Microscopic Magnetic Properties of $(V_{1-x}Ti_x)_2O_3$ near the Phase Boundary of the Metal-Insulator Transition

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Abstract

Magnetic susceptibility ($\chi$) and $^{51}$V NMR have been measured in $(V_{1-x}Ti_x)_2O_3$ near the phase boundary of the metal-insulator transition. It is established that the transition from antiferromagnetic insulating (AFI) to antiferromagnetic metallic phases near $x_c \approx 0.05$ is not quantum critical but is discontinuous with a jump of the transition temperature. In the AFI phase at 4.2 K, we observed the satellite in the zero-field $^{51}$V NMR spectrum around 181 MHz in addition to the "host" resonance around 203 MHz. The satellite is also observable in the paramagnetic metallic phase of the $x = 0.055$ sample. We associated the satellite with the V sites near Ti which are in the V$^{3+}$-like oxidation state but has different temperature dependence of the NMR shift from that of the host V site. The host d-spin susceptibility for $x = 0.055$ decreases below $\sim 60$ K but remains finite in the low-temperature limit.

Key words: A. oxides, D. magnetic properties, D. nuclear magnetic resonance
PACS: 71.30.+h, 75.50.Ee, 76.60.-k, 75.40.Cx

1 Introduction

Magnetic excitations from the anomalous metallic phase of $V_2O_3$ and its derivatives have received continued interest for more than three decades in connection with a famous temperature-induced metal-insulator transition (MIT)

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Preprint submitted to Elsevier Science 22 March 2022
Among various methods to stabilize the metallic phase against the antiferromagnetic insulating (AFI) phase, introducing V vacancies has extensively been studied in the last decade [2–5]. While stoichiometric V$_2$O$_3$ remains paramagnetic once the metallic phase is stabilized by applying pressure [6–8], the ground state of metal-deficient V$_{2-y}$O$_3$ is a spin-density wave (SDW) state characterized by a small ordered moment ($\sim 0.15 \mu_B$) with a large fluctuating component ($\sim 0.32 \mu_B$) [3]. $^{51}$V NMR, on the other hand, has revealed the existence of V$^{4+}$-like magnetic “guest” sites in V$_{2-y}$O$_3$ [9,5], indicating a spatially inhomogeneous electronic state which is suspected to be incompatible with homogeneous SDW order [8].

Substitution of Ti for V also stabilizes the metallic phase, resulting in the SDW ground state similar to V$_{2-y}$O$_3$ [10]. However, magnetic guest sites have not been detected yet in Ti-doped V$_2$O$_3$, which makes it a puzzle whether the SDW order is intrinsic to a homogeneous system or to the system with some sort of inhomogeneities like magnetic guests. In this paper, we report on the magnetic susceptibility and $^{51}$V NMR measurements on (V$_{1-x}$Ti$_x$)$_2$O$_3$ near the MIT phase boundary. We found the V$^{3+}$-like guest sites distinguishable from the host site in both the AFI and paramagnetic metallic (PM) phases. The SDW order is therefore intrinsic to the doped V$_2$O$_3$ systems with a kind of magnetic impurities.

2 Experiments

Powder samples of (V$_{1-x}$Ti$_x$)$_2$O$_3$ were prepared by arc-melting of V$_2$O$_3$, Ti and TiO$_2$ followed by annealing in H$_2$ atmosphere at 950 °C for 48 hours. Magnetic susceptibility was measured using a SQUID magnetometer. A clamp-type Cu-Be cell suited for the SQUID magnetometer [11] was used for the measurement of the susceptibility under pressure. NMR measurements were carried out with a coherent-type pulsed spectrometer.

3 Results

3.1 Magnetic susceptibility and phase diagram

Figure 1 shows the temperature ($T$) dependence of the magnetic susceptibility $\chi = M/H$ ($M$ and $H$ being the magnetization and the external field, respectively) of (V$_{1-x}$Ti$_x$)$_2$O$_3$ measured at $H = 2$ T on heating. The results are in good agreement with those reported in the literature [12] except that $\chi$ for $x = 0.045$ and 0.046 are somewhat larger than the others. This comes from a nonlinear increase of $M$-$H$ curves at low fields for these samples due to a
trace of ferromagnetic impurities, of which existence does not affect seriously
the determination of transition temperatures because their response to the
external field is scarcely dependent on $T$.

We can see from Fig. 1 that a sudden drop of $\chi$ signaling MIT disappears
for $x \geq 0.052$. A kink then appears at low $T$ due to SDW ordering. The $T$-
$x$ phase diagram is shown in Fig. 2. Here we defined the MIT temperature
$T_{MI}$ as a mid-point temperature of the rapid drop of $\chi$ due to MIT. $T_{MI}$
decreases with $x$ almost linearly to $\sim 60$ K in a rate $dT_{MI}/dx \approx -23$ K/Ti %
and is terminated at the critical concentration $x_c \approx 0.05$. Above $x_c$, Néel
temperature $T_N$ appears at $\sim 18$ K and increases gradually with $x$. The phase
diagram clearly demonstrates that the MIT in $(V_{1-x}Ti_x)_2O_3$ with changing $x$
is not quantum critical but is strongly first order.

The bulk $\chi$ of $(V_{0.954}Ti_{0.046})_2O_3$ under pressure is shown in Fig. 3. The most
striking feature of the result is that both the anomalies due to MIT and
SDW ordering are observable at 0.15 GPa. This suggests that the insulating
and metallic phases coexist in some pressure region, i.e., MIT under pressure
is first order as Ti doping. The resulting $T$-$p$ phase diagram is shown in the
inset of Fig. 3. Applying pressure reduces $T_{MI}$ in a rate $dT_{MI}/dp \approx -80$ K/GPa
which yields a scaling 0.29 GPa $\approx$ Ti % for the MIT. As opposed to Ti doping,
$T_N$ is suppressed by pressure, but the rate $dT_N/dp = -5.3(2)$ K/GPa is only
one-fifth of that in $V_{2-y}O_3$ [2]. $dT_N/dp$ was found to decrease slightly with $x$
to $-4.6(2)$ K/GPa for $x = 0.065$.

3.2 $^{51}$V NMR in the paramagnetic metallic phase

Field-swept $^{51}$V NMR spectra in the PM phase of $(V_{0.945}Ti_{0.055})_2O_3$ are shown
in Fig. 4. The spectrum is asymmetric with a tail at lower fields and is broad-
ened significantly at low $T$. The asymmetric line profile suggests the existence
of V sites having different crystallographic and/or magnetic environment from
that in pure $V_2O_3$. We analyzed the spectrum by fitting to the sum of two
Voigt functions on the assumption that there exists another V site or the
“guest” site in addition to the “host” site. The results are also shown in
Fig. 4. The intensity ratio between the host (dashed line) and the satellite
(dashed-dotted line corresponding to the guest) resonances is about 4 : 1 and
is almost $T$-independent. This ratio can be understood by considering that
the satellite signal at lower fields comes from V nuclei with at least one Ti
atom on the four neighboring V sites, because in that case the intensity ratio
is $0.797 : 0.203 = 3.93 : 1$, agreeing well with the observed one. The guest site
should be in the $V^{3+}$-like electronic state as the host site, because Ti atoms
exist as trivalent ions in $(V_{1-x}Ti_x)_2O_3$ [1].

The $T$ dependence of the NMR shifts $K^h$ and $K^g$ ($h$ and $g$ denote host and
guest, respectively) at the V sites is shown in Fig. 5. $-K^h$ takes a maximum
around 60 K, following the NMR shift of $^{51}$V in $V_2O_3$ under pressure [7] as in $V_{2-y}O_3$ [4]. On the other hand, $-K^g$ decrease gradually with decreasing $T$ and exhibits an upturn below about 60 K. The different $T$ dependence of $K^h$ and $K^g$ indicates that the d-spin susceptibilities of host and guest sites behave rather differently. We also showed in Fig. 5 the scale of the d-spin susceptibility $\chi_{\text{spin}}$ for the observed shift $K$ calculated using the relation $\chi_{\text{spin}} = (K - K_{\text{orb}})/A_{\text{spin}} (i = h, g)$. Here $K_{\text{orb}}$ is the shift due to Van-Vleck orbital susceptibility and $A_{\text{spin}}$ is the d-spin hyperfine coupling constant, for which the values in $V_2O_3$, $A_{\text{spin}} = -132 \text{ kOe}/\mu_B$ and $K_{\text{orb}} = 1.45 \%$ [7] were used. Noted that the host $\chi_{\text{spin}}$ never vanishes in the $T \to 0$ limit after making a round maximum around 60 K as in $V_2O_3$ under pressure [7]. The origin of the $T$ dependence of $\chi_{\text{spin}}$ for the host as well as the guest sites is not clear at present and remains as a future problem.

3.3 $^{51}$V NMR in the antiferromagnetic insulating phase

We have also observed the satellite in the zero-field $^{51}$V NMR spectrum in the AFI state. As shown in Fig. 6, the satellite appears at lower frequencies of the host resonance. The intensity of the satellite increases with $x$, suggesting that the satellite signal comes from V nuclei near Ti atoms. The hyperfine fields determined from the peak positions of the spectrum are listed in Table 1.

A periodic modulation of the spin-echo amplitude when varying the rf-pulse separation was observed for both the host and satellite resonances. From the modulation period, one can determine the splitting of the quadrupolar septet of $^{51}$V ($I=7/2$) [13]. For $x = 0.02$ the quadrupolar splitting of the host resonance is 218(2) kHz which is slightly larger than that of pure $V_2O_3$ (200 kHz) [14]. A smaller splitting of 135(5) kHz was found for the satellite in the $x = 0.02$ sample.

The appearance of the satellite near the host signal is indicative of the $V^{3+}$-like electronic state of the guest site in the AFI phase as in the PM phase. This is contrasted with the observation in $V_{2-y}O_3$ where the $V^{4+}$-like guests are identified via the zero-field $^{51}$V NMR [9,5]. We should note here that the relative intensity of the satellite to the host signal is consistent with the probability of finding V nuclei having Ti atoms on the four neighboring V sites as in the PM phase. It is therefore reasonable to consider that the existence of $V^{3+}$-like guest sites is characteristic of $(V_{1-x}Ti_x)_{2}O_3$ throughout its magnetic phase diagram.
Table 1

Hyperfine fields at the V sites in (V$_{1-x}$Ti$_x$)$_2$O$_3$ in the antiferromagnetic insulating state at 4.2 K.

| Ti (%) | host (kOe) | satellite (kOe) |
|--------|------------|-----------------|
| 0      | 185.9      | -               |
| 2      | 181.3      | 162.6           |
| 3      | 181.4      | 162.3           |
| 4.5    | 180.4      | 161.6           |
| 4.8    | 180.0      | 161.4           |

4 Discussion and Summary

The observation of the V$^{3+}$-like guest sites demonstrates that even in the metallic phase, the electronic state of (V$_{1-x}$Ti$_x$)$_2$O$_3$ is not so homogeneous as has been previously thought. In addition, the host site preserves the V$_2$O$_3$ character in spite of the fact that the number of $d$ electrons per vanadium is formally reduced by doping. These are nothing but a manifestation of strong Coulomb repulsion between electrons which favors the number of electrons per site being an integer. The Coulomb interactions as well as nesting of the Fermi surface are therefore indispensable for the SDW ordering in metallic V$_2$O$_3$.

It seems, however, that the presence of the magnetic guest sites is crucial in realizing the SDW order, because long-range order (LRO) is absent in pure V$_2$O$_3$ despite the nearly identical spin fluctuations in the metallic phase of pure, V-deficient and Ti-doped V$_2$O$_3$ [15,10]. A possible scenario is that metallic V$_2$O$_3$ is unstable to a perturbation destroying spatial coherence such as defects and impurities owing to the quantum critical nature of spin fluctuations [15]. This is reminiscent of impurity-induced LRO in low-dimensional quantum antiferromagnets with disordered ground states [16,17]. In metallic V$_2$O$_3$, V-vacancy induced V$^{4+}$-like sites and Ti-doping induced V$^{3+}$-like sites may serve as magnetic impurities, transforming the system into the SDW state. Local change due to doping of orbital fluctuations suppressing spin order [18] is also a likely source for long-range SDW ordering in the doped V$_2$O$_3$ systems.

In summary, we established the first-order doping-induced and pressure-induced MIT from AFI to AFM phases in (V$_{1-x}$Ti$_x$)$_2$O$_3$. The V$^{3+}$-like magnetic guest sites exist in the PM phase as well as in the AFI phase, indicating the importance of spatially non-uniform electronic states for the SDW ordering.
Acknowledgement

One of the authors (J.K.) was supported by Grant-in-Aid for Encouragement of Young Scientists from the Japan Society for the Promotion of Science (No. 12740218).

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Fig. 1. Magnetic susceptibility of \((V_{1-x}Ti_x)_2O_3\).

Fig. 2. Magnetic phase diagram of \((V_{1-x}Ti_x)_2O_3\). AFM denotes the antiferromagnetic metallic phase.
Fig. 3. Pressure dependence of the magnetic susceptibility of \((V_{0.954}Ti_{0.046})_2O_3\). \(T_{MI}\) and \(T_N\) are shown respectively by the solid and dashed arrows. The data are properly offset for clarity. Inset: magnetic phase diagram under pressure.

Fig. 4. Field-swept \(^{51}\)V NMR spectra in the paramagnetic state of \((V_{0.945}Ti_{0.055})_2O_3\) taken at 17.6 MHz. The vertical line indicates the field for zero shift. The dashed and dashed-dotted lines are the result of deconvolution (see text).
Fig. 5. Temperature dependence of the NMR shifts at the host (●) and guest (○) V sites in $(V_{0.945}Ti_{0.055})_2O_3$.

Fig. 6. Zero-field $^{51}V$ NMR spectra in the antiferromagnetic insulating phase of $(V_{1-x}Ti_x)_2O_3$ at 4.2 K.