A more complete treatment of the equations of motion should take into account the spatial inhomogeneity of the transverse and longitudinal electric field and the $\vec{q}$ dependence of the dielectric constants. Although lacking in this respect, the present treatment does demonstrate that for $\vec{E}\perp\vec{H}_0$ AK-CR the longitudinal depolarization field and the associated shift in resonance frequencies are essentially zero due to a combination of small AK-CR oscillator strengths and a large screening by the V-CR mode. It should be noted also that due to the absence of an appreciable longitudinal depolarization field in $\vec{E}\perp\vec{H}_0$ AK-CR, the presence of several types of carriers does not lead to hybrid resonances.[14,15] Thus, the AK-CR resonance frequencies for the different carriers will be independent of one another for $\vec{E}\perp\vec{H}_0$ as well as for $\vec{E}\parallel\vec{H}_0$.

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ORBITAL PARAMAGNETISM AND THE KNIGHT SHIFT OF D-BAND SUPERCONDUCTORS

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According to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity,[1] the spin susceptibility,[2] and therefore the Knight shift (k), should vanish exponentially as the temperature, T, of a superconductor approaches 0°K. Experiments on Hg,[3,4] Sn,[5] and V[6] appear to contradict this expectation since $k(0)/k(T_c)$ is 0.65 ± 0.04, 0.73 ± 0.03, and 1.0 ± 0.1 in the respective metals. (T_c is the superconducting transition temperature.) Numerous attempts have been made to modify the theory in order to account for these observations.[7] We wish to report measurements of k in the superconducting state of the metals V_3Si and V_3Ga which taken together with earlier measurements[8] in the normal state and their interpretation[9] show that (1) the d electrons are superconducting electrons, (2) at least 75% of the d spin susceptibility disappears at 0°K, and (3) substantial parts of the susceptibility and Knight shift arise from the temperature-independent orbital paramagnetism[10] to be expected in partially filled degenerate band metals. The magnitude of this orbital paramagnetism should be the same in both normal and superconducting states. Extrapolation of these results to vanadium metal indicates that the major part of k is of orbital origin and will be unaffected by the transition from normal to superconducting state. Furthermore the relaxation time in the normal state will be longer than that which one would predict from the Korringa relation. Preliminary calculations indicate that orbital paramagnetism makes an important contribution to the Knight shift in Sn, as well.

Nuclear magnetic resonance (NMR) studies below T_c require the use of particles (or films) small enough to permit complete penetration of the magnetic field. A characteristic property of all intermetallic compounds is their brittleness which makes possible the preparation of fine particles (~10^{-4} cm) by use of an automatic agate mortar and pestle. Particles of V_3Si and V_3Ga prepared in this manner are evidently small enough to permit nearly complete flux penetration at fields of 14 kOe since they are found to exhibit negligible diamagnetic rf susceptibility.[11] The NMR of V^{51} and Ga^{71} has been studied between 1.8 and 300°K and the k versus T data obtained are shown in Fig. 1. Two closely related features are to be noted: (1) For constant applied field the change in k_V and k_{Ga} as $T \to 0$ from T_c corresponds to a larger internal field and thus is opposite to the behavior previously observed in other superconductors. The observed shifts are also opposite to diamagnetic shielding effects resulting from partial flux exclusion,[3] and are of different magnitudes at the V site and the Ga site. (2) k is more positive at $T = 0$ than it is at any temperature in the normal state.

An interpretation of the observations below T_c may be given in terms of a model used previously to explain the k behavior in the normal state[9] but extended to include the effects of orbital paramagnetism. For example, in V_3Ga we write

$$k_V = \alpha\chi_s + \beta\chi_{orb} + \gamma\chi_d(T), \qquad (1)$$

$$k_{Ga} = \alpha'\chi_s + \beta'\chi_{orb} + \gamma'\chi_d(T), \qquad (2)$$

$$\chi = \chi_s + \chi_{orb} + \chi_d(T), \qquad (3)$$

where χ_s and χ_d are the molar spin susceptibilities resulting from the intersections of the Fermi

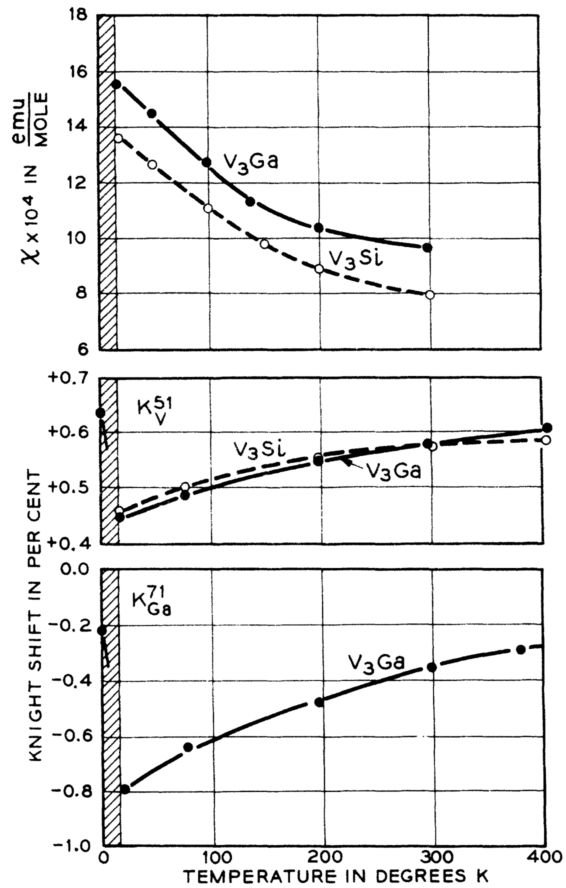

FIG. 1. The temperature dependence of the susceptibility and the V^{51} and Ga^{71} Knight shifts in V_3Ga and V_3Si for $T > T_c$ (14.6°K-V_3Ga; 15.8°K-V_3Si). For $T < T_c$ (shaded region) the Knight shifts at 1.8°K are indicated as well.

surface with the s and d bands and χ_{orb} is the molar orbital paramagnetism. In the normal-state experiments χ, as well as k_V and k_{Ga}, was found to be strongly temperature dependent. According to the above equations k_V and k_{Ga} are linear functions of χ_d, as found experimentally and shown in Fig. 2. The negative slopes of the k versus χ plots determined γ and γ' and were interpreted in terms of the exchange polarization of inner core s electrons by d electrons at the V site, and p electrons at the Ga site.[12] The positive increase in the k at both sites in the superconducting state clearly indicates a decrease in the d-electron spin susceptibility from which we conclude that the d electrons are actually superconducting electrons.

An estimated upper limit on χ_s is $\chi_s \simeq 0.30 \times 10^{-4}$ emu/mole corresponding to $\alpha\chi_s \simeq 0.1\%$. In the tight-binding approximation it may be shown

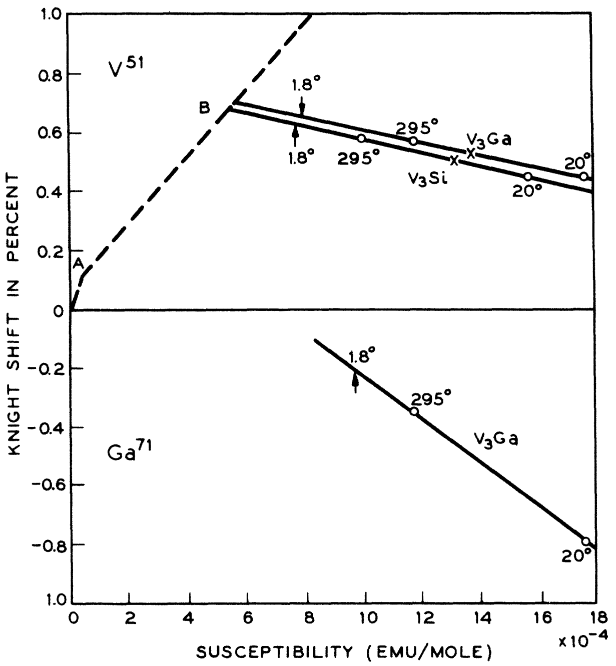

FIG. 2. The Knight shift versus susceptibility in V_3Ga and V_3Si. For $T > T_c$ a decreased dependence on temperature was found for the Knight shifts in particles smaller than 10^{-3} cm in size. For example, at 20°K the Knight shifts for the smallest particles are indicated by crosses and are to be compared with the corresponding values (circles) obtained from the large particles. Because of the relation between k and χ that was established in reference 9, this effect is taken to indicate a decreasing temperature dependence of the susceptibility with decreasing particle size.

that $k_{\mathrm{orb}} = 2(\chi_{\mathrm{orb}}/A)\xi\langle r^{-3}\rangle_{\mathrm{atom}}$ where A is Avogadro's number and $\xi = \langle r^{-3}\rangle_{\mathrm{metal}}/\langle r^{-3}\rangle_{\mathrm{atom}}$. Let us assume for the moment that χ_{orb} is associated with the V d electrons. In that case $\beta' = 0$ and $\beta = (2/3A)\xi\langle r^{-3}\rangle_{3d}$. We estimate[13] $\langle r^{-3}\rangle_{3d} = 2.0$ atomic units and $\xi \simeq \frac{3}{4}$ corresponding to $\beta = 11.25$. If $\chi_d = 0$, $k_{\mathrm{V}} = \alpha\chi_s + \beta\chi_{\mathrm{orb}}$ and must lie along the line in Fig. 2 extending from point A upwards with slope β. The intersection of this line (point B) with the line determined by the experimental points yields the value for which $\chi_d = 0$ or $\chi_{\mathrm{orb}} \simeq 5.2\times10^{-4}$ emu/mole.

The value of χ_{orb} so determined is a minimum value, for if we suppose $\beta' \neq 0$ (i.e., $\chi_{\mathrm{orb}}^{\mathrm{Ga}} \neq 0$) then the value of β will be reduced and the point B will shift towards larger χ. To obtain an upper limit on χ_{orb} we may use the value of k_{V} at 1.8°K since the spin susceptibility can only diminish in the superconducting state; $\chi_{\mathrm{orb}}^{\max} < 7.5\times10^{-4}$ emu/mole. An order of magnitude estimate[10] for $\chi_{\mathrm{orb}} \simeq 2\mu_B^2 NA\,|(0|L_z|i)|^2/\Delta$, where N is the number of d electrons for 3 V atoms and Δ the mean energy separation of filled levels $(0|$ from unfilled levels $|i)$, for which matrix elements of L_z exist, gives a value of $\chi_{\mathrm{orb}} = 6\times10^{-4}$ emu/mole for $N = 12$, $|(0|L_z|i)|^2 = 2$, and $\Delta = 2.5$ eV.

Let us now examine the significance of the observations below T_c. The values of k_{V} and k_{Ga} at a temperature $T \ll T_c$ correspond to a value of χ which is considerably smaller than the value observed at T_c. From our partitioning of the contributions to χ and k we determine, for $\chi_s + \chi_{\mathrm{orb}}$ remaining constant below T_c, that $\chi_d(0)/\chi_d(T_c)$ is bracketed by the values shown in Table I. This represents a more complete pairing of spins in the superconducting state than has been previously reported Note that if χ_s is less than has been estimated or has decreased in the superconducting state then the upper limits for $\chi_d(0)/\chi_d(T_c)$ would be still smaller. The fact that, in V_3Ga, the values of k_{V} and k_{Ga} for $T \ll T_c$ correspond to the different values of χ requires that

Table I. Parameters determined from NMR and χ measurements in the normal and superconducting states of V_3Ga, V_3Si, and V.

	$R \equiv \chi_d(0)/\chi_d(T_c)$	χ_{meas}	χ_{orb}	$\chi_{\mathrm{sp.ht.}}$	$\chi_{\mathrm{meas}}-\chi_{\mathrm{orb}}$	$N(0)V$ from Eq. (4)	$N(0)V$ from $[\ln(0.855\,\theta_D/T_c)]^{-1}$
		in units of emu/mole $\times10^{-4}$					
V_3Ga	$0 \le R \le 0.25$	17.9	5.2-7.5	14.0	12.7-10.4	0.13-0.39[a]	0.35[b]
V_3Si	$0 \le R \le 0.25$	15.7	5.2-7.5	10.7	10.5- 8.2	0.09-0.35[a]	0.35[b]
V		3.08	2.11	1.22	0.971		0.244[c]

[a]For V_3Ga and V_3Si the upper limit on χ_{orb}, which corresponds to $\chi_d(0)/\chi_d(T_c) = 0$, results in the larger values of $N(0)V$.

[b]Obtained from the relation given in the BCS theory and the experimental value of $N(0)$ and θ determined by Morin [F. Morin (to be published)]. Our thanks are due to Dr. Morin for a preprint of his work prior to publication.

[c]See reference 15.

the relative contributions of χ_s to k_V and k_{Ga} are different ($\alpha' > \alpha$).

The experimental evidence for the existence of a large χ_{orb} in V_3Ga and V_3Si resolves an apparent anomaly in the relation between the specific heat and susceptibility of these metals. The electronic specific heat coefficient γ determines the density of states at the Fermi surface $N(0)$ and thereby the susceptibility $\chi_{sp.ht.} = 3\mu_B^2\gamma/\pi^2k^2$. In the presence of a net attractive electron-electron interaction a simple theory, neglecting retardation effects, gives for the spin susceptibility

$$\chi_{spin} = \chi_{sp.ht.}[1+N(0)V]^{-1}, \qquad (4)$$

where V is the interaction parameter that appears in the BCS theory. This formula requires that $\chi_{spin} < \chi_{sp.ht.}$ whereas experimentally it is found that $\chi_{meas} > \chi_{sp.ht.}$ for the V_3X metals and for vanadium. This anomaly is removed if we recognize that $\chi_{spin} = \chi_{meas} - \chi_{orb}$. Using the limits on χ_{orb} given above we are able to bracket the values of $N(0)V$ as is shown in Table I. Interestingly, if we use the approximate relation given by BCS,

$$[N(0)V]^{-1} = \ln(1.14\langle\hbar\omega\rangle/kT_c), \qquad (5)$$

and let $\langle\hbar\omega\rangle = \frac{3}{4}\Theta_D$,[14] we find that the values of $N(0)V$ are bracketed by the values determined from our specific heat-susceptibility relations (see Table I.)

The identification of a large χ_{orb} in the V_3X metals depends upon there being temperature-dependent spin contributions to k and χ for $T > T_c$. Thus, a similar interpretation cannot be given a priori for vanadium. However, recent specific heat studies of Ti-V alloys have demonstrated that an essentially constant V satisfies Eq. (5) for all alloys in this system including vanadium,[15] for which $N(0)V = 0.244$. Applying the $[1+N(0)V]^{-1}$ correction to $\chi_{sp.ht.}$ we may calculate χ_{orb} from the relation $\chi_{orb} = \chi_{meas} - \chi_s - [1+N(0)V]^{-1}(\chi_{sp.ht.} - \chi_s)$. These values are collected in Table I. (χ_s is small and must be nearly the same in vanadium as it is in the V_3X metals.) The various predicted contributions to the Knight shift of vanadium for $T > T_c$ are $k_s = +0.10$, $k_d = -0.19$,[16] and $k_{orb} = +0.70$, resulting in a $k_V = +0.61$ whereas $k_{meas} = +0.58$ (all in %). If the contributions from k_s and k_d to k_V diminish below T_c the Knight shift will change at most by ~0.1 % in keeping with the experimental observations.[6] We may also estimate the relaxation time T_1 of the NMR for $T > T_c$ from our values of k_s and k_d. That the Kubo-Obata paramagnetism contributes to the Knight shift, but negligibly to the relaxation rate, arises from the fact that the major portion of χ_{orb} comes from the states that are at energies far removed from the Fermi energy, i.e., $E_F - E_0 \gg kT$ in contrast to the Pauli paramagnetism which arises from states within kT of E_F. No energy-conserving, nuclear moment-electron moment interactions can take place for these filled states and as a consequence no Korringa-like relation is to be expected for the orbital case. For independent s and d spin contributions to T_1 we have $T_1^{-1} = T_{1s}^{-1} + T_{1d}^{-1}$. Using the Korringa relation $T_1T = ck^{-2}$ where $c = 3.807 \times 10^{-6}$ sec °K for V^{51}, we find $T_1T = 0.83$ sec °K in essential agreement with the experimental value[17] $T_1T = 0.788$ sec °K. To summarize the situation in vanadium, orbital effects are the source of approximately all of k_{meas}, $\frac{2}{3}$ of χ_{meas}, and none of the relaxation rate of the V^{51} NMR.[18]

The situation in non-d group superconductors (e.g., Sn) is obscured by the fact that Landau diamagnetism precludes a partitioning of the relative contributions to χ as accomplished above. We wish only to remark that a reasonably small $\chi_{orb} = 0.18 \times 10^{-4}$ emu/mole with an estimated $\langle r^{-3}\rangle_{metal} = 14$ atomic units will account for all of the residual Knight shift in Sn for $T \ll T_c$ and the observation that the anisotropic Knight shift is unchanged at $T = 0$ from its value above T_c.

The experimental work reported herein is part of a detailed study of the NMR and χ studies in the V_3X metals and their alloys, done in collaboration with J. H. Wernick and H. J. Williams and to be published elsewhere.

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UPPER LIMIT FOR THE CRITICAL FIELD IN HARD SUPERCONDUCTORS

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Recently a number of reports have been made of extremely high critical fields observed in certain hard superconductors.[1-7] It is generally believed that these high critical fields arise from some sort of filamentary structure of the hard superconductors, possibly associated with dislocations.[1-10] A recent Letter,[11] reporting observations of nuclear magnetic resonance in the intermetallic compounds V_3Si and V_3Ga, shows that the spin susceptibility of these materials is reduced in the superconducting state at $T=0$ by more than 75% over the normal state. This observation sets a severe upper limit on the attainable critical field for these materials.

In a homogeneous, bulk superconductor, the transition from the superconducting to the normal state in a magnetic field occurs because of the extra free energy associated with the superconducting state due to the Meissner effect. If F_N and F_S are the free energies per unit volume of the normal and superconducting state, the critical field H_0 is given by

$$F_N = F_S + H_0^2/8\pi. \tag{1}$$

In a thin cylindrical conductor, the free energy associated with the Meissner effect is greatly reduced by partial penetration of the magnetic field. If the conductor is very thin, the critical field can be extremely large. Hauser and Helfand[9] find an enhancement factor of 45 for filaments of 400Å diameter.

We wish to point out that the critical fields observed and predicted for various superconductors are so high that they are approaching a limit that will exist even in the limit of no Meissner effect. In the normal state, a metal has a paramagnetic susceptibility χ_p due to the density of states at the Fermi level. In a magnetic field, the free energy will be lowered by an amount $\frac{1}{2}\chi_p H^2$. According to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity,[12] a superconductor at absolute zero will have no susceptibility due to electrons at the Fermi level. If this condition is realized in practice, in the absence of any Meissner effect, we should write in place of Eq. (1) at absolute zero,

$$F_N - \tfrac{1}{2}\chi_p H_0^2 = F_S. \tag{2}$$

In this equation we ignore the presence of any orbital paramagnetism that will be essentially the same in the normal and superconducting state. In terms of the density of states $N(0)$, $\chi_p = 2\mu_B^2 N(0)$, assuming a g factor equal to 2. According to the BCS theory[12] the free-energy difference $F_N - F_S = \frac{1}{2}N(0)\epsilon_0^2(0)$, where $\epsilon_0(0)$ is the energy gap at $T=0$. Equation (2) therefore becomes

$$(\mu_B H_0)^2 N(0) = \tfrac{1}{2}N(0)\epsilon_0^2(0)$$

or

$$\mu_B H_0 = (1/\sqrt{2})\epsilon_0(0) \tag{3}$$

with the density of states cancelling out. If we