Nuclear Magnetic Resonance and Magnetic Susceptibilities of Alloys of V with Al†

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Nuclear magnetic resonance properties of the V^{51} and Al^{27} isotopes and magnetic susceptibilities are reported for V-Al alloys in the body-centered cubic region up to 40 at. % Al in V and in the intermetallic compound V_5Al_8. In the bcc solid solution region the V^{51} Knight shift increases slightly from 0.567% in pure V to 0.586% in the 40 at.% Al alloy. The Al^{27} shift is negative, increasing from −0.038% at 5 at.% Al to −0.031% at 40 at.% Al. The magnetic susceptibility decreases monotonically from 287×10^{-6} emu/mole for pure V to 160×10^{-6} emu/mole for 35 at.% Al in V. These data, together with measured values of the electronic specific heat, are used to evaluate the various contributions to the Knight shift and susceptibility. It is shown that essentially all of the V^{51} Knight shift is the result of orbital paramagnetism, and that the latter accounts for most of the measured susceptibility in these alloys. The data support a band model in which the electrons in the *s-p* band have little or no interaction with the *d* band of the transition metal.

INTRODUCTION

THE present investigation is part of a continuing study of the electronic properties of transition metals and their alloys. In previous papers[1-3] we have described the behavior of the nuclear magnetic resonance and magnetic susceptibility in transition-transition metal alloys. The purpose of this paper is to describe the rather different outcome of a similar investigation of vanadium alloyed with aluminum. There has been a considerable amount of work devoted to studies of intermetallic compounds both of aluminum (with rare earths,[4] uranium,[5] and nickel[6]) and of vanadium.[7] The present investigation differs basically from these because it offers the possibility of studying the band structure of V-Al alloys using composition as the primary independent variable. The temperature dependences reported here do not represent as crucial a part of the development as they do for V_3Si or V_3Ga for example.[8]

The alloys to be discussed are the body-centered cubic substitutional solid solutions extending from pure V to V containing 40 at.% Al. The Knight shifts of both V^{51} and Al^{27} were measured over a range of external magnetic fields and at various temperatures from −150 to 100°C. The V^{51} absorption linewidth was also measured as a function of composition, external magnetic field, and temperature.

The interpretation of the data includes the partitioning of the Knight shift and paramagnetic susceptibility into portions associated with the *s* electrons, the *d* electrons, and the orbital paramagnetism. The latter is attributed to the V atoms alone as suggested by the data. Following an assumption concerning the *s*-selection density in these alloys the respective Knight shifts and susceptibilities are related, and the partitioning carried out in a self-consistent manner. Whereas the rigid band model proved useful in discussing transition-transition metal alloys, the V-Al data does not lend itself to such an interpretation. Rather, the Al conduction electrons seem to be independent of the V *d* band, in agreement with a previous, less extensive study, of the V-Tc-Al ternary alloys.[9]

EXPERIMENTAL

The alloys were prepared by arc melting requisite amounts of iodide vanadium and 99.9999 wt.% aluminum 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 negligibly small. Each specimen was homogenized at 1050°C for 1 week and then heat treated at 900°C for 1 week. 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.

The solid solubility of Al in V decreases from 49.5 at.% Al at 1670°C to 40.5 at.% Al at 500°C.[10] A γ-brass-

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TABLE I. Knight shifts, line widths, magnetic susceptibilities and lattice parameters of V alloys currently investigated.

Alloy (at. %)	Crystal structure	$K_V(\%)$ ($H_0=6.7$ kOe) ($T=297°K$)	δH_V(Oe) ($H_0=6.7$ kOe)	$K_{Al}(\%)$ ($H_0=13.1$ kOe)	χ in units (10^{-6} emu/mole) at 297°K	Lattice parameter (Å)
V-100% (Iodide V)	bcc	0.564±0.006			287	3.029
V-0.5% Al	bcc	0.572±0.006	10.8±0.6			
V-1% Al	bcc	0.568±0.006	11.0±0.6	−0.038±0.011	284	
V-2% Al	bcc	0.567±0.006	10.6±0.6	−0.036±0.009		
V-4% Al	bcc	0.570±0.01	10.8±0.7	−0.041±0.009	272	3.033
V-8% Al	bcc	0.573±0.006	11.6±0.6	−0.034±0.009	253	3.037
V-15% Al	bcc	0.573±0.006	12.1±0.6	−0.031±0.009	231	3.044
V-20% Al	bcc	0.584±0.006	14.2±0.9	−0.026±0.009	207	
V-25% Al	bcc	0.576±0.006	13.4±0.7	−0.028±0.009		3.054
V-30% Al	bcc	0.583±0.007	14.1±0.9	−0.024±0.009	174	
V-35% Al	bcc	0.598±0.01	15.9±1.2	−0.026±0.009	160	
V-40% Al	bcc	0.586±0.01	16.7±1.2	−0.024±0.009		
V-61.5% Al	γ-brass type	0.461±0.01		−0.031±0.011		
Al	fcc			0.161		

type intermetallic compound forms at the V_5Al_8 stoichiometry, and a two-phase region connects the bcc solid solution and this compound.

The magnetic susceptibilities were measured by the Faraday method. Details of this equipment and the low-temperature apparatus have been described previously.[2] The nuclear magnetic resonance apparatus and associated equipment[11] was of standard design. The specimens were filed by means of an automatic filing machine[12] and sieved to provide samples of 200 mesh and finer; the filings were placed under mineral oil to prevent oxidation. Since annealing was found to leave the line width and position unchanged while changing the intensity but little, all of the data presented were obtained using samples in the as-filed condition. The reference compounds used for the Knight shift measurements were V dissolved in nitric acid and an aqueous solution of aluminum chloride.
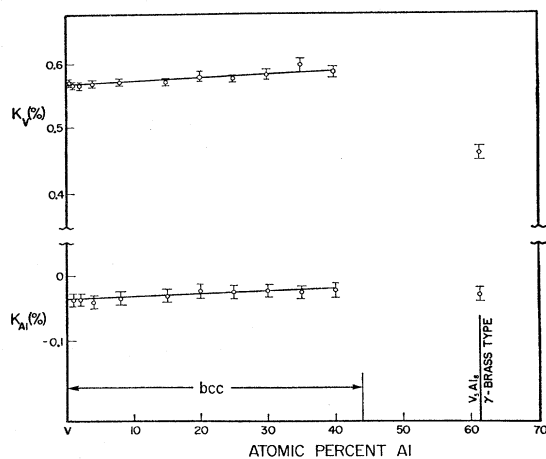
Measured values of the V^{51} Knight shift and linewidth, the Al^{27} Knight shift, the magnetic susceptibility and lattice parameter for the various alloy compositions considered appear in Table I. The Knight shifts as a function of composition are plotted in Fig. 1 in order to emphasize the rather small, apparently linear change over the 0–40 at.% Al region. The V^{51} linewidth increases by approximately 60% from its value in pure V over this same composition range. In order to obtain a usable signal-to-noise ratio for the Al^{27} resonance, modulation amplitudes were used which broadened the absorption lines artificially. The resulting signal was not sufficiently good to allow a satisfactory true Al absorption curve to be derived from it.

Tables II and III summarize the temperature and field dependence of the V and Al Knight shifts and the V linewidths in three representative alloys. The Knight shifts were found to be independent of temperature with one exception; the V^{51} in V-4 at.% Al exhibited an increasing shift with temperature. We have no explana-
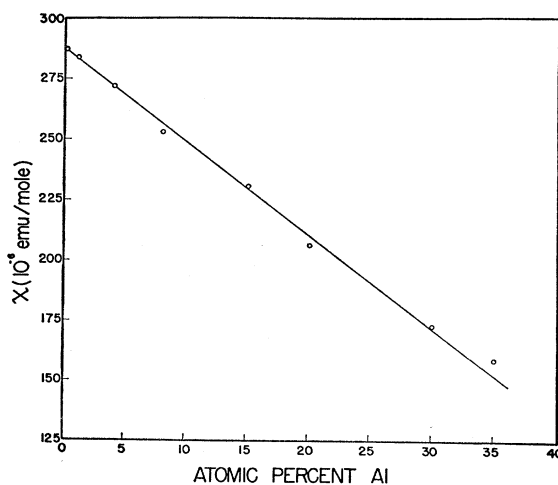

FIG. 1. Knight shifts of V^{51} and Al^{27} in V-Al alloys as a function of at.% Al.

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FIG. 2. Paramagnetic susceptibility of V-Al alloys at room temperature as a function of at.% Al.

tion for this unique case. The V^{51} linewidth decreases about ten percent in going from -150 to $100°C$. It seems probable that the temperature and field dependence of the linewidth are related to the same basic mechanism, the latter being primarily responsible for that part of the width in excess of the classical dipolar value. The field-dependent contribution to the linewidth is significantly greater for the higher Al alloys than it is for pure V or V-4 at.% Al.

Although the data are not included here, the susceptibility was also measured as a function of temperature and no variation was found within the experimental uncertainty over the range 77 to 300°K. The susceptibility versus composition is plotted in Fig. 2. There is only a slight deviation from linearity in the region of solid solubility under discussion. The susceptibility of the pure V was found to depend upon its preparation, as previous studies[1,13] have noted. The as-received crystal bar had a susceptibility of 298×10^{-6} emu/mole while a blank specimen, treated in the same manner as the alloys, gave the value listed in the table.

INTERPRETATION AND DISCUSSION

An analysis of the Knight shift and susceptibility will be given in the first section below. In the second section we offer brief arguments to show that certain sources of linewidth are highly improbable while others are likely. The fact that we are dealing with solid solutions rather than a structure having an identical electronic configuration at certain sets of atomic sites complicates the interpretation of the linewidth considerably.

1. Knight Shift and Susceptibility

The Knight shift is at present considered to derive from three distinct mechanisms. The contact hyperfine interaction between the nuclear magnetic moment and the field caused by the spin magnetization of the s conduction electrons was the first to appear in the literature.[14] The subsequent analysis will show that in the

TABLE II. Temperature dependence of the V^{51} and Al^{27} Knight shifts and of the linewidths of V^{51}.

Alloy (at. %)	$T°C$	$K_V (\%)$ ($H_0=14.0$ kOe)	$K_{Al}(\%)$ ($H_0=13.1$ kOe)	δH_V ($H_0=14.0$ kOe)
V	+24	0.566 ± 0.004		11.9 ± 0.5
	-75	0.563 ± 0.004		11.6 ± 0.5
	-150	0.560 ± 0.004		11.0 ± 0.5
V-4% Al	+100	0.588 ± 0.006		11.8 ± 0.6
	+24	0.578 ± 0.006	-0.035 ± 0.009	12.1 ± 0.9
	-75	0.571 ± 0.006	-0.035 ± 0.009	12.2 ± 0.6
	-150	0.571 ± 0.006		12.6 ± 0.6
V-20% Al	+100	0.601 ± 0.003		16.5 ± 0.9
	+24	0.596 ± 0.003	-0.026 ± 0.003	17.2 ± 0.6
	-75	0.599 ± 0.003	-0.028 ± 0.005	17.6 ± 0.6
	-150	0.602 ± 0.003		18.3 ± 0.9
V-35% Al	+100	0.606 ± 0.004		19.1 ± 0.9
	+24	0.599 ± 0.005	-0.024 ± 0.006	19.4 ± 1.2
	-75	0.608 ± 0.004	-0.024 ± 0.006	20.0 ± 0.9
	-150	0.601 ± 0.004		19.9 ± 0.9

[13] B. G. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. **5**, 1267 (1960).
[14] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

TABLE III. External field dependence of the Knight shifts of V^{51} and Al^{27} and of δH_V for the V-Al system at room temperature.

Alloy (at. %)	H_0(kOe)	$K_V (\%)$	δH_V (Oe)	H_0(kOe)	$K_{Al}(\%)$
V	4.5	0.547 ± 0.009	11.1 ± 0.7		
	6.7	0.561 ± 0.006	11.2 ± 0.3		
	10.9	0.567 ± 0.004	11.5 ± 0.3		
	14.0	0.566 ± 0.004	11.9 ± 0.5		
V-4% Al	4.5	0.534 ± 0.009	11.4 ± 0.6	8.1	-0.055 ± 0.01
	6.7	0.570 ± 0.006	10.8 ± 0.7	10.5	-0.045 ± 0.01
	10.9	0.573 ± 0.004	11.2 ± 0.7	13.1	-0.035 ± 0.004
	14.0	0.578 ± 0.003	12.1 ± 0.9	14.3	-0.032 ± 0.005
V-20% Al	4.5	0.529 ± 0.009	15.7 ± 0.7	8.1	-0.038 ± 0.014
	6.7	0.584 ± 0.006	14.2 ± 0.9	10.5	-0.029 ± 0.01
	10.9	0.594 ± 0.004	15.4 ± 0.9	13.1	-0.026 ± 0.003
	14.0	0.596 ± 0.003	17.2 ± 0.6	14.3	-0.016 ± 0.005
V-35% Al	4.5	0.554 ± 0.016	17.1 ± 1.0	8.1	-0.051 ± 0.014
	6.7	0.598 ± 0.010	15.9 ± 1.2	10.5	-0.024 ± 0.008
	10.9	0.602 ± 0.007	17.9 ± 1.4	13.1	-0.024 ± 0.009
	14.0	0.601 ± 0.004	19.9 ± 1.2	14.3	-0.019 ± 0.005

V-Al alloys this mechanism plays a relatively small role. This had been anticipated for V in the work on V_3Ga and V_3Si.[8] To estimate values for both the susceptibility and shift arising from the s electrons in V we assume the s band to be parabolic in shape and to contain 0.5 electrons per atom, as indicated by recent work on V-Cr alloys (see Ref. 21). This results in a density of two electron states $N_s(E_F)$ equal to 0.19 states/eV-atom and a susceptibility $\chi_s = 6.16 \times 10^{-6}$ emu/mole. Using this value in Eq. (16.1) of Knight's[15] article, together with the value of $a(s)$ to be found there gives $(\Delta H/H)_s = K_s = 0.128\%$. This assumes that $\xi = 1$, where ξ is the ratio of $\langle |\Psi_s(0)|^2 \rangle_F$, the probability density at the nucleus for s electrons near the Fermi surface, averaged over the Fermi surface, to $|\Psi(0)|_a^2$, the probability density at the nucleus for the outer s electrons in the free atom.

Another source of shift, also caused by a contact interaction, is the exchange polarization of inner s electrons by the polarized electrons in the conduction band.[16] The high density of electrons in the d band of the transition metals makes this an important process to consider. In the present case however, it seems that it is not particularly effective. The relation between the d-band contribution to the Knight shift K_d and the molar susceptibility χ_d of the $3d$ electrons may be written

$$K_d = b\chi_d = (8\pi/3)\langle\rho(0)\rangle_d \chi_d/N, \qquad (1)$$

where $\langle\rho(0)\rangle_d$ is the net unpaired spin density at the nucleus caused by one d spin averaged over the d states at the Fermi surface, in analogy with the corresponding equation for the conduction s contact shift, and N is Avogadro's number.

The remaining contribution to the paramagnetic susceptibility was pointed out by Kubo and Obata.[17] It is the induced orbital paramagnetism χ_{orb}, possible in partially filled degenerate bands such as occur in the

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[17] R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

TABLE IV. The measured susceptibility χ and contributions to it. The latter are the ionic χ_i, the total paramagnetic χ_{pm}, the Pauli s and d band χ_s and χ_d, the total orbital χ_{orb}, and the vanadium orbital $\chi_{orb}{}^V$, susceptibilities. The values given are in (emu/mole)$\times 10^6$.

Alloy	χ	χ_i	χ_{pm}	$\chi_s+\chi_d$	χ_{orb}	$\chi_{orb}{}^V$
pure V	287	−8	297	127	170	170
V-4 at.% Al	272	−7	281	114	167	174
V-10 at.% Al	248	−7	257	98	159	177
V-20 at.% Al	207	−7	216	72	144	180
V-30 at.% Al	174	−6	182	58	124	177
V-35 at.% Al	160	−6	168	52	116	178

transition metals. A contribution to the Knight shift may also arise from this source,[18] and in the present study it proves to be of particular importance.

The measured susceptibility χ includes diamagnetic contributions from the ion cores χ_i and from the conduction electrons, χ_L, i.e., $\chi=\chi_{pm}+\chi_i+\chi_L$, where χ_{pm} is the total paramagnetic susceptibility from all sources. Summing up the above contributions to the Knight shift and paramagnetic susceptibility we have the observed Knight shift for vanadium

$$K_V = K_s + K_d + K_{orb} \qquad (2)$$

and

$$\chi_{pm} = \chi_s + \chi_d + \chi_{orb}. \qquad (3)$$

Table IV lists values of the various contributions to χ for several compositions. χ_i is estimated using the values -7.7×10^{-6} emu/mole for V and -2.5×10^{-6} emu/mole for Al.[19] A constant χ_L of -2.0×10^{-6} emu/mole, which is 1/3 of χ_s in magnitude, is used for the Landau diamagnetism. We neglect the contribution to χ_L from the d band[13] which we estimate to be less than -0.5×10^{-6} emu/mole in the alloys under consideration. The total Pauli susceptibility $\chi_s+\chi_d$ is derived from the measured electronic specific heat[20] using the relation $\chi_s+\chi_d=5.74\times 10^{-2}\gamma$. Here the left-hand side is expressed in emu/mole and γ is in cal/mole deg.[2] The last column is included to demonstrate the constancy of the quantity $\chi_{orb}{}^V=\chi_{orb}/$(mole fraction V), the orbital paramagnetism per mole of vanadium contained in the alloys. In other words, we find the orbital paramagnetism per V atom to be essentially constant, and that for an Al atom to be zero. A plot of χ_{orb} vs composition also shows this clearly. The aluminum acts simply as a diluent in this case, and we introduce the relationship

$$K_{orb} = c\chi_{orb}{}^V = 2\langle r^{-3}\rangle_d \chi_{orb}{}^V/N \qquad (4)$$

between the Knight shift and the orbital paramagnetism of the vanadium. Here $\langle r^{-3}\rangle_d$ is the average value of r^{-3} for the 3d electrons of vanadium.

From above

$$K_V - K_s = b\chi_d + c\chi_{orb}{}^V \qquad (5)$$

considering both the experimental and interpolation errors involved in arriving at $\chi_{orb}{}^V$ in Table IV it is probably adequate to use the mean value 176×10^{-6} emu/mole to solve Eq. (5) for b and c. With $K_s=0.128\%$ and $\chi_s=6\times 10^{-6}$ emu/mole we find $b=-2.4$ mole/emu and $c=26.4$ mole/emu; on the other hand, taking the $\chi_{orb}{}^V$ directly from Table IV and $b=0$ gives an average $c=25.3$ mole/emu and values of the right-hand side of (5) within 2% of the left-hand side. Under the circumstances we feel confident only that b is near zero and probably negative. The value of $\langle\rho(0)\rangle_d$ is correspondingly small, lying between zero and -0.02×10^{25} cm^{-3}. The value of c depends somewhat on the value of K_s, but probably lies between 25 (from above) and 30, the latter corresponding to a K_s of 0.043% (a ξ of 1/3). Thus from Eq. (4) we have $0.75\times 10^{25}<\langle r^{-3}\rangle_d <0.90\times 10^{25}$ cm^{-3}. This may be compared with a value of 1.28×10^{25} cm^{-3} obtained by Butterworth in a study of V-Cr alloys.[21] Theoretical values of 1.20×10^{25} cm^{-3} for the V atom in the 3d^5 configuration and 1.68×10^{25} cm^{-3} for the neutral V atom have been quoted by Butterworth[21] and Shimizu,[22] respectively. The very small change in Knight shift accompanied by the drastic change in χ_d forces us to the conclusion that the coefficient b is small and that the Knight shift is primarily the result of orbital paramagnetism. We do not have the option of pairing off a large negative K_d with a positive K_{orb} in order to arrive at a larger K_{orb} and thus a larger c and $\langle r^{-3}\rangle_d$.

It remains to explain our results in terms of a plausible band structure for this type of alloy. The rigid band model, which appears to have some validity in the case of the body-centered cubic transition-transition element alloys[1-3,23] is not directly applicable here if, as would be supposed, Al additions to V decrease the electron/atom ratio (e/a) in V-Al alloys. If we count those electrons outside of closed shells as contributing to the band, then V would have $e/a=5$ and Al 3. A decrease in e/a would indicate a decrease in Knight shift, and an increase in the electronic specific heat as for Ti-V alloys.[1,24] Such behavior is contrary to the experimental data for V-Al alloys. Our interpretation of the data is consistent with recent specific-heat results on ternary Ti-V-Al and V-Cr-Al alloys[20] in which it is found that the electronic specific-heat coefficient γ decreases upon adding Al to Ti-V and V-Cr binary alloys. The decrease in γ appears to result from a decrease of $N_d(E_F)$ which in the simplest view is unaccompanied by any change in E_F. That is, the density-of-states curve shrinks to

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smaller values while E_F remains fixed at a value determined by the transition metal composition only. Meanwhile the $s-p$ band is enlarging. Since the s level in Al would correspond to an energy deep in the $s-p$ band the states at the Fermi surface are primarily p-like and thus make little or no positive contribution to the Knight shift of the Al, K_{Al}, via the contact interaction. The negative shift of the Al (cf. Table I) is quite probably caused by polarization of the core s electrons by the $3p$ electrons,[16] a process we have discussed previously in the case of V. The decrease in K_V with decreasing external field, most pronounced in the 4.5-kOe data (cf. Table III), is the result of significant second-order quadrupolar broadening of the observed central $(m=-1/2 \rightarrow 1/2)$ transition at these low fields.

2. Linewidth

The linewidth of the V resonance in V-Al alloys is contributed not only by the field-independent classical dipolar broadening, but by some field-dependent mechanisms. Twice the dipolar-root second moment (a measure of the width) calculated under the assumption that only the central line is observed,[25] and taking the change in lattice parameter into account, decreases linearly from 8.23 Oe for pure V to 6.68 Oe for V-40 at.% Al. The observed linewidth increases over this composition range, from 10.8 Oe to 16.7 Oe at $H_0=6.7$ kOe, and is somewhat field dependent. Of the various possible field-dependent contributions to the excess (over dipolar) linewidth, we can eliminate the inhomogeneous Knight shift, caused by random composition fluctuations, on the basis that the observed widths are not compatible with the small dependence of Knight shift on composition. A rough estimate of this contribution for the 40 at.% Al specimen, at $H_0=6.7$ kOe gives less than 1.5 Oe. The bulk paramagnetism of the samples must also be responsible for a small ($\lesssim 1$ Oe) contribution.[26] We conclude however that the largest part of the field-dependent component of the linewidth is contributed by second-order quadrupole and anisotropic Knight-shift effects. Estimates of the magnitudes of these, based on the electronic structure of the alloys, would be very difficult. The fact that the linewidth increases at low field after passing through a minimum at about 6 kOe strongly indicates the presence of the second-order quadrupole broadening mentioned previously in connection with the decrease in Knight shift at low field. The fact that the absorption is broadened but does not decrease appreciably in amplitude means that in fields of ~ 4.5 kOe the maximum quadrupole splitting is only about two to three times the dipolar width. This is not at all unreasonable, in fact the surprising thing is that the interaction is no larger.

The anisotropy in the Knight shift, to which we attribute the increase in linewidth at high fields, is in keeping with our concept of the electronic structure of this type of alloy. The wave functions of the d-band electrons will avoid the Al cells as if the Al were an obstacle. This will introduce anisotropy into the d function on a V atom where, in the absence of the Al, there would be cubic symmetry. The pronounced deviation from local cubic symmetry upon alloying is the result not only of the marked d character of the electrons on the V, but also the tendency of these electrons to avoid the Al cells. The latter part of this statement can be better appreciated if we make a comparison with the observations on V-Cr alloys.[27] The addition of Cr to V does not increase the V linewidth beyond that of pure V; there is even a general tendency for the width to decrease with increasing Cr content. This occurs in spite of the fact that the local atomic arrangements at a given composition should be the same for both V-Cr and V-Al alloys. This statement holds, of course, only if there is no ordering. Quadrupole effects are also less pronounced in the V-Cr system where they have no apparent influence on the linewidth. A Cr neighbor thus constitutes much less of a perturbation on the V band wave functions than does Al.

The temperature dependence of the V linewidth (cf. Table II) is not pronounced, but exceeds our estimated error. The slight increase in width as the temperature decreases is probably related to the anisotropy discussed above. As the lattice parameter decreases, the perturbation becomes more severe.

SUMMARY AND CONCLUSIONS

The Knight shifts of V and Al in V-Al alloys and the magnetic susceptibility of these alloys are interpreted in terms of the various contributions to the susceptibility. It is found that the orbital susceptibility per V atom is essentially independent of Al content and that the large change in observed susceptibility is due to significant decreases in both the orbital susceptibility (per mole of alloy) and the Pauli susceptibility. The rigid band model, which has been successfully applied to transition-transition element alloys in many instances, is thought to be inapplicable to V-Al and similar systems. The $s-p$ electrons appear to have little or no interaction with the d electrons which primarily determine the properties of the transition metals. The outer electrons of the Al are apparently not contributed to the V d band but instead constitute a low lying band, at the surface of which the wave functions are essentially p-like.

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