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

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atoms form a bcc lattice and the vanadium atoms are arranged in an array of straight lines, such that the distance d between nearest neighbors on the same line is considerably smaller than the distance between vanadium atoms belonging to different lines $[(3/2)^{\frac{1}{2}}d]$. If the tight binding approximation is used for the vanadium $3d$ electrons, this crystalline structure will result in extremely anisotropic electronic properties; namely, if only nearest neighbor interactions are considered, the vanadium $3d$ states form three degenerate bands: The $3d$ states belonging to the atoms that form the lines in the [100] direction, combine to form a band in which the electronic energy $\epsilon(\mathbf{k})$ depends only on k_x, the component of $\mathbf{k}$ in the [100] direction; similarly, states of atoms that form lines in the [010] and [001] directions form bands in which $\epsilon(\mathbf{k}) = \epsilon(k_y)$ and $\epsilon(\mathbf{k}) = \epsilon(k_z)$ respectively. The Fermi surface of each of these bands consists of two parallel planes, perpendicular to the corresponding line of atoms, as shown in Fig. 2. This electronic band structure has essentially one-dimensional properties.

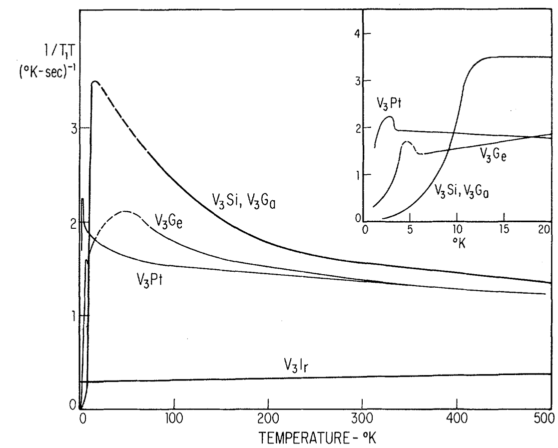

FIG. 1. The relaxation time T_1 of various V_3X alloys. $1/T_1T$ is plotted as function of temperature. The measurements were carried out on very fine powders, in a magnetic field of approximately 10 000 G.

One-dimensional models of metals have been investigated by Frohlich[8] and Overhauser.[9] Frohlich considered a one-dimensional model of a metal with electron–phonon interactions, and showed that such a metal is (for sufficiently strong electron–phonon coupling) a superconductor, with $kT_c \approx \epsilon_F \times \exp[-1/N(0)V]$ (vs $T_c \approx \theta_D \exp[-1/N(0)V]$ for a three-dimensional, isotropic, model[10]). In Frohlich's model, the self energy of the electrons in the *normal* state, due to their interaction with the phonon bath, is temperature dependent, and gives a contribution to the electronic specific heat of order $k(V/\epsilon_F)^2 \times \log(\epsilon_F/kT)$. This contribution can be phenomenologically described as due to an effective density of states, with the properties of the Jaccarino–Clogston peak. The contributions to the other electronic properties are similar. In an isotropic, three-dimensional model, this contribution is very much smaller [of order $k(V/\epsilon_F)^2(kT/\epsilon_F)\log(\epsilon_F/kT)$]. Overhauser also considered a one-dimensional metal, however, with direct electron–electron interactions. In Overhauser's model, there is also a transition to an ordered state at a relatively high temperature, and there are contributions to the specific heat similar to those of the Frohlich model (though, for the repulsive interactions considered by Overhauser, the ordered state has "giant spin waves" rather than BCS paired electrons). Consequently, it appears that the Clogston–Jaccarino peak is a property of a one-dimensional interacting electron gas, and does not depend very much upon the origin, or precise nature, of the interaction. It is a precursor effect, preceding the transition to the superconducting state.

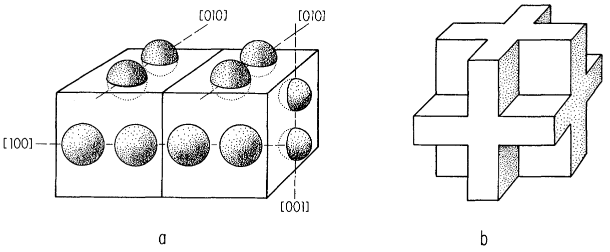

FIG. 2. (a) The crystal structure of V_3X compounds; (b) the Fermi surface of the vanadium $3d$ electrons in the tight binding approximation. There are 3 degenerate bands corresponding to electrons localized on the three groups of vanadium atom lines.

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Discussion 28

Coles: One rather interesting thing about a very strongly energy dependent density of state is that Pauli paramagnetism or the straightforward spin paramagnetism would show field dependence. Magnetization should not be linear in field. Has there been any evidence of this in high fields in the normal state of V_3Ga?

Jaccarino: I think that you'll find that the field dependence of the susceptibility is of the order of $(g\beta H/\Delta)^2$, where Δ = effective width of the band. This is still a rather small number; you only have field energies at best of the order of a degree or a couple of degrees and the widths of the bands are of the order of several hundred degrees. It would be very difficult to discern.

Chandrasekhar: This very unusual shape of the density of states at the Fermi surface—does this lead to any unusual ordinary transport properties? What sort of effect does it have on the normal state resistivity as a function of temperature or the thermal power?

Weger: I don't know about thermal power, but you would expect the Hall effect to be very different. If the *d*-electrons contribute to the resistivity then you should expect a different Hall effect and different magnetoresistance and things like that. Experimentally I know the thermoelectric power was measured and nothing strange was found —that's the measurement by Mrs. Sarachik.

Mrs. M. P. Sarachik, *Bell Telephone Laboratories:* These measurements were made by George Smith and myself. I can just quote what the results are. We found a peak in the thermoelectric power of V_3Ge which looks like a phonon drag contribution, and we did not find such a peak in the thermoelectric powers of the other three that we measured, namely V_3Si, V_3Ga and V_3Sn. They were all positive and about 10 μV per degree at room temperature. I was wondering if you could comment on these results since you do have them at your disposal.

Weger: It is very complicated. You have both *s*-electrons and *d*-electrons, and the question is how much of the thermal power is due to the *s*-electrons and how much to the *d*-electrons.

Pippard: If I remember correctly, the Fröhlich model involves a lattice displacement equal to the wave number at the Fermi surface in the one dimensional model. It is a finite displacement, is it not? What I am not clear about is whether you are allowed to have three mutually orthogonal finite displacements without their getting in the way of one another. I would like to ask Dr. Weger if that is so. The second point: Is there any possible way of verifying by x-ray methods that this displacement occurs?

Weger: If you look at the lattice there is no reason why they should interfere with each other because they are different atoms; there are three array of lines. Now in regard to x-rays—I don't know whether it can be seen by x-rays, but I believe that one could do an experiment with neutron diffraction. The theory by Kohn and Woll about the distortion of the phonon spectrum interacting with the electrons gives some singularities from this interaction which in three dimensions are very, very weak—discontinuous in the derivative—or something like that. Actually it has been observed by Brockhouse and his group in Pb, but after very very hard work because they are very small. Now if this model is true, then the singularities here should be much larger; they should not be discontinuous in the derivative but should show logarithmic infinities. So this would certainly be a way to confirm it or rule it out.

H. E. Rorschach, *Rice University:* If the Fermi surface has this very unusual shape, which seems necessary in order to give a cusp which moves with the Fermi surface, then it seems to me that one could hardly avoid the conclusion that there should be a superlattice formed in which this material should become essentially an insulator.

Nuclear Magnetic Resonance and Relaxation in Superconducting Vanadium*

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I. INTRODUCTION

Earlier nuclear magnetic resonance (NMR) experiments in superconducting mercury[1] and tin[2] suggested that the conduction electron spin susceptibility χ_s might not vanish[3] at $T = 0$. We undertook the work on vanadium[4] expecting the spin–orbit interaction[5] to be small. During the investigation Orgel[6] suggested that orbital contributions to the NMR shift should be appreciable. In the following we show that orbital effects are certainly important in vanadium although not necessarily overwhelming. The interpretation of the NMR shift in superconducting vanadium is qualified accordingly. A more

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* Supported in part by the U. S. Office of Naval Research.

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