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R. V. Yusupov, Dragan Mihailovic, Claire Colin, G.R. Blake, Thomas T. M. Palstra. Critical phenomena and femtosecond ordering dynamics associated with electronic and spin-ordered phases in YVO 3 and GdVO 3. Physical Review B: Condensed Matter and Materials Physics (1998-2015), 2010, 81, pp.075103. 10.1103/PhysRevB.81.075103 . hal-01002231

HAL Id: hal-01002231

https://hal.science/hal-01002231v1

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Published in:
Physical Review. B: Condensed Matter and Materials Physics

DOI:
10.1103/PhysRevB.81.075103

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Yusupov, R. V., Mihailovic, D., Colin, C. V., Blake, G. R., & Palstra, T. T. M. (2010). Critical phenomena and femtosecond ordering dynamics associated with electronic and spin-ordered phases in YVO3 and GdVO3. *Physical Review. B: Condensed Matter and Materials Physics*, *81*(7), 075103-1-075103-6. [075103]. https://doi.org/10.1103/PhysRevB.81.075103

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Critical phenomena and femtosecond ordering dynamics associated with electronic and spin-ordered phases in YVO_3 and $GdVO_3$

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(Received 28 October 2009; published 2 February 2010)

We present a systematic study of the electronic- and spin-excitation dynamics associated with the sequence of spin- and orbital-ordering phase transformations in the complex vanadates YVO_3 and $GdVO_3$ with ultrafast optical pump-probe reflectance spectroscopy. Relaxation dynamics occurs on a different time scale for each of the ordering transitions, which enables us to unambiguously associate the critical behavior in the dynamics with the observed ordering phenomena. Spin-ordering dynamics is observed on two time scales: $\tau_r \simeq 2$ ps (rise time) and $\tau_s \simeq 300-3000$ ps (decay time), observed below T_N in both compounds. In contrast, the relaxation dynamics associated with orbital ordering occurs in YVO_3 on a time scale of $\tau_o \simeq 20-50$ ps. From the temperature dependence of the dynamics, we observe that in both the G-type and C-type orbitally ordered (OO) phases of YVO_3 spin order develops in a second-order mean-field fashion with the Nèel temperature of the C-OO phase found from our data $T_N^C = 83 \pm 7$ K. In $GdVO_3$ we identify the emergence of a new ordered phase within the phase-separated state below 60 K. A new response component with a lifetime of ~ 60 ps is observed below 60 K together with other anomalies in the $\Delta R/R(\Delta t)$ data. This new phase is not resolved in x-ray diffraction and is not present in YVO_3.

DOI: 10.1103/PhysRevB.81.075103 PACS number(s): 71.27.+a, 75.40.Cx

I. INTRODUCTION

The simultaneous presence of comparable exchange, Coulomb and electron-phonon interactions leads to a diverse display of different collective ordering behavior of the strongly correlated electrons in complex oxides. In the last few decades, transition-metal oxides with a perovskite structure have attracted interest because of high-temperature superconductivity and colossal magnetoresistance. It is now commonly accepted that orbital and spin degrees of freedom, as well as charges and polaronic effects define the complex phase diagrams of these compounds, but the competing effects of the major interactions lead to very complex behavior in individual compounds, which presents a significant theoretical challenge. In manganites and cuprates diversity of the observed ordered states develops when the parent compounds are doped with Ca, Sr, etc.

The quasicubic vanadates RVO_3 (R=rare earth) are interesting because already the stoichiometric compositions such as YVO_3 reveal rather complex behavior. These compounds are Mott-Hubbard (M-H) insulators with the optical band gap of about 1.2 eV.[1] In the cubic approximation, vanadium ions (nominally V^{3+}) possess two electrons at the triply degenerate t_{2g} orbital and have thus an orbitally degenerate ground state. As a result of a cooperative Jahn-Teller (JT) effect, orbital ordering (OO) occurs in the whole family of RVO_3.[2] The electron-phonon interaction of electrons in t_{2g} orbitals is much weaker than in e_g states [manifested in the orbital ordering temperatures of $T_{OO}=800$ K in $LaMnO_3$ (Ref. 3) and $T_{OO}=200$ K in YVO_3]. Temperatures of the spin ordering (SO) are similar in stoichiometric manganites ($T_N=150$ K for $LaMnO_3$) and vanadates (116 K for YVO_3 and 119 K for $GdVO_3$). Thus, in vanadates the energy scales of the JT and exchange interactions are of the same order, leading to a strong interplay between the spin and the orbital degrees of freedom. One of the phenomena that obviously originate from such interplay is the temperature-induced magnetization reversal first reported in YVO_3.[4] Substitution of the R ion allows for a systematic control of the lattice parameters that in turn define the temperatures and properties of the phase transitions.

YVO_3 undergoes a well studied sequence of phase transformations: at $T_{OO}=200$ K, a second-order transition from orbitally disordered paramagnetic state to G-type orbitally ordered (G-OO) state is followed by a Néel transition to an antiferromagnetic G-OO/C-SO ordering at $T_N=116$ K. Finally, at $T_s \approx 77$ K a first-order transition involving both spin and orbital rearrangement to a C-OO/G-SO ordered state occurs.[2,5,6] At T_s the crystallographic symmetry *increases* from monoclinic $P2_1/b11$ to orthorhombic $Pbnm$ with decreasing temperature, which is quite unusual.

In $GdVO_3$ the evolution with temperature is even more complex. It has been shown recently with high-resolution x-ray diffraction that for the intermediate size R ions (Tb-Nd) the RVO_3 compounds below T_N are found in an electronically phase-separated state, presumably composed of the same C-SO/G-OO and G-SO/C-OO phases as, e.g., YVO_3.[7,8] In $GdVO_3$ phase separation develops gradually from T_N down and stabilizes at the C-OO/G-SO state volume fraction value of $\eta_C \approx 67\%$ at ~ 50 K. At $T_M \sim 8$ K another phase transition occurs in $GdVO_3$ that is clearly related to setting up of the long-range magnetic order in the Gd

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sublattice.[2,9] The magnetization reversal phenomenon is also observed in $GdVO_3$, but it is present over a much wider range of temperatures than in YVO_3, from T_N down to T_M.[9]

To elucidate the dynamics of the spin and charge excitations associated with spin and orbital ordering in these compounds, we present the results of an ultrafast all-optical study of YVO_3 and $GdVO_3$ single crystals in the near-equilibrium regime covering the temperature range of all the ordered phases. From the time response in different phases and T ranges, it becomes possible to distinguish the dynamics of the different excitations in the system. Recently, orbital-order melting under photoexcitation was studied in another member of the series $(LaVO_3)$.[10] Unfortunately, in $LaVO_3$ T_{OO} and T_N are almost equal, so the assignment of the different relaxation components have proved to be difficult.[10]

Meanwhile, a time-resolved pump-probe study of photoinduced phase transitions in YVO_3 (Ref. 11) was reported. The study of the excitation fluence and temperature dependencies allowed the authors of Ref. 11 to define the time scales and the destruction conditions for the SO and OO phases, respectively.

II. EXPERIMENTAL RESULTS

In our experiments the reflectivity transients $\Delta R/R(\Delta t)$ and their T dependencies were studied in a two-color pump-probe configuration. For pump the 400 nm (3.1 eV) light wavelength with a pulse duration of 50 fs and repetition rate of 100 kHz was used. The induced changes were probed at 800 nm (1.55 eV) on the low-energy wing of the M-H band. Freshly polished samples were mounted to the cold finger of the helium flow cryostat. The pump fluence value was $\sim 100\ \mu J/cm^2$ [which is well below the reported phase transition threshold value of 3 mJ/cm^2 for 400 nm pump wavelength in YVO_3 (Ref. 11)]. The linearity of the response as a function of pump fluence was verified experimentally for both crystals.

Representative $\Delta R/R(\Delta t)$ traces for YVO_3 and $GdVO_3$ with $\mathbf{E}_{probe}$ parallel to the c and a axes of the crystals are shown in Fig. 1. Responses of both samples were found to be strongly anisotropic below T_{OO} for YVO_3, in accordance with the optical studies,[12] and also above T_{OO} for $GdVO_3$. No dynamics of the anisotropy for $GdVO_3$ was observed above T_N up to $\Delta t = 1.5$ ns. In addition to exponential decays, some of the responses also have a weak oscillatory component originating from the interference of the beams reflected from the surface and from the traveling acoustic wave in the sample created by photoexcitation which has already been noted[11] and won't be discussed further here. Fast transients on a time scale of less than 1 ps are also present at all temperatures, which we attribute to initial avalanche relaxation of the photoexcited charge carriers as they relax toward the band extrema (i.e., the low-energy states). Since we are interested only in the dynamics of the states associated with ordering phenomena, we will confine our discussion to those components of the response which can be clearly identified by the response in the different phases.

The response was analyzed quantitatively by fitting the data to a sum of exponentials,

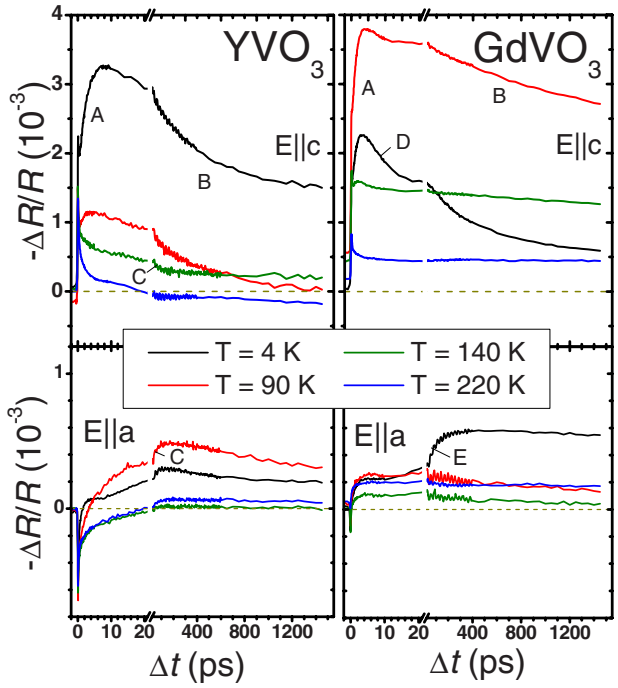

FIG. 1. (Color online) Polarized photoinduced reflectivity transients of YVO_3 and $GdVO_3$ crystals at four temperatures, corresponding to distinct regions of the phase diagrams [see Figs. 2(a) and 3(a)]. The components of the responses are marked according to Eq. (1).

$$\Delta R/R(\Delta t) = Ae^{t/\tau_r} + Be^{-t/\tau_s} + Ce^{-t/\tau_o} + De^{-t/\tau_1} + Ee^{-t/\tau_2}. \tag{1}$$

Significant difference in the observed time scales has allowed to characterize each component with high accuracy. Components $A-E$ are labeled in Fig. 1. The component with amplitude C is clearly observed only in YVO_3 while components D and E are observed only in $GdVO_3$.

Below T_N, the $\Delta R/R(\Delta t)$ responses of both samples with $\mathbf{E}_{probe} \| c$ reveal a relatively fast ($\tau_r \approx 2$ ps) rising component A and a slow ($\tau_s = 300-3000$ ps) relaxation B. The temperature dependencies of the amplitude and the lifetime of the long-lived component for YVO_3 and $GdVO_3$ are shown in Figs. 2(b), 2(c), 3(b), and 3(c), respectively. The lifetime of this component diverges in both compounds as T_N is approached from below while its amplitude simultaneously vanishes at T_N in accordance to expectations from mean-field theory.

Indeed, in the temperature range of $T_s < T < T_N$ (G-OO/C-SO phase) the amplitude variation in the slow relaxation component in YVO_3 can be described well with a mean-field expression

$$B(T) = B(0)(1 - T/T_c)^{\beta}, \tag{2}$$

where $\beta = 0.49 \pm 0.02$ and $T_c = T_N^G = 124.7 \pm 1.5$ K (G here refers to the type of the OO). The observed behavior is an unambiguous indication that the slow component is intimately related to the order parameter variation in the spin subsystem in the G-OO/C-SO state and thus reflects the spin order relaxation. In the region of T_s there are clear

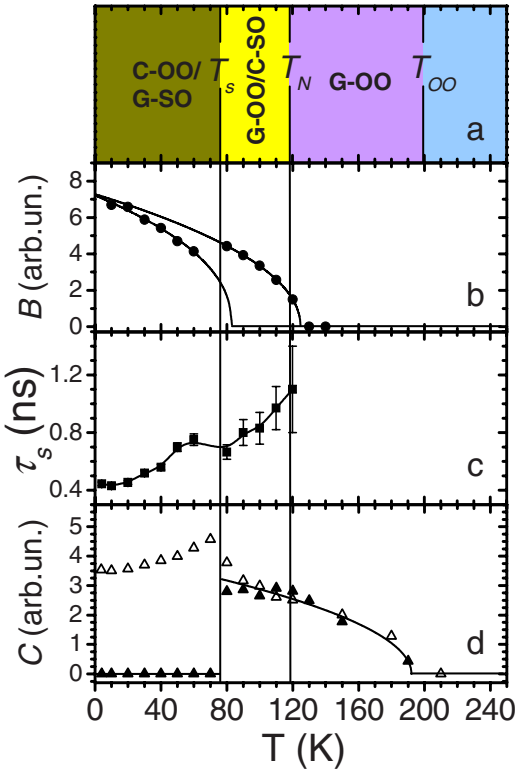

FIG. 2. (Color online) Phase diagram of YVO_3 (a) and temperature dependencies of the amplitude B (b) and the lifetime τ_s (c) of SO relaxation, and (d) of the ~40 ps component amplitude C in the $\mathbf{E}_{probe}\|a$ (△) and $\mathbf{E}_{probe}\|c$ (▲) $\Delta R/R$ responses. The solid lines in panels (b) and (d) are the fits of the data to Eq. (2).

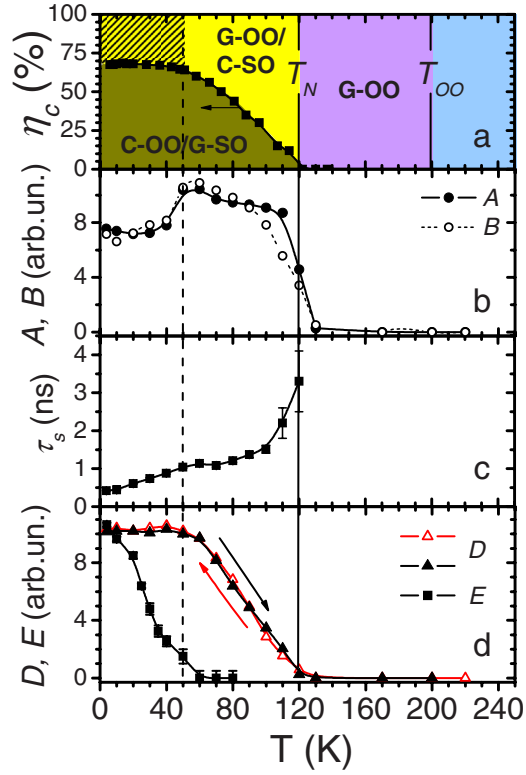

FIG. 3. (Color online) (a) Phase diagram of $GdVO_3$ with a dependence of a stable C-OO phase volume fraction (Ref. 8). (b) Temperature dependencies of the rise-time amplitude A (○), the relaxation amplitude B (●), and (c) the lifetime of SO. Temperature dependencies of the 5 ps component amplitude (on warming, ▲, and on cooling, △) and 60 ps component amplitude (■) are shown in (d).

peculiarities present in the amplitude and the lifetime temperature dependencies of this slow component. In fact, one can fit the amplitude dependence below T_s with Eq. (2) (Fig. 2) which gives fit parameters: $T_c = T_N^C = 83 \pm 7$ K and $\beta = 0.44 \pm 0.08$. The diverging behavior of $\tau_s(T)$ while approaching T_s from below is further indication of the second-order character of the spin ordering in the C-OO/G-SO phase. Thus, the transition to paramagnetic state would occur in C-OO phase of YVO_3 at T_N^C if the first-order transition to G-OO/C-SO state didnot take place at T_s.

The temperature dependence of the amplitude of this component in $GdVO_3$ is slightly different than in YVO_3 [Fig. 3(b)], and cannot be fit with the mean-field expression (2) near T_N. It has a clear anomaly below ~50 K but MF behavior is not evident at low temperatures either.

The temperature dependence of A and B follow each other very closely [Fig. 3(b)],[13] so we can deduce that in both C-OO and G-OO phases of YVO_3 and $GdVO_3$ the spin order is detectably perturbed by photoexcitation on the time scale of ~2 ps. [A similar rate was reported for the photoinduced SO melting in YVO_3 (Ref. 11)]. Component B can be unambiguously attributed to the SO relaxation.

The $\Delta R/R$ transients of YVO_3 also contain rather weak but clearly resolved component C with $\tau_o \sim 40$ ps. This component is present in the responses measured with $\mathbf{E}_{probe}\|a$ at any temperature below T_{OO} and only in the range $T_s < T < T_{OO}$ with $\mathbf{E}_{probe}\|c$. Its lifetime stays constant within experimental accuracy from T_s up to T_{OO} and shortens slightly down to ~25 ps below T_s. Its amplitude dependence on temperature [Fig. 2(d)] in the range $T_s < T < T_{OO}$ can be fit well with the MF expression (2), giving $T_{OO} = 192 \pm 14$ K and $\beta = 0.46 \pm 0.12$. This component is clearly related to the orbital order and most probably reflexes the time scale of the OO relaxation. It appears to be completely insensitive to the onset of spin ordering. Although a similar time scale 45 ± 10 ps was assigned to thermalization of the spin and the orbital subsystems in Ref. 11, our observation of this component above T_N up to T_{OO} and its clear relation to the orbital order doesnot support this assignment.

Temperature dependencies similar to the one obtained with $\mathbf{E}_{probe}\|c$ were found for some phonons in Raman[14] and IR spectra,[15] as well as for specific reflections in x ray[5,6] and neutron-diffraction patterns.[16] This behavior can unambiguously be assigned to the crystallographic symmetry lowering due to switching from the C-OO phase to G-OO at T_s.

Finally, let us discuss the additional low-temperature relaxation features for $GdVO_3$ (Fig. 3). In the transients with $\mathbf{E}_{probe}\|c$ in Fig. 1 a fast, $\tau_2 \sim 5$ ps, component is clearly seen. This component D is observed only below T_N and its lifetime doesnot vary significantly within this range. The temperature dependence of its amplitude is shown in Fig. 3(d). Remarkably, it reproduces almost exactly the temperature dependence of the low-T C-OO/G-SO phase volume fraction $\eta_C(T)$. Thus, the 5 ps component is directly related

to the C-OO/G-SO phase. As the SO relaxation has already been identified and occurs on the time scale of 10^2-10^3 ps, we attribute tentatively the 5 ps component to relaxation of the orbital order in the C-OO/G-SO phase. Importantly, this component variation is totally reversible with temperature [Fig. 3(d)].

One more relaxation component E, which is clearly seen in the raw $\Delta R/R(\Delta t)$ data for $GdVO_3$ at 10 K with $\mathbf{E}_{probe}\|a$ (Fig. 1) develops below ~60 K. Its relaxation time within this temperature range is essentially unchanged, $\tau_3=60\pm10$ ps. The amplitude variation with temperature is shown in Fig. 3(d). Remarkably, development of this component coincides in temperature with a sudden drop in the amplitude of the SO relaxation component (B).

III. DISCUSSION

A. Critical phenomena

The relaxation phenomena in YVO_3 are relatively straightforward to interpret, and our observations agree well with previous studies by x-ray diffraction and neutron scattering, as well as time-domain experiments by Mazurenko *et al.*[11] Based on the temperature dependencies of the amplitude and the lifetime of the slow, 300–3000 ps relaxation component in YVO_3, we conclude that the spin order both in the low-T C-OO and high-T G-OO phases develops as a second-order phase transition. This was previously known for the G-OO phase and from our data becomes clear now also for the C-OO phase. By extrapolating the amplitude variation in this component to the temperatures above T_s we are capable to estimate the Néel temperature $T_N^C=83\pm7$ K in the C-OO phase which is otherwise hidden by the first-order transition to the G-OO/C-SO phase at 77 K. The fact that orbital and spin rearrangement occurs just a few degrees below the Néel temperature of the C-OO phase T_N^C implies that the spin ordering provides the C-OO phase with the critical energy gain with respect to the G-OO/C-SO state and triggers thus the first-order transition at T_s. The temperature dependence of the 40 ps component C associated with the second-order transition to the orbitally ordered state at T_{OO} closely follows previous structural and Raman data.

However, the order parameters of the OO and SO in YVO_3 are not independent since both the orbital and spin structures rearrange simultaneously at T_s.[5] In such situation the transition to a higher crystallographic symmetry state as the temperature is decreased through T_s is no more a big surprise: the full symmetry group including the magnetic degrees of freedom should be used to describe the state fully.

The results on $GdVO_3$ are not as straightforward as in YVO_3, especially below T_N: in principle, we should consider the data as a combined response of two phases. Thus, the direct proportionality of the 5 ps component amplitude D to the C-OO phase volume fraction η_C and the coincidence of this amplitude temperature dependencies measured on cooling and on warming shows that phase separation in $GdVO_3$ occurs reversibly, similar as in $SmVO_3$.[7] This in turn indicates that the system is essentially in equilibrium at any given temperature within the phase separation range. Such observation demands a presence in the free energy of a term that stabilizes given phase volume ratio at a given temperature. In the recent publications[7,8] elastic deformations arising due to large difference in the lattice cell volumes of the G-OO/C-SO and C-OO/G-SO phases were suggested to stabilize the phase-separated state.

One of the most interesting experimental observations in $GdVO_3$ is the development of a new $\Delta R/R(\Delta t)$ response component E with $\tau_2\sim60$ ps below 60 K which is linked to a sudden drop of the SO amplitudes A and B. Interestingly, amplitudes A and B drop by ~30% below 60 K, which is similar to the volume fraction of the G-OO phase, which is ~33%. Thus we may explain the dip below 60 K by assuming that the SO response of the G-OO phase almost totally vanishes. Almost exactly in the same temperature range a significant modification of the monoclinic angle value in the G-OO phase of $GdVO_3$ was found with high-resolution x-ray diffraction.[8] Obviously, such coincidence is unlikely accidental. As there is a modification of the G-OO phase crystal structure, we assign the observed $\Delta R/R$ phenomena to the characteristic response of the phase-separated state, where the two fractions are fixed. This statement is supported also by the fact that the 5 ps component does not change in this temperature range: the phase separation has essentially already evolved and the phase volume fractions will experience only the minor changes on cooling down further to low temperatures. Yet, while the structural studies detect no symmetry break at ~60 K, the observation of new response component E which increases in a manner expected for an order parameter indicates clearly the emergence of a symmetry-broken phase within the nominally phase-separated G-OO/C-SO state. The 60 ps relaxation time of this phase strongly suggests that a new type of spin ordering is being observed, but the excitations are much more strongly coupled to the orbital degrees of freedom, so the lifetime is 60 ps, and not 300 ps as for the C-SO excitations.

The C-SO magnetic structure is common to all members of the RVO_3 series, although it exists only in an intermediate temperature range for rare earths smaller than Dy. The deviation of the monoclinic angle from 90° in the corresponding G-OO phase falls into two distinct ranges, varying from 0.02° to 0.03° for small rare earths and from 0.08° to 0.13° for large rare earths;[8,17] the G-OO phase within the phase-separated state of $GdVO_3$ appears to lie at the boundary between these two regimes. The orientation of the V spins within the C-SO phase has not been reported for all members of the series and its dependence on the rare earth is still rather unclear.[18] Available evidence provided by magnetization and neutron-diffraction measurements suggests that the V spins lie in the bc plane for RVO_3 with small rare earths[17,19] and in the ab plane for larger rare earths[16,20] but it should be noted that the ab-plane configuration is forbidden by symmetry arguments.[16,17] These two regions of the magnetic RVO_3 phase diagram coincide approximately with those defined by the G-OO phase monoclinic angle. Therefore, it is certainly possible that the V spins in the C-SO phase within the phase-separated state of $GdVO_3$ undergo a reorientation at the same temperature as the change in monoclinic angle; the exact temperature may be to some degree sample dependent. This scenario would become even more complex when spin and orbital fluctuations[21] are taken into

account; these seem to be most pronounced for RVO_3 with smaller rare earths where the fluctuations are strong enough to disrupt the G-OO and lower the symmetry.[17] Thus, the 60 K transition in the C-SO phase of $GdVO_3$ may also reflect a suppression of spin and orbital fluctuations upon cooling. Whatever the precise nature of the G-OO/C-SO phases in the "small" and "large" rare-earth regimes of the RVO_3 phase diagram, within the phase-separated state of $GdVO_3$ there seems to be a crossover between them that is manifested by the development of response component E below 60 K.

The peculiar feature of this 60 K transition is that it occurs *within* a phase-separated state. Sage *et al.*[8] considered the effect of oxygen octahedra tilting revealed experimentally by the monoclinic angle increase right below T_N in combination with exchange striction (ES) as a driving mechanism for the observed low-temperature behavior in RVO_3. Elastic strains arising from the large difference in the lattice cell volumes of the G-OO and C-OO phases were proposed to stabilize a given phase volume ratio at a given temperature. Taking into account that for RVO_3 compounds with R ionic radius $r < r_{Tb}$, lattice change due to ES are not observed because of lattice rigidness, we suggest that the phase transition we observe below 60 K in $GdVO_3$ is driven with exchange striction and is triggered with the lattice instability brought to the G-OO phase by elastic strains growing with the C-OO phase volume fraction.

B. Order dynamics

Our data allows to estimate the rates at which the spin and the orbital orders are perturbed under pulsed photoexcitation and at which they relax. We have unambiguous signatures of the SO: its perturbation is observed as the rise time of $\Delta R/R(\Delta t)$, and its relaxation—via the slow $\tau_s = 300-3000$ ps component below T_N. Thus, the time scale of the spin order perturbation from our study is 1.8 ± 0.5 ps, which is in full agreement with the high-fluence study of YVO_3.[11] The recovery of the SO is much slower, on the typical scale of the spin-lattice relaxation times.

The assignment of the ~ 40 ps component in YVO_3 and the ~ 5 ps component in $GdVO_3$ to the orbital-order relaxation is less unambiguous: we donot observe the critical slowing when approaching T_{OO} in YVO_3, and probably shouldnot observe in phase-separated $GdVO_3$ as the actual T_{OO} for the C-OO phase may be higher than T_N (where we start to observe the 5 ps response). Nevertheless, assuming that our assignment is correct, OO is perturbed almost instantaneously and relaxes with 25 ± 5 ps in the C-OO phase and 40 ± 10 ps in the G-OO phases of YVO_3 and within 5.3 ± 1.6 ps in the C-OO phase of $GdVO_3$. The last number is in good agreement with the study of $LaVO_3$, where thermalization of the orbital subsystem with the lattice occurred in the low-excitation range with a time constant of 2.9 ps.[2]

The instantaneous dynamics of the OO perturbation with a short light pulse is clear from the character of the created excitation. Absorption of the photon within the energy range of 1.2–4.3 eV (Ref. 1) (across the Mott-Hubbard gap) results in a charge transfer or d-d transition (or some mixture of the two). Thus, after a pulsed photoexcitation across the M-H gap RVO_3 compounds in the low-T spin-ordered and orbitally ordered phases experience the following sequence of the events (Fig. 4): (a) essentially instantaneous perturbation of an OO due to vanadium-vanadium electron transfers; (b) SO perturbation on the time scale of 2–3 ps that is governed most probably by the spin-orbit coupling (or thermalization of the orbital and spin subsystems); (c) the relaxation, probably only partial, of the OO on the scale of 5–50 ps; and (d) relaxation of the SO with $\tau_s = 300-3000$ ps, which occurs due to spin-lattice coupling.

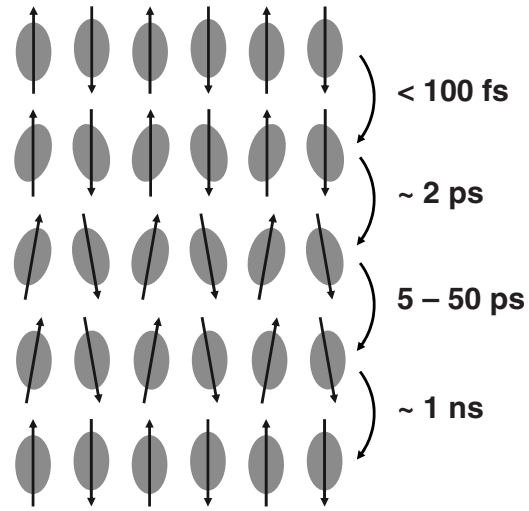

FIG. 4. Perturbation and relaxation of the orbital (ovals) and spin (arrows) order with the corresponding time scales in RVO_3.

Importantly, after all these relatively fast relaxation stages both YVO_3 and $GdVO_3$ at low temperature (10 K) are found far from equilibrium after 1.5 ns. This is probably a consequence of a wide >1 eV gap, and thus a slow rate of the over-the-gap multiphonon nonradiative transitions, as well as the radiative ones. This in turn creates the conditions for development of the photoexcited (and, probably, ordered) states. Indeed, similar conclusion was reached by Mazurenko *et al.*[11] In $GdVO_3$ a clear threshold behavior is observed in a spin-relaxation fluence dependence.[22]

IV. SUMMARY AND CONCLUSIONS

Summarizing, we have observed multicomponent photoinduced ultrafast reflectivity transients of the strongly correlated YVO_3 and $GdVO_3$ single crystals. In both samples the fast, ~ 2 ps, rising and slow, 300–3000 ps, decaying components have been clearly assigned to the perturbation and the relaxation of the spin order. In YVO_3 the SO develops in a second-order manner in both the C-OO and G-OO phases, the Néel temperature in the C-OO phase has been estimated as $T_N^C = 83 \pm 7$ K. Departure of the slow component variation with temperature from the critical behavior in $GdVO_3$ is most probably due to its inhomogeneous phase-separated state below T_N. The orbital-order relaxation is associated with the faster components of the reflectivity transients, occurring on the time scales of 25 ± 5 ps in the C-OO and 40 ± 10 ps in the G-OO phases of YVO_3 and 5.3 ± 1.6 ps in the C-OO phase of $GdVO_3$.

Our data indicate an occurrence of an unusual symmetry-breaking phase transition in the nominal G-OO/C-SO phase of $GdVO_3$ below 60 K. This transition takes place under the rare conditions of mesoscopic phase separation, driven presumably by exchange striction and is triggered by a lattice instability brought on by the elastic strains arising from phase coexistence. This transition was not observed in homogeneous phases of YVO_3, thus it is either a consequence of the phase separation or can only occur in a phase-separated state. The 60 ps relaxation time of this phase suggests that excitations are arising from a new hitherto unobserved spin-ordered state.

ACKNOWLEDGMENTS

We are grateful to V. V. Kabanov for valuable discussions. The work was supported within the FP6, Project No. NMP4-CT-2005-517039 (CoMePhS), R.Y. is grateful also for the support from RNP-6183 project by Ministry of Education and Science of Russian Federation.

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