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Giant positive magnetoresistance in metallic VO_x thin films

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We report on giant positive magnetoresistance (MR) effect observed in VO_x thin films, epitaxially grown on $SrTiO_3$ substrate. The MR effect depends strongly on temperature and oxygen content and is anisotropic. At low temperatures its magnitude reaches 70% in a magnetic field of 5 T. Strong electron-electron interactions in the presence of strong disorder may qualitatively explain the results. An alternative explanation, related to a possible magnetic instability, is also discussed.

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Transition-metal oxides (TMO) with strong electronic correlations show many fascinating phenomena, like high-temperature superconductivity, metal-insulator transitions, heavy fermion behavior, or colossal negative magnetoresistance. The rich physics of TMO is due to strong coupling of spin, orbital, and lattice degrees of freedom. Their complex interplay is controlled by a large number of structural and chemical factors, which makes the search for the new oxide materials, where the fine tuning of chemical composition and steric parameters might yield new unexpected electronic and magnetic properties of an apparent fundamental and applied interest.

A quite unexplored class of oxides containing transition-metal ions are the monoxides of vanadium and titanium. In these oxides the overlap of the metal t_{2g} orbitals can be tuned by changing the oxygen stoichiometry, which offers the control of the width of the t_{2g} band responsible for electron conductivity. Owing to a broad characteristic stoichiometry range, small changes in composition and/or local geometry can induce rather diverse physical properties. The oxygen content x in vanadium monoxide VO_x may deviate substantially from 1 ($0.8<x<1.3$). Remarkably, already small variations of x can induce changes in the electrical conductivity. A gradual transition from a metallic to a semiconducting behavior has been observed in the bulk[1] and in thin films.[2] Another important feature is an intrinsic disorder. Even stoichiometric VO contains ~16% atomic vacancies in both sublattices, distributed at random.

In this paper we report on giant *positive* magnetoresistance (up to 70% in a magnetic field of 5 T) observed at low temperatures in compressively strained metallic VO_x thin films ($0.8<x<1$). The positive sign of the effect, i.e., the *increase* of the resistance with applied magnetic field, implies different underlying physics as compared to metallic multilayers or manganite perovskites, where, as a rule, the resistance *decreases* with field.[3] We discuss possible mechanisms of this unusual effect, which might be related to electron-electron interaction in the presence of strong disorder, or to the proximity of the system to magnetic instability.

The 100-Å-thick VO_x films were grown on $SrTiO_3$ (001)(STO) substrates by molecular beam epitaxy. To prevent after oxidation, the films were capped with a thin MgO layer. The oxygen content x was determined using $^{18}O_2$-Rutherford backscattering spectrometry, as described in Ref. 2. Single-phase material was obtained for x values varying from 0.8 to 1.22. *In situ* reflection high-energy electron diffraction proved the *layer-by-layer* growth, with the same orientation as the underlying substrate. The high quality of our samples was further confirmed by x-ray analysis, which shows that the film grows in a full coherence with the substrate, i.e., the in-plane film and substrate lattice constants are identical (3.903 Å). The out-of-plane lattice constant varies between 4.003 Å for $x=0.8$ and 3.974 Å for $x=1.22$. Resistance and magnetoresistance (MR) were measured by the standard four-point probe method, in a commercial PPMS system, equipped with a rotatable sample holder, at temperatures between 2 and 300 K. For the MR measurements the magnetic field was varied between 5 T and −5 T, applied either perpendicular to the film plane, or in the film plane and parallel to the current. The Hall coefficient was measured in the square geometry using a conventional ac bridge. Electrical contacts of 10 nm of Cr metal were evaporated on the STO substrates, prior to deposition of the VO_x layers.

In a previous study we found that the resistivity of VO_x films grown under tensile strain on MgO substrates is orders of magnitude larger than for bulk material of the same composition.[2] Consistently, in this study we find much lower resistivities for VO_x films on STO. Apparently, this is due to the increase in the direct overlap between t_{2g} orbitals of neighboring metal ions in the compressively strained films. From Fig. 1 it is evident that there is a gradual transition from metallic to semiconducting behavior at about $x=0.94$.

In Fig. 2 we compare the temperature dependence of the resistivity ρ of the VO_x sample with $x=0.82$ measured in zero magnetic field H with that in an applied field of 5 T. $\rho(T)$ strongly decreases with decreasing temperature, reaches a minimum with the value of ~8 $\mu\Omega$ cm at $T=25$ K, and increases steeply at still lower temperatures. The strong T dependence of ρ and extremely low residual resistivity implies that the electronic conduction is mainly due to electron-electron scattering. The decrease of conductivity related to the steep upturn of $\rho(T)$ below 25 K follows very well a $\sqrt{T}$ law (see left inset in Fig. 2). As to the field dependence, the two curves, $\rho(T,H=0)$ and $\rho(T,H=5\text{ T})$

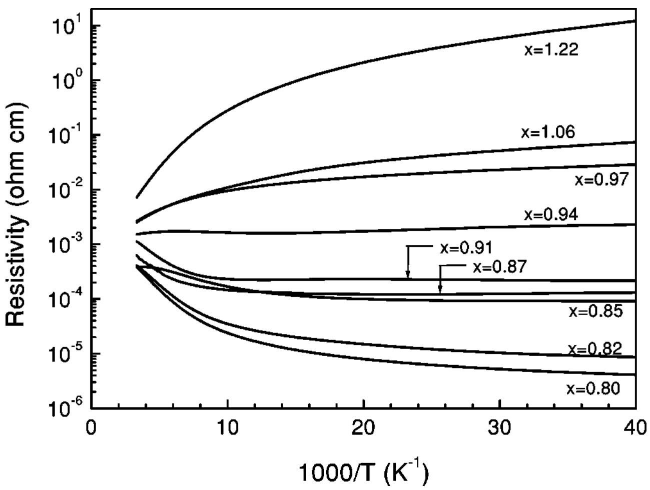

FIG. 1. Resistivity of VO_x/STO films for different x.

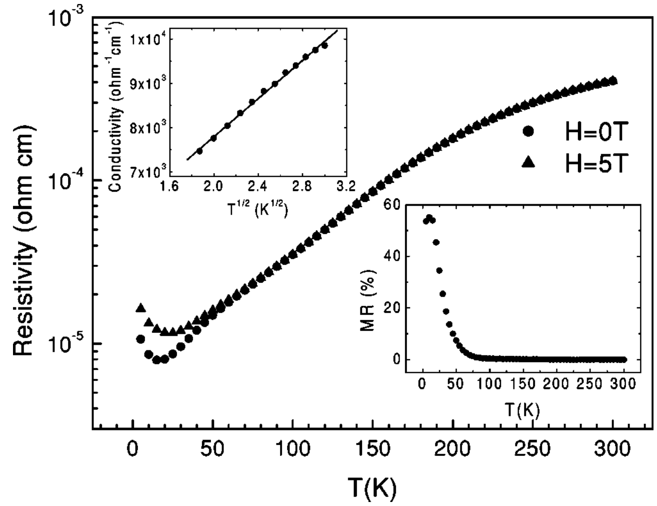

FIG. 2. The resistivity of VO_x film with $x=0.82$ at zero field and at $H=5$ T. In the inset at the right, the magnetoresistance is shown. In the inset at the left we show the fit of the low-temperature increase of resistivity by the $1/\sqrt{T}$ law.

are indistinguishable down to $\sim$70 K. Surprisingly, at lower temperatures the application of magnetic field increases the resistivity.

In the inset at the right of Fig. 2 we show the temperature dependence of MR defined as $\{[\rho(H)-\rho(0)]/\rho(0)\}$ 100%. The sign of the MR is positive and its magnitude increases smoothly with decreasing temperature, both in a drastic contrast to the negative colossal MR observed in the manganites.[4]

A representative field dependence of MR for the $x=0.85$ sample at several selected temperatures is shown in Fig. 3(a). The curves were obtained in all cases by increasing the field from 0 to 5 T, sweeping it then to -5 T and turning H finally back to zero. Under field cycles, the MR shows no hysteresis. Moreover, no sign of saturation is observed up to 5 T. Except for small fields, the MR is proportional to $\sqrt{H}$ at low temperatures and gradually changes to an almost linear and finally quadratic dependence with increasing temperature [see Fig. 3(c)].

A remarkable feature of the positive MR in VO_x films is its strong dependence on the oxygen stoichiometry [Fig. 3(b)]. The effect is largest in the sample with the smallest oxygen content $x=0.8$, where the MR amounts to 70% at 5 K in a magnetic field of 5 T. Increase of x results in the decrease of the MR which finally becomes unobservable for $x>0.94$, in an apparent correlation with the crossover from metallic to semiconducting regime of conductivity.

A clear dependence of the MR on the direction of the applied field was found. In Fig. 3(d) we present the MR of the $x=0.8$ sample at $T=5$ K with H perpendicular and parallel to the film plane and current direction. Positive transverse magnetoresistance (TMR) of about 70% and a longitudinal, still positive, magnetoresistance (LMR) of 40% was observed in a magnetic field of up to 5 T. Note that the TMR is always larger than the LMR.

The behavior of the MR is clearly correlated with the Hall effect. Our measurements show that the Hall effect is quite strong, negative and linear in fields up to 5 T. In Fig. 4 we plot the carrier concentration and Hall mobility obtained from the Hall effect and resistivity data of the sample with $x=0.87$. One can see that in the region of the strong change of the MR (for $T<\sim 50$ K) the carrier concentration is essentially constant, whereas the mobility which at low temperatures is pretty high, starts to decrease. The Hall measurements for different x show that effective carrier concentration decreases with increasing x for x between 0.8 and 1. The Hall constant changes sign for $x>1$.

Unfortunately, due to the small thickness and correspondingly total small mass of our films, it was not possible to measure their magnetization directly by superconducting quantum interference device. To elucidate magnetic properties of the VO_x films we have measured electron-spin resonance (ESR) of the samples with x ranging from 0.8 to 1.2. ESR has been measured using a Bruker spectrometer at X-band frequency 9.48 GHz and at temperatures between 1.9 and 300 K. A set of representative spectra [field derivatives of the absorbed microwave power $dP(H)/dH$] is shown in Fig. 5. The fingerprint of the VO_x/STO samples with $x<1$ showing a large positive MR is the occurrence at low temperatures of an intense broad microwave absorption consisting of several overlapping peaks. The signal emerges below 20–25 K. At still lower temperatures it increases in intensity and acquires a structure [Fig. 5(a)]. Remarkably, in the same temperature interval the resistivity shows an upturn (Fig. 2). In contrast, the samples with $x>1$ as well as the STO substrate itself are ESR silent and show only a small spurious signal at $H_{res}\simeq 3.3$ kOe [Fig. 5(b)], which can be attributed to the small amount of paramagnetic impurities in the substrate.

The signal observed in the VO_x films ($x<1$) is reminiscent of ferromagnetic resonance in strongly inhomogeneous ferromagnetic films, like, e.g., as-grown manganite films.[5] Owing to an inhomogeneous distribution of the magnetization across the film multiple broad lines occur in the spectrum. Apparently, a similar spectrum might be expected if the sample is not yet ferromagnetic but contains randomly distributed mesoscopic spin clusters.

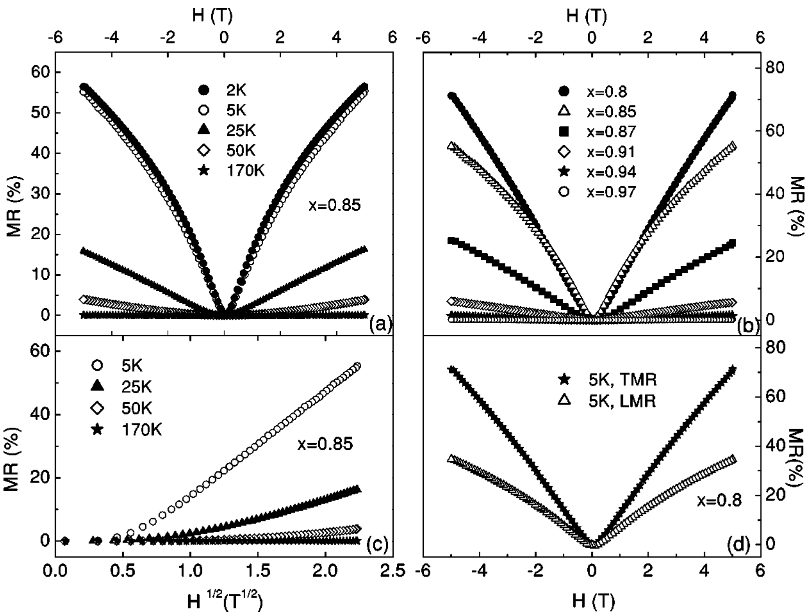

FIG. 3. (a) The magnetoresistance of VO_x film with $x=0.85$ for different temperatures. (b) The magnetoresistance of VO_x films at 5 K for different x. (c) $\sqrt{H}$ dependence of MR at low temperatures. (d) Comparison of the transverse and longitudinal MR for $x=0.8$ at 5 K.

The positive magnetoresistance which we found in the VO_x films is quite unusual in several respects. First of all, surprising is the very large magnitude of the effect. The ordinary positive MR in metals is usually rather small, less than a few percent. Its size is determined by $\omega_c\tau$, where $\omega_c=eH/m^*c$ is a cyclotron frequency, and τ the relaxation time, which is proportional to the mean free path l. Here e is the electron charge, m* is the effective carrier mass, and c is the speed of light. One may conclude that in our sample the value of l is rather large, as the residual resistivity is quite low. Still, it is difficult to expect a MR of 70%. Besides, the MR is also very large (~40%) for the parallel field geometry [see Fig. 3(d)] for which one would not expect a strong orbital contribution in our thin films.

Another feature which is different in our samples is the field dependence. The conventional MR in metals is quadratic in field (only at the ultraquantum regime it may be linear[6]), whereas as one sees from Fig. 3, it is not the case in our VO_x films. As is discussed above, the character of the field dependence changes gradually with increasing T from square root to linear and finally to quadratic. In particular, the linear regime resembles the MR in nonstoichiometric $Ag_{2\pm\delta}Se$, $Ag_{2\pm\delta}Te$ (Ref. 7) (for which positive MR is linear in field and larger in magnitude).

The explanation of the unusual behavior of the MR in VO_x films may be found in the specific electronic and crystal structure of this compound. On the one hand, as always in transition metal oxides, the electrons are apparently rather strongly correlated. On the other hand, there exists strong intrinsic disorder in VO_x, which always contains about 10–20 % of vacancies in both anion and cation sublattices. The role of the structural disorder has been recently discussed by Goodenough *et al.*[8] Thus, altogether one should view this system as the one with strong disorder and strong interaction.

Theory predicts (see, e.g., Ref. 9) that in metals with the electron-electron interaction and disorder, a square-root singularity appears in the density of states at the Fermi level, with the corresponding anomalies in transport properties, including MR. The correlation between the behavior of the MR

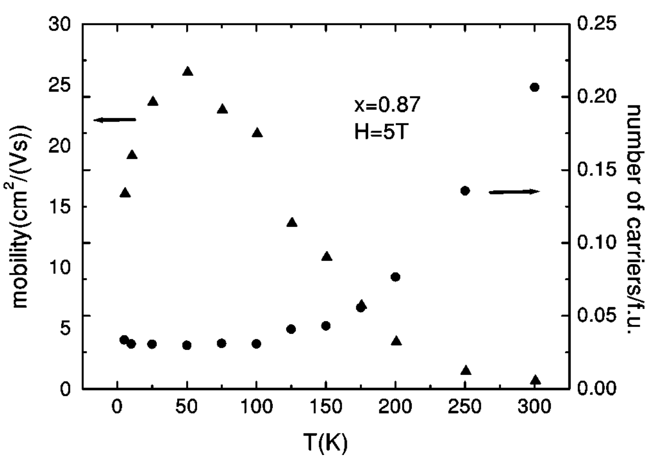

FIG. 4. The number of carriers/formula units and the Hall mobility of VO_x film with x =0.87 as the function of temperature in the field of 5 T.

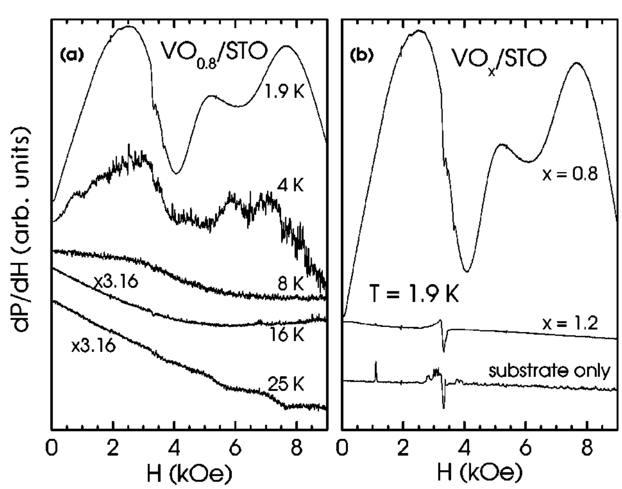

FIG. 5. ESR spectra of VO_x/STO samples, see text.

in VO_x films with that of the Hall effect, discussed above, suggests that indeed the interplay between interaction and disorder may be decisive for the observed effects. Thus, the low-temperature resistivity of our metallic films of VO_x is $\sim 1/\sqrt{T}$ (see left inset in Fig. 2), which agrees with this model. The MR should behave as $\sqrt{H}$ in high fields, at least for the case of relatively weak disorder and interaction, treated in these papers.[9] Our MR effect is qualitatively similar to this behavior, although it is much stronger than those expected from theoretical considerations.[10] One reason for this may be the much stronger disorder and interaction in our system. The effect may be also enhanced by the paramagnon scattering.[11]

In spite of the qualitative similarity with the case of the weakly interacting disordered systems, one still can not exclude alternative explanations of the observed large positive MR in the thin films of VO_x. In particular, one can expect that our system may be rather close to magnetic instability. Relatively broad bands and/or strong disorder may prevent the formation of long-range magnetic ordering, although short-range magnetic correlations may still exist. Indeed, our ESR study of VO_x films has shown that a rather strong but quite unusual (broad, consisting of several overlapping lines) ESR signal appears, which one might expect from, e.g., random magnetic clusters.

Our situation is definitely different from, e.g., that in phase-separated manganites (see, e.g., Refs. 12 and 13), where the presence of ''preformed'' ferromagnetic metallic clusters and their growth in size with field leads to the colossal *negative* magnetoresistance. However, we can visualize the following scenario: In our inhomogeneous system there may be no preformed magnetic clusters, but the magnetic susceptibility χ may be strongly spatially inhomogeneous, owing to, e.g., strong disorder. Then in the external field the parts of the film with larger χ will develop larger magnetization. But according to the conventional double-exchange model the energy of conduction electrons in these magnetized regions would decrease, and the electrons of our sample would redistribute. The electron concentration in these regions would increase, whereas the regions in between would be depleted. If the system is still below a percolation threshold, this would lead to the total increase of resistivity, owing to creation of more insulating barriers,[14] i.e., to the total positive MR. This picture is also consistent with the ESR data, although it is not clear whether it would give the observed dependence of the MR on H and T.

To conclude, we observed a surprisingly large (up to 70% in the field of 5 T) positive magnetoresistance in thin VO_x films, grown epitaxially on the $SrTiO_3$ substrate, which behaves at low temperatures as $\sqrt{H}$ in high fields. We argue that the possible explanation of the observed behavior may rely on the interplay of the electron-electron interaction and disorder. The effect observed above is much stronger than that predicted theoretically, but this can in principle be connected with the much stronger interaction and disorder in our case. Still, alternative explanations, e.g., relying on the inhomogeneous magnetic susceptibility and the proximity of our system to magnetic ordering, cannot be excluded. In summary, the compressively strained VO_x system seems to be quite unusual in many respects, and its properties, especially an extremely strong positive magnetoresistance, deserve further study, and possibly can be useful in applications, e.g., in spintronics.

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