

Knight Shifts and Magnetic Susceptibilities in V Alloys with Ti, Cr, and Tc*

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Knight shifts, K_V , of the V^{51} isotope have been measured in binary alloys of V with Ti, Cr, and Tc. The shifts, K_{Tc} , of the Tc^{99} nucleus have been measured over the whole composition range in the V-Tc system together with corresponding magnetic susceptibilities. The results on these bcc alloys indicate that the rigid band approximation is valid and nearly all electrons outside the closed $3p$ or $4p$ shell form a common conduction band with admixtures of s and non- s electronic states. Furthermore, these data augmented by electronic specific-heat measurements indicate that the proportion of electrons having s and non- s character changes with electron concentration within this common conduction band.

INTRODUCTION

THE relatively large changes in the Knight shifts that occur upon alloying have been the subject of several investigations,¹⁻⁵ and it is generally found that the solvent shift is a linear function of the solute concentration through the whole terminal solid solution phase. This is particularly well established in AgCd alloys and is at least approximately true in other simple systems studied to date which contain no transition metal atoms. Knight shifts in some dilute solid solutions of Cr, Mn, Fe, Co, and Ni in vanadium have been investigated by Drain⁶ and concentrated bcc solutions of the V-Cr system have recently been investigated by Barnes and Graham.⁷ The results indicate that the solvent shift is not a linear function of the solute concentration in the whole solid solution region. Due to the unfavorable nuclear properties of some of the solute elements previously studied, Knight shifts of the solutes have not been measured with accuracy in concentrated solid solutions of transition metal alloys. In this investigation, Knight shifts of V^{51} in V-Ti, V-Cr, and V-Tc binary alloy systems have been measured in the complete bcc solid solution region. Knight shifts of Tc^{99} and magnetic susceptibilities in the complete V-Tc binary system have also been investigated.

EXPERIMENTAL METHOD

The alloys were prepared by arc melting requisite amounts of electrolytic vanadium,⁸ technetium metal, iodide titanium, and commercial high-purity chromium in an argon atmosphere. The alloy compositions reported here are those of the weighed charges before melting, since the loss of weight upon melting was less than 0.1%

for 10-g specimens. Each specimen was homogenized at 1050°C for 3 days. The V-Tc alloys were then heat treated at 700°C for one week while the Ti-V and V-Cr alloys were heat treated at 900°C for the same time period. All of the heat treatments were in vacuum and the specimens were subsequently water quenched. The crystal structures and lattice parameters were determined by x-ray diffraction on powdered specimens.

At high temperatures, Ti and V form a continuous series of bcc solid solutions, while Ti-rich alloys transform to a hcp structure at lower temperatures. The transformation temperature, which is about 880°C for pure Ti, is lowered almost linearly by the addition of V. V and Cr form a continuous bcc solid solution across the whole binary system. In the V-Tc system, stable bcc solid solutions of V with Tc exist up to 60 at.% Tc and approximately 10 at.% V can be dissolved in hcp Tc. The two solid solutions exist in a two-phase field between 60 and 90 at.% Tc. A CsCl ordered bcc structure exists at the equi-atomic composition in this system.

Magnetic susceptibility measurements on bulk and powdered specimens were made by the Faraday method using an automatic weighing and recording microbalance. The estimate accuracy is $\pm 1.5\%$ relative to the susceptibility of Ta (0.85×10^{-6} emu/g) as standard. Each reported room-temperature susceptibility is an average of several measurements. A limited number of Tc alloys in the bcc region were measured at liquid nitrogen temperature. All measurements were performed under vacuum. Temperatures were measured with a copper-constantan thermocouple calibrated with a platinum thermometer. Ferromagnetic impurity corrections were applied as necessary.

Knight shift measurements were performed with a Varian NMR spectrometer. Most of the measurements were made in the V mode; however, for better signal-to-noise ratio for Tc^{99} in the reference solution, the U mode was employed. The resultant M -shaped curves had nearly equal peaks and the resonance field was taken to be that corresponding to the minimum in the curve. Each reported shift is an average of several measurements.

The specimens were either crushed or filed, depending

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¹ T. J. Rowland, *Acta Met.* **3**, 74 (1955).

² T. J. Rowland, *Phys. Rev.* **119**, 900 (1960).

³ H. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953).

⁴ L. E. Drain, *Phil. Mag.* **4**, 484 (1959).

⁵ M. B. Webb, *J. Phys. Chem. Solids* **20**, 127 (1961).

⁶ L. E. Drain, *Arch. Sci.* **13**, No. Fascicule Special 425-32 (1960).

⁷ R. G. Barnes and T. P. Graham, *Phys. Rev. Letters* **8**, 248 (1962).

⁸ The electrolytic vanadium used was kindly supplied by D. D. Blue of the U. S. Bureau of Mines.

TABLE I. Knight shifts, magnetic susceptibilities, and crystal structures of V alloys currently investigated.

Alloy (at.%)	Crystal structure	K_V (%)	K_{Tc} (%)	χ (10^{-6} emu/g) at 297°K		Lattice parameters (Å)
				Solid	Powder	
V-100% (Ames)	bcc	0.564 ± 0.006				
V-100% (Bureau of mines)	bcc	0.565 ± 0.006		5.48	5.85	$a_0 = 3.029$
V-100% (Union Carbide)	bcc	0.567 ± 0.006				$a_0 = 3.036$
V-10% Ti ^a	bcc	0.558 ± 0.01				$a_0 = 3.046$
V-20% Ti	bcc	0.547 ± 0.013				
V-30% Ti	bcc	0.530 ± 0.013				
V-40% Ti	bcc	0.518 ± 0.013				
V-50% Ti	bcc	0.491 ± 0.013				$a_0 = 3.157$
V-60% Ti	bcc	0.482 ± 0.015				
V-70% Ti	bcc	0.470 ± 0.015				$a_0 = 3.218$
V-80% Ti	bcc	0.472 ± 0.016				$a_0 = 3.251$
V-84% Ti	bcc	0.487 ± 0.019				
V-20% Cr ^a	bcc	0.600 ± 0.005				$a_0 = 3.028$
V-30% Cr	bcc	0.619 ± 0.004				
V-50% Cr	bcc	0.663 ± 0.003				$a_0 = 3.026$
V-60% Cr	bcc	0.688 ± 0.003				
V-70% Cr	bcc	0.671 ± 0.003				
V-80% Cr	bcc	0.631 ± 0.003				$a_0 = 3.024$
V-10% Tc ^b	bcc	0.590 ± 0.015	0.879 ± 0.015	4.37	5.05	
V-25% Tc	bcc	0.650 ± 0.015	0.930 ± 0.015		3.10	$a_0 = 3.026$
V-30% Tc	bcc	0.660 ± 0.015	0.854 ± 0.010	2.20		
V-40% Tc	bcc	0.610 ± 0.015	0.736 ± 0.015	1.68	1.95	$a_0 = 3.024$
V-50% Tc	CsCl	0.570 ± 0.015	0.640 ± 0.015		1.67	$a_0 = 3.023$
V-60% Tc	bcc	0.520 ± 0.015	0.365 ± 0.02	1.37	1.55	$a_0 = 3.034$
V-75% Tc	bcc+hcp			1.20		
V-95% Tc	hcp			1.16	1.48	
Tc	hcp		0.610 ± 0.010	1.22	1.58	$a_0 = 2.743^c$ $c_0 = 4.400$ $c/a = 1.604$

^a Alloys made from Bureau of Mines V.^b Alloys made from Union Carbide V.^c D. J. Lam, J. B. Darby, Jr., J. W. Downey, and L. J. Norton, Nature 192, 744 (1961).

on their brittleness, to 325 mesh or finer. All of the V-Ti samples were annealed in vacuum at 900°C for 1/2 h in order to reduce strains and then placed in oil to prevent oxidation. The V-Tc alloys are brittle and x-ray analysis showed little or no residual strain. The reported values of Knight shifts in this system and in the V-Cr system are all in the as-filed condition. Two V-Cr alloys were measured both in the as-filed condition and after annealing. Samples run in the latter condition showed a slight narrowing of the linewidth but the Knight shift was not affected.

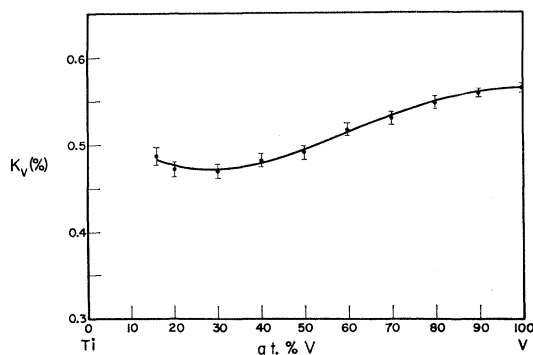
RESULTS

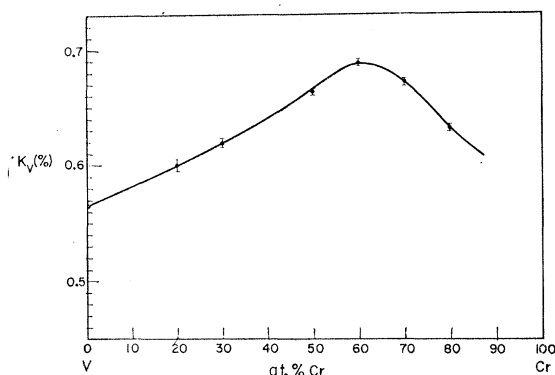
The Knight shift of V^{51} is relative to V dissolved in nitric acid and that of Tc^{99} is relative to a 35 mg/ml solution of NH_4TcO_4 . No chemical shifts were observed for Tc between the NH_4TcO_4 solution and a 350- μ g/ml solution of $CsTcO_4$ and for V in different nitrate concentrations. Typical resonance line shapes and widths of Tc^{99} and V^{51} in the V-Tc alloys have been previously reported.⁹

The Knight shifts of V^{51} and Tc^{99} , the crystal structure and room-temperature magnetic susceptibility of the alloys are given in Table I. The Knight shifts of V^{51}

in the Ti-V binary system show a slight minimum in the vicinity of 30 at.% of V in Ti (Fig. 1), whereas a broad maximum appears both in the V-Cr and V-Tc system (Figs. 2 and 3). Figure 3 shows that there is also a maximum in the shifts of Tc^{99} in the V-Tc system occurring on the V-rich side.

Magnetic susceptibility measurements on bulk and powdered samples of V-Tc alloys have been made across the whole binary system. The powdered specimens consistently show a higher value than that of the bulk samples. The susceptibilities decrease from pure V to the 50 at.% Tc alloy and then remain relatively inde-

FIG. 1. Knight shift of V^{51} in Ti-V alloys.⁹ D. O. Van Osteburg, H. Trapp, and D. J. Lam, Phys. Rev. 126, 938 (1962).

FIG. 2. Knight shift of V^{51} in V-Cr alloys.

pendent of composition to pure Tc. Preliminary low-temperature results indicate that the magnetic susceptibilities of these alloys in the bcc region are relatively temperature independent down to 77°K.

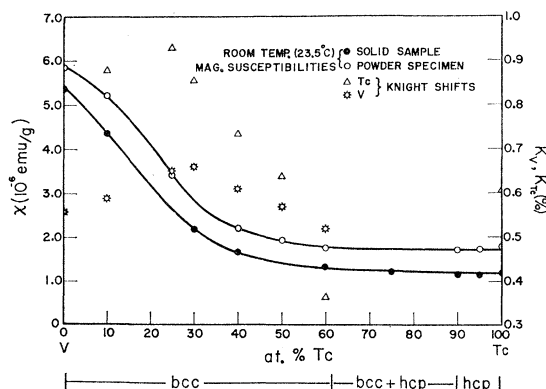
The electron:atom ratio, e/a , used in the subsequent plots, is determined from the number of electrons outside the $3p$ or $4p$ shells. The similarity of the dependence of the room-temperature magnetic susceptibility and the Knight shifts of V^{51} upon electron concentration in both the V-Cr binary system and the bcc region of the V-Tc system up to 50 at.% Tc can be seen in Fig. 4. Magnetic susceptibility data of the V-Cr binary system are obtained from the investigations of Childs *et al.*¹⁰

DISCUSSION

The Knight shift presented in its simplest form is given as follows:

$$K = (8\pi/3)\beta^2 n(E_F) \Omega \langle |\psi(\mathbf{k}, 0)|^2 \rangle_{av}.$$

β is the Bohr magneton, $n(E_F)$ the density of states evaluated at the Fermi level, $\psi(\mathbf{k}, 0)$ is the value at the nucleus of the wave function of momentum \mathbf{k} normalized over the atomic volume Ω , and $\langle |\psi(\mathbf{k}, 0)|^2 \rangle_{av}$ is the

FIG. 3. Knight shifts of V^{51} and Tc^{99} and magnetic susceptibilities in the V-Tc system.

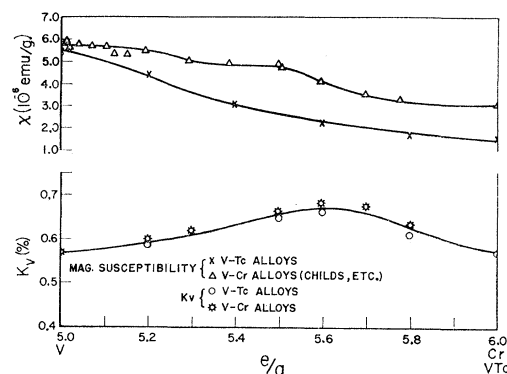
¹⁰ B. G. Childs, W. E. Gardner, and J. Penfold, *Phil. Mag.* **5**, 1267 (1960).

average of the square of the function $\psi(\mathbf{k}, 0)$ taken over all electronic states on the Fermi surface. In order to extract as much information from the current data as possible, the electron concentration dependency of each quantity in the above equation has to be examined individually.

Variations in $n(E_F)$ vs e/a can be obtained from low-temperature specific-heat and magnetic-susceptibility measurements, the former being the more accurate. The electronic specific-heat measurements of Cheng *et al.*¹¹ may be used to construct an $n(E_F)$ curve for the V-Cr and V-Ti systems. Childs *et al.* have proposed that their susceptibility data on V-Cr (which is essentially temperature independent) can also be explained in terms of a density of states curve. Both approaches lead to similar constructions for $n(E_F)$ vs e/a . The fact that the susceptibilities in the V-Tc system are almost temperature independent suggests that they may be used to construct a density of states curve (Fig. 3). Unfortunately, there are no low-temperature specific-heat data to corroborate this.

The similarity of the density-of-states curve for V-Tc obtained solely from susceptibility measurements to that of the V-Cr system obtained from both susceptibility and electronic specific-heat measurements suggests that the rigid band model may be applied to these two systems containing components from both the first and second long periods. A similar conclusion can be drawn from low-temperature specific heat¹² and superconductive transition temperature measurements¹³ in bcc alloys of other first and second long-period transition elements.

The atomic volume is proportional to the cube of the lattice parameter. From Table I it can be seen that for each system within a given phase the lattice parameter changes monotonically, and thus the atomic volume is a smooth function of electron concentration. V-Tc alloys

FIG. 4. Magnetic susceptibilities and Knight shifts of V^{51} in both the V-Cr and V-Tc system as a function of e/a .

¹¹ C. H. Cheng, C. T. Wei, and P. A. Beck, *Phys. Rev.* **120**, 426 (1960).

¹² W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **96**, 1442 (1954).

¹³ J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1569 (1961).

provide a unique experimental opportunity to observe the resonance of both components in a transition metal binary system. The similarity between the Knight shifts of V^{51} and Tc^{99} in the bcc region, as shown in Fig. 3, indicates that the increase in the number of d electrons on adding Tc to V affects both nuclear species in the same manner. That is, the electronic density responsible for the Knight shifts varies in approximately the same proportions in the vicinity of both Tc and V nuclei. This seems to rule out any localization of d electrons as well as s - d exchange polarization interactions which favor specific nuclei.

In the simple rigid band theory, the alloying of elements which are neighbors in the periodic table simply increases or decreases the number of electrons in the band without having any appreciable effect on the form of the band. The appropriateness of this point of view is supported by the close similarity between the results of the susceptibility and Knight shifts of V^{51} in the V-Cr and V-Tc alloys. The susceptibilities and Knight shifts

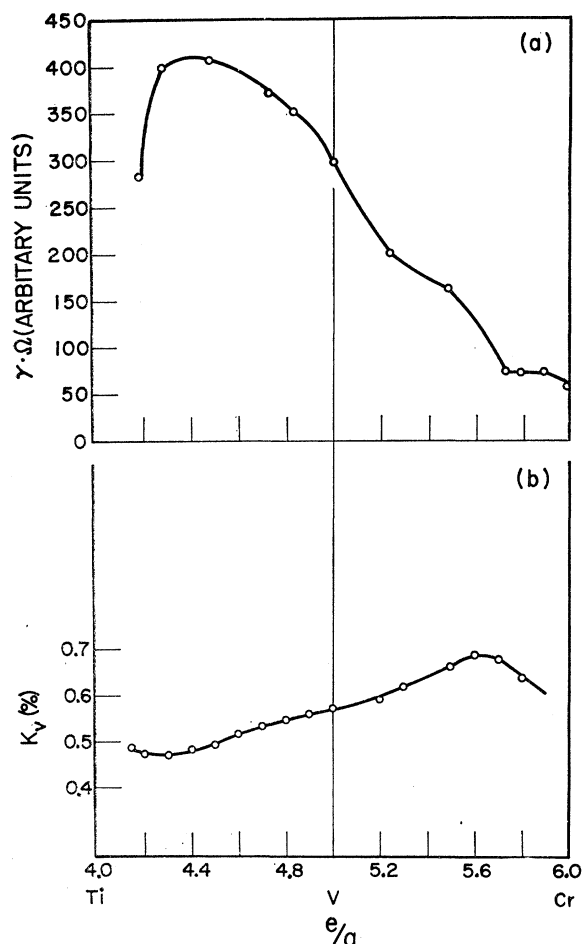


FIG. 5. Product of the electronic specific-heat coefficient with atomic volume, and the Knight shift of V^{51} in the V-Ti and V-Cr system as a function of electron concentration. (The electronic specific heat data were obtained from reference 11.)

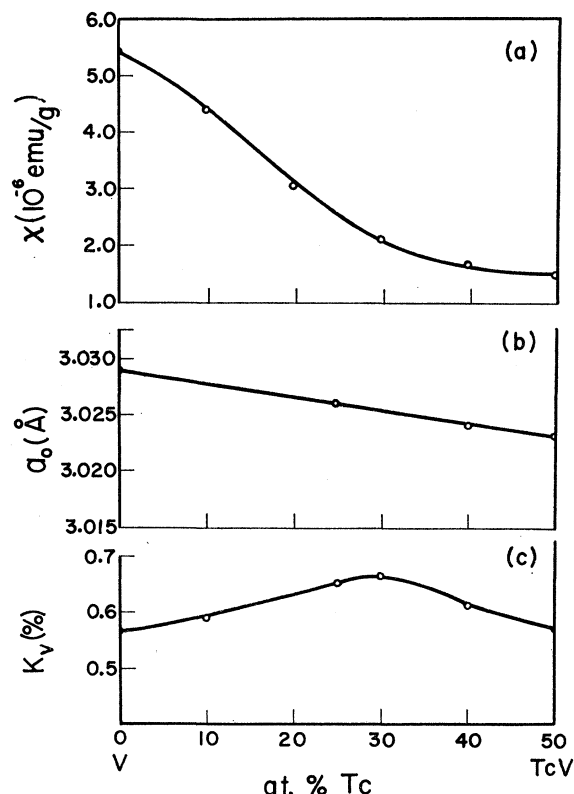


FIG. 6. Magnetic susceptibilities, lattice parameter (a_0), and K_V in the bcc region of the V-Tc system as a function of electron concentration.

of these alloys appear to depend only on the electron: atom ratio and not on the alloying element Tc. The results in these two systems also suggest that K_V is not controlled by $n(E)$ alone since the e/a dependence of the susceptibility and Knight shifts do not have the same form.

The solvent shift in the three systems investigated is not a linear function of the solute concentration through the whole terminal solid solution region as in the case of nontransition metal alloy systems previously investigated. The three factors upon which the Knight shift depends must be considered in order to interpret the results. Figure 5(a) shows the product of the electronic specific heat coefficient (\propto the density of states at the Fermi surface) and the atomic volume as a function of electron concentration for both the V-Ti and V-Cr binary systems. Figure 5(b) shows the Knight shifts of V^{51} in the same systems. The fact that the e/a dependence of $\gamma\Omega$ for the various systems is entirely unlike the dependence of K_V vs e/a strongly suggests that ψ^2 controls K_V . The fact that only s electrons predominantly contribute to $|\psi(\mathbf{k},0)|^2$ suggests that the proportionality of s -electron wave functions with momentum at the Fermi surface changes with e/a . At the Ti-rich end, the relative number of electrons at the Fermi surface having s character is apparently small. As the

electron concentration increases the proportion of the electrons having s character increases and reaches a maximum between V and Cr. Further increase of the electron concentration appears to cause a considerable admixture of s and non- s states, reducing the K_V values. A similar analysis can be applied to the change of proportionality of s and non- s wave functions in the bcc region of the V-Tc system, see Fig. 6.

An alternative view that one may put forth is that ψ^2 remains essentially independent of e/a and that $n_s(E)$, the density of states of the s electrons, changes in accord with K_V . Resistivity measurements in these alloy systems would aid in determining the validity of this argument. The high resistivity in transition metals is generally thought of as due to the scattering of conduction electrons from s to d states where the probability of such processes is proportional to the high density of states in the d band. The view adopted in this investigation is that the conduction electron wave function is composed of an admixture of s and d states with the electrons resonating between them. Thus, the resistivity should reach a maximum where the relative proportion of d states predominates and a minimum where the

relative proportion of s states predominates. Recently, Taylor and Llewellyn Smith¹⁴ have measured the resistivity in alloys of the V-Cr system and find a minimum very nearly in the vicinity where the current analysis postulates a maximum in s character. This strongly supports the view that it is ψ^2 which determines the K_V variation and not $n_s(E)$.

Information on the number of s electrons in pure V can be obtained from the nuclear magnetic relaxation measurements of Butterworth.¹⁵ He finds that the proportion of the electrons at the Fermi surface having s character is very low, roughly 0.17. The present measurements indicate that this value decreases on alloying V with Ti and increases on alloying V with Tc or Cr.

ACKNOWLEDGMENT

The authors wish to thank Dr. M. V. Nevitt for many helpful discussions throughout the preparation of the manuscript.

¹⁴ M. A. Taylor and C. H. Llewellyn Smith, *Physica* **28**, 453 (1962).

¹⁵ J. Butterworth, *Phys. Rev. Letters* **5**, 305 (1960).

Static Spin Temperature Experiments and the Approach to Thermal Equilibrium in the Rotating Reference Frame*

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Nuclear magnetic resonance experiments were performed which further verify Redfield's assumption that, for large rf fields $H_1(\nu)$, a nuclear spin system is properly described by a spin temperature in a reference frame rotating about the Zeeman field with frequency ν . As with similar experiments recently performed by Slichter and Holton, the interpretation of our results does not require any assumption about the spin-lattice relaxation mechanism. The measurements were made on the Na^{23} spins in NaCl and the F^{19} spins in CaF_2 . In both materials the agreement between experiment and theory was very good. From the sodium chloride results it is concluded that quadrupole interactions, caused by strains and imperfections, produce an unobservably small increase in the local field H_i in the crystals used.

Also studied was the rate at which the Na^{23} spin system in NaCl approaches thermal equilibrium in the rotating frame. In these experiments the magnetization M_z was measured as a function of the duration of a saturating pulse of amplitude $2H_1(\nu)$. The measurements were made over a time interval which was much shorter than the spin-lattice relaxation time. Our results provide quantitative verification of a recent calculation by Provotorov, who has shown that when $H_1 \ll H_i$, $M_z(\tau_a)$ approaches its equilibrium value (in the rotating frame) at a rate determined by a master equation. The master equation derived by Provotorov is in disagreement with the predictions of elementary perturbation theory except when the frequency of the rf field is equal to the Larmor frequency (or when τ_a is very short).

I. INTRODUCTION

THE experiments reported here provide additional verification of the hypothesis that spin systems in large rf fields can, at equilibrium, be characterized by a

spin temperature in a frame of reference rotating with the frequency of the perturbing rf field. This important assumption was advanced by Redfield^{1,2} and has, in recent years, been both tested and exploited in many experiments. We also report experiments that measure

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¹ Alfred G. Redfield, *Phys. Rev.* **98**, 1787 (1955).

² A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).