Probing phase transition in VO$_2$ with the novel observation of low-frequency collective spin excitation

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VO$_2$ is well known for its first order, reversible, metal-to-insulator transition (MIT) along with a simultaneous structural phase transition (SPT) from a high-temperature metallic rutile tetragonal (R) to an insulating low-temperature monoclinic (M1) phase via two other insulating metastable phases of monoclinic M2 and triclinic T. At the same time, VO$_2$ gains tremendous attention because of the half-a-century-old controversy over its origin, whether electron-electron correlation or electron-phonon coupling trigger the phase transition. In this regard, V$_{1-x}$Mg$_x$O$_2$ samples were grown in stable phases of VO$_2$ (M1, M2, and T) by controlled doping of Mg. We have observed a new collective mode in the low-frequency Raman spectra of all three insulating M1, M2 and T phases. We identify this mode with the breather (singlet spin excitation) mode about a spin-Pierls dimerized one dimensional spin $\frac{1}{2}$ Heisenberg chain. The measured frequencies of these collective modes are phenomenologically consistent with the superexchange coupling strength between V spin $\frac{1}{2}$ moments in all three phases. The significant deviation of Stokes to anti-Stokes intensity ratio of this low-frequency Raman mode from the usual thermal factor $\exp(h\nu/K_BT)$ for phonons, and the orthogonal dependency of the phonon and spinon vibration in the polarized Raman study confirm its origin as spin excitations. The shift in the frequency of spin-wave and simultaneous increase in the transition temperature in the absence of any structural change confirms that SPT does not prompt MIT in VO$_2$. On the other hand, the presence of spin-wave confirms the perturbation due to spin-Peierls dimerization leading to SPT. Thus, the observation of spin-excitations resulting from 1-D Heisenberg spin-$\frac{1}{2}$ chain can finally resolve the years-long debate in VO$_2$ and can be extended to oxide-based multiferroics, which are useful for various potential device applications.
set of V chains pair along the c₀ axis without being twisted and the V-V separations being 2.53 Å (bonding) and 3.25 Å (anti-bonding) along b₀, ↔ 2c₀ axis; while the V ions in the nearest neighbor V chains do not form pair but twist with respect to the c₀ axis with V-V separation of 2.93 Å (Fig. 1c)¹¹. The triclinic, T phase is reported as dimerized M2 phase Fig. 1d)¹². Along with temperature, application of external electric field¹³, use of hydrostatic pressure¹⁴, radiance¹⁵, and applied deformation¹⁶, initiate phase transition in VO₂. Furthermore, the transition temperature (T) is varied by controlling the density of charge carrier¹⁷, invoking deformation¹⁸, or by doping¹⁹ leading to a considerable change in the optical, electrical, and thermal properties of VO₂. These characteristics make VO₂ an attractive material, namely, windows with heat control²⁰, sensors for hazardous gas²¹, electrical switching device²², and cathode in Li-ion battery²³. Doping of metal (M) in VₓMoO₄ reduces²⁴ the Tₑ values for M = Ta²⁺, Nb²⁺, W⁶⁺, Mo⁶⁺, and increases²⁵ the Tₑ values for M = Cr³⁺, Al¹⁺, Ga³⁺.

As MIT is associated with SPT in this material, the debate remains, whether the electron-phonon coupling or strong electron-electron correlation trigger the phase transition²⁶,²⁷. In the present article, we study the cause of MIT and SPT and the correlation between them in details by our observation of collective spin excitation (spin-wave) for the first time in VO₂. As spin-wave propagates independently from the charge-density waves (spin-charge separation according to Tomonaga-Luttinger liquid theory), the SPT and MIT are understood by separate phenomenological model. We claim that local strain due to Mg doping leads to the transformation of the M1 phase into M2 and T phases in the V₁₋ₓMgₓO₂ system. Moreover, we claim that strong electron-electron correlation drives the MIT (Mott-Hubbard transition) and the V-chains in VO₂ can be considered as one-dimensional (1-D) non-interacting Heisenberg spin ½ chains. The structural phase transition is understood by the observed low-frequency Raman modes originated due to the dimerized 1-D chains resulting from Mott transition at a lower temperature. The experimentally observed Raman modes at low-frequency are compared with the calculated frequency for the singlet breather excitations in spin-Pierls dimerized state. The orthogonal dependency of the phonon and spin excitation, in the polarized Raman study helps in finding the origin of the low-frequency Raman modes as spin singlet breather excitations. Moreover, it is found that the Stokes to anti-Stokes intensity ratio of the low-frequency Raman mode differs considerably from the Boltzmann’s distribution law for bosons confirming it to be originated due to collective spin excitation. The role of doping in shifting the frequency of spin-wave as well as in increasing the transition temperature while maintaining the same structural phase is discussed in details introducing finite-size 1-D Heisenberg spin ½ chain model resolving the years-long debate in the phase transition of VO₂.

Results and Discussions

The x-ray crystallographic studies of the ground free-standing samples with different Mg dopant are shown in Fig. 2a. In sample S1, the diffraction peaks confirm the presence of monoclinic M1 phase of VO₂ (JCPDS # 04-007-1466)²⁷. Whereas the diffraction peaks for sample S2 match with the T phase of VO₂ (JCPDS # 01-071-0289)²⁸. The samples S3 (a–d) are found out as the M2 phase of VO₂ (JCPDS # 00-033-1441)²⁹.

We focused on the diffraction peaks at lower 20 values (Fig. 2b). For sample S1, the diffraction peak at 20 = 13.67° represents the (011) plane corresponding to monoclinic M1 phase (equivalent to (110)ₚ plane) of VO₂. In sample S2, two diffraction peaks observed at 20 = 13.47° and 13.81° may correspond to (−201) and (201) planes of T phase of VO₂. Similarly, for sample S3(a–d) the diffraction peaks equivalent to (−201) and (201) planes of the M2 phase of VO₂ are observed at ~ 20 = 13.38° and 13.84°. The twin peaks in samples S2 and S3(a–d) are equivalent planes of (110)ₚ phase, which is responsible for twin crystalline formation. The T and M2 phases of VO₂ are reported as the strained (tensile strain along the rutile c₀ axis) step for the M1 phase of VO₂. Since the samples were synthesized for different percentage of the Ar flow; there would be a different percentage of Mg dopants present in the samples. The dopant percentage can introduce strain in the sample and helps in stabilizing the T and M2 phases of VO₂. All the samples in S3 series are found out to be stabilized in M2 phase of VO₂, though the splitting of the twin peaks is observed to decrease from sample S3a (∆θ = 0.42°) to S3d (∆θ = 0.35°). A simultaneous decrease in the splitting of the twin peaks implies the increase in strain from sample S3a to S3d.
In order to determine the dopant percentage in the samples, the x-ray photoelectron spectroscopy (XPS) studies were carried out for the samples S1, S2, and S3. The XPS spectra for different elements for sample S1 to S3 with the characteristic electronic transitions are shown in Fig. 3.

For sample S1, V 2p spin-orbit spectrum (Fig. 3a; 2nd panel) can be fitted with two curves with binding energy (BE) values of 516.3 and 523.7 eV, which are assigned as the transition from 2p3/2 and 2p1/2 spin-orbits of V4+ oxidation state, respectively31,32. No trace of Mg was observed in sample S1 (Fig. 3a; 1st and 4th panels). In case of sample S2, Mg 1s and Mg Auger peaks are observed at 1304 and 306.1 eV, respectively33, which are reported to be observed for the Mg ion bonded with O (Fig. 3b; 1st and 4th panels). The V 2p spin–orbit spectrum for sample S2 can be fitted by four peaks with BE values 516.2, 518.2, 523.6, and 524.8 eV (Fig. 3b; 2nd panel). The V 2p1/2 and 2p3/2 peaks, observed at BE values of 516.2 and 523.6 eV, respectively for sample S2, can be assigned to V4+ oxidation state. The peaks, observed at BE value of 518.2 and 524.8 eV, can be assigned to 2p1/2 and 2p3/2 transitions for V5+ oxidation state32. In sample S3a, the peaks are identified at 516.3 and 523.7 eV for 2p1/2 and 2p3/2 transitions of V4+ oxidation state, respectively. Similarly, for V5+ oxidation state, the peaks are identified at 518.2 eV and 524.8 eV as 2p1/2 and 2p3/2 transitions in sample S3 (Fig. 3c; 2nd panel). The spin–orbit spectrum for Mg 1s and Mg Auger peak, in the case of sample S3a, are observed at 1304 and 306 eV (Fig. 3b; 4th panel)33. On the other hand, for all the samples, O1s peak at low BE value (530 eV) is attributed to lattice O, and O1s peak with high BE value (531.5 eV) corresponds to absorbed O species (Fig. 3; 3rd panel)34,35. The atomic percentage (at. %) of Mg, V, and O are calculated from the area under the curves considering appropriate sensitivity factors for each element and are tabulated (Table 1).

For the samples S3(b–d), we observed nearly similar results as that of sample S3a in XPS analysis except for a small increase in at. % of Mg from sample S3a to S3d (not shown in the manuscript). We have performed Laser-induced breakdown spectroscopy (LIBS) to reconfirm the identification of the trace elements present in the samples (Supplementary Fig. S1). In the case of samples S3(a–d), the intensities of Mg lines are found to increase gradually (Fig. S1). The XPS and LIBS studies confirm the presence of Mg in samples S2 and S3(a–d), which may help in stabilizing the T and M2 phase of VO2, respectively, by introducing strain in the system (as discussed in crystallographic structural studies section). The replacement of V4+ (d4) by Mg ion is more likely to produce an adjacent V5+ (d0) sites in the neighboring chains. We have also carried out the x-ray absorption near edge structure (XANES) measurements to find out the oxidation state of the V in the samples (Supplementary Fig. S2). By comparing spectra, we confirm sample S1 is in +4 oxidation state, whereas samples S2 and S3 are in mixed +4 and +5 oxidation states.

The Raman spectra of the samples were collected to obtain additional information about the structural phase of the as-grown samples. The Raman spectra for of S1, S2, and S3 samples collected at 80 K are depicted in Fig. 4a.
Eighteen Raman-active phonon modes are predicted by Group theoretical analysis for all low-temperature phases of VO₂ (for M1: 9A_g + 9B_g, and for M2 and T: 10A_g + 8B_g) at Γ point with different symmetries. However, we observed twelve vibrational modes for sample S1 (Fig. 4a).

Observed Raman modes at 141, 190 (A_g), 225 (A_g), 258 (either A_g or B_g), 307 (A_g/B_g), 335 (A_g), 390 (A_g/B_g), 440 (A_g/B_g), 497 (A_g/B_g), 611 (A_g), 665 (B_g), 823 (B_g) cm⁻¹ in sample S1 (Fig. 4a) conforms with pure M1 phase of VO₂.

| Sample | V⁴⁺ (at. %) | V⁵⁺ (at. %) | O (at. %) | Mg (at. %) | V⁵⁺/V⁴⁺ ratio |
|--------|-------------|-------------|-----------|------------|--------------|
| S1     | 31.66       | 0           | 68.34     | 0          | 0            |
| S2     | 21.42       | 8.19        | 69.57     | 0.81       | 0.38         |
| S3a    | 19.77       | 8.50        | 69.75     | 1.97       | 0.43         |

Table 1. The atomic percentage of the elements and V⁵⁺/V⁴⁺ ratio calculated from XPS spectra.

Figure 3. XPS spectra of the sample (a) S1, (b) S2, and (c) S3a denoted with the electronic transition of different elements. Open and solid symbols represent the data points and fitted curves, respectively.

Figure 4. (a) Raman spectra of the samples S1 to S3 collected at 80 K and (b) Raman spectra for the samples S3(a–d). The inset shows a zoomed view of the Raman spectra for samples S3(a–d) at lower frequencies.
In sample S2, thirteen mode frequencies are observed at 121, 201(A_g), 228(A_g), 267(A_g/B_g), 304(A_g), 343(A_g), 374(A_g/B_g), 413(B_g), 445(A_g/B_g), 503(A_g/B_g), 572(A_g), 636(A_g), and 828(B_g) cm$^{-1}$ (Fig. 4a), which match with the reported data for T phase of VO$_2$. For samples S3(a–d) we observed eleven Raman modes at ~ 50, 203 (A_g), 217(A_g), 229(A_g), 273(A_g/B_g), 297(A_g), 341(A_g), 432(A_g/B_g), 454(A_g/B_g), 651(A_g), and 831(B_g) cm$^{-1}$ (Fig. 4a), which exactly resemble with the reported M2 phase of VO$_2$. Raman spectroscopic studies at 80 K confirm the presence of three different phases of VO$_2$, i.e., M1, T, and M2 in samples S1, S2, and S3(a–d), respectively.

The Raman modes observed at 190 and 225 cm$^{-1}$ for sample S1 are assigned to the vibration of V ions along and perpendicular to the C$_3g$ axis, respectively. These modes are observed at 201 and 228 cm$^{-1}$ for sample S2 and 203 and 229 cm$^{-1}$ for sample S3. In the case of sample S3, one more Raman mode is also found to evolve at 217 cm$^{-1}$. The shift in frequency for the Raman mode ~190 cm$^{-1}$ for S1 → S2 → S3 transition is 13 cm$^{-1}$, whereas the frequency shift for the mode ~225 cm$^{-1}$ is only 4 cm$^{-1}$. The above observations imply that doping of Mg introduces strain along C$_3g$ axis and thereby stabilizing the T and M2 phase of VO$_2$ in samples S2 and S3(a–d), respectively. The Raman mode, observed at 611 cm$^{-1}$ in sample S1, is due to O–O stretching vibration which shifts from 612 to 636 and 651 cm$^{-1}$ in sample S2 and S3(a–d), respectively, indicating the length of V–O bond to be shorter with doping of Mg. In pure VO$_2$, V$^{4+}$ ion is positioned at the center of the octahedron constituting of oxygen atoms, and the principal axes of the octahedron are directed perpendicular to (110)M1 lattice plane. Each V atom shared its four electrons with six neighbor O atoms, and each O atom attracted adjacent electrons supplying by three nearest V atoms. After Mg$^{2+}$ ion occupies the native V$^{4+}$ (+4) place, the adjacent V$^{4+}$ (d$^0$) sites replace V$^{4+}$ (d$^1$) sites in the neighboring chains, as observed from XPS (Fig. 3) and XANES (Fig. S2) studies. As the V$^{4+}$ replaces V$^{4+}$, two apical O$^2-$ of the octahedron move closer to each other resulting reduction in the V–O bond length. The 141 cm$^{-1}$ band in sample S1 is reported as $A_g$ mode in few of the earlier reports. However, it is also reported as an external mode in one recent article, which can be viewed as relative motions of structural units with respect to each other. The mode is observed at 121 cm$^{-1}$ in sample S2 and ~50 cm$^{-1}$ for samples S3(a–d) (denoted by ‘*’ in Fig. 4a). The low-frequency Raman mode for samples S3(a–d) show a continuous blue-shift (inset of Fig. 4b) with an increase in doping while the other Raman peaks do not show any shift in frequency (Fig. 4b) with doping. VO$_2$ is reported to consist of 1-D long Heisenberg chains of V ions in two adjacent sub-lattices. As discussed before, in the M1 phase, the V atoms dimerize forming pairs, and the pairs tilt along the $C_a$ axis in both the sub-lattices. Whereas, in case of the M2 phase, the V chains along the $C_a$ axis pair without twisting in one sub-lattice, while in the other sub-lattice the V chains do not form pair. Instead, they twist with respect to the $C_a$ axis. The dimerized V chains of M2 phase slightly twist in the intermediate (between the M1 and M2 phases) T phase. The electronic structures of VO$_2$ were proposed by Goodenough in 1974. In the electronic band structure of VO$_2$, the O$^{2-}$ orbitals form the valence band with $\pi$ and $\sigma$ bonds and stay 2.5 eV below the Fermi level. In VO$_2$, there is single $d$ electron per V atom and the $d$ level splits into two states: the upper-lying doubly degenerate states $e_g$ states and lower-lying triply degenerate $t_{2g}$ states. The $t_{2g}$ states split again due to the tetragonal crystal field into an $a_{1g}$ state ($d_{xz}$, $d_{yz}$) and an $e_{g}$ ($d_{xy}$, $d_{z^2}$) doublet. In the low-temperature insulating phase of VO$_2$, V atoms dimerize along the $C_a$ direction which makes the $a_{1g}$ bands to be split into lower (bonding, $a_{1g}$) and upper (antibonding, $a_{1g}$) bands. Moreover, the twisting of the V–V pairs away from $C_a$ axis enhances the Vd–Op hybridization leading to a rise in the $e_g$ band above the Fermi level. As a result, a gap of ~0.7 eV opens up and makes the insulating phase stabilized. However, in the high-temperature metallic phase, the Fermi level crosses partially filled $a_{1g}$ and $e_g$ bands and the energy gap collapses. In this approach continuous changes in lattice parameters above transition temperature as well as sudden changes in lattice parameter due to V–V dimerization in the insulating phases is given as an input to calculate electronic structure, suggesting that it is the lattice that drives the MIT transition. In our previous report, we argued a very different scenario for MIT. In the high-temperature metallic phase three bands of different orbital characters overlap. The inter-orbital Coulomb repulsion pushes up the energy levels of the upper two bands, which leads to the transfer of electrons from the upper two bands to the lowest band. The electron transfer process leads to a further level of separation between bands. This process stops when two upper bands become empty, and the lowest band becomes half filled. The changes in lattice parameters above transition temperature are driven by the changes in relative band fillings with temperature. As soon as the lower band becomes half filled, the intra-orbital local Coulomb repulsion (Hubbard-type) takes over and drives a Mott-type MIT. The Mott insulating state is nothing but an assembly of parallel spin ½ antiferromagnetic Heisenberg chain. In 1-D, Heisenberg spin chain is driven to a spin-Pierls dimerized state. In 1D spin ½ Heisenberg system, the Hamiltonian reads as,
There are three kinds of spin excitations: soliton ($S$, spinon), antisoliton ($S'$; anti-spinon), and some breathers ($B_i$), which are the soliton-antisoliton (spinon-antispinon) bound states. The $n$th breather’s mass $E_n$ is related to $E_s$ (mass of soliton) via $E_n = 2E_s \sin[n\pi/(8K-2)]$.

With $n = 1, \ldots, [4/(K-1)]^{45}$. In SU(2)-symmetry, the soliton mass and second breather mass can be evaluated as

$$E_s \sim 1.5n^{2/3}J_1, \quad E_2 = \sqrt{3}Es$$

(Soliton, antisoliton and the first breather form a spin triplet with energy $E_s$. The second breather is a singlet excitation. Raman scattering from 1-D spin $\frac{1}{2}$ chain is theoretically explored by Sato et al.\textsuperscript{44}. It is reported that in case of dimerized chain, Raman intensity due to the triplets gives rise to a continuum background at frequencies $\omega \geq 2E_s$. Spin singlet breather $B_s$ appears as a $\delta$-functional peak at $\omega = E_2$ using form-factor approach (provided $T < fK$).\textsuperscript{46,47} However, in a practical case, a broadening in $\delta$-functional peak is expected as the experiment is carried out at non-zero temperature.

Pouget et al.\textsuperscript{48} reported the values of $J$ for the different phases of VO$_2$ by the nuclear magnetic resonance (NMR) and susceptibility studies. The value of $J$ for the M1, T, and M2 phases of VO$_2$ are found out as ~500 K, ~350 K, and ~320 K, respectively\textsuperscript{48}. The distortion ($\Delta$) dependence of Raman mode due to spin excitations is also reported for CuGeO$_3$, TiOOCr, and others\textsuperscript{49-53}. We have calculated the distortion ($\Delta = \Delta l/l$, where $l$ is the distance between two spins) for the three samples S1(M1), S2(T) and S3(M2) as $\Delta l_1 = 0.07$, $\Delta l_2 = 0.08$, and $\Delta l_3 = 0.12$, respectively. The Raman mode frequencies for the samples in M1 (S1), T (S2), and M2 (S3) phases are calculated using Eq. (4) as $\omega_1 = 152$ cm$^{-1}$, $\omega_2 = 117$ cm$^{-1}$, and $\omega_3 = 66$ cm$^{-1}$, respectively. The calculated and experimentally observed peaks are shown in Fig. 5a.

The little variation of experimental and calculated frequency is expected as the distortion $\Delta$ as well as exchange interaction $J$ depends on doping concentration and temperature. Since the breather mode frequency is proportional to $\Delta l/2l$, where $l$ is the dimerization order parameter, its variation with temperature mimics temperature dependence of order parameter. A background luminescence is observed in the case of sample S3 (Fig. 5a), which may be due to the tilted non-dimerized and randomly dimerized V- chains as reported by Sato et al.\textsuperscript{45}.

To reconfirm the origin of low-frequency Raman modes, we have calculated the intensity ratio of the Stokes to anti-Stokes ($I_s/I_{AS}$) Raman spectra for both the spin-wave and phonon vibration as a function of temperature. The Stokes and anti-Stokes Raman spectra collected at room temperature are shown in Fig. 5b. The presence of spin-wave in both Stokes and anti-Stokes sides close to the Rayleigh line for all the three samples are denoted by an arrow mark (Fig. 5b). The frequency-shift as well as the integrated $I_s/I_{AS}$ ratio for the spinon mode at the lowest frequency and the closest phonon mode originated due to V-V vibration ~200 cm$^{-1}$ (denoted by $*$ in Fig. 5b) are plotted as a function of temperature for all three samples (Fig. 6).

The $I_s/I_{AS}$ ratio is compared with the Boltzmann’s distribution law:

$$I_s/I_{AS} = \frac{v - v_m}{v + v_m} \frac{\hbar v_m}{K_B T}$$

where $v$ is the excitation frequency, $v_m$ is the phonon frequency, $\hbar$ is the Planck’s constant, $K_B$ is the Boltzmann’s constant, and $T$ is the temperature. The calculated values from Eq. (5) and experimentally observed values of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) Typical Raman spectra of all the samples S1 to S3 collected at 80 K and corresponding $\delta$-functional peak at the calculated Raman mode frequency (b) Stokes and anti-Stokes spectra for the samples S1, S2, and S3. The spin-wave and the phonon mode used for calculation of ($I_s/I_{AS}$) ratio are denoted by arrow and star sign, respectively.}
\end{figure}
Figure 6. The frequency-shift with temperature for sample (a) S1, (b) S2, and (c) S3. The observed and calculated Stokes to anti-Stokes (I$_{S}$/I$_{AS}$) ratio with temperature for sample (d) S1, (e) S2, and (f) S3. The solid and empty symbols represent calculated and observed (I$_{S}$/I$_{AS}$) ratio, respectively, with corresponding error values.

$I_{S}/I_{AS}$ ratio for both the spin-wave and the closest phonon mode are tabulated (Table 2). The calculated $I_{S}/I_{AS}$ ratio are plotted in Fig. 6(d–f) as a function of temperature. It is clear from Fig. 6 that though there is a continuous red shift with an increase in temperature (Fig. 6(a–c)) for both the spin-wave and phonon mode; there is a significant mismatch between the observed $I_{S}/I_{AS}$ ratio and the calculated one for the spin-wave. However, $I_{S}/I_{AS}$ ratio for the closest phonon mode ~200 cm$^{-1}$ follows the usual thermal factor of exp($hv/K_{B}T$) following Boltzmann's distribution law.

Whereas, the lowest frequency mode for all the three samples shows a considerable deviation of $I_{S}/I_{AS}$ ratio from the usual thermal factor exp($hv/K_{B}T$) for phonons and thus confirming the mode to be originated from spin excitation. We also performed the polarized Raman scattering on three single crystal microrods of the sample S1, S2, and S3. The FESEM image of the single microrod used for polarized Raman measurements along with randomly oriented microrods is shown in Supplementary Fig. S3a. The XRD data collected from a single microrod is also provided to confirm the orientation (Supplementary Fig. S3b). The incident excitation wave is considered along the Z direction, whereas, the growth direction of the microrods (C$_{B}$ axis) is chosen along the X-axis. According to Porto notation, in the parallel (Z(XX)Z) and perpendicular (Z(YX)Z) polarization configurations, the first and fourth letters represent the direction of the propagation of the incident (K$_{I}$) and scattered light (K$_{s}$) respectively, whereas the second and third letters inside the parenthesis represents the direction of the electric field of the incident (E$_{I}$) and the scattered light (E$_{s}$), respectively. Figure 7 shows the Raman spectra with both parallel (XX) and cross (YX) polarization configurations for the three samples. In case of parallel (XX) polarization, the intensity of the Raman mode arising due to V-V vibration parallel to C$_{B}$ axis (denoted as $\omega_{1}$ in Fig. 7) is more than that of the mode arising due to perpendicular to the C$_{B}$ axis (denoted as $\omega_{2}$ in Fig. 7). Whereas, the intensity flips in case of cross (YX) polarization condition. The above observations imply the microrods are aligned along the X-axis, i.e., along the C$_{B}$ direction$^{42}$. However, the intensity of the low-frequency Raman-modes (denoted as $\omega_{1}$ in Fig. 7) for all the three samples is observed to be high in case of cross-polarization condition (⊥ to C$_{B}$ axis), and falls rapidly for parallel polarization (∥ to C$_{B}$ axis). As the spin chains (V-ions) are aligned along the C$_{B}$ direction, the spinon vibration is expected to be produced parallel to the X-axis.

In an electromagnetic (EM) wave, the electric field vector (E) and magnetic field vector (B) propagates orthogonally to each other. As the excitation EM wave was incident along Z direction; while the E field propagates along the Y-axis, the B field propagates along X-axis and vice-versa. The collective spins get excited by the magnetic part of the electro-magnetic wave; therefore the maximum intensity is expected for the cross-polarization (YX) condition where E and B field propagates along the Y-axis and X-axis, respectively. Thus the orthogonal dependency of the phonon and spin excitation in the polarized Raman study reconfirms the origin of the low-frequency Raman modes as spin excitation.

We have carried out the temperature-dependent Raman spectroscopic analysis to study the phase transition of the V$_{1-x}$Mg$_{x}$O$_{2}$ samples. The temperature dependent Raman data for all the three samples S1, S2 and S3b are shown in Supplementary Fig. S4. Above the transition temperature, VO$_{2}$ became metallic in nature and we were unable to observe any Raman mode due to the screening effect. The temperature, at which sudden disappearance of all the Raman modes occurs, is considered as the transition temperature. We have also carried out temperature...
driven resistivity measurements (Supplementary Fig. S5) to reconfirm the transition temperatures. The resistance is observed to drop ~3 to 4 orders. Figure 8a shows typical temperature-dependent Raman spectra for sample S1. All the Raman modes disappear at 340 K for S1, 345 K for S2, 348 K for S3a, 350 K for S3b, 355 K for S3c, 358 K

Table 2. Comparison between calculated and experimentally observed \(I_s/I_{\text{AS}}\) ratio for the three samples.

| Sample | \(I_s/I_{\text{AS}}\) ratio | \(\omega_1\) (cm\(^{-1}\)) | \(\omega_2\) (cm\(^{-1}\)) |
|--------|---------------------|-----------------|-----------------|
| S1     | 100 ± 0.1          | 5.88 ± 0.2      | 8.12 ± 0.1      |
| S2     | 127.8 ± 0.1       | 3.41 ± 0.2      | 5.95 ± 0.1      |
| S3     | 63.0 ± 0.1        | 1.02 ± 0.05     | 1.40 ± 0.1      |

Figure 7. (a) Raman spectra at parallel (XX) and cross (YX) polarization condition for the three samples S1, S2, and S3.
was carried out at 1100 K for 3 h. The concentration of the Mg dopant was controlled by changing the flow rate of the flow of 20 sccm Ar, keeping other growth conditions same except the Mg powder. The XPS (VG ESCALAB (samples, S2, S3a, S3b, S3c, and S3d, respectively) in the presence of Mg powder. Sample S1 was prepared with the carrier gas. The synthesis was carried with the optimized flow of Ar (99.9%), e.g., 20, 40, 60, 80, and 100 sccm.

It is argued that strong electronic correlation drives the MIT and in turn, the Mott type MIT prompts a structural transition of spin-Peierls originating at a lower temperature. The insulating phases of VO2 can be considered as infinitely long 1-D dimerized Heisenberg spin ½ chains. The newly observed collective modes in the low-frequency Raman spectra of all three insulating M1, M2 and T phases are explained by the breather (singlet spin excitation) mode about a spin-Peierls dimerized 1-D spin ½ Heisenberg chain. The orthogonal dependence of the phonon and the singlet breathers in the polarized Raman study help in finding the origin of the low-frequency Raman modes as spin excitations. Moreover, it is found that the Stokes to anti-Stokes intensity ratio of the low-frequency Raman mode differs considerably from the Boltzmann’s distribution law confirming that SPT does not have any role in MIT. Spin-Peierls dimerized state comes from, spin-phonon coupling in Heisenberg spin ½ antiferromagnetic chain. Heisenberg spin chain presupposes a Mott transition in a half filled band. It is to be emphasized that this spin-mode is also observed in M2 phase (insulating) where only half the V-V chains are dimerized, and the other chains are not dimerized. The fact that the un-dimerized chains are not electrically conducting suggests the metal-insulator transition is a correlation driven Mott-transition which prompts a simultaneous SPT with reduction of temperature.

Conclusions

V1−xMgxO2 samples were grown in stable phases of VO2 (M1, M2, and T) by controlled doping of Mg. Random local strain due to Mg doping is found out as the main cause for the evolution of the M1 phase into T and M2 phases. The unrelaxed local strain in the metastable phases, however, does not bring metallicity in the system. It is argued that strong electronic correlation drives the MIT and in turn, the Mott type MIT prompts a structural transition of spin-Peierls originating at a lower temperature. The insulating phases of VO2, can be considered as infinitely long 1-D dimerized Heisenberg spin ½ chains. The newly observed collective modes in the low-frequency Raman spectra of all three insulating M1, M2 and T phases are explained by the breather (singlet spin excitation) mode about a spin-Peierls dimerized 1-D spin ½ Heisenberg chain. The orthogonal dependence of the phonon and the singlet breathers in the polarized Raman study help in finding the origin of the low-frequency Raman modes as spin excitations. Moreover, it is found that the Stokes to anti-Stokes intensity ratio of the low-frequency Raman mode differs considerably from the Boltzmann’s distribution law confirming its origin from spin excitations. The fact that the M2 phase is insulating even though half the V-V chains are not dimerized conclusively proves that MIT is a Mott-Hubbard transition. The V vacancy, invoked by Mg doping, creates d0 sites (V5+) at the nearest neighbors and introduces finite-size scaling effect by reducing the effective length of the Heisenberg spin ½ chains. Thus, the role of doping in increasing the transition temperature is understood by introducing finite-size 1-D Heisenberg spin ½ chain model. As spin-wave propagates independently from the charge-density waves, the shift in the frequency of spin-wave with doping in the absence of any structural phase transition confirms that the SPT does not prompt the MIT and resolves the years-long debate in the phase transition of VO2.

Methods

V1−xMgxO2 microrods were grown by vapor transport process on high pure (99.99%) alumina boat using mixed VO2 powder and Mg powder (Sigma-Aldrich, 99%) as the source and Ar (99.9%) as the carrier gas. The synthesis was carried out at 1100 K for 3h. The concentration of the Mg dopant was controlled by changing the flow rate of the carrier gas. The synthesis was carried with the optimized flow of Ar (99.9%), e.g., 20, 40, 60, 80, and 100 sccm (samples, S2, S3a, S3b, S3c, and S3d, respectively) in the presence of Mg powder. Sample S1 was prepared with the flow of 20 sccm Ar, keeping other growth conditions same except the Mg powder. The XPS (VG ESCALAB
MK200X) analysis was performed for the elemental analysis of the VO2 samples synthesized at different growth conditions using an x-ray source of Al-Kα (1486.6 eV) with beam diameter around 3 mm. The C 1s reference peak was used for calculating the BE values. A mixture of Gaussian–Lorentzian line shapes was used for fitting the spectra after applying Shirley type background correction. The structural properties of the as-grown samples were studied using synchrotron x-ray diffraction with a wavelength of 0.76089 Å using Si(111) channel cut monochromator. A MAR345 image plate area detector was used to collect the diffraction data. The vibrational modes of the synthesized samples were studied using a micro-Raman spectrometer (inVia, Renishaw, UK) in the backscattering configuration. An Ar+ Laser (514.5 nm) was used as the excitation source along with a thermoelectrically cooled CCD camera as the detector. To carry out the polarized Raman studies, polarizer and half-wave plates were placed in the incident ray path to attain the desired configurations. The low-frequency Raman scattering measurements for the Stokes and anti-Stokes spectra were carried out using a micro-Raman spectrometer (Witec Alpha 300RA) equipped with the Bragg grating (Rayshield™). Nd-YAG laser source (532 nm) was used to excite the samples. The temperature-dependent Raman spectra were collected using a temperature-controlled stage (Linkam; THMS600) under long working distance 50X objective with a numerical aperture (N.A.) of 0.45.

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Author contributions

R.B. planned the work, executed experiments, analyzed data, and wrote the manuscript. V.S. carried out the XRD experiments. S.K.S. carried out the low frequency Raman experiments. S.B. performed the XPS experiments. M.S. and S.D. contributed in careful evaluation of manuscript and understanding. All authors discussed the results, commented on the manuscript and gave approval to the final version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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