PHYSICAL REVIEW B VOLUME 8, NUMBER 3 1 AUGUST 1973

Nuclear-Magnetic-Resonance Study of the Electronic Transition in Near-Equiatomic V-Ru Alloys*

L. B. Welsh
Department of Physics, Northwestern University, Evanston, Illinois 60201
C. W. Chu
Argonne National Laboratory,† *Argonne, Illinois* 60439, *and Department of Physics,*‡
Cleveland State University, Cleveland, Ohio 44115

(Received 27 October 1972)

For the near-equiatomic V-Ru alloys (46–50-at.% Ru) Chu *et al.* have observed dramatic changes in the electronic properties of these alloys with an accompanying tetragonal crystallographic distortion. Using the V^{51} nuclear magnetic resonance as a probe of the electronic properties, we have studied the Knight shift K and spin-lattice relaxation rate R in the high-temperature cubic phase and low-temperature tetragonal phase. The dramatic decrease in R and increase in K from the cubic to tetragonal phases are strongly concentration dependent. These results correlate well with the strongly concentration-dependent results for the bulk electronic properties. An analysis of the NMR and susceptibility data shows that the change in the electronic properties from the cubic to tetragonal phases results from a dramatic decrease of the d-electron density of states at the Fermi energy, and that R and K are dominated by the d-orbital contributions.

I. INTRODUCTION

The nonmagnetic alloys of vanadium with other $3d$ transition metals have been extensively studied by nuclear-magnetic-resonance (NMR) techniques over the past decade.[1–3] These alloy systems have provided a test of the validity of the rigid-band approximation in $3d$-transition-metal alloys and also a test of the tight-binding theory of NMR for the $3d$-transition-metal alloys. The interpretation of the NMR results of these systems normally has been in terms of a rigid-band model with a doubly peaked d-band density of states for systems such[2] as V-Cr, where the unshielded nuclear charge difference ΔZ is small, or in terms of a quasi-rigid-band model for systems such as V-Mn and V-Fe, where the difference in the local density of d states has been approximated by a relative shift of the rigid-d-band density of states in an attempt to take into account the effects of a larger-ΔZ value.[3] In these systems the vanadium NMR Knight shift and the bulk susceptibility have been satisfactorily partitioned[1–3] between the contributions from the s-electron-spin contribution and the d-electron-spin and orbital contributions as a function of the electron-to-atom ratio $\mathfrak{z}$. To a lesser extent the contributions to the vanadium spin-lattice relaxation rate have also been satisfactorily determined.[1–5]

The alloys of vanadium with the $4d$-transition-metal ruthenium have been studied as a function of $\mathfrak{z}$ by several authors.[6–9] While these alloys display properties similar to the V-$3d$-transition-metal alloys over much of the composition range, for the nearly equiatomic $V_{1-x}Ru_x$ alloys the superconducting transition temperature[8] T_c peaks sharply near $x = 0.455$, where $T_c > 5\,^\circ\mathrm{K}$. For $x > 0.455$, the existence of superconductivity is closely connected with the stability of the CsCl cubic phase. T_c is suppressed rapidly for those alloys which distort from the CsCl cubic phase to a CsCl tetragonal phase as the temperature is lowered.[8] Chu *et al.*[8] have measured a number of the bulk properties of the nearly equiatomic alloys and found dramatic changes in the electronic properties of the two phases. They suggest that the cubic to tetragonal distortion may be electronically driven. Studies of the NMR properties of the V-Ru alloys by Bernasson *et al.*[6,7] showed relatively complicated continuous-wave (cw) line shapes with several satellite lines. They also found that the vanadium Knight shift and spin-lattice relaxation rate showed a strong dependence on the thermal history of their samples. For the composition range $0.45 \le x \le 0.50$, their vanadium NMR results do not correlate well with the results of the bulk measurements of Chu *et al.*[8]

In this paper we present a study of the vanadium NMR properties in annealed $V_{1-x}Ru_x$ alloys for $0.45 \le x \le 0.50$ in both the cubic and tetragonal phases. Our NMR results show that the local electronic properties at the vanadium site correlate well with the bulk properties measured by Chu *et al.*[8] Furthermore, by combining the results of the NMR and bulk-property measurements we have a better picture of the electronic properties in the cubic phase and the changes occurring in the electronic properties in the cubic-to-tetragonal distortion than is obtainable from an analysis of the bulk properties alone. Finally, the vanadium NMR results are discussed in terms of the various electron-spin and orbital contributions. We find that the d-orbital contributions dominate both the vanadium Knight

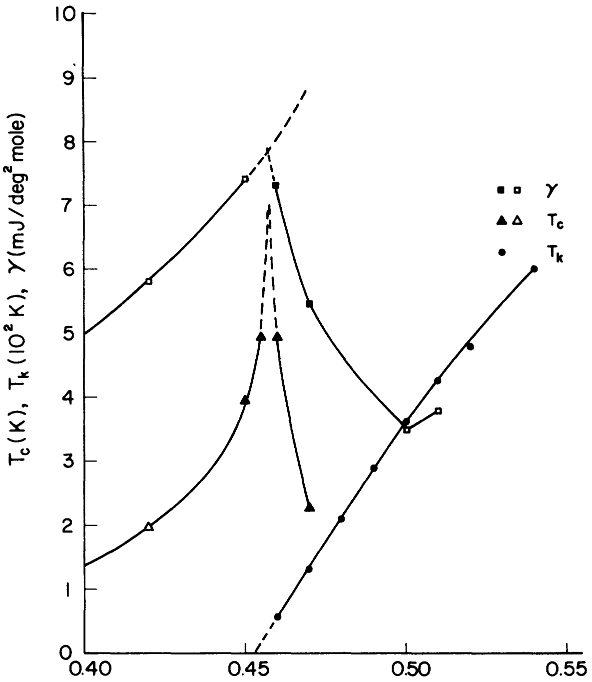

FIG. 1. Electronic transition temperature T_k, the superconducting transition temperature T_c, and the coefficient of the electronic specific heat γ vs x for the $V_{1-x}Ru_x$ alloys. These results are taken from Ref. 8.

shift and spin-lattice relaxation rate in both phases, but that the changes in these quantities as the alloy undergoes the cubic-to-tetragonal distortion are consistent with a dramatic decrease in the d-electron density of states at the Fermi energy.

II. EXPERIMENTAL RESULTS

The bulk properties of the $V_{1-x}Ru_x$ alloys for $0.40 \leq x \leq 0.55$ may be summarized in Fig. 1, which is taken from Chu *et al.*[8] Here the electronic-specific-heat coefficient γ, the superconducting transition temperature T_c, and the temperature T_k, describing the onset of the cubic-to-tetragonal transition as the sample is cooled, are plotted versus x. The values of T_k in Fig. 1 were determined from the resistivity and magnetic-susceptibility measurements, which show a dramatic change in these quantities from the cubic to tetragonal phases. For $x < 0.455$, only the cubic phase exists. For $0.455 \leq x \leq 0.50$, the cubic phase exists above T_k and the tetragonal phase exists below T_k. In this composition region T_k, T_c, and γ are strongly concentration dependent. Above $x = 0.50$ an additional hexagonal phase coexists with the cubic and tetragonal phases complicating the interpretation of both the bulk properties and the NMR measurements.[6]

Samples were prepared in an argon atmosphere by arc melting appropriate amounts of V (Semi-element Inc., three passes) and Ru (Johnson Matthey, Grade I). Each sample button was turned and remelted at least seven times to homogenize it. The weight loss during this process was less than 0.2%. Hence the quoted compositions were the nominal ones. The button was ground to 325- or 250-mesh powder. The powder after being magnetically cleaned was annealed in vacuum from room temperature to 1000 °C in approximately 1 h, then at 1000 °C for 1 h before it was finally air cooled to room temperature. The effects of heat treatment on the NMR measurements have been discussed by Bernasson *et al.*[6,7] Judging from the NMR results, our powder samples appear to be well ordered crystallographically after the above annealing.

Line Shapes

The most striking features of vanadium cw-NMR-line spectra for the composition range $0.45 \leq x \leq 0.50$ are the increase in the Knight shift, the decrease in the intensity of the line, and an increase in the linewidth in going from the cubic to tetragonal phases. Over the cubic-to-tetragonal transition region, the intensity of the tetragonal phase line grows rapidly at the expense of that of the cubic phase line. In neither phase is the cw line symmetric. Satellite lines of the type observed by Bernasson *et al.*[6] distort the line in the cubic phase and are thought to result from regions where the atomic ordering is incomplete since their intensity depends on heat treatment. In the tetragonal phase the intensity of the line is roughly a factor of 5 smaller than that of the NMR line in the cubic phase as a result of first-order quadrupolar wipe-out. In the tetragonal phase the cw line appears to be nearly symmetric at 8 kOe (except for the $V_{55}Ru_{45}$ sample), where the bulk of the NMR measurements were taken, but at 12.5 kOe the NMR line was definitely asymmetric. The line shape at 12.5 kOe could be accounted for qualitatively with the assumption of an anisotropic Knight-shift broadening of a Gaussian line, where $3K_{ax} = +0.10 \pm 0.10\%$, in qualitative agreement with Bernasson *et al.*[6] The behavior of the linewidth at 8 kOe is 6.8 Oe (peak-to-peak separation of the derivative curve) in the cubic phase independent of temperature, jumps to 10.0 Oe for the tetragonal phase at 180 °K and increases slowly to 13.0 Oe at liquid-helium temperatures.

The line shape was also studied in the tetragonal phase by integrating the quadrupolar spin echo observed in these samples at 8 kOe. An almost-symmetric central line was observed on a broad (~120 Oe) background resulting from nuclear-spin transitions other than the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. The noncentral peaks of the quadrupolar NMR spin-echo spectra are apparently smoothed out by the fairly broad distribution of electric field gradients in these samples. This may result from some concentration dependence of the volume change in the cubic-to-tetragonal distortion and minor variations of the local value of x.

Knight Shift

The V^{51} Knight shift was measured in both the cubic and tetragonal phases relative to VNO_3 or to the Al^{27} resonance in Al metal which was used as a secondary standard. The results of these Knight-shift measurements are shown for $0.45 \leq x \leq 0.50$ in Fig. 2 along with the results of Bernasson *et al.*[6,7] at 293° K. The tetragonal phase Knight shift is strongly concentration dependent, while the Knight shift in the cubic phase is nearly concentration independent. The cubic phase Knight shift for $x \leq 0.50$ was obtained at room temperature. The Knight shift in the $x = 0.50$ alloy was obtained at 340 K since at room temperature about one-third of this sample is in the tetragonal phase. It is particularly interesting to note from the data of Fig. 2 that the difference between the high- and low-temperature-phase Knight shifts disappears near $x = 0.455$ in agreement with the observed decrease of $\Delta\chi$ and $\Delta\rho$ as x approaches 0.455. No appreciable temperature dependence of the vanadium Knight shift was observed in the cubic phase although a slight increase was observed for the tetragonal phase Knight shift as the temperature was lowered. For both the cubic and the tetragonal phase lines the Knight shift was found to be temperature independent in the transition region. For the $x = 0.49$ and 0.50 samples, both lines were observed over a temperature range of ~40 K, which corresponds well with the temperature range of the transition observed in the bulk properties. Since T_k varies so rapidly with composition, the width of the transition probably results primarily from the distribution of local environments, i.e., the local values of x, indicating that the spread of x existing in these samples is on the order of $\Delta x \approx 0.002$ about the stated value.

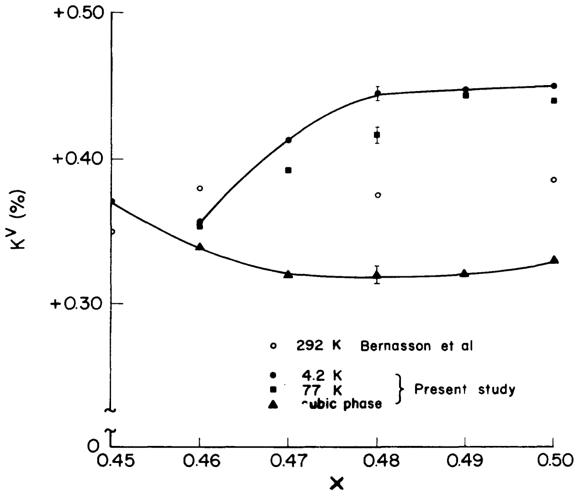

FIG. 2. V^{51} Knight shift for the high-temperature-cubic and low-temperature-tetragonal CsCl phases vs x for the $V_{1-x}Ru_x$ alloys. The open circles are data taken from Refs. 6 and 7.

Spin-Lattice Relaxation Rate

The V^{51} NMR spin-lattice relaxation time was measured in both the cubic and tetragonal phases by observing the recovery of either the free-induction-decay signal or the quadrupolar echo following a train of rf pulses which saturated the NMR signal. In all cases an exponential recovery of the NMR signal was observed. The composition dependence of the relaxation rate $R = (T_1 T)^{-1}$ is shown for both phases in Fig. 3. The relaxation rate in the tetragonal phase is given at 77 and 4.2 K. In the cubic phase the relaxation rate is given at room temperature for all samples except $x = 0.50$, where the relaxation rate was measured at 340 K. The relaxation rates display the same general behavior shown by the V^{51} Knight shift and the bulk properties. The relaxation rate in the cubic phase is roughly concentration independent except for $x = 0.50$ (this may be due to internal strains caused by the possible presence of some hexagonal phase since this sample is right on the phase boundary). The relaxation rate in the tetragonal phase is much more concentration dependent, and the difference of the cubic and tetragonal relaxation rates for $x > 0.45$ extrapolates to zero near $x = 0.45$. (No temperature dependence of R was observed between 1.5 and 4.2 K.) The relaxation rates obtained by Bernasson *et al.*[6,7] in the tetragonal phase are smaller and more concentration independent than those reported here. They report that their relaxation rates increased as the samples were better annealed giving better atomic ordering. This suggests that the observed differences between our NMR results and theirs may be due to differing heat treatments.[10] Since the relaxation rate apparently increases with increasing atomic order, we believe, that the samples we report on here are probably better ordered than those studied by Bernasson *et al.*[6,7]

III. DISCUSSION

In comparing the V^{51} NMR results presented here with those for the bulk properties obtained by Chu *et al.*,[8] the point of most importance is to what extent the properties of the V^{51} NMR reflect the variation of the bulk electronic properties. It has been suggested[6-9] that the difference in the electronic properties of the cubic and tetragonal phases results primarily from changes in the d-electron den-

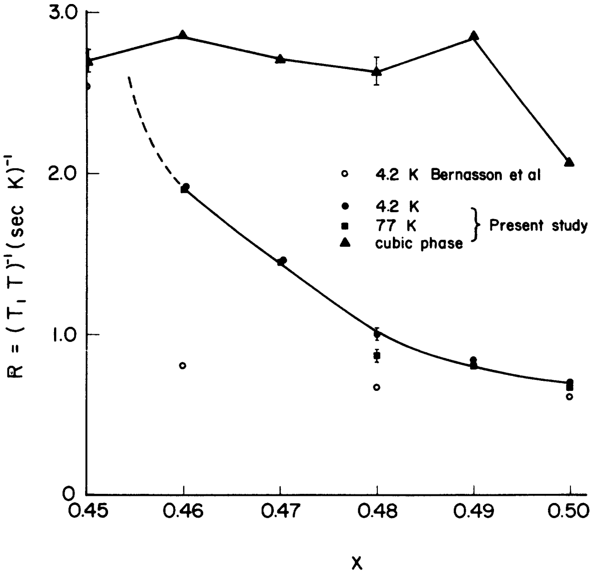

FIG. 3. V^{51} spin-lattice relaxation rate $R=(T_1T)^{-1}$ for the high-temperature-cubic and low-temperature-tetragonal CsCl phases vs x for the $V_{1-x}Ru_x$ alloys. The open circles are data taken from Refs. 6 and 7.

sity of states at the Fermi energy $N_d(0)$. Generally, for the vanadium-3d-transition-metal alloys the vanadium spin-lattice relaxation rate is thought to arise mainly from the local d-electron density of states at the vanadium site $N_d^V(0)$. Thus, $R^{1/2} \approx cN_d^V(0)$, where c is a constant. (This assumption will be examined in more detail below.) The density of states at the Fermi energy can be determined from $\gamma/(1+\lambda)$, where λ is the electron-phonon coupling constant.[11] In Table I we show the values obtained for the ratio of the T_1-determined local density of states at the vanadium site to the bulk density of states, $R^{1/2}(1+\lambda)/\gamma$, using the values of γ determined from Fig. 1 and the values of λ calculated by Chu *et al.*[8] in the McMillan formalism.[11] The values of γ and λ for several values of x were estimated by interpolating the data of Chu *et al.*[8] The values obtained for $R^{1/2}(1+\lambda)/\gamma$ suggest that in the tetragonal phase, the local density of states at the vanadium site scales with the bulk density of states. Similar correlation exists for the cubic phase as is clear from the fact that R and χ are nearly x independent. As discussed by von Meerwall and Schrieber for the case of the V-Mn alloys[3] (and is undoubtly the case where the unscreened nuclear charge difference is greater), the local density of states may differ significantly at different sites. Thus, it is possible that the rapid variation of the bulk properties may be more strongly reflected in the variation of the local density of states at the V site than at the Ru site.

TABLE I. Values of $R^{1/2}(1+\lambda)/\gamma$ at 4.2 K determined from the λ and γ values from Ref. 8 for the $V_{1-x}Ru_x$ alloys, $0.46 \le x \le 0.50$, where R is in units of $(\text{sec K})^{-1}$ and γ is in units of $\text{mJ}/(\text{K}^2\text{ mole})$.

x	0.46	0.47	0.48	0.49	0.50
λ	0.57	0.48	0.40	0.40	0.40
$R^{1/2}(1+\lambda)/\gamma$	0.30	0.33	0.30	0.31	0.31

As stated above, the difference in the electronic properties of the cubic and tetragonal phases is believed to result from changes in $N_d(0)$. Chu *et al.*[8] showed that $\Delta\rho/\rho$, $\Delta\gamma/\gamma$, and $\Delta\chi/\chi_{\text{spin}}$ have the same qualitative variation with x for $0.45 \le x \le 0.50$, where the quantities in the denominators are taken for the cubic phase. In the case of $\Delta\gamma/\gamma$ it was assumed that γ in the cubic phase could be extrapolated for $x > 0.45$ by the dashed line shown in Fig. 1. If we assume that $R^{1/2}$ tracks the bulk density of states in the cubic phase as well as in the tetragonal phase, then the concentration dependence of γ in the cubic phase can be estimated more accurately. Since R is roughly concentration independent, the values used for γ in the cubic phase and $\Delta\gamma$ are probably overestimated. In Fig. 4 we plot the concentration dependence of $\Delta R^{1/2}/R^{1/2}$ and $\Delta\gamma/\gamma$ using the concentration independent γ of 7.8 mJ/K^2 mole in the cubic phase (see Fig. 1). The concentration dependence of these quantities appears to be similar.

In determining the value of χ_{spin} to use in plotting $\Delta\chi/\chi_{\text{spin}}$ vs x, Chu *et al.*[8] assumed that the Van Vleck susceptibility $\chi_{vv} = \chi - \chi_{\text{spin}}$ was concentration independent and the same for both the cubic and tetragonal phases. With the same assumption the

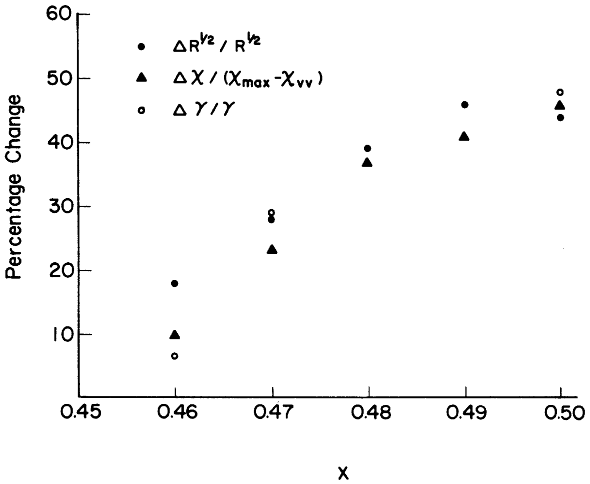

FIG. 4. Fractional change in the susceptibility, coefficient of electronic specific heat, and spin-lattice relaxation rate from the cubic-to-tetragonal phases vs x for the $V_{1-x}Ru_x$ alloys. The χ and γ data are taken from Ref. 8.

concentration dependence of $\Delta\chi/\chi_{\text{spin}}$ is also shown in Fig. 4, where we find that $\chi_{vv} = 65\times10^{-6}$ emu/mole gives the best agreement between the concentration dependence of $\Delta\chi/\chi_{\text{spin}}$, $\Delta\gamma/\gamma$, and $\Delta R^{1/2}/R^{1/2}$. This value of χ_{vv} is less than the 90×10^{-6} emu/mole determined by Chu *et al.*[8] from γ assuming no exchange enhancement of the spin susceptibility, although the difference in the resulting values of $\Delta\chi/\chi_{\text{spin}}$ is not large.

Using the V^{51} Knight shift and the bulk-susceptibility results, the assumption that the change in these quantities from the cubic to tetragonal phases results from a change in $N_d(0)$ can be tested. The relation between the Knight-shift components K_i and the various paramagnetic susceptibility contributions χ_i is given by[12]

$$K_i = (\mu_B N)^{-1} H_{\text{hfs}}^{(i)} \chi_i, \qquad (1)$$

where the $H_{\text{hfs}}^{(i)}$ are the appropriate hyperfine fields (in Oe/μ_B) and N is Avogadro's number. Normally, the assumption is made that the hyperfine-field values[1-3] do not vary significantly with x. In vanadium and the vanadium–transition-metal alloys only the s-spin, d-spin, and d-orbital contributions to χ have been found to be important[1-5] and they affect the vanadium nuclear spin via the s contact, d-core polarization, and d-orbital hyperfine interactions, respectively. Normally, the s-spin susceptibility and the V^{51} s-contact Knight-shift term are thought to be small in the vanadium alloys (von Meerwall and Schrieber estimated $K_s \approx +0.01\%$ in the V-Mn alloys[3]). Since the measured Knight shifts are positive while the d-core polarization contribution is negative, the largest Knight-shift contribution results from the orbital hyperfine interaction for both phases.

An effective hyperfine field H_{eff} can be determined from the quantity $\Delta K^V/\Delta\chi = H_{\text{eff}}/\mu_B N$, which is the change in the V^{51} Knight shift relative to the change in the bulk susceptibility. If the s-spin and d-orbital Knight shift and susceptibility contributions do not change appreciably from the cubic to tetragonal phases, then $\Delta K^V = \Delta K_d^V$, $\Delta\chi = \Delta\chi_d$, and $H_{\text{eff}} = H_{\text{hfs}}^{(d)}$. Table II shows that the values of H_{eff} are larger in magnitude than the value of $H_{\text{hfs}}^{(d)}$ obtained for vanadium[3] of -1.10×10^5 Oe/μ_B. This cannot result from a decrease in χ_{vv} since this would give a value of H_{eff} of smaller magnitude than $H_{\text{hfs}}^{(d)}$. Since the change in the V^{51} Knight shift reflects the change in the local susceptibility at the V site χ^V, it is possible that the change in χ_d^V per V atom is larger than the average change in χ_d per compound atom by ~ 20%, suggesting that the local properties at the V and Ru sites differ. Such a difference in the local properties is consistent with the magnitude of the V^{51} relaxation rate as discussed below.

TABLE II. Effective hyperfine field determined from $\Delta K^V/\Delta\chi$, the ratio of the V^{51} Knight-shift change to the change in the bulk susceptibility between the cubic and tetragonal phases for the $V_{1-x}Ru_x$ alloys. The $\Delta\chi$ values were taken from Ref. 8. The numbers in parentheses indicate the estimated uncertainty in the preceding digit.

x	0.46	0.47	0.48	0.49	0.50
$\Delta K/\Delta\chi$ (mole/emu)	−28(15)	−25(2)	−22(2)	−25(2)	−23(2)
H_{eff} (10^5 Oe/μ_B)	−1.5(1.0)	−1.36(15)	−1.21(15)	−1.36(15)	−1.26(15)

With the assumption that exchange enhancement of the spin susceptibility is unimportant for these alloys, the V^{51} spin-lattice relaxation rate is given by [2,4,5,12]

$$R = (T_1T)^{-1} = 4\pi\gamma_n^2 k_B \hbar \{N_s^2(0)(H_{\text{hfs}}^{(s)})^2 + N_d(0)[(pH_{\text{hfs}}^{(\text{orb})})^2 + (qH_{\text{hfs}}^{(d)})^2]\}, \qquad (2)$$

where the $N_i(0)$ are the s- or d-electron density of states at the Fermi-energy-per-spin direction and p and q are the orbital reduction parameters which depend on the orbital degeneracy of the d states at the Fermi energy.[4,5,12] Equation (2) applies to relaxation for nuclei in cubic environments and thus is not strictly correct for the tetragonal phase. Narath[13] has shown that for an environment with hexagonal symmetry, two important effects can be introduced in the tight-binding calculations for the relaxation rate. The first is the existence of an interference term between the s contact and d-core polarization relaxation rates. The second effect is the appearance of anisotropic orbital reduction factors. Since in the tetragonal phase the distortion from the cubic phase is small and $\Delta R^{1/2}/R^{1/2}$ appears to scale with $\Delta\gamma/\gamma$ and $\Delta\chi/\chi_{\text{spin}}$ (as shown in Fig. 4), we believe that these additional effects on the relaxation rate will be small, and that the relaxation rates for the tetragonal phase should be reasonably well described by Eq. (2).

The results for the V^{51} relaxation rates in both the cubic and tetragonal phases have been calculated using the V^{51} hyperfine fields for vanadium[3] of $H_{\text{hfs}}^{(d)} = -1.10\times10^5$ Oe/μ_B and $H_{\text{hfs}}^{(\text{orb})} = 2.30\times10^5$ Oe and are listed in Table III. Uniform degeneracy of the d band was assumed, i.e., p and q were taken to be 0.4 and 0.2, respectively.[4,5,12] The s-contact contribution to the relaxation rate was determined from the Korringa product[14] (K^2T_1T/S) using a value[3] of $K_s^V = 0.10\%$. The values of $N_d^V(0)$ for the cubic phase have been estimated assuming that γ was constant at 7.8 mJ/K^2 mole, an assumption upon which the calculated relaxation rates depend critically since $R \propto N_d^V(0)^2$. From the result (obtained from the value of $\Delta K/\Delta\chi$ in Table II) that $\Delta\chi_d^V$ might be ~ 20% larger than the average $\Delta\chi_d$, we might assume that $N_d^V(0)$ is 20% larger than the average value of $N_d(0)$. Even with this larger value

TABLE III. Estimates of the V^{51} spin-lattice relaxation rate in the cubic and tetragonal phases of the $V_{1-x}Ru_x$ alloys for $0.46 \leq x \leq 0.50$. The calculated relaxation rates given in parentheses are for $H_{\text{hfs}}^{(\text{orb})} = 2.8 \times 10^5$ Oe.

	Cubic phase				
x	0.46	0.47	0.48	0.49	0.50
$N_d^V(0)$ $\left(\frac{\text{states}}{\text{eV atom spin}}\right)$	1.35	1.43	1.51	1.51	1.51
$(T_1T)^{-1}_{\text{calc}}$ (sec K)$^{-1}$	1.70 (2.35)	1.90 (2.60)	2.05 (2.85)	2.05 (2.85)	2.05 (2.85)
$(T_1T)^{-1}_{\text{meas}}$ (sec K)$^{-1}$	2.85	2.72	2.64	2.86	2.08
	Tetragonal phase				
x	0.46	0.47	0.48	0.49	0.50
$N_d^V(0)$ $\left(\frac{\text{states}}{\text{eV atom spin}}\right)$	1.23	0.95	0.89	0.77	0.70
$(T_1T)^{-1}_{\text{calc}}$ (sec K)$^{-1}$	1.46 (1.99)	0.97 (1.28)	0.88 (1.16)	0.73 (0.93)	0.64 (0.81)
$(T_1T)^{-1}_{\text{meas}}$ (sec K)$^{-1}$	1.90	1.45	1.0	0.83	0.70

for $N_d^V(0)$ the calculated relaxation rates given in Table III fall substantially below the measured rates in both the cubic and tetragonal phases. This disagreement probably results from one of two sources. Either the value of λ determined using the McMillan formalism[11] is overestimated and hence $N_d(0)$ is underestimated, or the value of $H_{\text{hfs}}^{(\text{orb})}$ determined from vanadium[3] is too small. The calculated relaxation rates listed in Table III in parentheses are for $H_{\text{hfs}}^{(\text{orb})} = 2.8 \times 10^5$ Oe, which is the free-atom value.[3,15] The agreement between the calculated and measured relaxation rates is much improved with this value of $H_{\text{hfs}}^{(\text{orb})}$. Irrespective of whether the λ or $H_{\text{hfs}}^{(\text{orb})}$ values are suspect, the d-orbital relaxation rate appears to dominate the V^{51} relaxation rates in both the cubic and tetragonal phases.

IV. CONCLUSIONS

The NMR measurements presented here support the conclusion of previous authors that the changes observed in the bulk properties for the cubic-to-tetragonal distortion for the $V_{1-x}Ru_x$ alloys for $0.45 \leq x \leq 0.50$ result primarily from a decrease in the density of the d-electron states at the Fermi energy. The observation of a nearly x-independent V^{51} spin-lattice relaxation rate in the cubic phase indicates that $N_d(0)$ is nearly x-independent suggesting that T_c is not likely to be as high for the stabilized V-Ru cubic compounds with $x > 0.45$ as the extrapolation from alloys with $x < 0.45$ would suggest. The magnitude of the vanadium spin-lattice relaxation rate in these alloys suggests that either the values of the electron-phonon coupling constant λ are overestimated for these alloys by the McMillan formalism or else the d-orbital hyperfine field is larger than determined in vanadium and close to the value calculated for the free atom.

ACKNOWLEDGMENTS

We would like to thank Dr. G. S. Knapp and Dr. J. B. Darby, Jr. for the supply of V and Ru metals. Preparation of part of the samples by R. Conner is greatly appreciated.

---

*Supported by Air Force Office of Scientific Research Grant No. 71-2012 and by NSF through the Northwestern University Materials Research Center.

†Work performed under the auspices of the U. S. Atomic Energy Commission.

‡Permanent address.

[1] L. E. Drain, J. Phys. Radium 23, 745 (1962).

[2] J. Butterworth, Proc. Phys. Soc. Lond. 83, 71 (1964).

[3] E. von Meerwall and D. S. Schreiber, Phys. Rev. B 3, 1 (1971). This reference includes a comprehensive listing of other recent vanadium–transition-metal alloy studies.

[4] Y. Obata, J. Phys. Soc. Jap. 18, 1020 (1963).

[5] Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).

[6] M. Bernasson, P. Descouts, F. Donze, and A. Treyvand, J. Phys. Chem. Solids 30, 2453 (1969); M. Bernasson, P. Descouts, J. L. Page, and R. Prina, J. Phys. F 1, 334 (1971).

[7] J. L. Page (private communication).

[8] C. W. Chu, E. Bucher, A. S. Cooper, and J. P. Maita, Phys. Rev. B 4, 320 (1971).

[9] M. Marezio, P. D. Dernier, and C. W. Chu, Phys. Rev. B 4, 2825 (1971).

[10] In order to determine if an additional heat treatment of the powered samples alters the NMR properties, an additional $V_{51}Ru_{49}$ sample was prepared and annealed for 10 h at 1000 °C instead of 1 h. The relaxation rate increased by less than 10% and the Knight shift increased by ~0.01% in the cubic phase and ~0.03% in the tetragonal phase. These changes are much smaller than the differences between the unannealed and annealed samples reported by Bernasson *et al.* (Refs. 6 and 7) on the NMR properties or the difference between our NMR results and theirs. It is important to note that the data reported here are for samples which have received the same heat treatment, so that while the absolute values of the relaxation rates and Knight shifts might increase by a few percent upon further extended annealing, no substantial variation of the concentration dependence of these quantities would be expected.

[11] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[12] For a review of NMR in metals and alloys, see A. Narath, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York 1967).

[13] A. Narath, Phys. Rev. 162, 320 (1967).

[14] J. Korringa, Physica (Utr.) 16, 601 (1950).

[15] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. IIA.