Effect of disorder on the metal-insulator transition of vanadium oxides: Local versus global effects

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In this paper we investigate the effect of disorder on highly correlated electron systems, which exhibit metal-insulator transition (MIT) and structural-phase transition (SPT). We show that the effect of ion irradiation is strikingly different between V_2O_3 and VO_2, two otherwise similar materials. Upon irradiation, the MIT and SPT temperatures in V_2O_3 decrease drastically at low absolute dosages, much lower than for VO_2. At a low threshold dose, the insulating state of V_2O_3 drastically collapses into a metallic state. Contrary to this, irradiation of VO_2 leads to a much milder reduction of the MIT and SPT temperatures and to a weak, gradual decrease of the insulating state resistivity—not suppressed even at one order of magnitude higher doses than the V_2O_3 threshold. These major differences imply that the phase transition in V_2O_3 arises from global (rather than local as in VO_2) physical mechanisms that are extremely sensitive to disorder. This shows that the MIT and SPT may have substantially different physical origins in different systems, with the consequent major implications for theoretical descriptions of the MIT in highly correlated electron systems.

Strong electron correlations in materials [1,2] cause some of the most spectacular properties of solids such as superconductivity [3], colossal magnetoresistance [4], and metal-insulator transition (MIT) observed in a plethora of transition metal oxides [5]. Despite their relevance, electronic correlations are often poorly understood. The MIT in transition metal oxides is experimentally characterized by a several orders of magnitude resistivity change, a coincidental structural phase transition, and sometimes magnetic phase transitions. These effects, which may lead to revolutionary applications, have posed a long-standing theoretical challenge (Ref. [6] and references therein). Even the most basic issue, whether the microscopic mechanism that produces the MIT is due to short-range ("local") or long-range ("global") correlations, is under debate. An example of global correlations is the appearance of long-range order (magnetic or structural), which doubles the unit cell. This in turn opens up a gap at the Fermi surface of a half-filled metallic band [7], giving rise to the MIT. The more local correlations giving rise to the MIT arise from the competition between the kinetic energy, which favors electron transport, and the Pauli exclusion principle, which inhibits electron hopping [8]. Small amounts of disorder may affect differently these two types of electronic mechanisms, i.e., they may disrupt long-range electronic correlations but have only a minor effect on the local ones. An important and crucial issue is therefore whether disorder has the same effect on the MIT of different transition metal oxides. This would clarify whether global or local correlations are operational.

To address this crucial issue we have studied the effects of irradiation-induced disorder in two very similar oxides,

VO_2 and V_2O_3. Both exhibit very similar, large—several orders of magnitude—first order MIT, coincidental with a structural phase transition (SPT) at a stoichiometry-dependent temperature T_C [8]. Disorder induced by ion irradiation has been used in the past in order to fine control the amount of damage produced [9]. Surprisingly, we found that disorder induced by O^+ ion irradiation has qualitatively and quantitatively very different effects in V_2O_3 and VO_2. While VO_2 is robust, V_2O_3 degrades substantially with two orders of magnitude smaller irradiation doses. The insulating state resistivity of V_2O_3 remains constant initially, while the T_C starts decreasing at the smallest doses. Above a small threshold dose, the insulating state abruptly collapses and the resistivity decreases by six orders of magnitude. Contrary to this, even with two orders of magnitude higher irradiation doses, the VO_2 T_C drops only slightly. Moreover, the insulating state is preserved with only a gradual reduction of its resistivity. This shows that the SPT and MIT are much more sensitive to disorder in V_2O_3 than in VO_2, which implies that global effects play a more important role in V_2O_3 than in VO_2. These observations have important implications for theories being developed to understand the MIT [10,11], especially regarding the role of long range versus local correlations. These results unambiguously illustrate the unexpected, strikingly different nature of the electronic correlations in two otherwise very similar materials.

V_2O_3 and VO_2 thin films were deposited on *R*-plane sapphire substrates by rf magnetron sputtering [12]. More details on sample preparation are elsewhere [13–15]. In as-grown V_2O_3 [Fig. 1(a)] the out-of-plane, rhombohedral (012) x-ray diffraction (XRD) peak shifts from $2\theta = 24.30°$ above the SPT (300 K) to the monoclinic (011) [16] $2\theta = 24.05°$ below it (100 K) [17]. For VO_2 [Fig. 1(b)], the shift is from $2\theta = 37.26°$ at 360 K to $2\theta = 37.10°$ at 300 K, which

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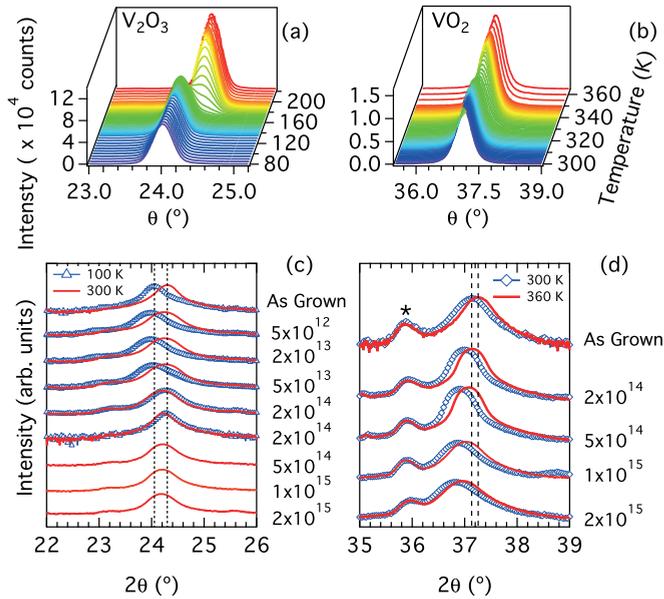†ischuller@ucsd.edu

FIG. 1. (Color online) (a) and (b) XRD at different temperatures across the SPT for V_2O_3 and VO_2, respectively. (c) and (d) XRD at two different temperatures and different doses as indicated (dose in units of ion/cm^2). The curves in (c) and (d) are shifted along the vertical axes for clarity. Upper curves on both panels correspond to nonirradiated reference samples measured under the same experimental conditions. Peaks marked with (*) belong to the sample holder.

corresponds to the tetragonal (101) to monoclinic (200) SPT [2]. During the SPT (around ~170 K for V_2O_3 and ~328 K for VO_2) the diffracted intensity is gradually redistributed between the two diffraction angles corresponding to the different lattice parameters of the two structural phases [Figs. 1(a) and 1(b)]. The virgin SPT and MIT temperatures can vary by ±5 K from sample to sample, which is substantially smaller than the effects observed due to O$^+$ irradiation.

Temperature dependent electrical transport was performed in all samples. As-grown V_2O_3 shows a six orders of magnitude change in resistivity at T_C ~ 165 K [black curves in Figs. 2(a)–2(d)]. As-grown VO_2 shows a four orders of magnitude change in resistivity at T_C ~ 348 K [black curves in Figs. 2(e) and 2(f)] [12].

Following the initial characterizations, each of the V_2O_3 and VO_2 films was irradiated with O$^+$ ions at doses ranging between 5×10^{12} and 2×10^{15} ions/cm^2, at a constant 110 keV energy. A "low" flux of ~1.5×10^{12} ions s^{-1} cm^{-2} was used to avoid sample heating during irradiation. SRIM simulations [18] of the ion damage in both materials were performed, assuming the same 30 keV threshold displacement energy for all atomic species. The simulations show that most of the oxygen ions traverse the thin film and reach the substrate: at most 10% of the ions are implanted in the vanadium oxide. Even for the highest dose 2×10^{15} ions/cm^2, the expected oxygen content increase due to implantation is only ~0.1%, which can be neglected. The evolution of the XRD and of the metallic-state resistivity with increasing irradiation dose [see discussion below Figs. 1(c), 1(d), and 3(c)] suggest that, both in VO_2 and V_2O_3, the irradiation damage produces
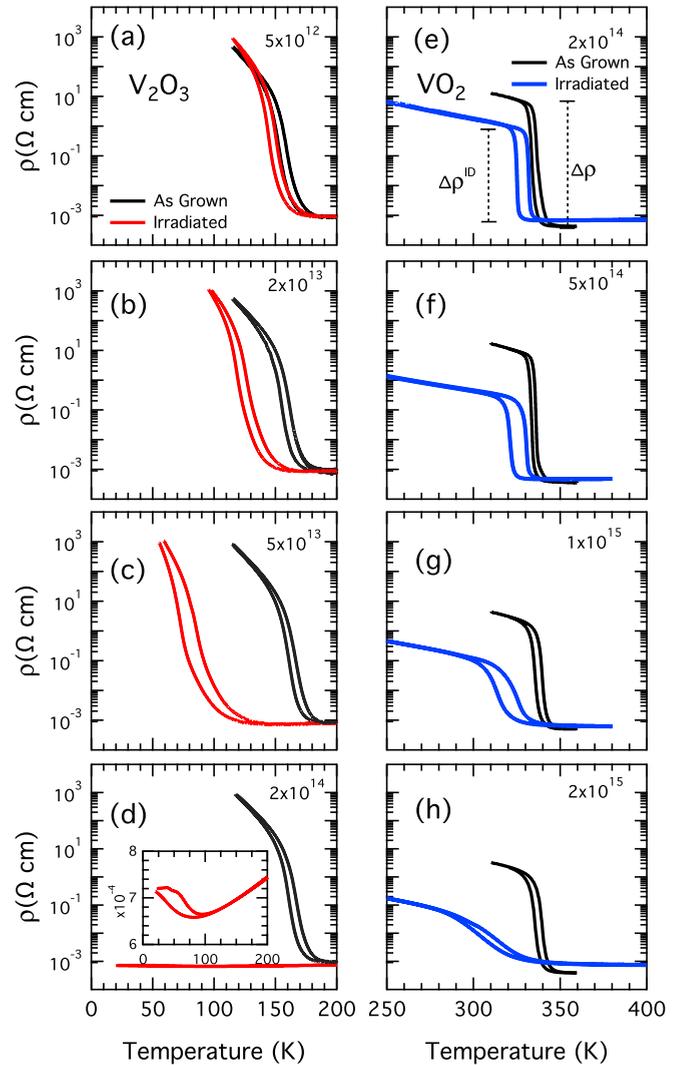

FIG. 2. (Color online) Resistivity as a function of temperature for (a)–(d) V_2O_3 and (e)–(h) VO_2 as-grown films (black solid lines) and after oxygen irradiation (red solid lines for V_2O_3 and blue solid lines for VO_2). Note the different doses used as indicated inside the plot. The definition of the resistivity changes $\Delta\rho$ and $\Delta\rho^{ID}$ (see text) is indicated in (e). Inset on (d) depicts the post-irradiated resistivity in linear scale.

a nonsaturating accumulation of subnanometric clusters or quasipoint defects [12].

The very same samples were investigated after ion irradiation using quantitative structural and transport measurements as described above. Figures 1(c) and 1(d), respectively, show a series of $\theta-2\theta$ XRD diffraction data for V_2O_3 and VO_2 films irradiated with different doses. The XRD spectra of as-grown samples are included for comparison. For each dose, the high-temperature XRD above the SPT (red line) is compared to the low-temperature one below the SPT (blue symbols).

The first remarkable observation is that both materials preserve their high-temperature crystal structure under irradiation, as indicated by the absence of a significant change in the XRD [red line, Figs. 1(c) and 1(d)]. After irradiation a shift in 2θ is observed at room temperature which reaches 0.10° for V_2O_3 and $\Delta2\theta \sim 0.23°$ for VO_2. These shifts
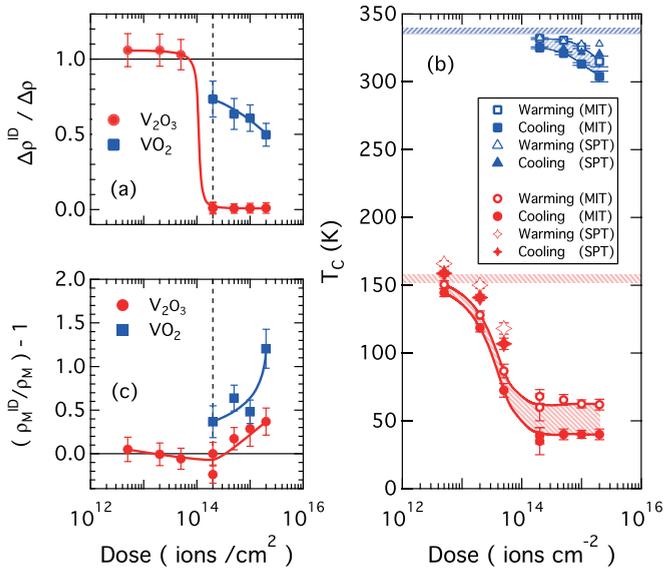
FIG. 3. (Color online) (a) Relative change of the resistivity calculated as $\Delta\rho^{\mathrm{ID}}/\Delta\rho$ for V_2O_3 (circle) and VO_2 (square). The dashed line marks the 2.0×10^{14} ions/cm^2 dose threshold. (b) Transition temperature obtained from curves in Fig. 2 after irradiation, for VO_2 (upper) and V_2O_3 (lower). Values from the cooling and heating branches are presented and the hysteretic region is indicated. The solid lines are guides to the eye. (c) Metallic state resistivity ρ_M^{ID} as a function of the irradiation dose for VO_2 and V_2O_3, normalized to the resistivity prior to irradiation ρ_M.

are similar to differences in 2θ observed among different samples and therefore considered to be insignificant. The diffraction peak width is unaffected by the irradiation and in-plane measurements (not shown) confirm that all crystal symmetries are preserved. No signs of amorphization appeared in the XRD spectra after irradiation. All of the above is a clear indication that, for both materials, the O^+ irradiation does not induce major structural changes even at the highest doses, which suggests that the ion damage creates point defects and/or subnanometric defect clusters [12].

Figure 1(c) shows that the V_2O_3 SPT is observable only below 2×10^{14} ions/cm^2: above this dose the structure remains in the rhombohedral symmetry [19] at all temperatures. Contrary to this, for VO_2 the SPT is observed for all doses, even at the highest 2×10^{15} ions/cm^2 [Fig. 1(d)]. The diffraction data show that the SPT hysteresis widens with increasing dose. No trace of residual insulating (metallic) phases are observed at temperatures well below (above) the phase transition, indicating that the SPT and the reduction in transition temperature is homogeneous across the sample.

The effect of irradiation on the transport properties of V_2O_3 [Figs. 2(a)–2(d)] and VO_2 [Figs. 2(e) and 2(f)] is drastically different between the two materials.

For V_2O_3, T_C is markedly reduced with increasing dose [red curves in Figs. 2(a)–2(c)]. A clear shift of the T_C is found even for the lowest dose 5×10^{12} ions/cm^2 [Fig. 2(a)]. On the other hand, the resistivity change at the MIT essentially remains unchanged with increasing dose until a 2×10^{14} ions/cm^2 threshold is reached. Then a drastic (six orders of magnitude) collapse of the resistivity takes place [see Fig. 2(d)] and only a

small transition ($\sim 10^{-4}\ \Omega$ cm) remains below 60 K [see inset Fig. 2(d)].

VO_2 shows a much milder decrease in T_C with increasing dose [blue curves in Figs. 2(e)–2(h)] similarly to the SPT [Fig. 1(d)]. Only a small (a few Kelvin) T_C decrease occurs at around 100 times higher doses than for V_2O_3. On the other hand, the MIT is not suppressed even for the highest doses: a two orders of magnitude MIT remains at 2×10^{15} ions/cm^2.

A quantitative comparison between the irradiation effects on V_2O_3 and VO_2 is shown in Fig. 3. To characterize the irradiation effect on the resistivity change at the MIT, we define the "MIT magnitude" $\Delta\rho \equiv \log(\rho_I/\rho_M)$, where the high-temperature (metallic-state) ρ_M and low-temperature (insulating-state) ρ_I resistivities are taken at the temperatures at which the loop closes. Figure 3(a) shows $\Delta\rho^{\mathrm{ID}}/\Delta\rho$ for both V_2O_3 and VO_2, with $\Delta\rho$ and $\Delta\rho^{\mathrm{ID}}$ the MIT magnitude before and after irradiation damage (ID). Strikingly, the $\Delta\rho^{\mathrm{ID}}/\Delta\rho$ decrease for V_2O_3 (circles) is sharp and occurs at a well-defined threshold dose, whereas VO_2 (squares) shows a much more gradual decrease. Furthermore, at the doses at which the MIT is fully suppressed for V_2O_3, the MIT magnitude decreases by only 20%–50% in VO_2.

The irradiation effects on the MIT and SPT transition temperature are shown in Fig. 3(b). The horizontal shaded regions indicate the transition temperatures of the as-grown samples. For V_2O_3 a drastic reduction of the MIT temperature (10 K) is found even at the lowest dose and for 5×10^{13} ions/cm^2 the reduction reaches almost 70 K. This is in stark contrast with the much milder effects observed in VO_2, for which the reduction is only of 5 K at 2×10^{14} ions/cm^2 and 16 K for the highest dose 2×10^{15} ions/cm^2.

The relative change in the metallic-phase resistivity upon irradiation, $\rho_M^{\mathrm{ID}}/\rho_M$, is qualitatively similar in both oxides [Fig. 3(c)]. At low doses the resistivity is essentially constant, and a gradual increase is observed above $\sim 10^{14}$ ions/cm^2 for both materials. This is expected if the increasing dose leads to a proportionally higher concentration of defects—either point defects and/or very small subnanometric defects clusters—and thus to a shorter electronic mean free path. This implies that the defect creation does not saturate in the high-dose range, in agreement with earlier experiments in similar systems [19,20]. The resistivity increase is slightly higher in VO_2 (squares) than in V_2O_3 (circles), which suggests a higher defect density in the former than in the latter. This is in stark contrast with the fact that the irradiation effects on the MIT and SPT are considerably stronger in V_2O_3 than in VO_2.

Furthermore, we have ruled out the effect of charge doping by comparing the expected increase of oxygen content from SRIM simulations (around 0.1% approximately for the highest dose) with existent literature values. For instance, in order to change the T_C value by 10 K, the chemical substitution or the increase of the oxygen content has to be around 1% for both VO_2 [7,21] and V_2O_3 [22–24]. This is far from the 0.1% we obtained from SRIM simulations and suggests that the irradiation damage does not produce significant chemical doping but a nonsaturating accumulation of subnanometric clusters or quasipoint defects [12].

In summary, while the XRD and electrical transport studies show that O^+ irradiation produces only minor structural changes at room temperature and an increase in the

metallic-state resistivity—both for VO_2 and V_2O_3—the effects on the MIT and SPT are quite striking and very different between the two materials:

(1) VO_2 is much less affected by irradiation than V_2O_3. The doses needed to get an observable effect on the VO_2 MIT and SPT are a factor of ~ 100 larger than for V_2O_3.

(2) In V_2O_3 the T_C starts dropping from the minimal dose, whereas in VO_2 T_C remains more or less constant in comparison, even for higher absolute doses.

(3) In V_2O_3 the resistivity change at the MIT is robust up to a threshold where a drastic drop occurs. Contrarily, in VO_2 the resistivity gradually decreases and the MIT is not suppressed even for 100 times higher doses.

All of the above leads to an inescapable, interesting, qualitative conclusion: the MIT and SPT in V_2O_3 are much more sensitive to disorder than in VO_2. This conclusion clearly should play a major role in the theoretical understanding of the MIT in these materials, especially considering that disorder is always present and unavoidable in them.

Several possible theoretical explanations have been advanced for the MIT in transition metal oxides, vanadium oxides in particular. In general, it is not clear whether the MIT is caused by the SPT or whether strong correlations drive both transitions [25,26]. Many theories rely on the opening of a collective gap in the half-filled metallic conduction band due to the doubling of the unit cell. This can be caused by global effects, such as structural distortions ("Peierls") due to the formation of V-V dimers in VO_2 [6], or antiferromagnetic order ("Slater") for instance suggested in V_2O_3 [27]. A more local description relies on the Hubbard Hamiltonian, such as expected for a "Mott-Hubbard" insulator [8]. In the latter model the MIT arises from the competition between the kinetic energy, which favors electron transport, and the Pauli exclusion principle, which inhibits electron hopping. These types of local effects are supported for instance by NMR and EPR experiments in VO_2 with Cr doping [28] or uniaxial pressure [29]. Based on a series of Ti and Cr doping experiments, it was also claimed that pure V_2O_3 (without doping) becomes insulating because of a Mott transition [30,31]. If the same mechanism drives the MIT in VO_2 and V_2O_3, the effect of disorder should be the same in both materials. However, the major experimental differences observed here between these two otherwise similar oxides imply that in each of them different (or additional) mechanisms must be playing a crucial role. It is indeed possible that several mechanisms act together,

as it is presumably the case for VO_2, where dimer formation produces a Peierls transition which may at the same time "assist" the Mott mechanism by reducing the electron kinetic energy [32].

The large differences in the sensitivity of the electrical transport to irradiation damage show that quite similar systems may exhibit very different mechanisms for the development of the MIT. Particularly the insensitivity to irradiation damage of the MIT in VO_2 seems to arise from a much more local origin than in V_2O_3. Therefore, the insulating phase of VO_2 has much more Mott-Hubbard character than V_2O_3. The experimental results described above are indeed in agreement with these recent theoretical calculations, which have claimed that the Mott transition assisted by the Peierls instability should be insensitive to the presence of disorder [32]. On the other hand, the extreme sensitivity of V_2O_3 to disorder suggests that in this material a long-range global mechanism—for instance the Slater transition associated to antiferromagnetic order—plays a dominant role.

In summary, a systematic structural and transport study comparing the effect of O^+ irradiation shows that the insulating state and the MIT of VO_2 are much more robust and less susceptible to disorder than for V_2O_3. Structural measurements, on the other hand, are insensitive to irradiation with O^+ ions, thus indicating that no major structural changes or formation of secondary phases occur. The striking and qualitatively different responses to O^+ irradiation in the transport show that the formation of the MIT and SPT in VO_2 are dominated by local properties, whereas in V_2O_3 global effects play a more important role.

[1] E. Morosan, D. Natelson, A. H. Nevidomskyy, and Q. Si, Adv. Mater. **24**, 4896 (2012).

[2] F. J. Wong, S.-H. Baek, R. V. Chopdekar, V. V. Mehta, H.-W. Jang, C.-B. Eom, and Y. Suzuki, Phys. Rev. B **81**, 161101 (2010).

[3] D. N. Basov, R. D. Averitt, D. van der Marel, M. Dressel, and K. Haule, Rev. Mod. Phys **83**, 471 (2011).

[4] E. Dagotto and Y. Tokura, MRS Bull. **33**, 1037 (2008).

[5] E. Abrahams and G. Kotliar, Science **274**, 1853 (1996).

[6] Z. Yang, C. Ko, and S. Ramanathan, Annu. Rev. Mater. Res. **41**, 337 (2011).

[7] J. B. Goodenough, J. Solid State Chem. **3**, 490 (1971).

[8] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).

[9] M. Nastasi and J. W. Mayer, Mater. Sci. Eng. R **12**, 1 (1994); G. S. Was, *Fundamentals of Radiation Materials Science—Metals and Alloys* (Springer, Berlin, 2007); M. Sirena, A. Zimmers, N. Haberkorn, E. E. Kaul, L. B. Steren, J. Lesueur, T. Wolf, Y. Le Gall, J.-J. Grob, and G. Faini, Phys. Rev. B **81**, 134439 (2010); J. Trastoy, M. Malnou, C. Ulysse, R. Bernard, N. Bergeal, G. Faini, J. Lesueur, J. Briatico, and J. E. Villegas, Nat. Nanotechnol. **9**, 710 (2014).

[10] P. Stoliar, L. Cario, E. Janod, B. Corraze, C. Guillot-Deudon, S. Salmon-Bourmand, V. Guiot, J. Tranchant, and M. Rozenberg, Adv. Mater. **25**, 3222 (2013).

[11] V. Guiot, L. Cario, E. Janod, B. Corraze, V. Ta Phuoc, M. Rozenberg, P. Stoliar, T. Cren, and D. Roditchev, Nat. Commun. **4**, 1722 (2013).

[12] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.91.205123 for details on the sample preparation and irradiation damage procedures.

[13] A. Sharoni, J. G. Ramírez, and I. K. Schuller, Phys. Rev. Lett. **101**, 026404 (2008).

[14] J. G. Ramirez, A. Sharoni, Y. Dubi, M. E. Gómez, and I. K. Schuller, Phys. Rev. B **79**, 235110 (2009).

[15] M. K. Stewart, D. Brownstead, S. Wang, K. G. West, J. G. Ramirez, M. M. Qazilbash, N. B. Perkins, I. K. Schuller, and D. N. Basov, Phys. Rev. B **85**, 205113 (2012).

[16] P. D. Dernier and M. Marezio, Phys. Rev. B **2**, 3771 (1970).

[17] Variations of $\pm 0.1°$ of the absolute 2θ values are observed for V_2O_3 and VO_2 between different samples. This is connected to a natural spread in sample morphology and slight deviations in the instrumental alignment and does not affect the relative shift in 2θ due to the SPT and the MIT.

[18] L. Thomé, S. Moll, A. Debelle, F. Garrido, G. Sattonnay, and J. Jagielski, Adv. Mater. Sci. Eng. **2012**, 1 (2012).

[19] A small shift towards higher 2θ values is observed with decreasing temperatures due to lattice thermal contraction. This shift is opposite to the difference expected from the phase transition.

[20] A. Debelle, A. Boulle, F. Rakotovao, J. Moeyaert, C. Bachelet, F. Garrido, and L. Thomé, J. Phys. D: Appl. Phys. **46**, 045309 (2012).

[21] N. R. Mlyuka, G. A. Niklasson, and C. G. Granqvist, Appl. Phys. Lett. **95**, 171909 (2009).

[22] D. McWhan, J. Remeika, T. Rice, W. Brinkman, J. Maita, and A. Menth, Phys. Rev. Lett. **27**, 941 (1971).

[23] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice, Phys. Rev. B **7**, 1920 (1973).

[24] W. Bao, C. Broholm, S. A. Carter, T. F. Rosenbaum, G. Aeppli, S. F. Trevino, P. Metcalf, J. M. Honig, and J. Spalek, Phys. Rev. Lett. **71**, 766 (1993).

[25] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Phys. Rev. Lett. **72**, 3389 (1994).

[26] T. M. Rice, H. Launois, and J. P. Pouget, Phys. Rev. Lett. **73**, 3042 (1994).

[27] J. C. Slater, Phys. Rev. **82**, 538 (1951).

[28] J. P. Pouget, H. Launois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, and P. Hagenmuller, Phys. Rev. B **10**, 1801 (1974).

[29] J. P. Pouget, H. Launois, J. P. Dhaenens, P. Merenda, and T. M. Rice, Phys. Rev. Lett. **35**, 873 (1975).

[30] S. A. Carter, J. Yang, T. F. Rosenbaum, J. Spalek, and J. M. Honig, Phys. Rev. B **43**, 607 (1991).

[31] J. Spalek, A. Datta, and J. M. Honig, Phys. Rev. Lett. **59**, 728 (1987).

[32] C. Weber, D. D. O'Regan, N. D. M. Hine, M. C. Payne, G. Kotliar, and P. B. Littlewood, Phys. Rev. Lett. **108**, 256402 (2012).