Dynamic signature of orbital selective Mott transition in the metallic phase of VO$_2$

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Abstract

An orbital-selective technique, nuclear magnetic resonance (NMR) spectroscopy, which could simultaneously probe the atomic structure and electronic properties, was employed to address the ‘bad metal’ behaviors, i.e., negligible electron thermal conductivity in the metallic phase of VO$_2$. The measured electric field gradients at V sites by $^{51}$V NMR were found to evolve significantly in the pure metallic phase within the vicinity of structural phase transition temperatures, unexpected in a simple metal within this temperature region according to structural analysis by diffraction. This abnormal temperature-dependent local symmetry evolution can be well explained by a simple phenomenological model of orbital selective Mott transition in this multiorbital system.

Transition metal oxides and chalcogenides with strong electron correlations have great scientific interest and potential applications in superconductors, ultrafast field effect transistors, and smart coatings [1–5]. Among them, vanadium dioxide (VO$_2$) is particularly appealing because it exhibits a metal-to-insulator (MI) transition close to room temperature ($T_i \sim 340$ K), which is distinct from its counterparts and has received considerable attention [6–16]. Below $T_i$, VO$_2$ has a monoclinic crystal structure (M$_1$) with a modest band gap of $\sim$0.7 eV, while above $T_i$ it is metallic with a rutile structure (R). Recently, interest has been raised in the thermal experiments showing ‘bad-metal’ behaviors, i.e., electronic thermal conductivity of the metallic phase of VO$_2$ remains unusually low with respect to electronic conductivity across the MI transition [17]. This quite unusual behavior suggests that electronic and thermal transport properties could be tuned independently, which might provide another clue to design advanced thermoelectric materials with high electrical conductivity while low thermal conductivity, reminiscent of phonon-glass electric-crystal materials [18].

To understand the above abnormal transport properties in VO$_2$, Mott–Hubbard, Peierls and cooperative Mott–Peierls models have been proposed [19–23]. The key difference between these proposals lies in the role of Mott physics that plays in the band gap formation and the driving force in triggering the MI transition. Extensive efforts have been carried out to distinguish the role of electronic correlations from Peierls distortion from a microscopic point of view. The nature of the MI transition in pure VO$_2$ is, however, still under hot debate [24]. One of the reasons might be due to the lack of experimentally determined electron density distribution information in VO$_2$. It has been suggested that electron correlation induced orbital ordering should also show up in its metallic phase [2, 14, 25]. Nonetheless, the evolution of electron density distribution in the metallic phase of pure VO$_2$ remains to be measured. To be noted, the anisotropy of electron density distribution information can be probed by orbital-selective techniques such as nuclear magnetic resonance (NMR) spectroscopy while it could hardly be accessible by neutron diffraction techniques in systems with small...
scattering cross section of neutrons. The anisotropy of valence electron density distribution at a nucleus can be extracted from electrical field gradients (EFGs) \( \text{[26]} \). At the same time, the principal vector \( (V_{zz}) \) of EFGs at a quadrupole nuclear can be probed by NMR through quadrupole interactions \( \text{[27]} \). The investigation of EFGs at atomic sites in \( R \) phase at various temperatures should be of most relevance for deeper understanding the mechanism of MI transition and the so called ‘bad metal’ behavior in pure VO\(_2\) \( \text{[28]} \). Surprisingly, such EFG information in metallic VO\(_2\) toward the above understanding has not been reported yet in prior NMR studies \( \text{[29−36]} \), as far as the authors were concerned.

In this work, we systematically examined the EFGs of pure VO\(_2\) crystals by \( ^{51}\text{V} \) NMR spectroscopy at various temperatures. \( ^{51}\text{V} \) (spin \( I = 7/2 \)) NMR is selected as an atomic probe because \( ^{51}\text{V} \) is a quadrupole nucleus and EFGs at V sites directly links V 3\text{d} orbital ordering. Our results show that the measured \( ^{51}\text{V} \) EFGs evolve significantly in the metallic VO\(_2\) and then remain nearly unchanged at well above \( T_c \), unexpected in a simple metal within this temperature region according to lattice structure analysis by diffraction. In combination with first-principles calculations, the evolution of EFGs is found to originate from the dynamics of orbital selective Mott transition in the metallic phase. The observed correlation-driven orbital selection in metallic VO\(_2\) is relevant for better understanding the MI transition mechanism and ‘bad metal’ behavior such as negligible electronic thermal conductivity, \( 0.5 \text{ W m}^{-1} \text{ K}^{-1} \) and only \( 1/10 \) of the magnitude as predicted from Wiedemann–Franz law in the metallic phase near the MI transition.

Stoichiometric VO\(_2\) powdered crystals of large primary particle size (typically \( > 10 \mu m \)) were well annealed and used in this study. This product (Alpha Chemical Ltd) was bought from the Sinopharm Chemical Reagent Co. Ltd. Powdered crystals were checked by x-ray diffraction and found to be free of complicating insulating phases. Solid state \( ^{51}\text{V} \) NMR experiments were performed at 9.39 Tesla on a Bruker Avance III 400 HD spectrometer at variable temperatures from 200 to 400 K with high precision of \( \pm 0.1 \text{ K} \). To prevent spectral distortion, careful selections of r.f. pulse durations and power were chosen. \( ^{51}\text{V} \) chemical shifts were referenced to pure V metal at room temperature (~5200 ppm). Resistivity measurements were carried out following a four-wire method inside the NMR spectrometer coil. Temperatures were monitored and controlled at the same precision as NMR experiments.

VO\(_2\) crystallizes into metallic phase \( (R) \) above 340 K with one-dimensional vanadium chains evenly running along the c axis (figure 1(b)). VO\(_2\) transforms into nonmagnetic insulating phase, \( M_1 \) with strong dimerization (V–V pairing) at lower temperatures, as shown in figure 1(a). All V atoms in the \( R \) phase are equivalent in symmetry. It is the same case for the \( M_1 \) phase. The difference between two structures in terms of local symmetry at V sites is illustrated in the inset of figures 1(c) and (d), respectively. The local symmetry at V sites can be quantitatively evaluated by \( ^{51}\text{V} \) NMR.

Figures 1(c) and (d) show the \( ^{51}\text{V} \) NMR spectra of VO\(_2\) powders for \( M_1 \) phase at 300 K and \( R \) phase at 341.6 K, respectively. A point-by-point technique is used to map the entire spectrum. Selective pulse with low power (~1 W) and long pulse width (50 \text{ ms}) was chosen to map the full spectra with no spectral distortion. The frequency interval is around 100 ppm (~10 kHz). Central transition lines along with full first-order satellites for
Table 1. Experimentally measured $^{51}$V NMR quadrupole coupling constant ($C_Q$) and quadrupole frequency, $\nu_Q = 3C_Q/(2I(I+1)) = C_Q/14$, asymmetry parameter $\eta=(V_{zz}-V_{xx})/V_{zz}$, and total electric field gradients, EFGs ($V_{zz} = 4.136C_Q$(MHz)/Q(b) for M$_1$ (30 K) and R phase (341.8 K), respectively. Here, $\sin \theta = 7/2$, quadrupole moment Q(b) = 0.052 b for $^{51}$V nucleus. Only the absolute value of the $V_{zz}$ can be measured. Calculated EFGs tensors including valence and lattice contributions along with asymmetry parameter (\eta) for M$_1$ (300 K) and R phase (453 K), respectively, are also listed. Here, 'valence EFG’ is defined as the EFG inside the muffin tin sphere only; 'latticeEFG’ refers to the contribution from the interstitial region. The total EFG is the sum of valence EFG and lattice EFG.

|     | Expt. $\nu_Q$ (MHz) | Expt. $\eta$ | Expt. EFG ($10^{21}$ V m$^{-2}$) | Calc. total EFG ($10^{21}$ V m$^{-2}$) | Calc. valence EFG ($10^{21}$ V m$^{-2}$) | Calc. lattice EFG ($10^{21}$ V m$^{-2}$) | Calc.$\eta$ |
|-----|---------------------|-------------|-------------------------------|--------------------------------|---------------------------------|---------------------------------|-------------|
| M$_1$ | 0.49                | 0.5         | 5.5                           | 5.01                           | 0.43                            | 4.58                            | 0.6         |
| R    | 0.3                 | 0.5         | 3.3                           | $-2.4^a$                      | 0.72                            | $-3.12$                         | 0.3         |

$^a$ Here, the negative sign indicates that the main component of EFG takes an opposite direction to $C_Q$ axis.

$M_1$ phase can be clearly seen. The sharp features in the NMR powder patterns for $M_1$ phase indicate the high quality of the sample largely free of either impurities (i.e. V$_2$O$_3$, ~609 ppm at 300 K [36]) or site distributions. The homogeneously broadening of the line shape for the R phase is also resolved (see figure S1 in the supplemental materials available online at stacks.iop.org/NJP/20/073026/mmedia). However, it seems that only inner satellite lines can be seen in the R phase. Quadrupole coupling constants, $C_Q$ and hence EFGs can be obtained by fitting the experimental spectra with SIMPSON software [37]. The principal vector of EFG tensor, $V_{zz} = 4.136 \times 10^{19}C_Q$(MHz)/Q(b) (V m$^{-2}$), where Q(b) refers to electric quadrupole moment, Q in unit barn. Q = 0.052 barn for $^{51}$V nucleus. In addition, anisotropy in either central transition or satellite lines for both phases can be seen, indicating large contributions from Knight shift anisotropy at high magnetic field. This anisotropy hinders a good fitting for the powder spectra. Fortunately, as illustrated in figures 1(c) and (d), one can directly read the splitting ($\nu_Q'$) of first order inner satellite transitions $(\pm \frac{1}{2} \rightleftarrows \pm \frac{3}{2})$, marked as ‘$a'$ and ‘$b'$ in the figure, which measures $C_Q$ directly. Here, $C_Q = 2(2I(I+1)\nu_Q/3$, where $\nu_Q = \nu_Q/(1-\eta)$ and asymmetric parameter, $\eta = (V_{yy}-V_{xx})/V_{zz}$ = 0.5 for the $M_1$ phases [29]. $C_Q$ values are around 7 MHz for the $M_1$ phase at 300 K and 4.2 MHz for the R phase at 341.6 K, respectively. The $C_Q$ values for both phases are listed in table 1. The measured $C_Q$ values are in agreement with previous reports [29, 31]. The smaller values for the quadrupole interaction in the R phase reflect the less distorted coordination of vanadium in this phase. Quadrupole coupling constants can be also estimated by line intensity analysis. For instance, nutation experiments were performed for the $M_1$ phase (see figure S2). The measured $C_Q$ value for $M_1$ phase from nutation experiments are compared very well with the $C_Q$ value listed in table 1.

Figures 2(a) and (b) show the temperature dependence of $^{51}$V NMR spectra of VO$_2$ polycrystalline powders after several thermal cycling. This one-pulse measurement of $C_Q$ provides a great opportunity to perform systematic temperature dependent study in VO$_2$. One can see that $^{51}$V isotropic Knight shifts change from 2100 ppm to about $-4500$ ppm at around 337.8 K (see figure 2(c)). This transition temperature is close to 340 K, which has been well documented in literatures [1]. By the way, magnetic field effects on the transition temperature can be neglected up to 9 T (not shown). In the R phase, the large negative Knight shifts are primarily of core polarization origin [34, 35]. Neglecting the small diamagnetic magnetism, the Knight shifts in metals come from three potential sources, that is: \( K = K_v + K_a + K_w = H^{HF} \chi_v + H^{pd} \chi_a + H^{sd} \chi_w\), \( K_v \) is from the Fermi-contact contribution associated with s character conduction electrons, the others refer to the direct core polarization, \( K_a \) and orbital contributions, \( K_w \) from 3d conduction electrons. The major difference between them lies in the temperature dependence. Only \( K_v \) is usually temperature dependent. This argument on the origin of the negative Knight shifts is strongly supported by the observation that the measured bulk magnetic susceptibility ($\chi$) show almost linearly with Knight shifts ($K$) with temperature as an implicit parameter [34, 35] and hyperfine fields ($H^{HF}$) are temperature insensitive. More importantly, a sharp transition of EFGs across this temperature can be also observed, indicating that (1) it is structural phase transformation (SPT); (2) the SPT is displacive. The small hysteresis ($\sim 5$ K) of transition temperature during thermal cycling further confirms the high quality of the sample. There are no observable changes of central line width and $C_Q$ values in the $M_1$ phase below $T_c$ within the temperatures investigated, suggesting no metastable and spatial phase separations associated with other insulating/semiconducting phases, such as M$_2$ or T [10]. From figure 2(d), one can see the measured $C_Q$ values for the R phase increase monotonically with temperatures and then saturate within the temperatures investigated. This finding is our major result. The increase of $C_Q$ values for the R phase upon heating is unexpected for a simple metal. Enhanced diffusion usually averages out local magnetic field fluctuation ($\Delta H$) or electric field gradients at a nuclear and leads to a decrease of $C_Q$ values upon heating in a simple metal. The observed abnormal evolution of $C_Q$ values in metallic VO$_2$ indicates that it is a metal, as evidenced from Korringa-like relaxation behavior [34], but quite strange.
Based on their distinctive line shape and line shifts in $M_1$ and $R$ phases of VO$_2$, more information can be obtained from $^{51}$V NMR spectroscopy. The coexistence of both phases is demonstrated by NMR (figures 2(a) and (b)). This phase coexistence in VO$_2$ has also been observed by mid-infrared near-field spectroscopy [38].

Beyond that, the volume fractions of $M_1$ ($\lambda$) or $R$ phases ($1 - \lambda$) within this complex structure can be estimated by NMR. For simplicity, $^{51}$V NMR central line integral is proportional to the number of nuclear spins or V atoms in a phase within a limited temperature range near the transition. To check if the volume fraction of electric conducting phase has any effects on electronic transport properties, electronic conductivity of VO$_2$ crystals was measured at variable temperatures. Sharp MI transition can be clearly seen (see figure 2(e)). Figure 2(f) gives the volume fraction of $M_1$ phase versus conductivity with temperature as an implicit parameter. A sharp transition of electronic conductivity occurs when $\lambda$ reaches say $\sim 80\%$ (an estimation, it should not be taken too literally).

Electronic structures for both phases were calculated from first principles. A semilocal combination of the modified Becke-Johnson exchange and LDA correlation potentials (mBJLDA) within the density functional theory framework were employed in the computations for the $M_1$ phase. The computations were implemented in the WIEN 2k code [39]. Electron correlations are supposed to be treated with a similar accuracy as GW and hybrid methods in mBJLDA [40]. To be noted, LDA/GGA functional always produces a metal, i.e., not only for

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**Figure 2.** $^{51}$V NMR spectra as a function of temperature, (a) for $M_1$ phase; (b) for $R$ phase. (c) The $^{51}$V isotropic shifts at various temperatures for both phases. The shifts were extracted from central lines shown in (a) and (b). (d) The distance of the inner satellite transition lines in terms of quadrupole splitting as a function of temperatures for both phases. The data were read from first-order satellites shown in (a) and (b). (e) Electronic conductivity versus temperatures. The inset illustrates the experimental setup in an NMR spectrometer coil. To obtain Ohmic contact, electrodes were placed on the surface using silver glue and the electrode areas were no less than 1 mm$^2$. (f) The relation between electronic resistivity and volume fraction of $M_1$ phase with temperature as an implicit parameter.
the R phase but also for the M₁ phase. This aspect is an indication of strong electron correlation effects in this material. The calculated quadrupole coupling constants, $C_Q$ and asymmetry parameters ($\eta$) for the M₁ phase are summarized in table 1. For the M₁ phase, the calculated EFG is $5.01 \times 10^{21}$ V m$^{-2}$, in good agreement with experiment, $5.5 \times 10^{21}$ V m$^{-2}$. For comparison, the calculated absolute value of EFG by LDA is $2.4 \times 10^{21}$ V m$^{-2}$ for the R phase, in reasonable agreement with experiment. The measured value is $3.3 \times 10^{21}$ V m$^{-2}$ for the R phase, as shown in table 1. It is worthy of noting here that the measured EFG (from $C_Q$) is a scalar while the calculated one is a principal vector with negative sign $'-'$. When the direction of the principal vector of EFG is anti-parallel with the $c_R$ axis of R phase (see figure 1(b)), a negative sign $'-'$ will be put in front of the number. It is worth noting here that, for the R phase (say at 450 K), mBJLDA functional is not recommended. The calculated EFG using this functional for this phase is much larger than the measured one. To calculate EFGs more accurately for both phases, a new method is called for. Anyway, our calculations are encouraging. The principal component of EFGs can be reasonably estimated with the implementation of mBJLDA and GGA for M₁ and R phases, respectively. More importantly, one can see EFGs at V sites consist of two components based on computations (see table 1). The component of lattice EFG dominates in both phase. The sign of valence EFG is opposite to that of lattice EFG in the R phase. In addition, figures 3(a) and (b) show the calculated band structure of the M₁ and R phases. The calculated energy gap is about 0.705 eV in the M₁ phase, which is close to previous reports $^{14, 40}$. The difference of EFGs between two phases is reflected by their charge density map. Figures 3(c) and (d) present the computed charge density distributions of (100) for M₁ phase and (001) of R phase. One can see M₁ is distinguished from R phase in the directionality of the bonding between V and O atoms. The charge density distribution at V sites in the R phase is more isotropic than that in the M₁ phase. The more isotropic electron density distribution, the less EFGs or $C_Q$ values are.

Dynamic signature of orbital selective Mott transition can be revealed from the observation of the anomalous temperature dependent EFGs in VO₂. There are usually two possible mechanisms that contribute to the evolution of charge density distribution. To lower the potential energy of $V^{4+}$ ions upon cooling, the degeneracy of three V 3d $t_{2g}$ orbitals can be removed by two ways: (a) lattice distortion; (b) orbital selective Mott transition. The latter case (b) is not necessarily associated with any lattice symmetry reduction. Temperature dependent x-ray diffraction studies show that no lattice symmetry change occurs in R phase $^{7, 41}$. Thermal-
Incompletely dimerized VO₂, these results exclude the possibility of any significant contribution from lattice distortion to the EFGs measured in the R phase within the temperatures investigated. The observed large temperature dependent EFGs should point to the contribution from charge density distribution in the R phase. We emphasize that it is the energy difference ($\Delta = U - k_B T$) that drives the V 3d $t_{2g}$ energy bands splitting when $U$ is larger than $k_B T$ in magnitude, which leads to the redistribution of the electron density. In this case, no lattice symmetry reduction will be expected but at the price of accumulation of local stress inside the octahedron. This type of electron density redistribution is continuous [43], resulting from the competition between $U$, $k_B T$ and elastic energy ($= Y \varepsilon$, where $Y$ is Young’s modulus and $\varepsilon$ is strain) (figure 4). Larger anisotropy of charge density distribution and hence higher EFG from valence electrons can be expected because of orbital ordering (i.e., lift of $t_{2g}$ orbital degeneracy). When the orbital occupation of $d_{z^2}$ is dominant and approaching the critical point of half-filling, the occupation of other two $t_{2g}$ orbitals of $d_{xx} + d_{yy} (\pi^*)$, in which electrons are itinerant becomes nearly empty. We note that the sign of valence EFG is opposite to that of lattice one and the absolute value from valence contribution is less than that from lattice in the R phase (see table 1). Clearly, valence EFG will become larger in absolute value when approaching $T_c$ from R to M₁ phase. In other words, valence EFG will cancel the lattice EFG more and yield a smaller total EFG when approaching the MI transition from R to M₁ phase. The above lines of arguments are in excellent agreement with observed temperature dependency of EFGs, revealing the hidden dynamics of correlation-driven orbital ordering in the R phase when approaching the MI transition. Our EFG results support the proposal that the degenerated V $t_{2g}$ orbitals are gradually lifted and selectively occupied in $d_{z^2}$ upon cooling even in the metallic phase, leaving $\pi^*$ orbitals pretty low even before the MI transition from R to M₁. The ‘bad-metal’ behaviors such as negligible electronic thermal conductivity across MI transition can thus be understood qualitatively. On the other hand, for itinerant electrons occupied in $\pi^*$ bands that transport thermal energy, the density of states at the Fermi level is low within the vicinity of MI transition. On the other hand, for strongly correlated (or localized) electrons occupied in $d_{z^2}$ bands crossing the Fermi level, as illustrated in figures 3(a) and (b), the ratio of the electronic contribution of the thermal conductivity to the electrical conductivity deviates from the Lorentz number and approaches to zero at high temperatures, see [28]. That means the strongly correlated electrons in the ‘bad-metal’ plays an essential role of participating in electrical transport rather than thermal transport. Beyond the above, quadrupole effects in NMR seems to be also ideal for examining charge density distribution in other chalcogenides such as Fe-(Se, Te), Ni-(Se, S) or SrCaRuO [44–46], where orbital selective Mott transition are expected to take place. For instance, an iron based superconductor BaFe₂As₂ with orbital selective Mott transition, another well-known example of multiorbital system, shows similar temperature dependent anomaly in charge density distribution but at much lower temperatures [47].

Recently, attentions have been paid again on other phases of VO₂ such as $M₂$, a semiconducting monoclinic phase with similar lattice structure to $M₁$. It is worth noting here that the pure VO₂ sample used in this work is doping-free and strain-free. Our work is different from the previous ones [20, 32, 33, 48] which measured the incompletely dimerized $M₂$ phase that could be stabilized by either chemical-doping or uniaxial tensile stress according to the phase diagram (see figure 4). Their conclusion on MI mechanism was associated with the $M₂$ phase and $R \leftrightarrow M₂$ transition [20, 32, 33]. Our NMR results are not associated with $M₂$ phase. Firstly, there are

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**Figure 4.** Sketch of phase diagram for VO₂, showing the electronic OSMP state in the R phase. The data points were referred to literatures [8, 33]. It is the kinetic energy ($k_B T$) that breaks the balance with the effective $U$ and drives the formation of orbital selective Mott phase (where the occupation of $d_{z^2}$ becomes dominant). This orbital ordering will yield internal stress inside the octahedron along $c$ axis of the R phase, according to the crystal-field theory. Compressive stress along this axis will then promote the orbital selection and hence decrease the transition temperature.
two crystallographically non-equivalent V sites in the $M_2$ phase while there is only one in the $M_1$ phase. The sharp features of central lines and satellites (see figure 1(c)) can only be assigned to a single $M_1$ phase with only one V site (or two equivalent sites). Secondly, temperature dependent NMR and XRD results of our sample above $T_t$ up to 450 K indicate the only existence of monoclinic $M_1$ below $T_t$ and tetragonal rutile $R$ phase above $T_t$, as shown in figures 2(a), (b) and figures S1 and S4. Significant amount of other phases can be ruled out in our sample. Above all, the revealed dynamic signature of orbital selective Mott transition is for the $R$ phase when approaching the $R \leftrightarrow M_1$ transition.

In summary, atomic structure and electronic properties of pure VO$_2$ were systematically examined by $^{51}$V solid state NMR at various temperatures from 290 to 500 K. The measured EFGs in the metallic phase are gradually enhanced upon heating in the vicinity of the MI transition temperature and then nearly saturate at higher temperatures within the temperatures investigated. In combination with the first principles computations, this unusual EFG evolution in the $R$ phase of VO$_2$ is found to originate from the orbital selective Mott transition, providing a dynamic signature of the orbital selective Mott transition. This NMR study is relevant for better understanding the origin of the MI transition mechanism and ‘bad-metal’ behaviors in VO$_2$.

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