave functions. It is possible to write a Korringa-like relation for each of the contributions *s*, *d*, and *o*, and one which combines all three. Combining Eqs. (1), (4) and (2), (5), and (3), (6) we obtain:

$$K_s^2T_{1s}T=\left(\frac{\hbar}{4\pi k}\right)(\gamma_e/\gamma_n)^2=S, \tag{12}$$

the usual Korringa relation[5]

$$K_d^2T_{1d}T=S\epsilon^{-1}, \tag{13}$$

$$K_o^2T_{1o}T=S\eta^2, \quad \eta=\frac{4f(1-f)\langle r^{-3}\rangle_D}{a^{1/2}\Delta N_d(\zeta)\langle r^{-3}\rangle_d}. \tag{14}$$

If we now express K_d and K_o and $1/T_{1d}$ and $1/T_{1o}$ in terms of K_s and $1/T_{1s}$, respectively, so that

$$K=K_s+K_d+K_o=K_s(1+\alpha+\beta), \quad K_d=\alpha K_s$$
$$K_o=\beta K_s \tag{15}$$

and

$$1/T_1=1/T_{1s}(1+\gamma+\delta), \quad 1/T_{1d}=\gamma 1/T_{1s}$$
$$1/T_{1o}=\delta 1/T_{1s}. \tag{16}$$

From Eqs. (12)–(16) we have

$$\gamma/\alpha^2=\epsilon, \quad \delta/\beta^2=1/\eta^2$$

so that we obtain finally

$$K^2T_1T=\rho^2S, \quad \rho^2=\frac{(1+\alpha+\beta)^2}{1+\alpha^2\epsilon+(\beta/\eta)^2}. \tag{17}$$

The experimental values of ρ are given in Table I. As can be seen, ρ_{La} and ρ_{Sc} are very nearly the same. This is just what we would expect if $\alpha_{Sc}=\alpha_{La}$, $\beta_{Sc}=\beta_{La}$, $\epsilon_{Sc}=\epsilon_{La}$ and $\eta_{Sc}=\eta_{La}$. The first two equalities can be shown to follow directly from the previously assumed Eq. (11),

$$c_{di}=c_{dj}, \quad c_{oi}=c_{oj}$$

and

$$K_{di}/K_i=K_{dj}/K_j, \quad K_{oi}/K_i=K_{oj}/K_j$$

---

[15] S. Alexander, E. Corenzwit, B. T. Matthias, R. G. Shulman, and B. J. Wylnda, Phys. Rev. **129**, 2481 (1963).

[16] D. Zamir and R. M. Cotts, Phys. Rev. **124**, A666 (1964).

which were obtained by observing that H alloying produced similar changes in K and T_1T for each Group III*b* metal. The equalities $\alpha_{\text{Sc}}=\alpha_{\text{La}}$ etc., could have just as well been similarly deduced by comparing the pure metal ρ's without resorting to similarities in H alloying behavior. It naturally follows than that we should expect $\rho_{\text{La}}'\approx\rho_{\text{Sc}}'$ with $\alpha_{\text{Sc}}'\approx\alpha_{\text{La}}'$, $\beta_{\text{Sc}}'\approx\beta_{\text{La}}'$, $\eta_{\text{Sc}}'\approx\eta_{\text{La}}'$. The similarity in the (ρ')'s is reasonably good. The fact that the (ρ)'s and (ρ'/ρ)'s for the different metals are similar is at least a necessary condition for their having similar electronic band structures. It should be pointed out that considering only the effects of H alloying which gave

$$K_i'/K_i\cong K_j'/K_j$$

and

$$(T_1T)_i'/(T_1T)_i\cong(T_1T)_j'/(T_1T)_j\,,$$

we should have expected only that

$$\rho_i'/\rho_i\approx\rho_j'/\rho_j\,.$$

We may exploit Eq. (17) for further information by making use of the boundary conditions, (1) that all the terms must be real, (2) that necessarily

$$\epsilon,\,\rho,\,\eta,\,\beta\geq 0$$

and (3) we will assume that

$$\alpha\lesssim 0\,.$$

For the MeH_2 which have $\rho'>1$, we find irrespective of α, ϵ, and η that

$$\beta'\geq(\rho'-1)$$

which tells us that an orbital interaction does indeed exist in at least the alloys. For $\rho'\approx 2$, $\beta'\gtrsim 1$ which says that the orbital contribution of K is as large or larger than the *s*-contact term. That some orbital interaction exists in the pure metals (which have $\rho<1$) follows from the fact that only with $\eta\equiv 0$ will $\beta=0$. It is reasonable to expect that $0.1\lesssim\eta\lesssim 10$ which places a lower limit on β of $\beta\approx 0.5$. Again, irrespective of α it can be shown that when $\rho\sim\eta$, $\beta\sim\infty$ or that the orbital contribution far exceeds the *s* contact contribution.

As was suggested earlier from temperature-dependence considerations, $|\alpha|$ is probably small, at least small enough such that we may neglect it in the determination of η which follows. We may write, solving Eq. (17) for η, $\eta^2=\beta^2\rho^2/(1+\alpha+\beta)^2-\rho^2(1+\alpha^2\epsilon)$ and for $\alpha=0$, $\eta^2=\beta^2\rho^2/(1+\beta)^2-\rho^2$. Consider for the moment that β and $\beta'\gg 1$ (as an example take $\beta\approx 10$ which makes $\sim 90\%$ of the Knight shift orbital in origin and $\sim 10\%$ from the *s* contact term) then $\eta\approx\rho$. A point of interest is the ratio of $\eta'/\eta=\rho'/\rho\cong 5$. (Recall that the primes refer to the H alloys.) Looking at the expression for η, Eq. (14), we see that the $N_d(\zeta)$ must be reduced by H alloying by more than this factor of 5 to offset the decrease in $f(1-f)$. (We assume that the other quantities in 14 are not greatly modified by H alloying.)

Alternatively if we assume $\beta<1$ for the pure metal [note that we are not allowed to assume this for the alloy since $(\beta\gtrsim\rho-1)$] while taking β large for the H alloy, we have very approximately

$$\eta\approx\beta\rho\,,\quad \eta'\approx\rho'$$

so that

$$\eta'/\eta=\rho'/\beta\rho\approx 5/\beta\,,\quad \beta<1$$

which implies that $N_d(\zeta)$ must be reduced by much more than the factor of 5 previously found. Note that if we had taken for the alloy the smallest possible β', $\beta'=\rho'-1$ then $\eta'\rightarrow\infty$. The large decrease in the density of states upon H alloying illustrated in the above two cases is consistent with and follows from the apparent vanishing of $(T_1T)^{-1/2}\propto N(\zeta)$ near $\text{H}/Me=2.2$. If $N(\zeta)$ is small, then so also must be K_s and K_d, but since K_o does not depend on N at the Fermi level, but on the entire distribution of occupied and unoccupied states in the band, it can persist. Hence it is reasonable to assume β large and the dominance of an orbital interaction at least in the H alloys. The fact that η need only be approximately equal to ρ in order that orbital effects dominate is well within the realm of possibility for the pure metals as well as the alloys.

From the constancy of the ρ's and the measured values of K_{Y}, we may predict the T_1T for Y and YH_2. These values are included in Table I. A value for ρ for vanadium is also included in Table I, for in some sense it is tempting to regard V as the pure metal counterpart of the MeH_2 transition alloys, since V is also considered to have 5 electrons per *Me* atom in its conduction band. Butterworth has concluded that the orbital contribution is also dominant in pure V.

ACKNOWLEDGMENTS

The author wishes to thank Dr. David Zamir for informing him of his spin lattice relaxation time and Knight shift measurements of V in the V-H system prior to their publication.

Note added in proof. It is worthwhile to note that a recent measurement of $T_1T=0.358$ sec. $-$°K for Nb^{93} in niobium metal by Dr. J. Butterworth, who kindly informed the author of this work, yields a value of ρ for niobium of $\rho=2.4$ which is, perhaps, significantly close to that of $\rho=2.5$ for vanadium. Again resonance similarities now among the Group V*b* metals and between the pure metals and H alloys are seen and seem to suggest that there may be similarities in the electronic band structure of this group of metals.