If this is a real effect, then we would expect to observe a normal isotope effect in lanthanum and thorium, and a partial one in niobium. Since, unfortunately, each of these metals only has one reasonably abundant stable isotope, our values of φ may be the only experimental check on any future theoretical estimate of ζ.

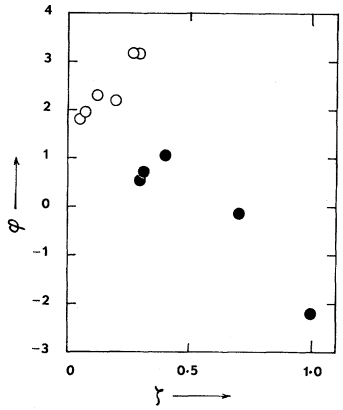

FIG. 1. Plot of experimental values of $\varphi = \partial \ln N(0)\, V/\partial \ln v$ against Garland's value of ζ. ● transition metals, ○ other metals.

Table II shows that φ does not vary much among the simple nontransition elements. If this is so, then it is to be expected that it will be approximately constant for a given metal under a wide range of pressure unless some new areas of Fermi surface overlap are established at the Brillouin zones by high pressures. In this case we may integrate (3) taking φ as a constant and obtain

$$\ln (T_c/\theta) \propto v^{-\varphi}. \tag{5}$$

We may therefore expect that the $T_c - v$ relation will no longer be linear, but that T_c will only approach zero asymptotically with decreasing volume instead of falling to zero at a particular pressure.

We chose aluminium as a particularly suitable substance in which to look for this effect. Measurements have now been made to pressures of 20 000 atm which reduce T_c to 0.71° K. We find that there is a clear deviation from linearity, and that this deviation is in fact that predicted by our expression (5).

ACKNOWLEDGMENTS

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NUCLEAR MAGNETIC RESONANCE

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Orbital Paramagnetism and the Knight Shift in Transition Metal Superconductors

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INTRODUCTION

One of the consequences of the BCS[1] microscopic theory of superconductivity is that the spin susceptibility of the conduction electrons will vanish exponentially as the reduced temperature, T/T_c approaches zero.[2] (This is shown in Fig. 1.) This follows from the fact that all states are chosen to be eigenstates of the total spin and that the ground state of the superconductor is one for which the expectation value of the spin is zero. Since the remaining states are removed in energy by an amount Δ (the energy gap) it requires, as a minimum, an amount of energy 2Δ to excite a Cooper pair to those states for which $\langle |S_z| \rangle \neq 0$.

It is, therefore, of some interest to measure the temperature dependence of the spin paramagnetism

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[2] K. Yosida, Phys. Rev. 110, 769 (1958).

below T_c. Any bulk measurement of the magnetization suffers from the fact that the diamagnetism resulting from the Meissner effect overwhelms the normal-state spin paramagnetism by many orders of magnitude. However, the spin paramagnetism of the conduction electrons produces a hyperfine field at the atomic nuclei and, via nuclear magnetic resonance (NMR) techniques, changes in this hyperfine field are easily discerned. Indeed, Knight and his coworkers[3] and Reif[4] have examined either thin films or colloids of Sn, V, and Hg below T_c in a manner in which at least one of the dimensions d was sufficiently small so that the condition $d < \lambda_0$, the zero field penetration depth, was satisfied. The difficulties encountered in preparing hundreds of metal films of the order of several hundred angstroms thickness deposited on insulating bases are considerable.

The Knight shift of the NMR in metals has usually been thought to arise from the contact hyperfine interaction between the nuclear magnetic moment and the field arising from the spin magnetization of the s conduction electrons.[5] If one compares the

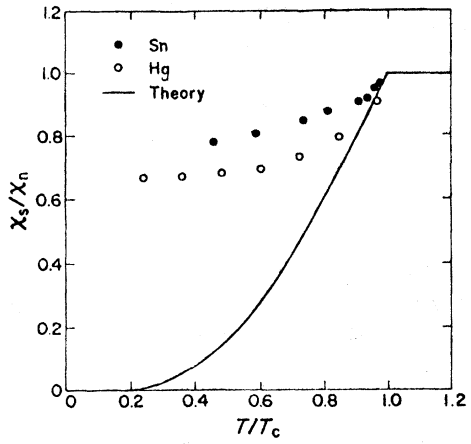

FIG. 1. The solid line is the reduced spin susceptibility versus the reduced temperature as calculated by Yosida (Ref. 2) using the BCS theory (Ref. 1). The experimentally obtained reduced Knight shifts for Sn and Hg are indicated by the points.

NMR frequency in a metal with that of a nonmagnetic, nonmetallic substance, the *fractional* shift K in the resonance frequency is just $8\pi/3$ times the spin magnetization density at the nucleus or

$$K = (8\pi/3)\chi_V\Omega\langle|\Psi_s(0)|^2\rangle_F\,, \qquad (1)$$

where χ_V is the volume spin susceptibility [$\chi_V = 2\mu_B^2 N(E_F)$], Ω the atomic volume, and $\langle|\Psi_s(0)|^2\rangle_F$ is the probability density at the nucleus for s conduction electrons of energies close to E_F, averaged over the Fermi surface. For other than s electrons, $|\Psi(0)|^2 = 0$ and in cubic symmetry the spin dipolar fields of non-s electrons vanish in the absence of spin–orbit coupling. The proportionality of K and χ_V then allows for a direct determination of the fractional change in χ below T_c since $K(T)/K(T_c) = \chi(T)/\chi(T_c)$.

The results on Sn and Hg (see Fig. 1) indicated that $K(0)/K(T_c) \simeq \frac{2}{3}$. Still more surprising are the measurements on V for which $K(0)/K(T_c) \simeq 1$.

Many suggestions have been made to explain these disturbing results and it would be out of place here to review the merits of each. However, one of the most reasonable theories, that of spin–orbit scattering by an impurity[6] or by surface irregularities, is capable of further experimental testing, and has relevance to the experimental work to be presented. Because of spin–orbit scattering by an impurity the wave functions are no longer eigenfunctions of **S**. From the uncertainty principle we may argue that the energies of all states are broadened by an amount

$$\delta E = h/\tau_{s.o.} \qquad (2)$$

where $1/\tau_{s.o.}$ is the frequency of spin–orbit scattering, related to the average distance $l_{s.o.}$ an electron at the Fermi surface travels between collisions by $l_{s.o.} = V_F\tau_{s.o.}$. If $\delta E \gg \Delta$ the one-electron states are strongly admixed and $\chi(0)/\chi(T_c) \rightarrow 1$. Since $hV_f/\Delta \simeq \xi_0$, the correlation distance, the above conditions on χ and K may be expressed as

$$\xi_0/l_{s.o.} \gg 1, \text{ then } \chi(0)/\chi(T_c) \simeq 1\,, \qquad (3a)$$

$$\xi_0/l_{s.o.} \ll 1, \text{ then } \chi(0)/\chi(T_c) \simeq 0\,, \qquad (3b)$$

as one might expect from the simplest physical argument. For the heavier metals Sn and Hg the choice of reasonable values for $l_{s.o.}$ will reproduce the observed small decrease in K below T_c.[6] However, for V, where the atomic spin–orbit coupling is smaller than in Sn or Hg, a large change should be obtained contrary to what is observed experimentally.

THE SUSCEPTIBILITIES AND KNIGHT SHIFTS OF TRANSITION METALS

Although detailed consideration will be given only to certain transition metal intermetallic compounds,

[3] W. D. Knight, G. M. Androes, and R. H. Hammond, Phys. Rev. **104**, 852 (1956); G. M. Androes and W. D. Knight, *ibid.* **121**, 779 (1961); R. J. Noer and W. D. Knight, Bull. Am. Phys. Soc. **6**, 122 (1961).

[4] F. Reif, Phys. Rev. **106**, 208 (1957).

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

[6] R. A. Ferrell, Phys. Rev. Letters **3**, 262 (1959); P. W. Anderson, *ibid.* **3**, 325 (1959); A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **42**, 1088 (1962) [English transl.: Soviet Phys.—JETP **15**, 752 (1962)].

some remarks of a quite general nature concerning susceptibilities and Knight shifts in transition metals may be made. Many d band metals have characteristically large paramagnetic susceptibilities and electronic specific heats—both of which have come to be

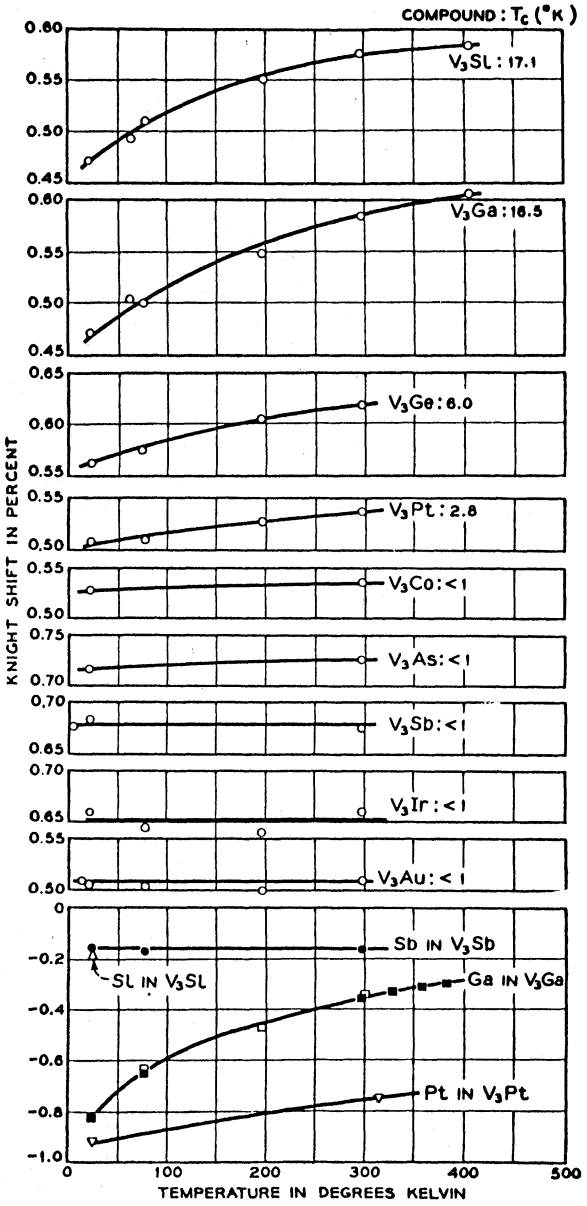

FIG. 2. The temperature dependence of the Knight shifts *above* T_c in the V_3X metals. A strong correlation is seen to exist between $\partial K/\partial T$ and T_c.

associated with the relatively high density of states $N(E)$ in the d bands. All of the d band paramagnetism is *not* of spin origin, however. There is an orbital contribution, that arises in the second order of perturbation theory,[7] which is the analog in metals of the more familiar Van Vleck temperature-independent paramagnetism of free ions. Quite generally, one may expect the spin and orbital contributions to be comparable in magnitude.

The hyperfine fields, and therefore the Knight shifts, in transition metals will reflect these additional contributions to the paramagnetism. Though, as previously remarked, no direct dipolar contribution to the Knight shift appears in cubic symmetry, the spin paramagnetism of the d electrons, via the core polarization of inner s shell electrons, may produce an appreciable contribution to the Knight shift, which is usually *negative*. The orbital contribution to the Knight shift, which may be directly related to the orbital paramagnetism,[8] in the approximation of tight binding, is *positive* in sign.

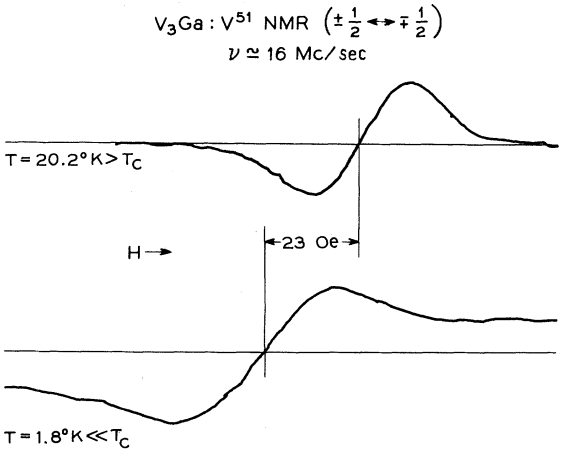

FIG. 3. The derivative of the NMR of V^{51} in V_3Ga above and below T_c.

In consideration of the fact that the exchange and correlation effects may modify the d spin paramagnetism from that which one would calculate knowing the electronic specific heat and that a detailed knowledge of the band structure is required to obtain the orbital paramagnetism, it would appear a formidable task to disentangle the various contributions to the susceptibility and Knight shift in a transition metal. If, however, the susceptibility and Knight shift are temperature-dependent, it becomes possible, within the framework of a simple model to affect a separation. This is best illustrated using the results obtained on the superconducting intermetallic compounds V_3X where, for example, X may be Ga, Si, Ge, As, etc.

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

[8] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. (to be published).

NORMAL STATE RESULTS ON THE V_3X METALS

A study of the NMR above T_c revealed that a correlation existed between the temperature dependence of the Knight shift and T_c for any given V_3X metal[9]; specifically, the higher T_c the larger was the temperature dependence of the Knight shift (see Fig. 2). Later measurements[10] revealed a siimlar correlation

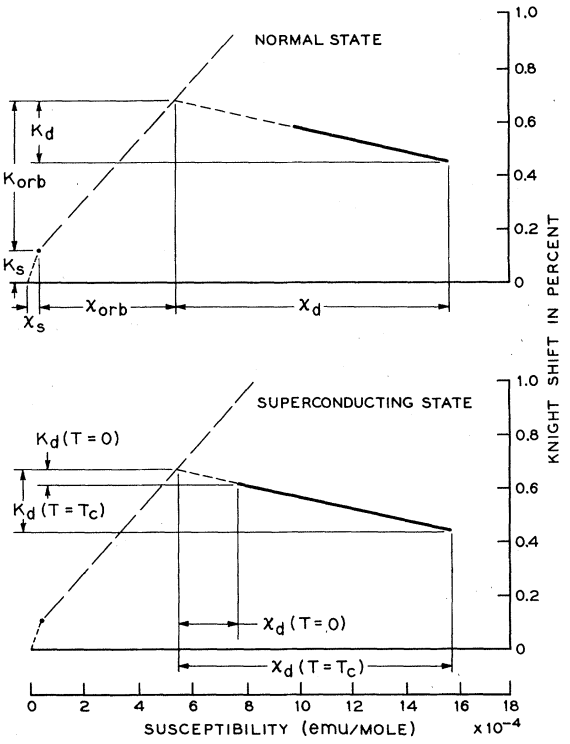

FIG. 4. The Knight shift versus susceptibility for the V^{51} NMR in V_3Si; (a) above and (b) below T_c. The various contributions to K and χ are explained in the text.

to exist with respect to the temperature dependence of the susceptibility and T_c. The V^{51} NMR in V_3Ga is shown in the upper part of Fig. 3 for $T > T_c$.

It was further noted that the Knight shift, at both sites, was proportional to the susceptibility, with temperature the implicit parameter. This provided the motivation for an interpretation[11] in which it was assumed that the temperature dependence of the susceptibility and that of the Knight shift resulted from the Fermi level intersecting a rather narrow, high $N(E)$ peak in the d band. (Subsequent electronic specific heat measurements have confirmed this surmise.[12])

[9] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters 5, 149 (1960).
[10] H. J. Williams and R. C. Sherwood, Bull. Am. Phys. Soc. 5, 430 (1960).
[11] A. M. Clogston and V. Jaccarino, Phys. Rev. 121, 1357 (1961).
[12] F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).

If we take a two band (s and d) model to analyze the electronic properties of these metals and, furthermore, assume only the d spin susceptibility and Knight shift to be temperature-dependent then we may write[13] (take V_3Si, for example)

$$\chi(T) = \chi_s + \chi_{orb} + \chi_d(T) , \tag{4}$$

$$k_V(T) = \alpha\chi_s + \beta\chi_{orb} + \gamma\chi_d(T) , \tag{5}$$

where χ_s and $\chi_d(T)$ are the respective s and d band spin susceptibilities, and χ_{orb} the orbital susceptibility of the degenerate d band.[7] (All susceptibilities are molar.) The quantities α and γ are proportional to the hyperfine field per spin of s and d electrons, respectively. In the approximation of tight binding it may be shown[8] that $\beta = (2/A)\xi\langle r^{-3}\rangle_{atom}$, where A is Avogadro's number and $\xi = \langle r^{-3}\rangle_{metal}/\langle r^{-3}\rangle_{atom}$.

We may construct a K vs χ diagram as follows: Using a free electron estimate for χ_s, assuming one

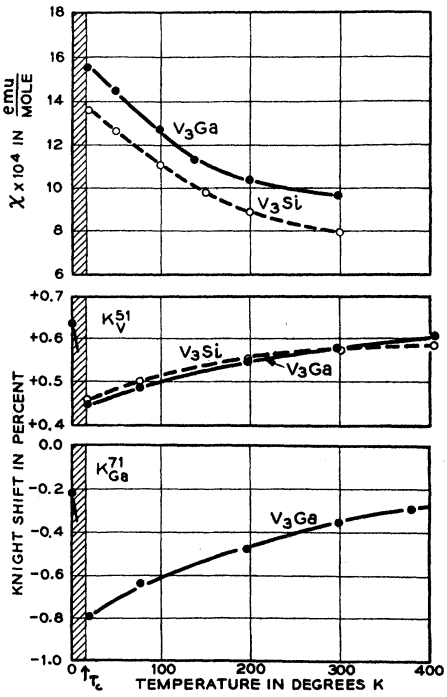

FIG. 5. The temperature dependence of the susceptibility of V_3Ga and V_3Si above T_c and the temperature dependence of the V^{51} and Ga^{71} NMR Knight shifts in the same metals above and below Tc.

4s electron per V atom we find $\chi_s \simeq 0.3 \times 10^{-4}$ and $K_s \simeq 0.1\%$. This is indicated by the short dashed line extending to the dot in Fig. 4(a). Using a value of $\langle r^{-3}\rangle_{atom} = 2.0$ a.u. and assuming $\xi = \frac{3}{4}$ (i.e., the 3d functions are expanded in the metal) we determine

[13] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters 9, 262 (1962).

$\beta = 11.25$. A dashed line from the dot is drawn with this slope. Now on the same figure, the observed K vs χ data are shown by the solid straight line the slope of which is seen to be *negative* indicating the d spin hyperfine field is produced via core polarization.

The intersection of the extrapolation of the solid line with the line previously indicated ($\Delta K_{\text{orb}}/\Delta\chi_{\text{orb}}$) permits a separation of spin and orbital contributions to be made. This is indicated on the ordinate and abscissa of the same figure. Similar analyses may be made for the X site Knight shifts and for other of these intermetallic compounds.

SUPERCONDUCTING STATE

For $T \ll T_c$ it is observed (see Fig. 5) that the Knight shift at both the V and X sites becomes more *positive* than it is anywhere above T_c. (The V^{51} NMR in V_3Ga below T_c is shown in the lower part of Fig. 3.) This is opposite to the spurious effects arising from the Meissner effect in which incomplete field penetration results in an apparent less positive Knight shift. Moreover, the change in the field for resonance is different at the V and X sites, showing the effect to be atomic rather than macroscopic in character.

Of the three contributions to the susceptibility and Knight shift only the orbital one will be relatively unaffected by the change from normal to superconducting state. The major part of the orbital paramagnetism arises from matrix elements of $\mathbf{L}$ which admix states $|n,k\rangle$ of the unfilled portion of the band into states $\langle n',k|$ of the filled portion of the band, *only a small fraction of which have energies such that* $|E_1 - E_F| \leq kT_c$. Let us assume first that only the *d spin* paramagnetism decreases below T_c. Then the observed changes in the Knight shift must appear as points along the heavy line shown in Fig. 4(b) and, in particular, must, at the lowest temperature, correspond to the ordinate change indicated. We see that no less than 75% of the d spin susceptibility has disappeared at $T = 0°K$. If we assume that *both* s and d spin susceptibility diminish below T_c then the observed change in Knight shift corresponds to a decrease in χ_d that exceeds 75%.

The behavior of the Ga Knight shift in V_3Ga is also consistent with a large reduction of the spin susceptibility as is shown in Ref. 13. These experiments represent the most complete spin pairing in the superconducting state observed to date.

When the values of the deduced spin susceptibilities for V_3Si and V_3Ga in the normal state are compared with those obtained from the electronic specific heat, according to the relation $\chi_{s.h.} = 3\mu_B^2\gamma/\pi^2k^2$, assuming that the electronic specific heat is not affected by the electron–phonon interaction, it is found that $\chi_d < \chi_{s.h.}$. It may be shown[8] that if the net electron–electron interaction is attractive, then the spin susceptibility will be reduced according to the relation

$$\chi_{\text{spin}} = \chi_{s.h.}[1 + N(E_F)V]^{-1} \tag{6}$$

providing one neglects retardation effects.[14] Here V is the interaction parameter of the BCS theory and is approximately related to kT_c via $[N(E_F)V]^{-1} = \ln(1.14\,\langle h\omega\rangle/kT_c)$. Using $\langle h\omega\rangle/k \simeq \frac{3}{4}\,\Theta_D$ it is found that the values deduced for χ_d are consistent with Eq. (6). They are collected in Table I of Ref. 13.

CONSISTENCY OF THE V_3X KNIGHT SHIFTS WITH THE SPIN-ORBIT SCATTERING THEORY

Recent measurements of λ on V_3Si[15] when combined with the known $N(E_F)$ and T_c permit a calculation of ξ_0. A comparison of the values of λ and ξ_0 for Sn and V_3Si are made in Table I. Even if we take $l_{s.o.}$ in V_3Si to be an order of magnitude smaller than that assumed for Sn we see that $\xi_0 < l_{s.o.}$. Consequently, appreciable spin pairing is to be expected below T_c as is observed in V_3Si and V_3Ga.

TABLE I. A comparison of the parameters that enter in the spin–orbit scattering theory of Ref. 6 for Sn and V_3Si. All dimensions are given in angstroms. The parameter d is the size of the particles (thickness of film) for the V_3Si (Sn) NMR experiments.

	T_c (°K)	$\lambda(0)$ (Å)	ξ_0 (Å)	$l_{s.o.}$ (Å)	$\frac{2\pi}{3}\frac{\xi_0}{l_{s.o.}}$	d (Å)
V_3Si	17.0	1500	23	$>10^2$	<0.5	10^4–10^5
Sn	3.7	500	1630	10^3	3.4	10^2

V AND NB METAL

In view of the important contribution that orbital effects make to the V_3X metals it is of interest to determine χ_{orb} and K_{orb} in other transition metals. A detailed analysis has been made for platinum[8] which exhibits a temperature-dependent Knight shift and susceptibility. For the superconducting metals V and Nb, neither K nor χ is temperature-dependent. However, by use of Eq. (6) and the known electronic specific heats we may deduce χ_d from the measured susceptibility and thus obtain χ_{orb}. Again, a free electron ($n = 1$; $m/m^* = 1$) estimate for χ_s will

[14] See, however, J. J. Quinn, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (J. Wiley & Sons, Inc., New York, 1960), p. 58 for a discussion of the electron–lattice and electron–electron interaction effects on the specific heat.

[15] T. J. Greytak and J. H. Wernick (private communication).

suffice as a reasonable means for obtaining K_s. Using values for the core polarization hyperfine fields that have been obtained in ionic crystals and computed values of $\langle 1/r^3 \rangle$ we are able to calculate the separate contributions to the Knight shift for V and Nb. The results are given in Table II. Clearly, orbital effects are of primary importance to both susceptibility and Knight shift. As to spin pairing below T_ci, t is particularly interesting to note that the complete suppression of the spin contributions at $T \ll T_c$ would have little effect on the Knight shift since the latter is primarily of orbital origin and the s and d contributions are small and of opposite sign.

TABLE II. The calculated contributions to the Knight shift in the normal state of V and Nb metal. The corresponding calculations for the superconducting state are also given in which the extreme case of complete spin pairing is assumed. It is seen that nearly all of the observed Knight shift is of orbital origin.

		K_s	$K_{d\text{-}sp}$	$K_{d\text{-orb}}$	K_{calc}	K_{exp}
V	Normal	0.10	—0.16	0.70	0.64	0.58
	Supercond.	0.0	0.0	0.70	0.70	0.58 ± 0.06
Nb	Normal	0.37	—0.23	0.74	0.88	0.85
	Supercond.	0.0	0.0	0.74	0.74	

The Electronic Band Structure of V_3Si and V_3Ga*

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The electronic properties of a certain class of alloys, having the composition V_3X, have been investigated in detail by Jaccarino, Clogston, Gossard, Morin, Maita, and others.[1] They found that the electronic susceptibility and Knight shift are strongly temperature dependent, and that the electronic specific heat is very large. Clogston and Jaccarino suggested that these properties can be described by a one-electron model in which the density of states $\rho(E)$ has a sharp maximum at (or very near) the Fermi level.[2] Upon the suggestion of Jaccarino, the nuclear magnetic relaxation time T_1 of V^{51} in various V_3X alloys was measured.[3] In "normal" metals, $1/T_1T$ is temperature independent,[4] proportional to $\rho(E_F)^2$, and apparently less affected by electron–electron correlations than the susceptibility and the Knight shift.[5] Consequently, a measurement of T_1 should yield a direct measure of the density of states at the Fermi surface. The measured values of $1/T_1T$ vs temperature are plotted in Fig. 1. It is seen, that below the transition temperature, T_1 behaves pretty much like in Type I superconductors.[6] It is shorter than predicted by Korringa's relationship just below T_c, and it gets longer at temperatures considerably below T_c. However, above T_c, T_1T is not constant, as is the case in the superconductors investigated so far (including vanadium metal[7]). Rather, $1/T_1T$ decreases as the temperature is increased. The higher T_c, the sharper this decrease.

Theoretically, a rigid, narrow band should cause T_1T to be temperature dependent, according to the relationship $1/T_1T = a + bT^2$, where a and b are temperature independent. This relationship is not observed experimentally; the observed variation being stronger at low temperatures. These observations, in conjunction with the susceptibility and Knight shift data,[1] indicate that a density of states function that can account for the observations, must have the following properties: (1) The peak of $\rho(E)$ is very narrow, much narrower than the width of the $3d$ band commonly observed in transition metals, (2) if the width of the peak is determined from the slope of the $1/T_1T$ vs T curve (or susceptibility, or Knight shift vs. T) at a given temperature, the width is of the same order as this temperature, (3) if the concentration of conduction electrons is varied, (say, by investigating the compounds $V_{3-x}Ga$, $0 \leqslant x \leqslant 1$), the peak stays at the Fermi surface.

The following model is proposed to account for the experimental observations. The V_3X alloys have the $\beta - W$ crystal structure (Fig. 2), in which the X

* Work supported by the National Science Foundation, Washington, D. C.

[1] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962); F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

[2] A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

[3] M. Weger, Bull. Am. Phys. Soc. **7**, 613 (1962).

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

[5] D. Pines, Solid State Phys. **1**, 420 (1955).

[6] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

[7] J. Butterworth, Phys. Rev. Letters **5**, 305 (1961).