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Nuclear Magnetic Resonance in Vanadium Chromium Hydride*

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The Knight shift K and the spin-lattice relaxation time T_1 of the nuclear magnetic resonance of ^{51}V are measured in the system $V_{1-x}Cr_xH_y$. Values of K_V and $(T_1)_V$ in the binary systems $V_{1-x}Cr_x$ and VH_x are compared with present measurements in the ternary system using a rigid-band model. Both K_V and $(T_1)_V$ depend, to a good approximation, upon the electron-per-atom ratio of the alloy, $\mathfrak{z}=5+x+y$, and are independent of relative concentrations of Cr and H. Data are consistent with the screened positive-ion model for hydrogen in the metal in which the hydrogen atom contributes its electron to the conduction band of the system. No Knight shift of the ^{1}H spins has been detected. The temperature dependence of T_1 for ^{1}H was measured in several alloys. A minimum in $(T_1)_H$ is attributed to thermally activated diffusion of protons. Activation energies measured range from 1.5 to 8 kcal/mole.

I. INTRODUCTION

TRANSITION metals in groups III B, IV B, and V B of the Periodic Table are known to absorb relatively large amounts of hydrogen into interstitial sites. The resulting mixtures are metallic and many of their physical properties suggest that they can be treated as alloys of the transition metal.

The hydrogen is assumed to be an alloying element that contributes its electron to the conduction band of the host metal. The positive hydrogen ion is screened by conduction electrons in the metal, and the resulting ionization potential is reduced well below that of the atom in vacuum.[1]

There has been an increasing number of experiments which indicate that the hydrogen ion is not negative as, for example, in the alkali hydrides. Measurements of magnetic susceptibility,[2] electronic specific heat,[3] and nuclear magnetic resonance (NMR)[4,5] give support to the assumption of the positive ionic state. An additional assumption of a rigid-band model has been invoked in analyzing the NMR data.[4,5] In the rigid-band model, electrons from the solute, hydrogen, change the electron density of states in the solvent conduction band. The NMR Knight shift K and spin-lattice relaxation time T_1 of the solvent nuclei are sensitive to changes in the electron density of states. Zamir[5] tested the rigid-band model by comparing solvent NMR parameters in the alloy system $V_{1-x}Cr_x$ with those in the VH_x and in the isolectronic systems $Nb_{1-x}Mo_x$ with NbH_x. Comparison of the vanadium K and T_1 in, $V_{1-x}Cr_x$ with K and T_1 in VH_x is made for equal values of the electron per atom ratio $\mathfrak{z}$. According to the rigid-band model $\mathfrak{z}$ would equal $5+x$ in both $V_{1-x}Cr_x$ and VH_x. Zamir found K_V and $(T_1)_V$ had essentially the same dependence on $\mathfrak{z}$ in VH_x as in $V_{1-x}Cr_x$. He proposed that the effect of the addition of H to V was equivalent to the addition of Cr to V in affecting the electron density of states.

As a further test of the above assumptions, we have measured K_V and $(T_1)_V$ in the V-Cr-H ternary alloy system. The V-Cr alloy system was selected because of the especially strong dependence of the density of states upon $\mathfrak{z}$ in the region $\mathfrak{z}=5.0$ to $\mathfrak{z}=5.5$.

Also, there exists a considerable amount of data on electronic specific heat,[6] magnetic susceptibility,[7] superconducting transition temperatures,[8] and NMR[9,10] in the V-Cr alloy. The results of the vanadium NMR measurements in the $(V_{1-x}Cr_x)H_y$ ternary alloy system is reported here. The purpose of these experiments is to determine whether K_V and $(T_1)_V$ depend principally upon $\mathfrak{z}$ and are independent of relative concentrations of Cr or H. Measurements of electronic specific heat of some of the same alloys are reported elsewhere.[11]

II. EXPERIMENTAL PROCEDURES

A. Sample Preparation

V-Cr alloys were prepared in the Cornell Materials Science Center High Temperature Facility from the highest-purity commercial materials available at the time of preparation. The vanadium and chromium had stated purities of 99.8 and 99.99%, respectively. The metals were weighed to an accuracy of 0.2% and subsequently alloyed in an electron-beam furnace. To assure homogeneity, the alloy buttons were turned and

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remelted. A 2-day anneal in a Vycor vial at 1000°C was followed by a rapid cooling.

Fine metal powder, free of Fe contamination, was produced from these alloys by heating the sample in a H furnace to 1000°C where they absorbed about 0.1 H per host metal ion. They were then cooled and crushed in an alumina mortar and pestle. Particles with a dimension less than 44 μ were selected with a sieve. The absorbed H was driven from the metal powder by heating to 600°C in a vacuum for several hours. After rehydriding to the desired H concentration the metal was sealed in thin-walled glass tubes under a He atmosphere and annealed for 12 h at 350°C to ensure uniform H distribution.

Hydrogen concentrations of up to 0.75 H per host metal ion were attained for pure V metal. V-Cr alloys took up decreasing amounts of H with an increasing proportion of Cr in the alloy. Stated H concentrations are accurate to 2%.

B. Experimental Observations

Knight-shift, line-shape, and linewidth measurements were performed on a wide-line NMR spectrometer using the Varian rf unit, crossed-coil probes, and a Varian 12-in. electromagnet. Vanadium resonances were observed at 11 MHz, while proton resonances were observed at 16 MHz. Frequency was held constant to within 5 Hz by means of external crystal controlled oscillator driving the Varian rf unit. For all resonances the center of the line was taken to be at the field where the first derivative went through zero. The linewidth of the absorption curve was taken to be the full width of the line between turning points of the first derivative.

The Knight shifts of V in the alloys were measured using the V resonance in sodium metavanadate ($NaVO_3$) as a reference marker. The Na resonance in $NaVO_3$ was identified and avoided.

Spin-lattice relaxation times were measured with a pulsed, phase coherent, NMR spectrometer. All measurements were made at 11.65 MHz. Measurements were made at 4, 77 and between 200 and 400°K with two crossed-coil probes. Measurements of the proton spin-lattice relaxation time T_1 were made using the "90-90" technique which consists of two 90° pulses applied with variable spacing. In the case of V it was never possible to saturate the entire spin system with the initial 90° pulse. The vanadium quadrupole interaction (spin $\frac{7}{2}$) splits the nuclear spin levels causing only the central transition to be saturated by the applied rf field. However, spin-spin interactions which occur in a short time compared to T_1 equalize the spin level populations and saturation is approached. For this reason a pulse "comb" of six or eight 90° pulses was applied saturating approximately 95% of the signal intensity. The vanadium T_1 was measured by applying a single monitoring 90° pulse at varying spacing after the last pulse in the pulse comb.

III. DATA

A. Vanadium Knight Shifts

The V Knight shifts were measured as described above and the uncertainty in the reported values is ±2% of the shift.

Knight shifts were measured both at room-temperature (protons motionally narrowed) and at liquid-nitrogen temperature. The measured V Knight shifts in the alloy hydrides and are plotted in Fig. 1, as a function of the electrons per atom ratio. Knight-shift measurements made by Drain[10] in the V-Cr system are also plotted in the same figure for comparison. In pure V there is a systematic difference between our value of K_V [$(+0.55\pm0.01)\%$] and the value published by Drain[10] [$(+0.580\pm0.001)\%$]. The difference equals about 25% of the linewidth; it is outside the probable error, and the difference is not understood. Our principal interest here is not in the absolute value of K_V, but in the change ΔK_V and its dependence upon relative concentrations of H and Cr.

Specific values of K_V are shown in Table I. Figure 1 also shows values of K_V for the V-H_y system from the measurements of Zamir.[5]

B. Vanadium Spin-Lattice Relaxation Times

The spin-lattice relaxation times of V in several V-Cr-H samples are shown in Fig. 2, where $(T_1T)^{-1}$ (T is the absolute temperature) is plotted as a function of the electron per atom ratio. T_1 was measured at 77 and 4.2°K. The product T_1T is constant over this temperature range to an uncertainty of 10–15%, which is within the accuracy of measuring T_1. The data are compared to those of Butterworth[9] (open circles) in his study of the V-Cr alloy system. One particular alloy and a hydride prepared from this alloy are marked in the figure. This was done to emphasize the effect of adding

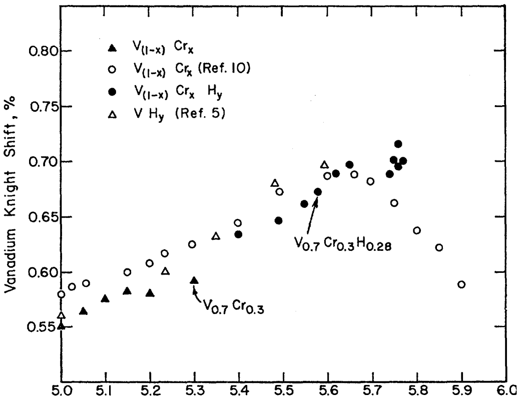

FIG. 1. Vanadium Knight shifts versus electron-per-atom ratio. All data points indicated by solid circles represent samples containing some hydrogen. Effect of addition of hydrogen to one alloy, $V_{0.7}Cr_{0.3}$, is shown as an example.

TABLE I. Summary of data for alloy hydrides.

Sample number	Composition	Knight shift 77°K (%)	T_1T V	Proton linewidth at 77°K (gauss, ±0.5 G)	$\mathfrak{z}$ (Electrons per atom)	V linewidth 77°K	Room temp.	Proton activation energy	
206	$V_{0.95}Cr_{0.05}H_{0.71}$	0.715	2.62	12.8	5.76	...	11.1	5.2	
207	$V_{0.85}Cr_{0.15}H_{0.50}$	0.696	2.62	13.4	5.65	...	11.8	...	
208	$V_{0.90}Cr_{0.10}H_{0.66}$	0.707	2.62	13.7	5.76	9.0	11.0	...	
210	$V_{0.90}Cr_{0.10}H_{0.65}$	0.700	2.35	13.6	5.75	13.4	...	8.5	2.3
211	$V_{0.90}Cr_{0.10}H_{0.30}$	0.634	1.46	13.2	5.40	17.7	11.0	5.5	
212	$V_{0.85}Cr_{0.15}H_{0.34}$	0.645	1.49	12.7	5.49	15.3	...	7.2	1.5
213	$V_{0.85}Cr_{0.15}H_{0.47}$	0.689	2.22	13.4	5.62	11.6	10.0	...	
214	$V_{0.6}\ Cr_{0.4}\ H_{0.34}$	0.687	2.00	14.0	5.74	11.9	9.3	6.7	
215	$V_{0.7}\ Cr_{0.3}$	0.590	1.23	...	5.30	12.3	11.6	...	
216	$V_{0.8}\ Cr_{0.2}$	0.580	1.08	...	5.20	12.2	11.6	...	
217	$V_{0.7}\ Cr_{0.3}\ H_{0.46}$	0.696	2.46	13.0	5.76	11.8	9.3	7.9	2.3
218	$V_{0.95}Cr_{0.05}H_{0.50}$	0.660	1.85	12.6	5.55	11.8	9.1	...	
219	$V_{0.7}\ Cr_{0.3}\ H_{0.28}$	0.670	1.92	11.8	5.58	13.4	10.7	4.8	
220	$V_{0.8}\ Cr_{0.2}\ H_{0.57}$	0.698	2.94	14.6	5.77	13.0	9.6	...	
221	$V_{0.6}\ Cr_{0.4}\ H_{0.37}$	0.693	2.52	11.9	5.77	12.4	...	...	
	$V_{0.6}\ Cr_{0.4}$	0.595	...	...	5.40				
	$V_{0.95}Cr_{0.05}$	0.563	...	...	5.05				
	$V_{0.85}Cr_{0.15}$	0.582	...	...	5.15				
	$V_{0.90}Cr_{0.10}$	0.575	...	...	5.10				
	V	0.550	...	...	5.00				

hydrogen to the lattice and is typical of the other data points. Values of T_1T also appear in Table I.

For alloy hydride samples with $5.0 \leq \mathfrak{z} \leq 5.6$, $(T_1T)^{-1}$ data appear to depend on the value of $\mathfrak{z}$ only and not the relative values of x and y.

C. Vanadium Linewidths

The linewidth of the V resonance was measured at 77°K and room temperature using the wide-line spectrometer. At room temperature the protons are diffusing rapidly and their contribution to the V linewidth is small. At 77°K rigid lattice conditions obtain and the vanadium linewidth increases due to the proton-V dipole coupling. V linewidths vary from 9 to 18 G at 77°K with a mean value of 12.8 G and from 9.3 to 11.8 G at room temperature with a mean value of 10.5 G.

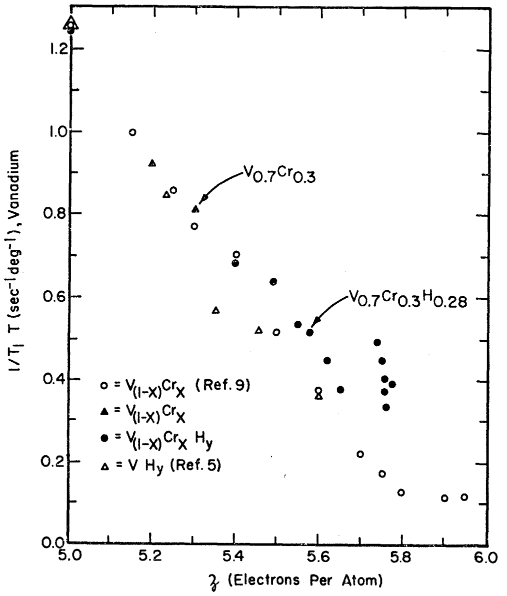

FIG. 2. Vanadium spin-lattice relaxation rate versus electron per atom ratio. Effect of addition of hydrogen to one alloy, $V_{0.7}Cr_{0.3}$, is shown as an example.

Many of the V resonances have an asymmetry which could be due to distribution of Knight shifts or second-order quadrupole interactions. No attempts were made to sort out the causes of the asymmetry in the line shape.

D. Proton Resonance

The proton spin-lattice relaxation time was measured in $(V_{1-x}Cr_x)H_y$ as a function of temperature from −65 to +300°C. The data are plotted in Fig. 3. The minima

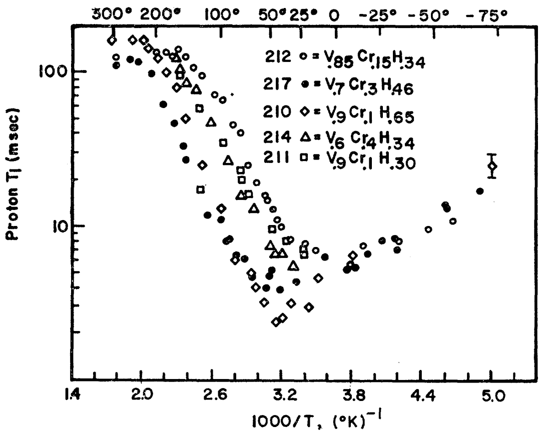

FIG. 3. Temperature dependence of proton spin-lattice relaxation time for several hydride alloys.

in the temperature dependence of T_1 for these samples occur near room temperature. Activation energies for proton diffusion were calculated from the temperature dependence of this curve and values obtained vary from 5 to 8.5 kcal/mole on the high-temperature side on the T_1 minima and from 1.5 to 2.3 kcal/mole at temperatures below 0–25°C.

The proton rigid-lattice linewidths, measured at 77°K, varied from 11.8 to 14.6 G in various samples. The large uncertainty in the linewidth, ±0.5 G, is due to a weak proton signal observed against a relatively large background resonance from H in the probe coil. Signal strength of the proton resonance is limited by the long T_1 of the proton spin system in the alloys at these low temperatures.

There was no evidence of a measurable shift in the resonant frequency of the proton resonance in these samples.

IV. DISCUSSION

A. Vanadium Knight Shift

In the interpretation of the NMR data, we assume that the magnetic susceptibility of V-Cr alloys can be partitioned into four contributions; the 4*s* conduction electron spin susceptibility χ_s, the 3*d* conduction electron spin susceptibility χ_d, the orbital paramagnetic susceptibility χ_0, and the diamagnetic susceptibility χ_{dia}, which is the only negative term. The total susceptibility of an alloy is

$$\chi_{\text{total}}=\chi_s+\chi_d+\chi_0+\chi_{\text{dia}}. \tag{4.1}$$

It is also assumed that K_{V} and $(T_1T)^{-1}$ can be partitioned into separate terms depending upon 4*s* electrons, core polarization, and orbital hyperfine fields, H_s, H_d, and H_0, respectively. Then,

$$K_{\text{V}}=K_s+K_d+K_0$$

or

$$K_{\text{V}}=(\beta N_0)^{-1}(H_s\chi_s+H_d\chi_d+H_0\chi_0)\,, \tag{4.2}$$

where K_{V} is a numerical fraction, the susceptibilities are in units (emu/mole), β is the Bohr magneton, N_0 is Avogadro's number, and $(\beta N_0)^{-1}=1.79\times10^{-4}$.

The 3*d* spin susceptibility χ_d is strongly dependent upon the *d*-band density of states which, in turn, depends strongly upon the value of $\mathfrak{z}$. Previous analysis of the V-Cr system indicates that the orbital and *s*-spin contributions to the total susceptibility are relatively weakly dependent upon $\mathfrak{z}$ in the range $\mathfrak{z}=5.0$ to $\mathfrak{z}=5.5$. We therefore assume that all of the $\mathfrak{z}$ dependence of the V Knight shift is due to the dependence of K_d upon $\mathfrak{z}$ through the dependence of the *d*-band density of states, $N_{bsd}(0)$, upon $\mathfrak{z}$.

We use[12]

$$\chi_d=2\beta^2N_{bsd}(0)/[1-N_{bsd}(0)V_c]\,, \tag{4.3}$$

where V_c is the correction factor for electron-electron interactions. Values of $N_{bsd}(0)$ obtained from electronic specific-heat data and corrected for electron-phonon interactions have been published by McMillan[13] for the V-Cr alloy system. The known susceptibility of V-Cr alloys[7] can be fit to Eq. (4.3) and a value of $V_c=0.3\pm0.05$ eV is obtained. The small contribution of *s*-band electrons to the electronic specific heat, estimated using the single-particle free-electron model, is subtracted from the experimental values of the electron specific heat before $N_{bsd}(0)$ is obtained. For pure V the value of χ_d is thus found to be $\chi_d=107\times10^{-6}$ emu/mole.

Curiously, this is within a few percent of the value that would be obtained from electron specific-heat data and the strict application of a single-particle free-electron model. The corrections for electron-electron and electron-phonon interactions essentially cancel.

A knowledge of hyperfine fields is needed to partition the Knight shift. Yafet and Jaccarino[14] used the values $H_d=-1.17\times10^5$ G obtained from paramagnetic resonance studies of the V^{2+}; $3d^3$ ion, $H_s=1.12\times10^6$ G by application of the Fermi-Segrè formula, and $H_0=1.9\times10^5$ G estimated from theory calculation of $\langle r^{-3}\rangle$. When the above value of H_s is used to calculate the V spin-lattice relaxation rate, it predicted that over 50% of the measured rate would be due to the *s* electrons. However, examination of the dependence of $(T_1T)^{-1}$ upon $\mathfrak{z}$ in V-Cr alloys (see Ref. 9 and Sec. IV C of this paper) indicates that the *s* electron contribution to $(T_1T)^{-1}$ is less than 25% of the total. In the absence of a better estimate of H_s, we use the above number, but with reservation that it is probably too large. The free-electron single-particle model is used to estimate $\chi_s=7.7\times10^{-6}$ emu/mole in pure V. From the above, K_s and K_d are calculated to be for pure V:

$$K_s=+0.15\%\,,\quad K_d=-0.23\%\,,$$

and from these, K_0 is obtained from the measured K_{V} and Eq. (4.2) as $K_0=+0.63\%$. The orbital interaction is the main contribution to K_{V}.

Electronic-specific-heat measurements[11] show that the addition of H to V reduces the *d*-band density of states. Therefore χ_d and thus K_d can be expected to be correspondingly reduced in absolute magnitude. Using the rigid-band model, we assume that K_s and K_0 remain constant as $\mathfrak{z}$ changes when H is added, as is the case for addition of Cr.

For example, in $\text{VH}_{0.5}$, the electronic-specific-heat coefficient is[11] 4.55 (mJ/mole °K^2) compared to 9.25 (mJ/mole °K^2) for pure V. Therefore, using the same electron-phonon and electron-electron corrections as in $\text{V}_{0.5}\text{Cr}_{0.5}$, we estimate that for $\text{VH}_{0.5}$,

$$\chi_d=48\times10^{-6}\text{ emu/mole}.$$

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TABLE II. Comparison of calculated K_V and measured K_V.

Sample	$N_{bsd}(0)$ (electrons/ erg atom) (10^{11})	χ_d (emu/ mole) (10^{-6})	K_d (calc)	K_V(tot) (calc) (%)	K_V (meas) (%)
V^a	7.19	107	−0.23	0.55	0.55
$V_{0.8}Cr_{0.2}$	6.07[b]	83.5	−0.18	0.60	0.58
$V_{0.8}Cr_{0.2}H_{0.1}$	5.78[b]	78.1	−0.165	0.615	061
$V_{0.8}Cr_{0.2}H_{0.3}$	3.58[b]	42	−0.09	0.69	0.65
$V_{0.6}Cr_{0.4}$	4.8[b]	61	−0.13	0.65	0.60
$VH_{0.5}$	3.97[b]	48	−0.10	0.67	0.685[c]

[a] The V Knight shift was used as the experimental basis for these calculations and is shown for comparison only.
[b] Reference 11.
[c] Reference 5.

Thus, from Eq. (4.2) for $VH_{0.5}$,

$$K_d = -0.10\%$$

and the total calculated Knight shift is

$$K_{\text{total}} = K_s + K_d + K_0 = 0.68\%.$$

The Knight shift[5] for $VH_{0.5}$, 0.685% and the shift corresponding to an electron per atom ratio of 5.5 in Fig. 1 in V-Cr-H, 0.655%, compare favorably with this value. The Knight shifts have been calculated for $V_{0.8}Cr_{0.2}$, $V_{0.8}Cr_{0.2}H_{0.1}$, $V_{0.8}Cr_{0.2}H_{0.3}$, and $V_{0.6}Cr_{0.4}$ using electronic-specific-heat data of Ref. 11, and values of K_V are shown in Table II.

There are other features of the Knight-shift data that are consistent with the idea of a contributed H electron. Between $\mathfrak{z}=5.0$ and $\mathfrak{z}=5.75$, the Knight shift generally increases. It is interesting to note in Fig. 1 the shift behavior of an alloy approximately in the middle of this range upon hydriding. The $V_{0.7}Cr_{0.3}$ alloy and its hydride, $V_{0.7}Cr_{0.3}H_{0.28}$, which contains 0.28 H per transition-metal ion, can be picked as examples. If the H contributes its electron to the conduction band, then $\mathfrak{z}=5.3+0.28=5.58$ and the Knight shift should increase. If the H removed an electron from the metal conduction band to form a negative ion, $\mathfrak{z}=5.3-0.28 \approx 5.0$. The second alternative would result in a shift comparable to that of pure V (0.55%). The actual shift is 0.67%. The first alternative, that of a contributed electron, seems to be more representative of the data. All other alloys behave in a similar fashion. In general, the Knight shift does not depend on the relative amounts of Cr and H, but only on the ratio of electrons per atom computed by assuming a contributed H electron.

B. Susceptibility

As a check for internal consistency in the above partition of K_V, the susceptibility will be considered. The orbital susceptibility χ_0 can be estimated from K_0 as

$$\chi_0 = K_0/(1.79\times10^{-4}H_0)$$

or

$$\chi_0 = 185\times10^{-6}\ \text{emu/mole}.$$

The total susceptibility is given by Eq. (4.1). Because of the high effective mass of the d-band electrons, the Landau diamagnetism can be assumed[9] to be less than 10×10^{-6} emu/mole. Thus, the above empirical estimates of χ_s, χ_d, and χ_0 would indicate that for pure V

$$\chi_{\text{total}} = (7.7+107+185-10)\times10^{-6}\ \text{emu/mole}$$
$$= 290\times10^{-10}\ \text{emu/mole}.$$

Published measured values[7] of χ_{total} range from 300 to 310×10^{-6} emu/mole, in good agreement with the above.

For $VH_{0.5}$, χ_{total} is estimated to be

$$\chi_{\text{total}} = (7.7+48+185-5)\times10^{-6}\ \text{emu/mole}$$
$$= 236\times10^{-6}\ \text{emu/mole}.$$

Interpolation of the Zanowick-Wallace[2] data to $VH_{0.5}$ yields $\chi_{\text{total}} = 260\times10^{-6}$ emu/mole as an experimental value. The satisfactory agreement between these estimated and published measured total susceptibilities supports the above partitioning of the Knight shift as well as the idea that the H atom contributes its electron to the host-metal conduction band.

C. Vanadium T_1

The relaxation rate in a metal is proportional to both the absolute temperature and the square of the electron density of states at the Fermi surface. In vanadium and VCr where both the s and d electrons contribute to the relaxation, it is assumed as in the discussion of Knight shifts that the s and d bands are separable. Therefore, the relaxation rate can be written as the sum of the s and d contributions:

$$(T_1T)^{-1} = C_sN_s^2(0) + C_dN_{bsd}^2(0)\,, \tag{4.4}$$

where

$$N_{\text{total}}(0) = N_s(0) + N_{bsd}(0)\,,$$

C_s and C_d are constants, and $N_s(0)$ is the s-band density of states at the Fermi surface. The 4s contact term is the only interaction contributing to C_s, while core polarization, orbital and dipole interactions contribute to C_d.

A model has been developed[14] that expresses the four contributions to the relaxation rate in terms of the hyperfine fields at the nucleus. The four contributions to the relaxation rate can be written

$$(1/T_1T)_s = (4\pi/h)[\gamma_nH_sh]^2N_s^2(0)k_B\,,$$
$$(1/T_1T)_d = (4\pi/h)[\gamma_nH_dh]^2N_{bsd}^2(0)k_B \times[\tfrac{1}{3}f^2+\tfrac{1}{2}(1-f)^2]\,,$$
$$(1/T_1T)_0 = (4\pi/h)[\gamma_nH_0h]^2N_{bsd}^2(0)k_B\tfrac{2}{3}f(2-\tfrac{5}{2}f)\,,$$
$$(1/T_1T)_{\text{dip}} = 1/25(4\pi/h)[\gamma_nH_0h]^2N_{bsd}^2(0)k_B\,, \tag{4.5}$$

where f is the average fractional admixture of $3d(\Gamma_5)$ states at the Fermi surface. The orbital hyperfine field H_0 depends upon $\langle r^{-3}\rangle$, which is averaged over the d

TABLE III. Comparison of calculated and measured $(T_1T)_V^{-1}$.

Sample	$N_{bsd}(O)$ (electron/erg atom) ($\times 10^{11}$)	$C_sN_s(O)^2$	$C_dN_{bsd}(O)^2$	$(T_1T)_{\text{calc}}^{-1}$	$(T_1T)_{\text{meas}}^{-1}$
V[a]	7.19	0.25	1.0	1.25	1.25
$VH_{0.5}$	3.97	0.25	0.30	0.55	0.56
$V_{0.8}Cr_{0.2}H_{0.1}$	5.78	0.25	0.64	0.89	0.80[b]
$V_{0.8}Cr_{0.2}H_{0.3}$	3.58	0.25	0.25	0.50	0.52

[a] The V relaxation rate was used as the experimental basis for these calculations and is shown here for comparison only.
[b] $(T_1T)_{\text{meas}}^{-1}$ for this concentration is obtained by interpolating between data points in Fig. 2.

states at the Fermi surface, whereas previously (Knight shift) it was averaged over all occupied states in the *d* band. There may be some difference between these two averages but this will be ignored.

Since relaxation rates are additive,

$$\frac{1}{T_1T}=\left(\frac{1}{T_1T}\right)_s+\left(\frac{1}{T_1T}\right)_d+\left(\frac{1}{T_1T}\right)_0+\left(\frac{1}{T_1T}\right)_{\text{dip}}. \quad (4.6)$$

Using the values of the hyperfine fields listed above and best available values of the density of states, Yafet and Jaccarino arrived at a value for $(T_1T)^{-1}$ that is approximately twice the measured value, 1.25 (sec deg)$^{-1}$, for pure V. Their value of the *s*-band contribution to the relaxation rate in V equals about 25% of their total calculated relaxation rate and 50% of the measured relaxation rate. Butterworth[9] suggests that the *s* band is responsible for only about 3% of the total relaxation rate.

A new experimental estimate of the *s*-band contribution can be obtained assuming $N_s(0)$ is constant and by plotting values of $(T_1T)^{-1}$ versus McMillan's values[13] of $N_{bsd}^2(0)$ for V-Cr alloys. A fit of Eq. (4.4) to such a plot yields $(T_1T)_s^{-1}=0.25$ (sec °K)$^{-1}$ which is less than the value of 0.64 (sec °K) obtained by Yafet and Jaccarino, but greater than 0.04 (sec °K)$^{-1}$ suggested by Butterworth.[9] A value of $C_d=1.93\times10^{-20}$ cgs units is obtained from the slope of that plot. By subtracting the *s*-band contribution to the relaxation rate from the measured value for a pure V, we find the *d*-band contribution: $(T_1T)_d^{-1}=1.0$ (sec °K)$^{-1}$. Using $N_{bsd}(0)$ for $VH_{0.5}$ and the above value of C_d, the value of $(T_1T)_d^{-1}$ for $VH_{0.5}$ is calculated to be 0.30 (sec °K)$^{-1}$. From Eq. (4.3) the relaxation rate for $VH_{0.5}$ should then be $(T_1T)^{-1}=0.55$ (sec °K)$^{-1}$. From Zamir's data[5] the interpolated value of $(T_1T)^{-1}$ at $\mathfrak{z}=5.5$ in the VH system is 0.56 (sec °K)$^{-1}$. Similar calculations have been made for two other alloy hydrides for which a value of $N_{bsd}(0)$ is known. The results are shown in Table III. The calculated relaxation rates are remarkably close to the observed values for the three samples.

The change in the electron specific heat upon hydriding which is attributed here only to a change in the *d* electron density of states leads to a reasonable prediction of the change in the relaxation time in the hydride. Also, the experimental relaxation rate in the hydride decreases in a manner similar to the rate in pure V-Cr alloys. From these calculations and comparisons one can see that the addition of H to V affects the relaxation rate (via the electron density of states) as if the H electron were contributed to the conduction band of the metal.

The relaxation rate measured for vanadium chromium hydrides is shown in Fig. 2 as solid circles. Butterworth's data for the relaxation rate in V-Cr alloys is shown as open circles. Data have been plotted on Fig. 2 as if the H electron were donated to the metal conduction band.

The rapid decrease in the relaxation rate between $\mathfrak{z}=5.0$ and $\mathfrak{z}=5.6$ is thought to reflect the change in the *d* electron density of states which is squared in the relaxation equation. Adding hydrogen to V-Cr alloys affects the relaxation rate as if more Cr had been added. A typical example, $V_{0.7}Cr_{0.3}$, and its hydride, $V_{0.7}Cr_{0.3}H_{0.28}$, are marked in Fig. 2 to illustrate this effect. The T_1 of the alloy hydride is very similar to that of a $V_{0.4}Cr_{0.6}$ alloy, $\mathfrak{z}=5.6$.

If a negative H ion had been proposed, then $\mathfrak{z}=5.3-0.28=5.0$. The measured (T_1T) for $V_7Cr_{0.3}H_{0.28}$ is distinctly different from $(T_1T)^{-1}$ measured at $\mathfrak{z}=5.0$ in pure V. Further, this assumption would produce a large scatter in the data that would depend on the relative amounts of Cr and H in each sample.

The spread in $(T_1T)^{-1}$ above $\mathfrak{z}=5.6$ cannot be explained. It is interesting to note, however, that it is in this regime where the vanadium relaxation rate and the electron density of states in other V binary alloys depends not only on the electrons/atom ratio, but also on the other element in the alloy.[15]

D. Proton T_1

Vanadium hydride, VH_x, exists as two phases,[2] bcc and body-centered tetragonal (bct), for values of x greater than 0.03 and less than 0.43. The bcc (α) phase has a lattice constant slightly greater than that of the vanadium metal. Above $x=0.43$ and below $x=0.9$ only the bct (β) phase exists. Above $x=0.9$ a new γ phase starts forming which could be a stoichiometric dihydride phase. No such phase information exists for the V-Cr-H system. It is possible that the two-phase region ($x=0.03$–0.43) does not exist in the vanadium-chro-

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[15] Y. Masuda, M. Mishioka, and N. Watanabe, J. Phys. Soc. Japan **22**, 238 (1967).

mium hydrides since the V resonance in the alloy hydrides does not have the distinctive overlapping absorption line found in the V resonance in low-concentration vanadium hydrides. The V resonance in the alloy hydrides is asymmetric but is similarly asymmetric before hydriding.

The hydrogen nuclei in the vanadium-chromium hydrides occupy fixed interstitial positions in the lattice at temperatures at or below 77°K. As the alloy hydride is warmed, the protons change sites through a thermally activated self-diffusion process where the jump frequency ν_c is given by

$$\nu_c = 1/\tau_c = \nu_0 e^{-E_A/RT}. \tag{4.7}$$

In Eq. (4.7), τ_c is the correlation time, ν_0 is the so-called "attempt frequency," E_A is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Modulation of the H-H and the H-V magnetic-dipole interactions by the translational diffusion is the primary mechanism for the proton spin-lattice relaxation. Interactions with the Cr^{55} will be neglected because of its small nuclear moment and natural isotopic abundance. In principle, this mechanism could also affect the relaxation of the V nuclei. Measurements of T_1 of V in the alloy hydrides were performed at temperatures of 77 and 4°K which are low enough to avoid any contribution to the relaxation from this mechanism.

In terms of the usual spectral densities $J^{(k)}(\omega)$, the spin-lattice relaxation time of proton system I in V-Cr-H interacting with the V spin system S can be expressed in terms of the correlation time τ_c and compared with experiment.[16] Thus,

$$\begin{aligned}1/T_1 = {}&(3/2)C_I[J^{(1)}(\omega)+J^{(2)}(2\omega_I)]\\ &+C_s[(1/12)J_{IS}^{(0)}(\omega_I-\omega_s)+(3/2)J_{IS}^{(1)}(\omega_I)\\ &+(3/4)J_{IS}^{(2)}(\omega_I+\omega_s)],\end{aligned}$$

where

$$C_I=\gamma_I^4\hbar^2 I(I+1), \quad C_s=\gamma_I^2\gamma_s^2\hbar^2 S(S+1), \tag{4.8}$$

γ_I and γ_s are the gyromagnetics ratios of the proton, and the V nuclei, respectively. The first term on the right-hand side of Eq. (4.8) represents proton relaxation caused by the dipole interaction with other protons, while the second term represents interaction with V.

Equation (4.8) can be expressed in terms of $J^{(1)}(\omega)$ only. If one assumes cubic symmetry and averages over the directional dependence of the spectral density, then for the powder samples used,

$$J^{(2)}(\omega):J^{(1)}(\omega):J^{(0)}(\omega)=4:1:6, \tag{4.9}$$

and Eq. (4.8) becomes

$$\begin{aligned}(1/T_1)={}&(\tfrac{3}{2}C_I)[J^{(1)}(\omega_I)+4J^{(1)}(2\omega_I)\\ &+0.48J_{IS}^{(1)}(0.74\omega_I)+1.45J_{IS}^{(1)}(\omega_I)\\ &+2.90J_{IS}^{(1)}(1.26\omega_I)],\end{aligned} \tag{4.10}$$

where

$$C_S=1.45C_I.$$

For most vanadium hydrides the lattice has tetragonal symmetry with the axis ratio $c/a=1.10$. This value of c/a is sufficiently near unity that, for the sake of simplicity and the limited purposes of this discussion, the ratios for cubic symmetry given in Eq. (4.9) are used in making a numerical estimate of $1/T_1$.

The usual form of the spectral density function is assumed:

$$J^{(1)}(\omega)=\left(\frac{2}{15}\right)\left[\frac{2\tau_c}{1+\omega^2\tau_c^2}\right]\sum_k (r_k^{-6}),$$

where the summation will be designated $\sum_i$ for the proton sites and $\sum_j$ for the vanadium sites. Equation (4.10) becomes

$$\begin{aligned}\frac{1}{T_1}=\frac{2C_I}{5\omega_I}\Bigg[&\left(\frac{1}{1+(\omega_I\tau_c)^2}+\frac{4}{1+(2\omega_I\tau_c)^2}\right)\omega_I\tau_c\sum_i(r_i^{-6})\\ &+\left(\frac{0.48}{1+(0.74\omega_I\tau_c)^2}+\frac{1.45}{1+(\omega_I\tau_c)^2}\right.\\ &\left.+\frac{2.90}{1+(1.26\omega_I\tau_c)^2}\right)\omega_T\tau_c\sum_j(r_j^{-6})\Bigg].\end{aligned} \tag{4.11}$$

The maximum value of $1/T_1$ occurring at a value of $\omega\tau_c\approx 1$ can be estimated when the lattice sums are known. Some model for the position of the H in the lattice must be assumed in order to estimate the sums. In a bcc lattice, there are two possible types of interstitial sites usually referred to as the octahedral and the tetrahedral sites. In a bct lattice, the octahedral sites can be further identified as two types shown as O_1 and O_2 in Fig. 4. The tetrahedral sites T are also shown in Fig. 4. We are not aware of experiments which have determined which of the sites are occupied by H in the β phase of vanadium hydrides. Therefore, it will be assumed that all sites are possible.

Because of the relatively large average spacing between H atoms in the lattice, the contribution of the

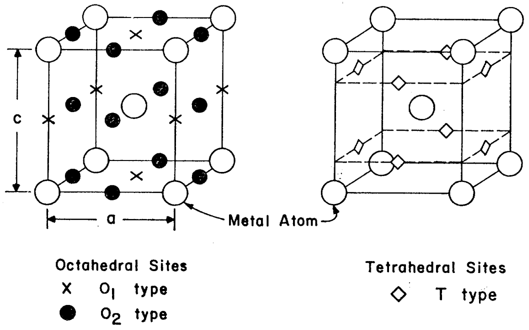

FIG. 4. Octahedral (O) and tetrahedral (T) interstitial sites in bct lattice. Metal ions show as the large open circles. In a bcc lattice, O_1 and O_2 sites are indistinguishable.

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[16] D. Zamir and R. M. Cotts, Phys. Rev. **134**, A666 (1964).

H-H term in Eq. (4.11) is for any one type of interstitial site less than 10% of H-V term. The relaxation rate therefore would seem to be controlled by H-V dipolar interactions.

The lattice sums in Eq. (4.11) have been evaluated for each type of interstitial site in the bct phase using[2] $c=3.36$ Å and $a=3.302$ Å. For the V-H summations it is found that the value of $\sum_j (r_j^{-6})$ is $108/a^6$, $160/a^6$, and $177/a^6$ for interstitial sites O_1, O_2, and T, respectively. When these sums are substituted in Eq. (4.10) the respective minimum calculated values of T_1 are 1.6, 1.1, and 1.0 msec for VH_y with zero Cr concentration. Contributions of H-H interactions have been omitted, and their inclusion would reduce each value of T_1 by about 10%. For an alloy $\text{V}_{1-x}\text{Cr}_x\text{H}_y$, the above estimates of T_1 should be divided by the quantity $1-x$.

Experimental values of the minimum value of T_1 vary from about 2.5 msec to about 7 msec, depending upon the Cr and H concentrations. Corresponding experimental values of T_1 are a factor of 1.5 to 4 times greater than the calculated values. The $(1-x)^{-1}$ dependence of T_1 upon the V concentration is obeyed approximately in samples 210, 214, and 217. But, the samples 211 and 212 with smaller Cr concentrations have larger values of T_1 than other alloys, which disagrees with the expected $(1-x)^{-1}$ dependence.

The fact that the calculated relaxation times are shorter than measured values could indicate that the proton jumps to adjacent interstitial sites are too short for full modulation of the dipolar interactions. Hence relaxation rates are overestimated.

The proton self-diffusion activation energy E_A can be determined from the temperature dependence of T_1 for the protons.

For samples where data at temperatures below the T_1 minimum are available, two activation energies for each sample are observed.

In the high-temperature region, $50°\text{C} \lesssim T \lesssim 150°\text{C}$, the activation energies range from 5 to 8.5 kcal/mole. Below about 0°C, the values of E_A range from 1.5 to about 2.3 kcal/mole in the samples where data exist.

Two values of E_A in separated temperature ranges are also observed in the isoelectronic niobium[16] and tantalum[17] hydrides. In comparing V-Cr hydrides to Nb and Ta hydrides it is noted that in Nb and Ta hydrides the value of E_A is high at low temperatures, and E_A is low at high temperatures. The high-temperature values of E_A in Nb and Ta hydrides were measured in the cubic α phase. The low-temperature values were measured in the β phase.

If the V-Cr hydrides behave in a similar way then our low temperature values of E_A would represent β-phase data, and our high-temperature range would actually correspond to the transition region between the β and α phase. This transition was discontinuous in TaH_x, steep in NbH_x, and no values of E_A were specified for the transition region.[16,17] The transition region, under this assumption, in V-Cr hydride is broadened enough to allow the relatively high values of E_A to be determined. Our T_1 data have very low temperature dependence above 200°C, in what is probably the α phase, but not enough data are available for analysis.

V. CONCLUSIONS

Measurements of K_V and $(T_1T)^{-1}$ for V have been made in a number of V-Cr hydrides. The relaxation rate is more strongly dependent upon the assigned electron per atom ratio than is the Knight shift. If it is assumed that the H contributes its electron to the conduction band, the value of $\mathfrak{z}$ for a $\text{V}_{1-x}\text{Cr}_x\text{H}_y$ alloy is calculated to be $\mathfrak{z}=5+x+y$. Plots of K_V versus $\mathfrak{z}$ and $(T_1T)^{-1}$ versus $\mathfrak{z}$ for a wide range of values of x and y indicate that K_V and $(T_1T)^{-1}$ are to a good approximation dependent on $\mathfrak{z}$ and essentially independent of the relative values of x and y. The interpretation indicates that a rigid-band model is a good approximation for the hydride alloys as well as for the V-Cr system.

The partitioning of K_V and $(T_1T)^{-1}$ in pure V has been reexamined in view of recently available electron-phonon and electron-electron interaction constants. It is found that the partitioning of K_V is not substantially different from others previously published.[9,18] The partitioning of $(T_1T)^{-1}$ indicates that the 4s electron hyperfine field is less than predicted from the Fermi-Segrè formula. Analysis of the dependence of $(T_1T)^{-1}$ upon $N_{bsd}(0)^2$ for V-Cr alloys indicates that $H_s \approx 0.7 \times 10^6$ G, which is about $\frac{2}{3}$ of the value previously used.[14]

Where data on electronic specific heat of hydride alloys is available, values of K_V and $(T_1T)^{-1}$ have been calculated based upon the understanding of K_V and $(T_1T)^{-1}$ in pure V. Reasonably satisfactory agreement between these calculated values again supports the idea that the rigid-band model is a good approximation in the alloy hydrides and that H enters the lattice as a screened-positive ion.

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[18] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962); A. Narath and A. J. Fromhold, Jr., Phys. Rev. **139**, A794 (1965).