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^{51}V Quadrupolar Effects in V–Transition-Metal Alloys and Solutions of O and N in V†

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The ^{51}V NMR in several V-based alloys with 3*d*, 4*d*, and 5*d* transition metals, and in dilute solid solutions of O and N in V, was used to study quadrupolar effects due to alloying. The results show these effects to be several times smaller for transition-metal (substitutional) solutes than for interstitial O and N in V. The solute dependence suggests that the field gradients around substitutional atoms arise mainly in response to local lattice distortion rather than to the shielding of the excess charge of the solute. A line-shape simulation based on an r^{-3} radial dependence of q produces good agreement with the observed absorption spectra. The all-or-nothing wipeout model, when applied to the interstitial alloys, yields wipeout numbers $n_1 = 126 \pm 7$ for N in V, and $n_1 = 194 \pm 12$ for O in V. The observed magnitude of the effective field gradients in V-based alloys is believed to result from a partial cancellation of the Sternheimer antishielding tendency by the overshielding effect of a large density of states near the Fermi level at the V atoms.

I. INTRODUCTION

Since the early work of Drain[1] it has been known that the nuclear-quadrupole interaction has a relatively small effect on the ^{51}V NMR in vanadium metal and V-based alloy systems. The spin of ^{51}V is $\frac{7}{2}$, and its electric-quadrupole moment is -0.05_2 b,[2] about one-third the value for ^{27}Al, ^{63}Cu, and ^{65}Cu, nontransition metals on which alloy studies have been previously made. For some alloys the decrease with solute concentration of the observable resonance intensity has been interpreted in terms of an all-or-nothing quadrupolar wipeout model[3] to yield an effective first-order (satellite) wipeout number n_1. For the ^{27}Al NMR in Al:Cu, $n_1 \approx 170$,[4] while 3*d*-transition-metal solutes in Al, because of the presence of resonant ($l = 2$) conduction-electron scattering,[5] cause even larger wipeout: n_1 (^{27}Al) for Fe or Mn in Al is about 800.[4] In all of these cases, the spectrum is also affected to second order in the quadrupolar interaction e^2qQ/h and is essentially unobservable at higher solute concentrations.

By contrast, the ^{51}V NMR has been observed at all solute concentrations at least in the cubic phases, and where no magnetic interactions exist, in V-Ti,[6,7] V-Cr,[1,8] V-Mn,[1,9,10] V-Fe,[11,12] V-Co,[1] V-Ni,[1] and also in V-Nb,[13] V-Tc,[7,14,15] V-Ru,[16] and V-Al.[17] In none of these cases does the peak-to-peak NMR intensity per V nucleus seem to be reduced more than an order of magnitude from that of pure-V metal. In the interstitial β-VH (V lattice body-centered tetragonal, $c/a \geq 1.10$[18]), not even first-order distortion could be observed at room temperature.[19] A detailed study of the effects of alloying on the NMR line shape in V-Mn has been reported by von Meerwall and Schreiber.[10] Their findings, as they pertain to the quadrupolar distortions of the vanadium resonance, may be summarized as follows:

(a) There is a first-order wipeout effect of the peak-to-peak intensity, complete by about 15-at.% Mn in V ($n_1 = 36$), but there is no second-order broadening above 4 kOe at any concentration.

(b) The satellite intensity is removed symmetrically from the line center, but remains close to it. There is no discernible structure in the wings. Upward of 90% of the total expected intensity remains within ±120 kHz of the center. The peak-to-peak width decreases slightly from pure V to 1.5-at.% Mn in V, and remains nearly constant to well above 15-at.% Mn in V.

(c) The electric field gradients remain below about 10^{24} cm^{-3} even at the V nuclei nearest to a Mn atom (using $^{51}Q = -0.05$ b).

(d) Cold working during the powdering of the NMR samples has no noticeable effect on the spectra.

The results of earlier work,[1] especially on V-Cr,[8] are qualitatively compatible with (a), (b), and (d) above. The purpose of this work is to extend the study of nuclear-quadrupole effects over a range of V-based transition-metal alloys, with particular attention to the possible origin of the field gradients, and their dependence on radial distance from the solute atom, as well as the effectiveness of various shielding and antishielding mechanisms. Moreover, there is little detailed knowledge of the effect of interstitial impurities on the vanadium NMR, partly because such impurity content is difficult to analyze. Several works by Drain[1,8,20] suggest that a considerable drop in peak-to-peak intensity, and some line-shape distortion, may be due to interstitial impurities even in samples nominally at least 99.6 at.% pure. This study was, therefore, extended to include N and O dissolved in solid V. A preliminary report of part of this work has been published.[21]

II. EXPERIMENTAL

Alloy specimens for this study were prepared by arc melting several times in an argon atmosphere. The starting vanadium (Leico, Materials Research Corporation) was at least 99.97 wt% pure of oxygen, nitrogen, and transition metals, and the transition-metal solutes were typically 99.5 to 99.99 wt% pure. The resulting ingots were wrapped in Mo foil, enclosed in quartz capsules under an argon atomosphere, homogenized for 50 h at 1140 °C, and furnace cooled. A mechanical filing machine produced fine powder, which was magnetically separated by passing it several times near the poles of a strong permanent magnet. For room-temperature NMR, only particles passing through a 200-mesh sieve were selected, while for low-temperature work a 325-mesh sieve was used.

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The most consistent results for N and O dissolved in V were obtained by outgassing 0.012-in.-thick vanadium strips at rising temperature, terminating near 1275 °C and 10^{-7} torr. Except for a pure-V standard, a measured amount of gas was admitted at this temperature and allowed to diffuse into the metal. The NMR samples consisted of sections of these strips, separated from each other and from interspersed 0.0005-in.-thick Cu strips by insulating layers, and formed into stacks. The NMR intensity was corrected for the varying rf penetration depth, using the resistivity data of Hörz,[22] and for small differences in geometry and receiver sensitivity as determined from the ^{63}Cu NMR intensity.

Peak-to-peak intensity measurements were performed at 300 K near 4 and 10 MHz using a Varian wide-line spectrometer modified to accept a standard signal to calibrate sensitivity. Measurements were performed at constant rf, modulation amplitude, and sample geometry and volume. We define peak-to-peak intensity as peak-to-peak height h_1 of the absorption derivative times the square of the peak-to-peak width, normalized to spectrometer sensitivity, sample weight, and weight fraction of V constituting the alloy. During a run, at least two measurements were performed on each sample. The intensity was finally divided by that of an identically prepared sample of pure V taken during the same run. This final quantity will be referred to as $I_0(c) = I_{pp}(c)/I_{pp}\,(c=0)$.

For the purpose of studying the entire line shape at high signal-to-noise ratios, runs were performed at 4.2 K near 10 MHz, using a crossed-coil spectrometer employing electronic balancing.[23] Because the superconducting critical field for 4.4-at.% Ti in V at 4.2 K is near 10 kOe,[24] the line shape for this alloy was obtained at 77 K.

III. RESULTS AND DISCUSSION

A. Results

In order to check the effect on resonance intensity of initial purity and of possible contamination introduced during arc melting of the alloys, the peak-to-peak intensity of a sample filed from an ingot of nominally 99.97-wt%-pure V was compared with that of a powder of identical material after arc melting and heat treatment. The intensity was found to be 0.94 ± 0.02 of the former value. An ingot of 99.2-wt%-pure vanadium (Alfa Inorganics) was similarly arc melted and heat treated. Its intensity was found to be 0.65 ± 0.02 of the value for the untreated 99.97-wt% V sample above. The contamination present in the last sample is described as consisting of approximately equal amounts of transition metals and gaseous impurities. As will be apparent, the small amount of transition-metal impurities present should be able to reduce the relative intensity to no less than about 0.9, so that the excess reduction is attributable to the presence of interstitial impurities. It is possible that the small intensity decrease accompanying arc melting and heat treatment is caused by the gettering of any oxygen remaining in the argon atmosphere after first melting a titanium getter button. In a series of V-Cr alloys, prepared for an earlier study from less pure V, we find the intensities $I_0\,(c)$ to lie well below those of our present preparations at comparable Cr concentrations.

1. N *and* O *as Solutes*

Metallographic examination of our VN_x and VO_x samples containing $x \leq 1$ at.% impurity was con-

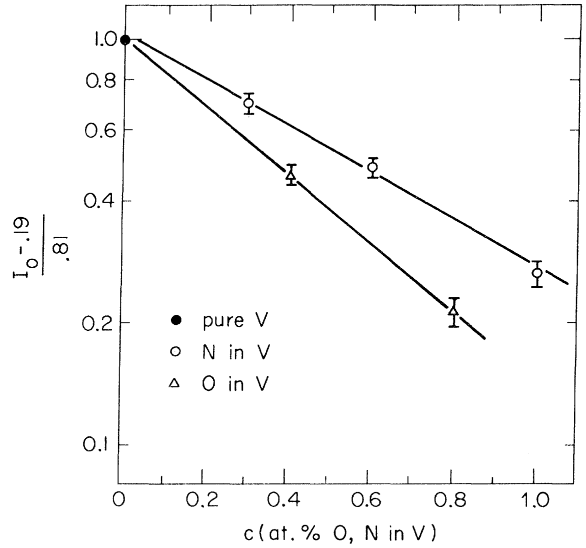

FIG. 1. ^{51}V NMR satellite wipeout for O (triangles) and N (circles) dissolved in vanadium. The wipeout numbers n_1 are 194 ±12 for O and 126 ±7 for N in V.

sistent with the existence of a solid solution. In a sample containing 1-at.% carbon, a precipitate was observed near the grain boundaries. The line shapes in VN_x and VO_x differ from those in our purest V samples again as described for V-Mn in Sec. I, with the difference that the line distortion for a given concentration of interstitial is roughly comparable to that in substitutional alloys with a solute concentration about five times greater.

The peak-to-peak intensity I_0 and linewidth in several samples were unchanged between 4 and 10 MHz, so that second-order effects can be ruled out at these and higher frequencies. The concentration dependence of the satellite intensity contained in the region of the central line, $(I_0 - 0.19)/0.81$, is shown in Fig. 1 and is consistent with an all-or-nothing wipeout model.[3] The wipeout numbers are $n_1 = 126 \pm 7$ for N in V, and $n_1 = 194 \pm 12$ for O in V. Since most or all of the resonance intensity remains in the close vicinity of the original line, wipeout must here be modified to mean a removal of the satellite intensity from the peak-to-peak region only.

Several batches of the purest V prepared by MRC and Leico had nearly the same peak-to-peak intensity: $I_0 = 1.00 \pm 0.04$, given an experimental uncertainty near ±2%.[25] From a comparison with Fig. 1 it is plausible that these samples may differ from one another in O or N content by no more than 0.04 at.%; this is probably also the upper limit of their total interstitial impurity content. The differences among the relatively impure V samples available to Drain[1,8,20] are adequately explained by the presence of up to several tenths of 1% of N or O.

2. *Transition-Metal Solutes*

In the study of V-based transition-metal alloys, we find the NMR spectra to be remarkable in their resemblance to one another at similar solute concentration. Except for small quantitative differences they are, again, substantially described by the observations for V-Mn (Sec. I). The line shape of the central portion of the peak continues to resemble that of V metal within $\pm 0.8\Delta H$ of the center, where ΔH denotes peak-to-peak width in the differential spectrum. With addition of solute, quadrupolar satellite intensity moves symmetrically away from the center, but in all cases remains within a region of about 120 Oe on either side of it. The absorption amplitude decreases monotonically with distance from the center; this decrease is least rapid in the wings in high-concentration samples. The parameters of the spectra are independent of temperature between 4.2 and 300 K, although the absence of structure in the wings limits the precision of this comparison. From a double integration of the entire observable line shape, essentially the full absorption intensity (0.90 ± 0.20) expected per V nucleus was observed even in the highest-concentration sample prepared (13.8-at.% Cr in V). The second moment of the V resonance rises from 122 ± 8 Oe^2 in the pure-V standard to 780 ± 40 Oe^2 for 13.8-at.% Cr in V, and to about 1×10^3 Oe^2 in $V_{72}Mn_{28}$, where the quadrupolar distortion appears to be complete in first order.

In order to ascertain whether the concentration dependence of the peak-to-peak intensity in these alloys is still describable by the modified all-or-nothing model used above for N and O, a study of concentration dependence was performed for V-Cr. The results are shown in Fig. 2. When taken together with the constancy of the total integrated intensity, and from a comparison of the alloy line shapes with that of pure V, it is apparent that a large part of the satellite intensity remains close to the line center. However, since the observed central intensity ratio $I_0(c)$ approaches the quadrupolar central fraction $I_c(\frac{7}{2}) = \frac{4}{21} = 0.19$ with increasing concentration, almost all V nuclei at higher concentration must experience strong enough field gradients to remove from within the region between the derivative peaks the infinities of the powder spectrum[26] arising from even the innermost satellite transition ($m_1 = \pm\frac{3}{2}$ to $\pm\frac{1}{2}$). The concentration dependence of ΔH above 5-at.% Cr in V is adequately explained[8] by a decreasing nuclear-dipolar width and by the presence of inhomogeneous Knight-shift broadening. These effects are moderate below 14-at.% Cr in V, and cannot explain the observed (present investigation and Ref. 8) 12% decrease in ΔH between pure V ($\Delta H = 13.3 \pm 0.2$ Oe at 10 MHz)

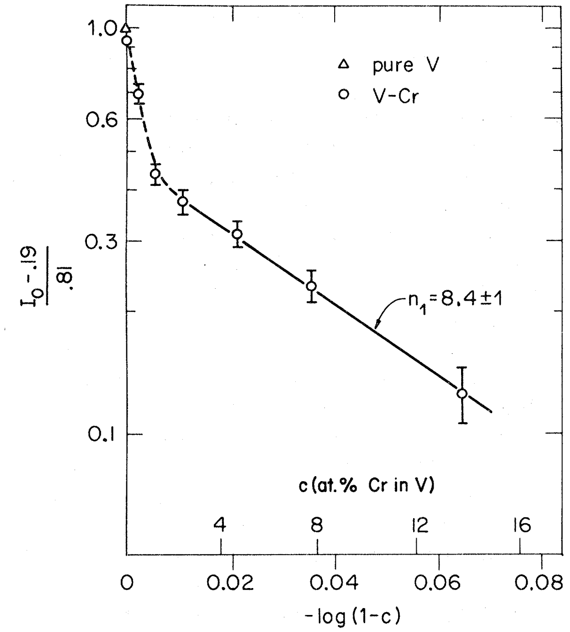

FIG. 2. Fraction of the satellite intensity contained in the region of the central ^{51}V resonance, as function of Cr content. The experimental wipeout number $n_1 = 8.4 \pm 1$ must be determined from data at the higher concentrations (see text).

and the 4.8-at.% Cr alloy. This effect may be attributable either to the lower value of the second moment of the central quadrupolar component as compared with that of the entire unsplit spectrum,[27] or to the presence in the pure V samples of small but finite quadrupolar splittings whose peaks fall within the region bounded by the derivative extrema.

The concentration dependence of I_0 below about 5-at.% Cr in V is less easily understood, but may be the result of splittings of the magnitude of the linewidth, which become statistically less likely at higher concentrations. In such a case, the wipeout number must be determined from high-concentration behavior. The straight-line portion of the curve in Fig. 2 bears out this expectation and yields a wipeout number $n_1 = 8.4 \pm 1$, the bcc coordination number. The initial sharp decrease of I_0 suggests the presence of significant gradients out to the fourth shell of neighbors; this effect will be discussed in Sec. III B. In V-Mn, where $n_1 = 36 \pm 6$,[10] a similar but smaller departure from over-all linearity is seen, whereas no such effect is observed in VO_x or VN_x (at least below 1 at.%), where n_1 is larger still.

For the purpose of comparing field gradients in V-based alloy systems, the most marked differences in I_0 were desired. Experience with the V-Mn system suggested a solute content near 5 at.%. The results of the corresponding experiment are shown in Table I. In order to estimate the relative importance of possible sources of field gradients, correlations of satellite-intensity loss (Table I, column 3) with other quantities are useful. One such quantity is ΔZ, the excess solute charge. The correlation, however, is far from satisfactory: V-Cr ($\Delta Z = +1$) has the smallest intensity loss, whereas V-Nb ($\Delta Z = 0$) and Vi-Ni ($\Delta Z = +5$) have large, nearly equal, intensity losses. On the other hand, the intensity loss seems to correlate with the solute-induced lattice distortion as reflected in the derivative of the x-ray lattice constant a with respect to the solute concentrations c near $c = 0$, where those data are available (Refs. 7, 10, 11, 13, and 28). Not unreasonably, the intensity loss increases with increasing lattice distortions, but is unaffected by its sign; a reversal in the sign of q would leave both the spectrum and the central intensity unaffected. The data thus strongly suggest that the field gradients in these alloys reflect differences in atomic size—but not excess charge—between vanadium and the transition-metal solutes. The lack of evidence for a correlation with charge dif-

TABLE I. Effect of alloying on ^{51}V NMR and lattice constant.

Solute c (at.%)	Central intensity $I_0(c)$	$1-[(I_0-0.19)/0.81]$	e^2AQ/h[a] (10^{-20} kHz cm^3)	$\frac{1}{a}\frac{da}{dc}$[b]
4.4% Ti in V	0.35 ± 0.02	0.80 ± 0.03	2.90 ± 0.1	+0.085
4.8% Cr in V	0.43 ± 0.02	0.70 ± 0.03	1.50 ± 0.1	−0.050
4.8% Mn in V	0.35 ± 0.02[c]	0.80 ± 0.03[c]	2.30 ± 0.1	−0.074
4.8% Fe in V	0.34 ± 0.02	0.81 ± 0.03	2.32 ± 0.1	−0.088
4.8% Co in V	0.33 ± 0.02	0.83 ± 0.03	1.63 ± 0.1	...
4.8% Ni in V	0.28 ± 0.02	0.89 ± 0.03	1.70 ± 0.1	...
4.8% Nb in V	0.30 ± 0.02	0.86 ± 0.03	2.60 ± 0.1	+0.103
4.8% Mo in V	0.40 ± 0.02	0.74 ± 0.03	1.05 ± 0.1	+0.022
4.8% Ta in V	0.27 ± 0.02	0.90 ± 0.03	3.10 ± 0.1	+0.112
4.8% W in V	0.29 ± 0.02	0.88 ± 0.03	2.20 ± 0.1	+0.035
4.8% Pt in V	0.25 ± 0.02	0.92 ± 0.03	1.95 ± 0.1	...

[a] For definition, see text.

[b] Taken from Refs. 7, 10, 11, 13, and 28.

[c] Taken from Ref. 10.

TABLE II. Details of the line-shape simulation for $c = 0.14$.

Shell of first occupation; i	Probability of occurence P_i	Radius R_i (Å)[a]	Occupation B_i
≥ 5	$P_{50}(0,\ 0.14) = 0.001$	large	...
4	$P_{26}(0,\ 0.14)P_{24}(1^+,\ 0.14) = 0.019$	5.02	3.3[b]
3	$P_{14}(0,\ 0.14)P_{12}(1^+,\ 0.14) = 0.101$	4.28	2.01[b]
2	$P_8(0,\ 0.14)P_6(1,\ 0.14) = 0.118$	3.03	1
2	$P_8(0,\ 0.14)P_6(2,\ 0.14) = 0.048$	3.03	2
2	$P_8(0,\ 0.14)P_6(3^+,\ 0.14) = 0.012$	3.03	3.90[c]
1	$P_8(1,\ 0.14) = 0.390$	2.62	1
1	$P_8(2,\ 0.14) = 0.222$	2.62	2
1	$P_8(3,\ 0.14) = 0.072$	2.62	3
1	$P_8(4^+,\ 0.14) = 0.017$	2.62	4.26[c]

[a] Lattice is bcc, $a_0 = 3.027$ Å.

[b] Most probable occupation of shell.

[c] Most probable occupation of a shell, provided its occupation exceeds the next higher entry in column 4.

ference seems to indicate that any excess charge is screened well within the wipeout radius (see Ref. 10 for a discussion of this point). This behavior may be attributed to the high density of states of these alloys (see Sec. III C). Moreover, the charge-density oscillations, proportional to ΔZ, arising from conduction-electron scattering from the impurities, must have very small amplitude or range to be compatible with our data. A theoretical treatment of this case using the arguments of Kohn and Vosko[29] or Brettell and Heeger[4] in their original form is clearly inappropriate.

B. Line-Shape Simulation

Because the NMR line structure is unresolved in these alloys even at the lowest concentrations, and because the spectra represent averages over angles characteristic of powder patterns, a simulation of the line shape is appropriate. From comparisons with the observed spectra the characteristic magnitudes of the quadrupole interactions are deduced. The simulation consists of a superposition of first-order quadrupole powder patterns[26] whose relative intensities and relative splittings are characteristic of the statistically expected occupancies of the shells surrounding a V atom. A number of simplifying assumptions have been made, some of which are designed to apply to moderately small solute concentrations:

(i) An asymmetry parameter $\eta = 0$ has been assumed in all cases.

(ii) The field gradient due to an isolated impurity is assumed to be proportional to the inverse third power of its distance from a V atom: $q = A/r^3$.

(iii) Because of the strong radial falloff of q, the size of the total (principal component of the) field gradient at any V atom is approximated knowing its distance from the closest shell i occupied by any impurities, by the number of impurities B_i that shell contains, and by the average occupation $\langle B_{i+1}\rangle$ of the next outer shell. For the more distant shells, only the most probable occupancy of that shell is used to calculate the average gradient arising from it. The effect of the presence of several impurities at comparable distances and various angles is reproduced approximately by estimating an average-field-gradient correction (close to unity) depending on the occupancy of each shell.

(iv) V atoms having no impurity neighbors within a cutoff radius (larger than the wipeout radius) of four shells are assigned zero-field gradient.

(v) The solute distribution is assumed to be random; probabilities for the occurrence of certain shell occupancies are evaluated from binomial probabilities $P_N(n, c)$ of finding n impurities in a chosen set of N sites at fractional solute concentration c. The symbol n^+ will denote n or more impurities.

By way of illustration, Table II shows the details of a simulation for a 14-at.% alloy. The simulation consists of components of relative strengths P_i, each with quadrupole interaction

$$\frac{e^2 q_i Q}{h} = \frac{e^2 Q}{h}\frac{A}{R_i^3} f_i\left(B_i + \frac{R_i^3}{R_{i+1}^3} f_{i+1}(\langle B_{i+1}\rangle)\right), \qquad (1)$$

where R_i is the radius of the contributing shell and A is chosen to give the best agreement with the observed spectrum. The function f_i accounts for the approximate effects of the presence of two or more impurity atoms in one shell and thus depends on the shell i as well as on its occupation B_i. By definition, $f_i(1) = 1$ in all shells; estimates for higher occupancies in the bcc structure gave values of f_i between 0.7 and 1.1 for the four inner shells, depending on occupation. Because of its relative computational efficiency, this method is judged preferable to accumulating histograms of the quadrupole interaction over finite lattices. An exact evaluation of a statistical model such as this would be prohibitive because of the number of possible configurations involved.

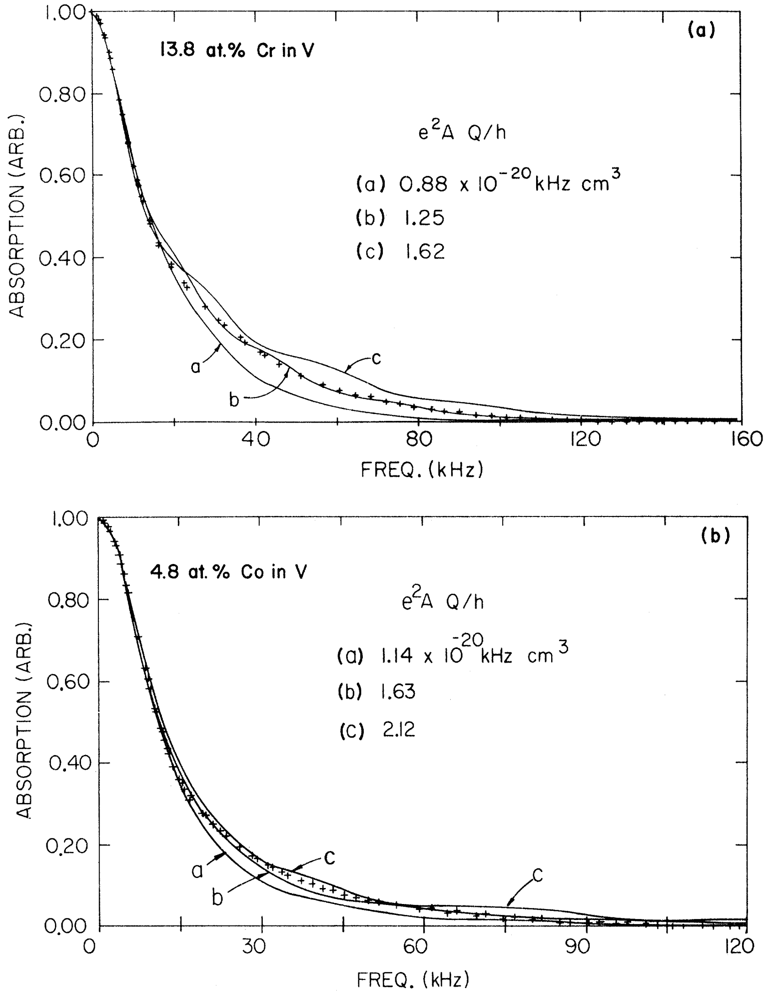

FIG. 3. ^{51}V NMR absorption in alloys containing 13.8-at.% Cr in V (a), and 4.8-at.% Co in V (b). The observed derivative spectra have been integrated and their left half reflected about the center, showing their symmetry (crosses). The solid lines are simulations (see text) using different values of the quadrupole interaction; in each case, (b) gives the best visual fit.

The details of the simulation were carried out with a computer program which generated and summed the appropriate powder patterns and convoluted the result with the line shape observed in pure-V metal. The corresponding experimental NMR spectrum was integrated by the program and (in view of its symmetry) folded about its centroid, normalized to unit height, and plotted with the synthesis. Figure 3 shows two such comparisons of the experiment (+) with syntheses. The contents of Table II apply to Fig. 3(a); similar comparisons were performed for two lower concentrations of Cr in V. It is found that the value of A necessary to produce the best fit to the spectra increases slightly (by less than 15%) as the concentration is lowered. Because the model is designed for low concentrations, and in the interest of uniformity, the values for 4.8-at.%-solute content are selected for all alloys. From an inspection of Table II, column 2, using the assumed r^{-3} dependence of q, it is evident that at higher solute concentrations the field gradients experienced by over 97% of all V nuclei lie within a factor of 4 of each other. Using a value for $Q(^{51}\mathrm{V})$ of$^2 - 0.05$ b and the value of A from the appropriate synthesis, we find that this range of field gradients for Cr in V is $1.1\times 10^{23} \lesssim q \lesssim 4.8 \times 10^{23}$ cm^{-3} at V nuclei.

The lack of detailed agreement between spectra and syntheses may indicate a departure from the assumed r^{-3} dependence of q; this is certainly to be expected at small r. From the appearance of specifically the lowest concentration simulations it may be inferred that the r^{-3} law overestimates q in the first shell surrounding an impurity. It must be added that the good agreement of our simulations with the spectra should not be regarded as evidence against an oscillatory (or other) radial falloff of q.

A requirement imposed on the simulations is the need to account for essentially all resonance intensity under the curve within about 150 kHz of the center, for reasons discussed in Sec. III A. This condition is satisfied in every case; the best-fitting syntheses in Fig. 3 both contain over 95% of the

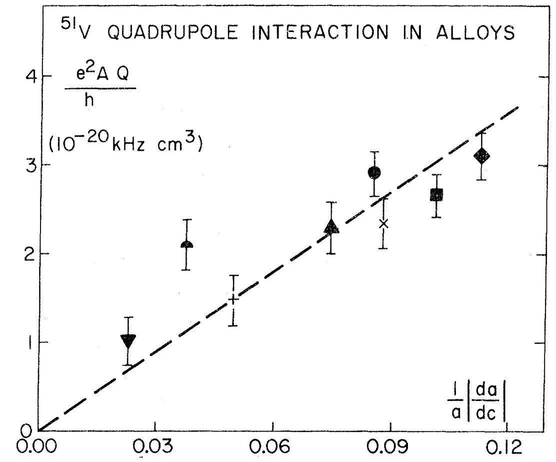

FIG. 4. Magnitude of the quadrupole interaction found from line-shape simulation for alloys containing 4.8-at.% solute vs absolute value of the fractional lattice-parameter change on alloying. The solutes are Ti (circle), Cr (plus), Fe (cross), Mn (triangle), Nb (square), Mo (inverted triangle), Ta (diamond), and W (semicircle). Of these, only Cr, Fe, and Mn decrease the vanadium lattice parameter.

total resonance intensity.

Since the Knight shift in V-Cr depends on solute concentration,[8] the effect of shift inhomogeneity at 10 MHz was included in the simulations. Each of the components in Table II was given a shift on the basis of an assumed sensitivity of the shift to the occupancy of two neighbor shells.[8] Using a broadening line shape whose $\Delta\nu$ is 13.2 kHz in all cases, the combination of shift inhomogeneity and quadrupole distortion satisfactorily accounts for the linewidth increase from 13.2 kHz at 4.8-at.% Cr to 13.4 kHz at 7.9-at.% Cr and to 14.3 kHz at 13.8-at.% Cr.

Upon inspection of the separate powder patterns generated in the course of the syntheses for V-Cr, it is apparent that even the outermost satellite contributions of those atomic configurations for which the third or fourth shells are the nearest to be populated by Cr atoms never fall beyond two to four ΔH on both sides of the center. The effect of this is to diminish markedly the intensity at the lowest concentrations, a situation not susceptible to description by a simple wipeout model. At higher concentrations, V atoms with no Cr neighbors within three shells are sufficiently rare as to have little effect on further intensity reduction.

Line-shape simulations were also carried out for the other vanadium alloys. The values of e^2AQ/h appropriate to these spectra are listed in Table I, column 4, and plotted in Fig. 4 against the change in lattice parameter with concentration. The correlation evident from Fig. 4 reinforces our earlier conclusion that lattice distortion is mainly responsible for the field gradients in V-based alloys, at least for substitutional solutes. An expected correlation between our measurements of quadrupole interaction and satellite-intensity loss $1-(I_0-0.19)/0.81$ may be masked by the close grouping among the values of I_0 relative to their experimental error. Another conclusion to be drawn from these simulations is that in all the substitutional alloys investigated, the field gradient at V nuclei does not exceed $q_{\max}=10^{24}\ \text{cm}^{-3}$ except at an insignificant fraction of V nuclei. It might be noted here that the smallness of the first- and second-order quadrupole splittings is primarily the result of the small quadrupole moment (−0.05 b) and the large spin ($I=\frac{7}{2}$) of ^{51}V as compared with, say, Cu (−0.15 b, $I=\frac{3}{2}$).

C. Effect of Solvent Density of States

No general discussion of nuclear-quadrupole effects in alloys of transition metals has been given. In particular, the effects of the Fermi-surface electrons on the screening of the excess solute charge are not well understood. It may be useful, in the absence of a detailed knowledge of the dependence of the electric field gradients (EFG) on the distance from the solute atom in a transition metal host, simply to estimate the local amplification of an impurity-induced EFG at the host resonant nucleus. We may regard all EFG originating outside a suitably defined host-metal atomic sphere as a semiempirical parameter q_{latt} (unique to each V atomic site), and estimate the response of the electrons inside the sphere to q_{latt}. We employ the theory of Watson, Gossard, and Yafet,[30] expressing the total EFG q at a host nucleus by

$$q=q_{\text{latt}}\,(1-\gamma_\infty)+q_{\text{loc}}\,(1-R_Q), \tag{2}$$

where γ_∞ and R_q are the appropriate Sternheimer antishielding factors. In the first half of the $3d$-transition-metal series, it is generally found that $1-\gamma_\infty\approx 12$,[31] while $1-R_Q$ is close to unity.[30] The local field gradient, arising inside the atomic sphere, has been written[30]

$$q_{\text{loc}}=q^0+q'+q'', \tag{3}$$

where q^0 arises from the noncubic symmetry of the perturbed Bloch wave functions, which have the local symmetry of the crystal, while q' is caused by the redistribution of the occupied states near the Fermi surface and q'' is associated with the spatial distortions of the Bloch functions. Reference 30 gives a method of estimating q' which may be simplified for $3d$ transition metals as follows:

$$q'\approx-\tfrac{4}{49}\,\alpha\, n(E_F)\, e^2\langle r^2\rangle\langle r^{-3}\rangle\, q_{\text{latt}}\ , \tag{4}$$

where $n(E_F)$ is the bare density of states at the Fermi surface, r is the electronic radius, and α

is a constant which corrects for the effects of self-consistency, and is estimated for V to be $\alpha \approx 0.65$ by interpolation between the results for Ti and Co.[30] Substituting the values for $n(E_F) = 1.80$ states/eV atom,[32] $\langle r^2 \rangle = 4.5$ a.u.,[33] and $\langle r^{-3} \rangle = 1.8$ a.u.,[33, 34] we find

$$q' = -21 q_{\text{latt}} . \tag{5}$$

This term always overshields q_{latt} and will tend to cancel the antishielded direct lattice gradient.

While it would be difficult to calculate q^0, it is thought to be small in $3d$ transition metals and will, moreover, be partially cancelled in a self-consistent calculation of q'. It will be neglected here.

A reasonably low upper limit on q'' may be found in terms of N, the number of conduction electrons per site, and the orbital angular momentum l:

$$q'' \lesssim q_{\text{latt}} \, | \gamma_\infty (l) | \, \frac{N}{2(2l+1)} . \tag{6}$$

For V, $N = 5$, $l = 2$, and $\gamma_\infty(2)$ will be the dominant contribution to γ_∞.[32] We approximate $\gamma_\infty = \gamma_\infty(2)$ and have

$$q'' \approx + 6 q_{\text{latt}} . \tag{7}$$

Combining the results and making reasonable guesses for the uncertainties in the estimated quantities, we find that even the sign of q/q_{latt} is indeterminate:

$$q \approx q_{\text{latt}} (12 + 6 - 21) = -(3 \pm 5) q_{\text{latt}} . \tag{8}$$

The possibility of appreciable cancellation between antishielding and overshielding tendencies is evident. In the presence of a much smaller $n(E_F)$, q' will tend to become insignificant, allowing a non-transition-metal nucleus to experience more nearly the full effect of the antishielding amplification of the EFG, irrespective of the origin and spatial dependence of the latter.

IV. CONCLUDING REMARKS

In V-based transition-metal alloys and oxygen and nitrogen solid solutions, the quadrupole interaction energies at V nuclei are relatively small, of first order only above 4 kOe, and not sensitively dependent on solute species. The details of the modest dependence on solute suggest that the source of the field gradients is not primarily the excess solute charge, or the consequences of its shielding, but the distortion of the lattice in the vicinity of the solute atom. The data on interstitial O and N in V are consistent with this interpretation considering that in both cases[22] $a^{-1}\,(da/dc) = 0.158$ and is thus larger by a factor of 2 than in representative substitutional alloys. Earlier work[28] had suggested that $a^{-1}\,(da/dc)$ may be substantially higher. We may of course also expect the electron distribution near these elements to be different from that for the substitutional metallic solutes.

The EFG from lattice distortion may be expected to obey an r^{-3} radial dependence beyond the first shell of neighbors. The success of line-shape simulations based on this law is consistent with, but does not compel here, such an interpretation. A modified first-order wipeout model may be applied in the case of N and O in V, in which the field gradients are highest. It is still useful for V-Mn,[10] but requires reinterpretation for V-Cr, in which the field gradients are smallest.

It is suggested that the observed EFG in both the transition-metal alloys and the interstitial solutions may involve a sizeable cancellation between a Sternheimer antishielding of q_{latt} and an overshielding resulting from a redistribution of the occupied electronic states near the Fermi surface.

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New Technique for Determining the Diffusion Mechanism by NMR: Application to Cl^{35} Diffusion in TlCl†

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A major problem in the study of atomic motions is the determination of the dominant mechanism responsible for translational diffusion. Recently Ailion and Ho predicted that the rotating-frame spin-lattice relaxation time $T_{1\rho}$ would have an angular dependence which depends on the diffusion mechanism in the ultraslow-motion region. In this paper we have extended these ideas to TlCl for which the dominant mechanism is known by other experiments to be Cl vacancy diffusion. We observed experimentally an angular dependence consistent with the dominant mechanism being Cl vacancy diffusion, thereby corroborating the basic ideas of Ailion and Ho. We have also been able to eliminate Cl interstitialcy diffusion as a possible dominant mechanism. We measured an activation energy of (0.733 ± 0.012) eV, in agreement with results of other experiments.

I. INTRODUCTION

In this paper we report the experimental verification of a new technique for determining diffusion mechanisms in solids.[1] This technique was proposed theoretically by Ailion and Ho,[2] who predicted that in the ultraslow-motion region[3] the rotating-frame spin-lattice relaxation time $T_{1\rho}$ would depend upon the angle which the external magnetic field H_0 makes with respect to the crystal axes. In particular they predicted that this angular dependence could vary significantly with diffusion mechanism and could, for example, be measurably different for vacancy, interstitialcy, and interstitial diffusion. Direct comparison of the experimental data with the results of calculations could then be used to distinguish the dominant mechanism from alternate possibilities.

We chose to perform our experimental study on a solid for which the diffusion mechanism has been determined to a high degree of probability by other techniques. In particular we studied TlCl for which the dominant mechanism, as determined by Friauf,[4] is chlorine vacancy diffusion. Our results are in excellent agreement with the results of Friauf and strongly corroborate the ideas of Ailion and Ho.

II. BACKGROUND

A. Strong-Collision Theory

The theoretical calculations for $T_{1\rho}$ in TlCl utilize the strong-collision approach, originally developed by Slichter and Ailion[5] (SA). We now review the strong-collision theory and the conditions under which it is valid. The motivation for a strong-collision theory arises when we attempt to study the spin-lattice relaxation time in very weak Zeeman fields. Under conditions such that the external magnetic field is less than or comparable to the local field, weak-collision[6–8] theories which