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Nuclear magnetic resonance of ^{51}V in $(Ti_{1-x}V_x)_2O_3$ $(0 < x < 1)$ powders

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^{51}V nuclear magnetic resonance in $(Ti_{1-x}V_x)_2O_3$ powders with $0 < x < 1$ has been studied at room temperature. For $x < 30\%$, the ^{51}V Knight shift (KS) is strongly negative. It becomes rapidly less negative when $x \sim 30\%$, then varies slowly at higher V concentrations. Mechanisms responsible for the Knight shift are proposed. The results are discussed in connection with a previous study of the magnetic phase diagram of $(Ti_{1-x}V_x)_2O_3$ which reveals two markedly different magnetic behaviors, namely, a spin-glass or mictomagnetic regime at low temperatures and low values of x $(x < 30\%)$ and a metallic antiferromagnetic regime at higher values of x $(x \gtrsim 40\%)$. From this study it is concluded that the steep variation of KS with x is due to a decrease of the core polarization hyperfine field associated with a transition from a V local-moments magnetic regime to an itinerant magnetic regime.

I. INTRODUCTION

Ti_2O_3, V_2O_3, and the mixed compounds $(Ti_{1-x}V_x)_2O_3$ have been extensively studied during the last decade, both experimentally and theoretically, mainly because of their temperature-induced semiconductor to metal transitions.[1]

Pure Ti_2O_3 is a semiconductor at low temperature with a small Van Vleck type paramagnetism. It undergoes a gradual transition from semiconductor to metal in the temperature range from 400 to 500 K. The incorporation of 0.5% V induces both local magnetic moments on the vanadium atoms and a metallic conductivity. These properties lead to a remarkable spin-glass behavior for $0.5\% < x < 10\%$, at low temperature. Energy-band schemes which account for the magnetic and electrical properties have been proposed.[2,3]

At ~150 K, pure V_2O_3 exhibits a first order transition from a semiconducting antiferromagnetic to a metallic paramagnetic phase. Doping V_2O_3 with Ti decreases the transition temperature and stabilizes completely the metallic phase for Ti concentrations of ~5%.[4]

$(Ti_{1-x}V_x)_2O_3$ forms a continuous solid solution for $0 < x < 1$ and is isostructural with α-Al_2O_3 for all x. The c parameter increases with x for $x < 40\%$ then remains constant while the a parameter decreases monotonically with x.[5]

Magnetic properties of $(Ti_{1-x}V_x)_2O_3$ $(0 < x < 1)$ have been recently reported.[6] The spin-glass regime observed for $x < 10\%$ extends into a mictomagnetic phase for $x < 40\%$. Above 40%, magnetic susceptibility, high-field magnetization, electrical resistivity data give experimental evidence for a metallic antiferromagnetic phase with Néel temperature T_N ranging from 60 to 10 K depending on x. Recently, Mössbauer data have confirmed the existence of this phase.[7] The magnetic phase diagram which has been obtained is shown in Fig. 1.

At high temperature $(T > T_N)$, the bulk susceptibility can be described by a Curie-Weiss-type law:

$$\chi = \chi_0(x) + C(x)/[T - \theta(x)] \ , \qquad (1)$$

where $\chi_0(x)$ is a temperature-independent contribution. χ_0 was found to increase linearly with x for $10\% < x < 40\%$, then to saturate for $x > 50\%$ as shown in

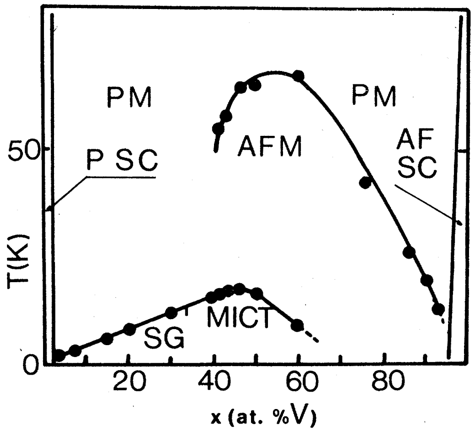

FIG. 1. Phase diagram of $(Ti_{1-x}V_x)_2O_3$. P, paramagnetic; SG, spin-glass; MICT, mictomagnetic; AF, antiferromagnetic; M, metal; and SC, semiconductor.

Fig. 2. The effective magnetic moment per vanadium atom, $p = (3K_BC/2Nx\mu_B^2)^{1/2}$ where N is the Avogadro number, first decreases with x at small x from $\sim 3.8\mu_B$, is nearly constant for $x < 60\%$, then increases slightly for $x > 60\%$ to $\sim 2\mu_B$ as shown in Fig. 2. The paramagnetic Curie-Weiss temperature $\theta(x)$ shows a remarkable behavior; θ is small, positive, and increases with x for $x < 20\%$, then θ decreases sharply, becomes equal to zero for $x = 30\%$, and is strongly negative for $x > 30\%$ ($\theta = -50$ K for $x = 50\%$).

The magnetic study[6] of $(Ti_{1-x}V_x)_2O_3$ suggests that two markedly different behaviors occur, depending on the value of x:

(i) At low x ($x < 10\%$), the magnetic properties are due to V virtual bound states. The magnetic couplings between the local moments are of the Ruderman-Kittel oscillatory type and are predominantly ferromagnetic as indicated by positive values of θ.

(ii) At larger x, the high negative values of θ indicate that the local-moments model is no longer valid. The magnetic behavior has been described in terms of a polarization of the $3d$ conduction band with antiferromagnetic exchange interactions.[6]

Despite the wealth of macroscopic information that has been obtained from the magnetic study, no clear picture of the transition for electrons from local-moments behavior to itinerant behavior has emerged so far. In order to clarify the magnetic properties of the $(Ti_{1-x}V_x)_2O_3$ solid solution we have performed ^{51}V nuclear magnetic resonance at room temperature on these samples. Up to now, only pure V_2O_3 and Al- or Cr-doped V_2O_3 had been studied by NMR.[8,9] The near 100% abundance of the ^{51}V nuclear species make it particularly suitable to the measurements of frequency shifts and linewidths.

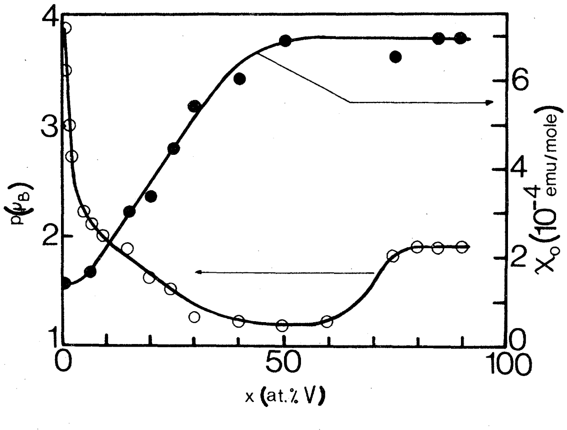

FIG. 2. Temperature-independent contribution to the susceptibility χ_0 (right scale) and effective magnetic moment per vanadium atom p (left scale) vs V concentration.

In this paper, we unveil new features of the NMR behavior of ^{51}V in $(Ti_{1-x}V_x)_2O_3$ as x is increased: The Knight shift is found to exhibit a sharp change from large negative values to less negative values near $x = 30\%$. We will relate these results to the V concentration dependence of the magnetic behavior of $(Ti_{1-x}V_x)_2O_3$ found in previous measurements.[6]

II. EXPERIMENTAL PROCEDURE

The samples used in this study have been prepared by arc-melting the constituents Ti_2O_3 and V_2O_3 in the appropriate proportions under an argon atmosphere. The $(Ti_{1-x}V_x)_2O_3$ compounds being metallic, the arc-melted buttons were then crushed for the NMR experiments. The typical particle size of the powders was ~ 50 μm. This size allows an essentially complete penetration of the external rf magnetic field. Details of the sample preparation and characterization are given elsewhere.[10] It has not been possible to obtain homogeneous samples for $x > 90\%$.

NMR measurements were made at room temperature with a conventional cw Varian 4210A wideline spectrometer unit using standard lock-in technique and a Varian 4230B crossed coil probe. The measurements were made using a Harvey Wells electromagnet whose field was calibrated with a HW G502 NMR gaussmeter. The ^{51}V frequency-shifts measurements were made at fixed frequency. The ^{51}V resonance in vanadium powder, corrected for its Knight shift of -0.57% (Ref. 11) was used as a reference. The magnetic field was swept slowly through the resonance and was modulated at about 30 Hz with a modulation amplitude of ~ 4 G peak to peak. Some measurements have been made at 77 K. In this case, the samples were placed in the tip of a glass Dewar mounted in the probe.

III. EXPERIMENTAL RESULTS

A. ^{51}V NMR frequency shift

Typical room-temperature ^{51}V NMR spectra are shown in Fig. 3 for various V concentrations. The additional ^{27}Al resonance is due to the aluminum in the NMR probe.

The results of the study of the composition dependence of the ^{51}V Knight shift in $(Ti_{1-x}V_x)_2O_3$ are shown in Fig. 4. The room-temperature susceptibility is also given in this figure. The estimated accuracy of the Knight-shift measurements is $\pm 0.2\%$. Negative resonance shifts are obtained throughout the range of concentrations studied. The main feature is the rapid rise of the Knight shift towards less negative values for $x \sim 30\%$. For $x > 80\%$, the Knight shift is ap-

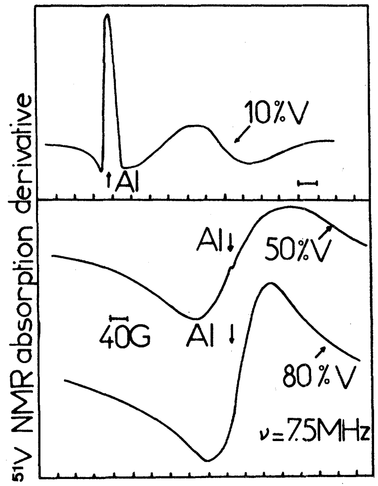

FIG. 3. Typical room-temperature spectra of the ^{51}V NMR signal in $(Ti_{1-x}V_x)_2O_3$. The Al signal is due to the Al NMR probe.

proximately the same as in pure V_2O_3.[8]

It has been possible to measure the Knight shift at 77 K only for high values of x. For $x = 90\%$, the Knight shift is -0.4% at 77 K, while it is -0.2% at room temperature. In preliminary experiments, it had been found, for $x = 10\%$, that the Knight shift was -5.1% at 273 K and -2.7% at 373 K.[12]

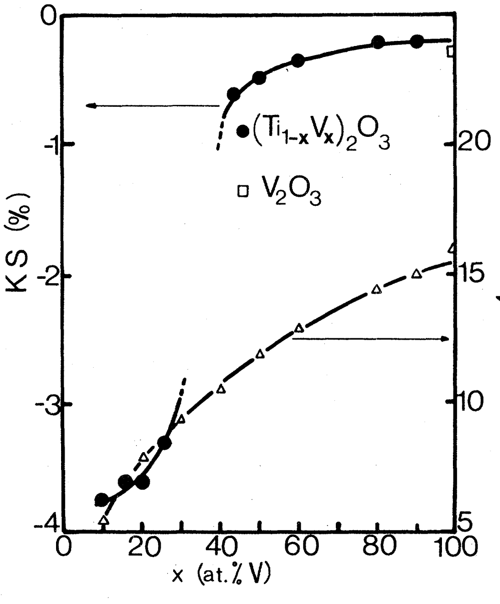

FIG. 4. Left scale: ^{51}V frequency shift vs V concentration at room temperature. (●), $(Ti_{1-x}V_x)_2O_3$; (□), V_2O_3. Right scale: magnetic susceptibility vs V concentration at room temperature (Δ).

Our results are in disagreement with those obtained by Myako and Ito[13] for $x \lesssim 10\%$. These authors had observed a temperature-independent and a concentration-independent Knight shift at low values of x. We suggest that the signal that these authors had observed could be due to the aluminum of the probe.

B. NMR linewidth

It can be seen from Fig. 3 that the NMR line is symmetrical at low x ($x \sim 10\%$) and at large x ($x \sim 80\%$). In the intermediate range of concentration ($x \sim 50\%$), the line is asymmetrical. Typical values of the peak-to-peak linewidth ΔH are $\Delta H \simeq 100$ G for $x = 10\%$ and $\Delta H \sim 60$ G for $x = 90\%$ (Fig. 5). For all x, ΔH is larger than in pure V_2O_3 for which $\Delta H \sim 20$ G.[8] ΔH is found to be field dependent and increases with the magnetic field. A similar behavior has been observed in Nb-doped VO_2.[14]

A search for the ^{51}V resonance signal was also made at 77 K. The linewidth was found to increase with decreasing the temperature and was observable only at high values of x. In preliminary experiments[12] a decrease in ΔH with increasing temperature has been found for $x \sim 10\%$. ΔH was ~ 100 G at room temperature and ~ 85 G at 373 K.

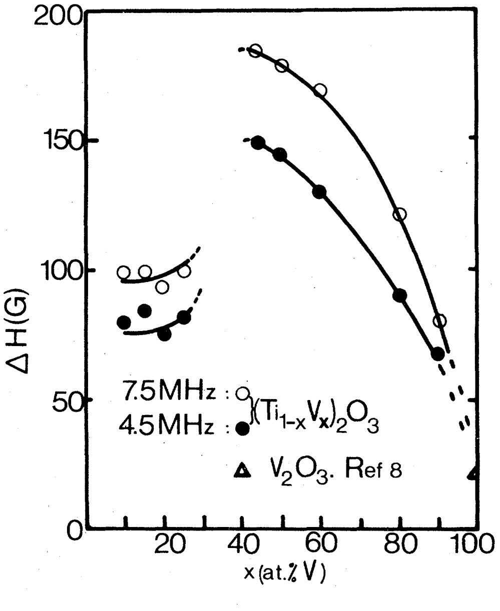

FIG. 5. ^{51}V nuclear resonance linewidth vs V concentration at room temperature. ○, data taken at 7.5 MHz; ●, data taken at 4.5 MHz.

IV. DISCUSSION

The NMR data described above suggest that, for $x \sim 30\%$, a change in the magnetic interactions of V in $(Ti_{1-x}V_x)_2O_3$ occurs. We will first compare our results with those obtained in various vanadium oxides; then, we will discuss the variations of the Knight shift as a function of x. We will also discuss possible contributions to the linewidth. We will propose mechanisms responsible for the rapid changes in the Knight shift near $x = 30\%$ in relation with the other magnetic properties of $(Ti_{1-x}V_x)_2O_3$.

A. Comparison with other vanadium oxides

In Table I, typical Knight shifts, linewidths, and susceptibilities of various metallic vanadium oxides are summarized. Our data obtained for $V_2O_3 + 10\%$ Ti exhibit some similarities with those obtained on pure metallic V_2O_3 or $V_2O_{3+\epsilon}$. The origin of these similarities could be explained by the fact that the matrix is the same and also by the presence of narrow $3d$ bands in all these materials. However, we wish to point out some differences:

(a) The core-polarization hyperfine field $(H^{\mathrm{hf}})_{\mathrm{cp}}$ is low in VO_2 (-85 kG/μ_B) (Ref. 16) and high in $(Ti_{0.9}V_{0.1})_2O_3$ (~ -280 kG/μ_B) (see Sec. IV B); in pure V_2O_3 a value of -140 kG/μ_B is obtained.[8] It does not seem possible to explain these differences only by different spin susceptibilities χ_d. For example, $\chi_d = 8 \times 10^{-4}$ emu/mole V in V_2O_3 at 155 K and $\chi_d = 6.2 \times 10^{-4}$ emu/mole V in VO_2 at 370 K. The ratio $\chi_d(V_2O_3)/\chi_d(VO_2)$ is 1.30 while the ratio $(H^{\mathrm{hf}})_{\mathrm{cp}}(V_2O_3)/(H^{\mathrm{hf}})_{\mathrm{cp}}(VO_2)$ is 1.65.

(b) The linewidth is field independent in pure V_2O_3 (Ref. 19), while it is field dependent in $(Ti_{1-x}V_x)_2O_3$ and $(V_{1-x}Nb_x)O_2$.[14]

B. ^{51}V Knight shift

1. *Sources of the Knight shift*

The Knight shift arises from a combination of several contributions: s-band Pauli paramagnetism χ_s, temperature-dependent d-band spin paramagnetism $\chi_c(T)$ via core polarization, and d-band Van Vleck paramagnetism χ_{VV}.

Neglecting the diamagnetism, the Knight shift is given by

$$K = K_s + K_{\mathrm{cp}} + K_{\mathrm{VV}} \;, \tag{2}$$

where

$$K_s = \frac{8\pi}{3N} \langle |\psi_s(0)|^2 \rangle \chi_s \;, \tag{3}$$

$$K_{\mathrm{cp}} = \frac{8\pi}{N} \langle \rho(0) \rangle_d \chi_d(T) \;, \tag{4}$$

$$K_{\mathrm{VV}} = \frac{2}{N} \langle r^{-3} \rangle_d \chi_{\mathrm{VV}} \;. \tag{5}$$

Here $\langle |\psi_s(0)|^2 \rangle$ is the s electron density at the nucleus averaged over the Fermi energy E_F; $\langle \rho(0) \rangle_d$ is the spin density at the nucleus induced by $3d$ electrons at E_F, and $\langle r^{-3} \rangle_d$ is the average of r^{-3} for the free ion. N is the Avogadro number. K_s and K_{VV} are positive while K_{cp} is negative.

The d-spin core-polarization term K_{cp} arises from exchange polarization of inner core s electrons of vanadium atoms by $3d$ electrons producing a distortion of ion core. It will be shown below that K_{cp} is

TABLE I. Summary of ^{51}V Knight shifts (KS), linewidths (ΔH), and susceptibilities (χ) of some metallic vanadium oxides. Data for pure vanadium have been included. Data are taken at 300 K, except for VO_2 and V_2O_3 under pressure.

	V	$VO_{1+\epsilon}$	VO_2[a]	V_2O_3[b] (26 kbar)	V_2O_3	$V_2O_{3+\epsilon}$	$V_2O_3 + 10\%$ Ti	V_3O_5	V_4O_7
Reference	11	15	16, 17	18	19	20	This work	21	22
KS (%)	+0.57	+0.4	−0.4	~ -0.8	−0.3	−0.3	−0.2	−1.6 (V^{4+}) −3.6 (V^{3+})	−2.2 (V^{3+})
K_{VV} (%)			+0.6		+1.5				
K_{cp} (%)			−1		−1.8				
ΔH (G)	13.5	~ 200	30 at 8 kG 18 at 14 kG	~ 300	~ 20	~ 20	60		~ 50
χ (emu/mole)	8×10^{-6}	6×10^{-3}	6×10^{-4}		1.7×10^{-3}	2.2×10^{-3}	1.5×10^{-3}	1.7×10^{-3}	2×10^{-3}

[a] Data taken at 350 K above the metal insulator transition.
[b] Data taken at 4.2 K.

the main source of the concentration dependence of the ^{51}V Knight shift.

In $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$, the s-contact term K_s is not expected to contribute significantly because s electrons are essentially localized on the oxygen atoms. On the other hand, in Eq. (4), $\chi_d(T)$ is the d-spin susceptibility of the V ions and in Eq. (5), χ_{VV} the Van Vleck susceptibility of V ions only.

The total Knight shift can be expressed in terms of χ_{VV} and χ_d if χ_s is negligible:

$$K = K_{\mathrm{cp}} + K_{\mathrm{VV}} = \alpha\chi_d + \beta\chi_{\mathrm{VV}} \ , \tag{6}$$

where α is a constant proportional to the core-polarization hyperfine field $(H^{\mathrm{hf}})_{\mathrm{cp}}$ and β to the orbital hyperfine field $(H^{\mathrm{hf}})_{\mathrm{cp}}$. Measurements of $K(T)$ and $\chi(T)$ together yield the value of α and χ_d if β is known. The values of α and χ_d will be given by a K vs χ plot.

In $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$, a K vs χ plot need not be linear because χ is the total susceptibility which contains the contribution of both Ti and V ions. A tentative K-χ plot for $x = 10\%$ gives $(H^{\mathrm{hf}})_{\mathrm{cp}} \sim -280$ kG/μ_B.[12]

For large values of x ($x \sim 90\%$), the susceptibility χ is of the same order of magnitude as in pure $\mathrm{V}_2\mathrm{O}_3$. The value of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ is ~ -140 kG/μ_B in pure $\mathrm{V}_2\mathrm{O}_3$ and very likely of the same order of magnitude in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$ for $x \sim 90\%$.

2. *Concentration dependence of the ^{51}V Knight shift*

From our data it is clear that there is a steep change in the Knight shift near $x = 35\%$, while the room-temperature susceptibility increases continuously with x. The behavior of χ_d with x cannot explain this result since an increase of χ_d would lead to a more negative Knight shift. The temperature-independent term χ_{VV} shown in Fig. 2 increases monotonically; this variation explains only partly the change of the shift to less negative values.

We rather propose that the steep variation of the Knight shift is due to a rapid decrease of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ near $x = 35\%$. We do not expect any concentration dependence of $(H^{\mathrm{hf}})_{\mathrm{VV}}$ because it involves only an average radius $\langle r^{-3}\rangle_d$ of the vanadium ion. From our K-χ plot we have obtained $(H^{\mathrm{hf}})_{\mathrm{cp}} \sim -280$ kG/μ_B for $x = 10\%$, while $(H^{\mathrm{hf}})_{\mathrm{cp}} \sim -140$ kG in pure $\mathrm{V}_2\mathrm{O}_3$.[8] In order to explain the observed change in K a drop of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ by a factor of 2 has to be invoked.

The origin of such a strong concentration dependence of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ could be

(i) a possible change of the band structure which would be reflected in the increase of the c parameter[5] for $x \sim 30\%$. The polarization of vanadium core s electrons caused by a partially filled $3d$ band is sensitive to band overlap between $3d$ orbitals of vanadium ions and outer orbitals of neighboring titanium ions and oxygen anions. A change of the band structure when x is increased could affect $(H^{\mathrm{hf}})_{\mathrm{cp}}$. We do not expect a rapid variation of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ from this mechanism.

(ii) The most likely mechanism seems to be the transition from a V local moments magnetic regime ($x \sim 10\%$) to an itinerant magnetic behavior ($x \sim 40\%$). At low x, Ruderman-Kittel interactions and at large x antiferromagnetic interactions within the d band are predominant. At low x ($x \sim 10\%$) local V magnetic moments would give strong values of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ and therefore strongly negative shifts while at large x ($x > 40\%$), the itinerant moments would give lower values of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ and less negative shifts. This is consistent with the fact that the sharp variation of the Knight shift occurs approximately at the same concentration for which the paramagnetic Curie temperature θ is zero and for which a low-temperature antiferromagnetic metallic phase is observed.

3. *Temperature dependence of the ^{51}V Knight shift*

There are some similarities in the temperature dependence of the Knight shift in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$ and in $\mathrm{V}_2\mathrm{O}_3$ or VO_2. In all these materials, it has to be related to the temperature dependence of the spin susceptibility. In $\mathrm{V}_2\mathrm{O}_3$ or VO_2 a K-χ plot where the temperature is the implicit parameter gives values of $(H^{\mathrm{hf}})_{\mathrm{cp}}$ and $(H^{\mathrm{hf}})_{\mathrm{VV}}$ but, in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$, such a plot is doubtful as discussed in Sec. IV B 1.

C. ^{51}V NMR linewidth

1. *Origin of the linewidth*

Several mechanisms can contribute to the linewidth: nuclear dipolar interaction, quadrupolar interaction, some distribution of the Knight shift due to inhomogeneities, relaxation due to the interaction with s or d conduction electrons, exchange interactions between nuclear spins and local magnetic moments, and exchange interactions between local magnetic moments. We consider these contributions in turn.

In pure $\mathrm{V}_2\mathrm{O}_3$, the nuclear dipolar linewidth is about 3 G.[8] It is even smaller in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$. Therefore, dipolar interactions cannot explain the values of ΔH observed.

Any nucleus of the iron group which has a magnetic moment has also an electric quadrupolar moment; in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$ the local environment of V ions is noncubic and the ^{51}V quadrupolar moment interacts with the field gradient. The resonance line is split into several lines which are unresolved in our powdered samples. If one observes the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition only, the line will be broadened only by the second-order quadrupolar interactions which vary as

$1/H$. Since we observe an increase of ΔH with the field, this mechanism cannot explain our results.

One likely source of linewidth in a disordered system is a variation in Knight shift from site to site. For example, for $x \sim 40\%$, concentration for which the Knight shift depends strongly on x, a fluctuation of concentration $\Delta x = 5\%$ would give rise to a variation of the Knight shift $\Delta \mathrm{KS} \sim 1\%$. This leads to a linewidth $\Delta H \sim 65$ G. Therefore, a fluctuation of concentration is not negligible in the ^{51}V linewidth. Besides, this mechanism could be responsible for the asymmetry of the line for $x \sim 50\%$.

The contribution of s electrons to the relaxation is negligible for all x because s electrons are essentially localized on oxygen anions. A relaxation via the d conduction electrons would lead to an increase of ΔH with temperature in disagreement with the experimental results. Moreover, these contributions would not lead to a field-dependent linewidth.

The Van Vleck paramagnetism will contribute negligibly to the relaxation because this mechanism involves states at energies far above E_F, while the Pauli paramagnetism contribution arises from states without $k_B T$ of E_F.

The relaxation can arise from interactions between nuclear spins and magnetic local moments. In $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$, the linewidth decrease with increasing temperature indicates that the relaxation is essentially due to interactions between nuclear spins and V magnetic moments. Exchange interactions between magnetic moments produces mutual spin flip of the electrons which in turn produce nuclear relaxation. This mechanism is very likely to be efficient in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$.

2. *Concentration dependence of the linewidth*

Our results show that ΔH is larger in $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$ than in pure $\mathrm{V}_2\mathrm{O}_3$ and that ΔH seems to decrease when x is increased $(0 < x < 100\%)$. This variation could be related to to the concentration dependence of the magnetic polarization around the V atoms. At low x $(x < 30\%)$, the polarization would be inhomogeneous and would lead to mictomagnetism. At large x $(x > 80\%)$, the polarization would become more homogeneous and would lead to the antiferromagnetic regime observed at low temperatures.

V. CONCLUSION

In summary, our ^{51}V NMR results on $(\mathrm{Ti}_{1-x}\mathrm{V}_x)_2\mathrm{O}_3$ show large negative frequency shifts which become rapidly less negative near $x = 30\%$. The linewidth seems to decrease with x. It is shown to be field dependent. A consistent explanation of the results is based on the existence of a sharp transition near $x = 30\%$ from a V magnetic local-moments regime to an itinerant magnetism. The variation of the Knight shift has been attributed to a sharp variation of the core-polarization hyperfine field. The linewidth was shown to be due to nuclear spins and magnetic local-moments interactions. A sharp differentiation between the two magnetic regimes has been made possible by ^{51}V NMR.

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