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Nuclear Magnetic Relaxation in Vanadium

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Summary.

Measurements of the nuclear magnetic spin-spin and spin-lattice relaxation in the transition metal vanadium have been made at temperatures of 20.4° K, 77.3° K and 292° K. No evidence of the presence of localized unpaired electrons in vanadium was found. By comparison of the results with measured values of other physical properties of vanadium, it is deduced that there is such thorough admixture of *s*-states and *d*-states at the Fermi surface in vanadium that the spin susceptibility of the *s*-electrons is enhanced, by exchange interaction, to the same high degree as that of the *d*-electrons, namely, about 2.5 times. It is also deduced that the proportion of all the states at Fermi surface having *s*-character is roughly 0.17.

From a comparison of the measured values of the Knight shift, $\Delta H/H$, and the spin-lattice relaxation time, T_1, of the nuclear magnetic resonance in a metal, information can be derived about the state of the electrons in the metal. For, as Korringa showed [1], if the electrons responsible for the shift and the relaxation behave as uncorrelated electrons of largely *s*-character, the following simple relation exists between T_1 and $\Delta H/H$

$$T_1 \left(\frac{\Delta H}{H}\right)^2 = \frac{\hbar}{\pi k T} \left(\frac{\beta I}{\mu^2}\right)^2 \qquad (1)$$

where T is the absolute temperature, and β and μ are the magnetic moments of an electron and nucleus, respectively, while the other symbols have their conventional meanings. Conversely, departure from the Korringa relation indicates departure of the electrons from such simple behaviour.

Information about the electrons can also be obtained from measurements of the spin-spin relaxation, particularly if there is some question of the existence of localized states containing electrons of unpaired spin.

This note reports the results of measurements of T_1, and of the spin-spin relaxation of the ^{51}V resonance in vanadium metal, and some inferences drawn from them. The results are of some interest because they are the first reported accurate measurements of nuclear magnetic

relaxation in a transition metal, where the unfilled shell of *d*-electrons might be expected to influence strongly the nuclear magnetic resonance. As a probable consequence of these electrons the results show much the largest departure from the Korringa relation observed so far.

The sample consisted of 2.4 gram of vanadium powder obtained by grinding the metal on an alumina wheel and subsequently sieving it through a 200 mesh. The metal was initially prepared electrolytically by the U.S. Bureau of Mines Electrometallurgical Section, and was found by analysis to have a purity of 99.7%, the principal impurity being 0.09% by weight of dissolved iron.

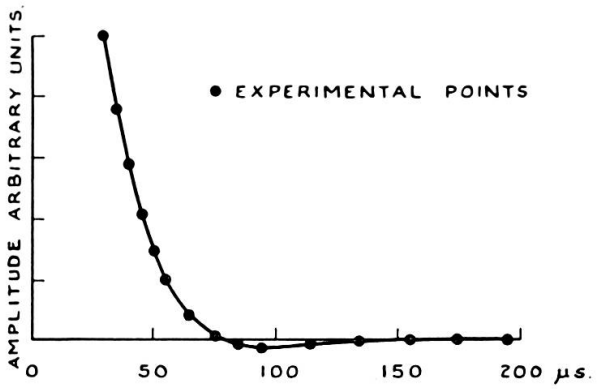

FIG. 1. INDUCTION DECAY, AFTER $\frac{\pi}{2}$ PULSE, FROM TRANSVERSE NUCLEAR MAGNETIC MOMENT OF ^{51}V NUCLEI IN VANADIUM METAL.

Fig. 1.

The measurements of relaxation were made at temperatures of 20.4° K, 77.3° K and 292° K, and at a frequency of 11.000 Mc/s, by a pulsed radio-frequency method incorporating coherent detection and post-detector integration. The pulse sequence used in the measurement of T_1 consisted of an initial $\pi/2$ pulse followed, after a variable period, by a further $\pi/2$ pulse, while measurement of the induction decay following a single $\pi/2$ pulse gave information about spin-spin relaxation.

The induction decay observed at all temperatures is shown in figure 1. We see from the overshoot that the decay is not that from a Gaussian line shape [2], for such a line would result in a decay having a time, t, dependence of the form $\exp(-\gamma^2\sigma^2t^2/2)$, where γ is the magnetogyric ratio of the nucleus, and σ^2 is the mean square deviation of the field at

the nuclei. The overshoot is a common feature of induction decays from rigid lattices [3]. The departure from Gaussian behaviour, however, does not begin until after some 60μs, as is shown by figure 2, where the induction decay is shown as a function of t^2. The value of σ^2 derived from the straight part of the curve is 31 gauss^2, which value may be compared with the calculated dipolar value [5] of 19.3 gauss^2, and that, derived from conventional measurements [5], of 32 gauss^2.

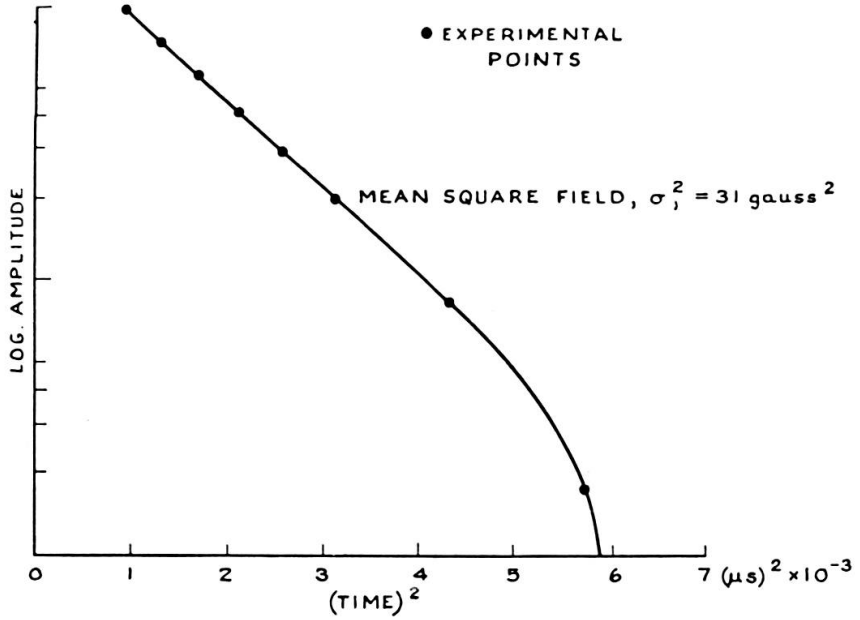

FIG. 2. AMPLITUDE OF INDUCTION DECAY, FROM ^{51}V NUCLEI IN VANADIUM METAL, AGAINST (TIME)^2

Fig. 2.

In the reasonable agreement of the calculated dipolar line width with that derived from the measurements, and the temperature independence of the latter, we see no evidence for the existence in vanadium of localized unpaired electronic spins. The extra broadening is attributed to indirect spin-spin coupling of the nuclei via the conduction electrons.

The values of T_1 obtained are given in Table 1, together with the product of T_1 and temperature T.

We see that, within experimental error, the value of T_1 varies inversely as the absolute temperature from 292° K down to 20.4° K, indicating that, over this temperature range, the dominant mechanism of spin-

lattice relaxation is the interaction between the nuclear spins and the spins of the conduction electrons. Thus, again, there is no sign of any effects due to spins of localised *d*-electrons.

TABLE 1.

Values of T_1 *and of* T_1T *against temperature.*

T (°K)	T_1 (m sec)	T_1T (sec. °K)
20.4	38.4 ± 1%	0.783 ± 1%
77.3	10.2 ± 1%	0.788 ± 1%
292	2.70 ± 1%	0.788 ± 1%

If we assume that the electrons producing the spin-lattice relaxation are behaving as uncorrelated electrons of mainly *s*-character and use the measured value of T_1T in equation (1), we can calculate the value of Knight shift such electrons would produce. By this means we derive a value for $\Delta H/H$ of 0.219%. Measured values, however, are some 2.5 times this, ranging from 0.55% [4] to 0.58% [5].

Such a discrepancy is in the wrong direction to be explained by invoking electron states of other than *s*-character, for such states would merely contribute to the relaxation without affecting the shift. Furthermore, because of their low spin density at the nucleus, their effect on relaxation would be small.

Consequently, we assume that T_1 is largely determined by the effective density of *s*-states at the Fermi surface. As this density appears, from the temperature-independence of T_1T, to be constant, and because of the lack of a plausible mechanism for prolonging T_1, we conclude that $\Delta H/H$ and, hence, the spin paramagnetism of the *s*-states is enhanced by a factor of about 2.5.

However, further information about the relation of the effective density of states of the conduction electrons to their spin paramagnetism, χ_p, can be derived from measurements of the coefficient of electronic specific heat, γ_e, and the magnetic susceptibility of the metal. For, if the conduction electrons behave as uncorrelated the following simple relation exists between χ_p and γ_e [6].

$$\frac{\chi_p}{\gamma_e} = \frac{3\beta^2}{\pi^2 k^2} \qquad (2)$$

This relation is analogous to the Korringa one, but refers to all the electronic states at the Fermi surface which are expected in vanadium to be of largely *d*-character, and not merely to those of *s*-character.

The measured value of γ_e in vanadium [7] is 8.8×10^{-3} Joule/gram atom. deg^2. If we again assume that the electrons are uncorrelated and insert the value of γ_e in equation (2) we obtain a value for the spin susceptibility of these electrons of 122×10^{-6} emu/gram atom. Childs et al [8] have measured the total susceptibility of vanadium and, after making small corrections for diamagnetism, have arrived at a value for the spin susceptibility of 308×10^{-6} emu/gram atom. Thus, the spin susceptibility of the mainly *d*-type electrons at the Fermi surface is also some 2.5 times greater than that expected from their effective density of states.

In the present state of theory the explanation of this surprising coincidence must be to some extent speculation, but in the absence of any better theory, it is suggested that the enhancement of the susceptibility is a result of exchange interactions between the conduction electrons, while one interpretation of the fact that the susceptibility of the *s*-electrons is enhanced to the same high degree as that of the *d*-electrons is that there is such thorough admixture of *s*-states and *d*-states at the Fermi surface, that they are equally affected by exchange effects.

From the measured values of T_1 and γ_e, we can deduce approximately the proportion, ξ, of the electrons at the Fermi surface having *s*-character, by means of Korringa's formula

$$T_1^{-1} = 2\pi k T \hbar^{-1} \xi^2 n^2 (E_0) a^2 (s) \qquad (3)$$

where $n(E_0)$ is the total density of states at the Fermi surface, obtained from γ_e, and $a(s)$ is the hyperfine coupling constant for an *s*-electron. Using the value of $a(s)$ calculated by Knight [9] in equation (3) leads to a value for ξ of 0.17. The fact that such a reasonable value for ξ can be obtained from T_1 alone tends to substantiate the view that the departure from the Korringa relation is mainly due to enhancement of the Knight shift.

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Relaxation magnétique nucléaire dans le Vanadium

Résumé.

Des mesures de relaxation magnétique nucléaire spin-spin et spin-réseau ont été effectuées dans le métal de transition Vanadium à des températures de 20,4° K — 77,3° K et 292° K. Aucune trace de présence d'électrons non appariés n'est apparue dans le Vanadium. La comparaison de ces résultats avec les valeurs mesurées à partir d'autres propriétés physiques du Vanadium permet de déduire qu'il y a un tel mélange d'états *s* et d'états *d* à la surface de Fermi du Vanadium, que la susceptibilité magnétique des électrons *s* est augmentée, par interaction d'échange, au même degré que celle des électrons *d*, à savoir environ 2,5 fois. On a également déduit que la proportion de tous les états à la surface de Fermi ayant un caractère *s* est environ 0,17.