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Magnetic ordering and structural phase transitions in strained ultrathin SrRuO₃/SrTiO₃ superlattice

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Abstract

Ruthenium-based perovskite systems are attractive because their structural, electronic and magnetic properties can be systematically engineered. SrRuO₃/SrTiO₃ superlattice, with its period consisting of one unit cell each, is very sensitive to strain change. Our first-principles simulations reveal that in the high tensile strain region, it transits from a ferromagnetic (FM) metal to an antiferromagnetic (AFM) insulator with clear tilted octahedra, while in the low strain region, it is a ferromagnetic metal without octahedra tilting. Detailed analyses of three spin-down Ru-*t*_{2g} orbitals just below the Fermi level reveal that the splitting of these orbitals underlies these dramatic phase transitions, with the rotational force constant of RuO₆ octahedron high up to 16 meV/Deg², 4 times larger than that of TiO₆. Differently from nearly all the previous studies, these transitions can be probed optically through the diagonal and off-diagonal dielectric tensor elements. For one percent change in strain, our experimental spin moment change is $-0.14 \pm 0.06 \mu_B$, quantitatively consistent with our theoretical value of $-0.1 \mu_B$.

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Strontium ruthenate [1] belongs to a broad scope of perovskites and has attracted extensive attention, due to its exotic properties. When slab thickness decreases, its itinerant ferromagnetic (FM) phase disappears [2]. This has motivated many experimental [3–6] and theoretical investigations [7–9] to search the origin of the loss of the FM metallic phase. Another perovskite, SrTiO₃ (STO), is a good insulator, and also has attractive physical properties such as superconductivity and two-dimensional electron gas on its surface and interfaces [10, 11]. It would be a fascinating idea to investigate a superlattice which consists of one layer of “conducting” SrRuO₃ and one “insulating” layer of SrTiO₃, or SRO/STO superlattice. Experimentally, thicker superlattices have already been fabricated [12–15]. The Curie temperature decreases [14, 15] with the decrease of the period of the superlattice. The magnetic moment of the Ru atom is suppressed, and no FM ordering was identified in a 1/1 superlattice. A question is thus raised whether there is indeed any magnetic ordering established in the SRO/STO 1/1 superlattice.

With the advent of the state-of-the-art molecular-beam epitaxy (MBE), pulse laser deposition (PLD) and other growth techniques, it is now possible to fabricate interfaces with atomic sharpness. This is particularly true for systems with a very small lattice mismatch, such as SRO/STO. More importantly strain can be controlled through different substrates. For instance, TiO₂ and MgO [16] can induce an in-plane strain of -4% and 7%, respectively. Piezoelectric substrates like PMN-PT even allow one to control the strain in real time [17]. This greatly facilitates materials engineering.

In this *Letter*, we report that such a superlattice undergoes an intriguing magnetic phase transition under epitaxial strain. Our experiment first shows that in a well prepared SRO/STO superlattice sample, ferromagnetic ordering can survive down to ultrashort period (1/1). We can tune its magnetic properties by applying different strains. Our first-principles calculations further reveal that the in-plane strain can drive the system from a ferromagnetic to an antiferromagnetic phase at a critical strain $\xi_c = 5\%$. Within the ferromagnetic phase, three structurally different phases are identified: below 0.25% (α phase), the RuO₆ and TiO₆ octahedra rotate in the opposite direction but without tilting; between 0.25% and 2.5% (β phase) tilting starts and the rotation angles of both RuO₆ and TiO₆ are reduced; and above 2.5% (γ phase), both RuO₆ and TiO₆ rotate in the same direction. To understand these dramatic changes, we carefully examine the borderline between phases and find that the frontier spin-down Ru- t_{2g} orbital is mainly responsible for the phase transition, where

its occupation changes with the strain. These phase transitions directly lead to a qualitative difference in dielectric tensor, a signature that can be probed experimentally.

We grew [SRO/STO]₃₀ superlattice samples using laser MBE on three different substrates: STO, Nb:STO and LaSrAlTaO (LSAT). The growth of 1/1 superlattice films was monitored by reflection high energy electron diffraction (RHEED), which showed a layer-by-layer growth mode, (see the Supplementary Materials for more details.) Lattice mismatches in terms of STO lattice constant for these substrates are 0%, 0.05% and -0.92%, respectively. The structures were characterized by x-ray diffraction (XRD) using the synchrotron radiation [18] beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF), shown in Fig. 1(a). The data shows unambiguously that the superlattices are smooth and free of any second phase. From the (002) peaks (see Fig. 1(a)), we estimate the out-of-plane lattice constants for these films to be 3.982 Å, 3.978 Å and 4.009 Å, respectively, meaning that the samples are strained according to the substrate lattice. The Laue oscillations of the peak due to the total crystalline film thickness indicate a good [001] orientation of the film. Surface atomic force microscopy (the inset of Fig. 1(a)) reveals that all these samples have a smooth termination with the roughness below 1 uc.

The magnetic properties were measured at 5K by vibrating sample magnetometer (PPMS VSM Option Release 1.2.4 Build 1). Although the magnetization is suppressed compared to the bulk SRO, clear hysteresis loops (M-H) are observed in all our samples. Superlattice recovers some of the lost FM ordering in SRO thin films. To our knowledge, this has not been reported before at 1 uc-thick SRO thin films and superlattices. Though the coercive field weakly depends on substrates, both the remanence and saturation field strongly depend on the substrates. The spontaneous magnetization changes from $0.12 \pm 0.03 \mu_B$ (on Nb:STO) to $0.30 \pm 0.03 \mu_B$ (on LSAT) per Ru. The Ru magnetic moment decreases as the strain increases (see the inset in Fig. 1(b)). For one percent change in strain, the magnetic moment change is $-0.14 \pm 0.06 \mu_B$. Since film thickness and growing conditions are the same for all our samples, the lattice mismatch, or the strain, is directly responsible for the magnetic properties change.

To understand the strain effects in this superlattice, we resort to first-principles calculations. For bulk SRO, extensive calculations have been performed to investigate changes in structural, electronic, and magnetic properties [8, 19–22], but very few on a superlattice [23–25]. We carry out first-principles calculations on a STO/SRO superlattice (see the inset

in Fig. 1(a)) within the local spin density approximation plus Hubbard on-site Coulomb repulsion (LSDA+U) [18, 26]. Within this scheme, the magnitude of U_{eff} is treated as an empirical parameter, which will be discussed in the following text and the Supplementary Materials.

The in-plane tensile strain ξ , defined as $\xi = (a - a_{\text{STO}})/a_{\text{STO}}$, is applied to the superlattice. Here a is the lattice constant in use while a_{STO} is that of the parent compound. The in-plane strain is changed from -4.5% to 6%. At each strain, the ion positions and the out-of-plane lattice constant are fully relaxed. There are three distinctive angles to characterize the structure change. One is the tilting angle ϕ around an axis parallel to (001) plane (see the inset in Fig. 1(c)). The other two angles θ_{Ru} and θ_{Ti} denote rotations around [001] axes of the RuO_6 and TiO_6 octahedra, respectively.

Figure 1(c) shows the energy difference between FM and AFM phases as a function of strain. In a wide range of strain, the FM alignment between the neighboring Ru atoms is energetically favored. The magnetic moment is $2 \mu_B$ per SRO formula unit, which is consistent with the calculated ferromagnetic ground state of bulk SRO [22]. However, when the tensile strain exceeds $\sim 5\%$, the structure with c-type AFM phase becomes more stable than that of FM. Therefore, a magnetic phase transition occurs at this critical strain. One notices that the total energy difference between the AFM and FM structures is linear with respect to strain but with three different slopes (see the caption of Fig. 1). This suggests structural phase transitions taking place as a consequence of strain variation.

The observation is indeed verified. Structurally, the FM region can be subdivided into three different phases: $\xi \leq 0.25\%$ (α phase), $0.25\% < \xi \leq 2.5\%$ (β phase) and $2.5\% < \xi \leq 5\%$ (γ phase) (see Figs. 1(c) and 1(d)). Within α phase the neighboring octahedra rotate counterclockwise with respect to each other, where θ_{Ru} is always positive but θ_{Ti} is negative (see Fig. 1(d)). There is no tilting, i.e. $\phi = 0^\circ$. The quenching of tilting renders the superlattice with a high symmetry of $P4/mbm$, making it easy to be detected (see below). Similar observations have been reported experimentally in single crystals [9, 27–29]. Once the strain exceeds 0.25%, the symmetry is reduced to $P2_1/c$. The β phase features a tilting ($\phi \neq 0^\circ$) and two octahedra TiO_6 and RuO_6 rotating in the opposite direction (see $\theta_{\text{Ti}} < 0$ and $\theta_{\text{Ru}} > 0$). In the γ phase the TiO_6 octahedron rotates in the same direction as RuO_6 .

To shed light on this structural phase transition, we zoom in a small region around $\xi = 0.25\%$ (see the small dashed box in Fig. 1(d)). We manually change four structural

parameters (ϕ , θ_{Ru} , θ_{Ti} and ξ) around their respective equilibrium values while keeping the rest unchanged. To make a quantitative comparison, we choose the structure at $\xi = 0.45\%$ with a tilting angle $\phi = 3.88^\circ$ as the reference structure since it is near the critical point. The energy difference curves are plotted in Fig. 2(a). The energy minimum is indeed at its global minimum, since each curve has a minimum at 0° , with a small deviation in $\Delta\theta_{\text{Ti}}$ due to our energy threshold of ± 1 meV in our optimization procedure. Contributions from each angle are very different. The rotational angle $\Delta\theta_{\text{Ru}}$ has the strongest effect on the energy change among all the angles. If we fit the energy change to a harmonic potential $\frac{1}{2}K_{\Delta\theta_{\text{Ru}}}(\Delta\theta_{\text{Ru}})^2$, we find $K_{\Delta\theta_{\text{Ru}}} = 16$ meV/Deg², or 53 eV/rad² [30]. This is much larger than that of $K_{\Delta\phi} = 1$ meV/Deg² and $K_{\Delta\theta_{\text{Ti}}} = 4$ meV/Deg². In addition, the energy change of $\Delta\theta_{\text{Ti}}$ is highly anharmonic. We expect experimentally Raman spectra can easily distinguish them.

It is conceivable that the above strongest contribution from $\Delta\theta_{\text{Ru}}$ must be associated with the electronic structure of Ru ions. To see this, we integrate the Ru- t_{2g} projected density of states from -10 eV to the Fermi level. Figure 2(b) shows that the occupation of these orbitals changes substantially with strain. If we compare its change with the phase change in Figs. 1(c) and 1(d), we find a very nice match between them. Starting from the strain away from the critical one, the occupations in d_{zx} and d_{yz} are similar. Near the phase boundary of the structural phase transition their occupations differ from each other. The d_{yz} orbital gains electrons while the d_{zx} loses electrons. After tilting sets in, the occupations of these two orbitals again become close to each other. No other element has these characteristic changes. Moreover, since the Fermi level is mostly contributed by the Ru-O hybridized states, this explains why the energy change with respect to the rotation of RuO_6 is most pronounced. At the FM/AFM phase transition point, electrons are transferred from the $d_{yz/zx}$ to the d_{xy} orbital. One spin down electron resides almost entirely in the d_{xy} orbital. More details are provided in the Supplementary Materials.

We also investigate the effect of the Hubbard U on the above phase transitions. Structurally, U_{eff} has a minor effect [8]. Changes in the rotation angles at strain $\xi = 1\%$ and $\xi = 4.5\%$ are too small to show. The largest change of about 2 degrees in the RuO_6 rotation (Fig.2(c)) is found at a highly strained case ($\xi = 6\%$). But none of these affects the above phase separation. Therefore, the $P4/mbm \rightarrow P2_1/c$ transition is robust [18]. Figure 2(d) shows that the band gap for the AFM phase is established for $U_{\text{eff}} \geq 1$ eV, and the total

energy favors the AFM phase for $U_{\text{eff}} > 1.5$ eV. This is expected since it is well known that the strong on-site correlation favors an AFM phase [31].

Since U_{eff} effectively splits and shifts band states, the spin moment is fixed. To compare with our experimental spin moment change, we set U_{eff} to zero [32] and compute the spin moment change. The results are shown in the inset of Fig. 1(b). For every percent change in strain, our theoretical magnetic moment change of $-0.1 \mu_B$ agrees with our experimental value of $-0.14 \pm 0.06 \mu_B$ quantitatively.

Finally, we demonstrate that both predicted structural and magnetic transitions are detectable optically. The structural phase transition at $\xi = 0.25\%$ breaks the mirror symmetry (C_{2v}), while the magnetic ordering transition changes the band structure. The former leads to a dramatic difference in the off-diagonal element of the dielectric tensor, and the latter leads to another big difference in the diagonal elements. In other words, we probe structural and magnetic phase transition using two different tensor elements. Since VASP does not include the intraband contribution, we decide to use Wien2K to compute the tensor since both interband and intraband transitions are taken into account [18].

The off-diagonal element of the dielectric tensor is used to probe the first order structural phase transition. In α phase, C_{2v} mirror symmetry exists and all the off-diagonal elements are zero. When tilting sets in and the mirror symmetry is broken in β phase, nonzero ε_{yz} emerges, a manifestation of the beginning of octahedra tilting (see Fig. 3(a) and more discussions in Supplementary Materials). At the critical point the metal-to-insulator transition occurs. To observe this transition, the diagonal element is used. In the metallic phase, the low energy excitation consists of a plasma contribution, and the diagonal elements of dielectric tensor diverge like $1/\omega$. In the insulating phase, on the other hand, only interband transitions are left. The low energy divergence no longer exists. Such change can be seen in Fig. 3(b). Thus the two major phase transitions can be detected through a simple optical setup.

In conclusion, we have shown that SRO/STO superlattice preserves its ferromagnetic ground state at ultra-short limit. Our experiment has demonstrated that their magnetic properties are tunable through different strains induced by different substrates. This is confirmed in our theory. Our theory further reveals a strain-dependent phase evolution for SRO/STO superlattice, where increase in strain can drive the superlattice from a ferromagnetic metallic phase to an antiferromagnetic insulating phase. There are three phases within FM. In the α phase, the RuO_6 and TiO_6 octahedra do not tilt, but in the β and γ phases,

they do. We have shown that the Ru- t_{2g} orbital underlies these multiple-facet changes, which can be detected experimentally. By examining the effects of Hubbard U, we find that our theory with LSDA+U does qualitatively support our experimental findings that the strain induces changes in magnetic properties. Therefore, our findings are significant as they reveal fascinating opportunities in the Ru-based strongly correlated electronic systems, which are crucial for future applications in ferroics and nano devices [33–35].

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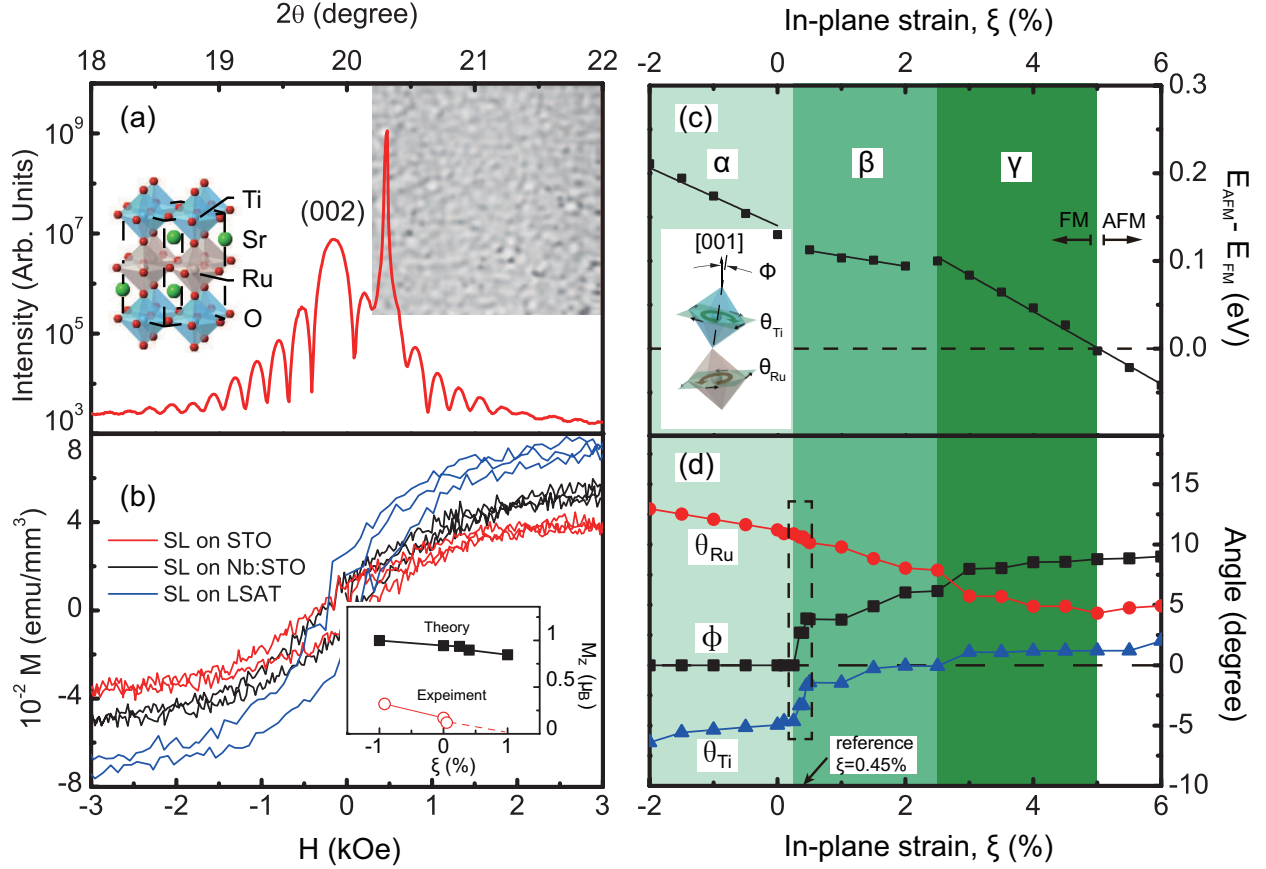


FIG. 1: (Color online) (a) X-ray diffraction pattern for the sample grown on STO substrate. Left inset: Superlattice structure, where Sr, Ru, Ti and O atoms are shown in green, brown, blue and red, respectively. Right inset: Surface AFM image for this sample. (b) Hysteresis loops for $[SRO/STO]_{30}$ superlattices grown on STO, Nb:STO, and LSAT substrates, respectively. The inset shows the magnetic moment of the Ru atom as a function of strain. (Exp: unfilled symbols and theory: filled symbols.) (c) Theoretical in-plane strain dependence of the total energy difference between AFM and FM phases. Three phases α , β and γ in FM phase are highlighted by shaded in three different colors. The slopes for the three fitting lines are -0.03, -0.01, -0.04 eV/percent in strain, respectively. Inset shows the tilting angle ϕ and two rotational angles θ_{Ru} and θ_{Ti} . (d) Optimized ϕ , θ_{Ru} and θ_{Ti} as a function of ξ . The dashed box is the region that is further examined in Fig. 2(a).

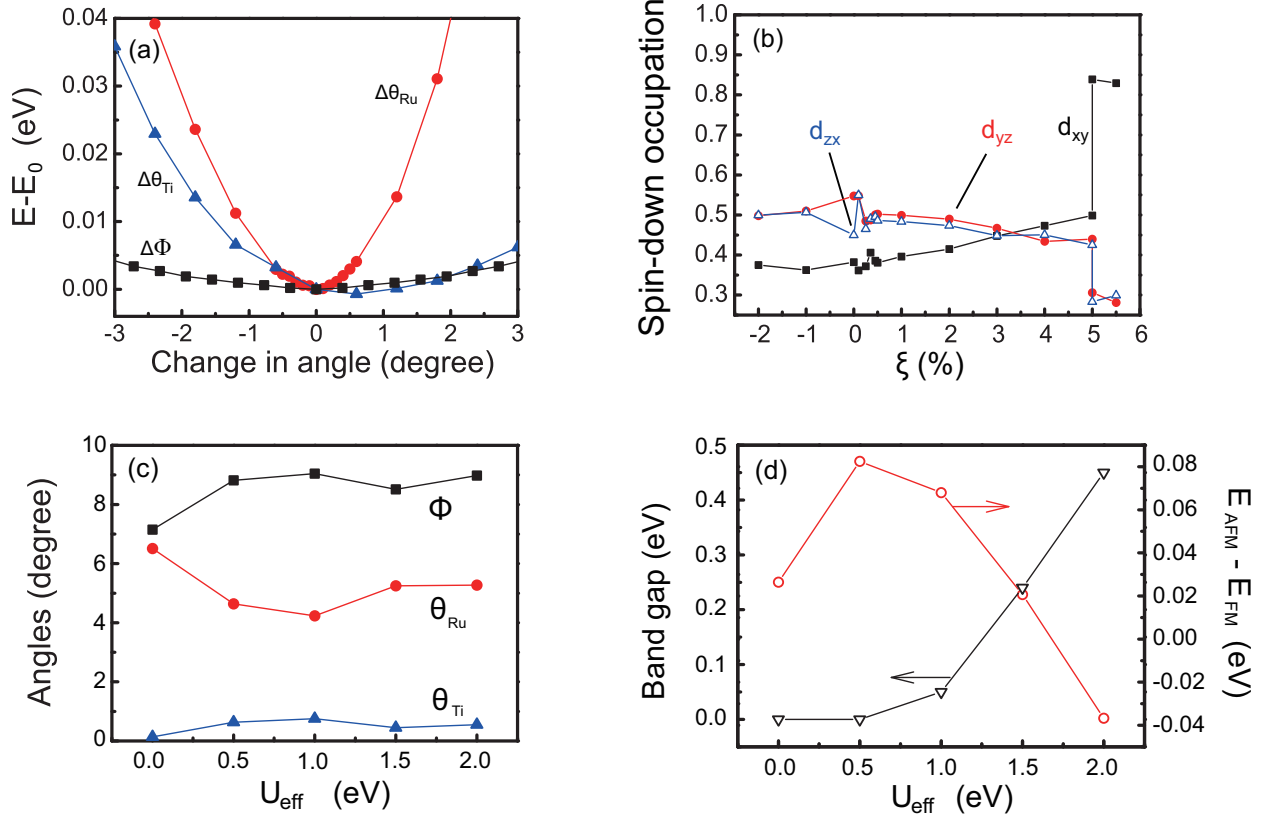


FIG. 2: (Color online) (a) Relative total energy as a function of the rotational and tilting angles. Here $\Delta\phi = \phi - \phi^0$, $\Delta\theta_{\text{Ru}} = \theta_{\text{Ru}} - \theta_{\text{Ru}}^0$, $\Delta\theta_{\text{Ti}} = \theta_{\text{Ti}} - \theta_{\text{Ti}}^0$, where ϕ^0 , θ_{Ru}^0 and θ_{Ti}^0 are their respective equilibrium values at the critical point ($\phi^0 = 0^\circ$, $\theta_{\text{Ru}}^0 = 10.9^\circ$, $\theta_{\text{Ti}}^0 = -4.7^\circ$). E_0 is the energy of the equilibrium structure. $\Delta\theta_{\text{Ti}}$ has its lowest point at $+0.6^\circ$, but this is within our relaxation accuracy of 2 meV. (b) Spin-down occupation of the three Ru t_{2g} orbitals. See spin-up occupation in the Supplementary Materials. The occupation is calculated by integrating the projected DOS from -10 eV to the Fermi level within the Wigner-Seitz radius of 1.402 Å. (c) Tilting and rotation angles at $\xi = 6\%$ as a function of U_{eff} . (d) Band gap for the AFM phase and total energy difference as a function of U_{eff} .

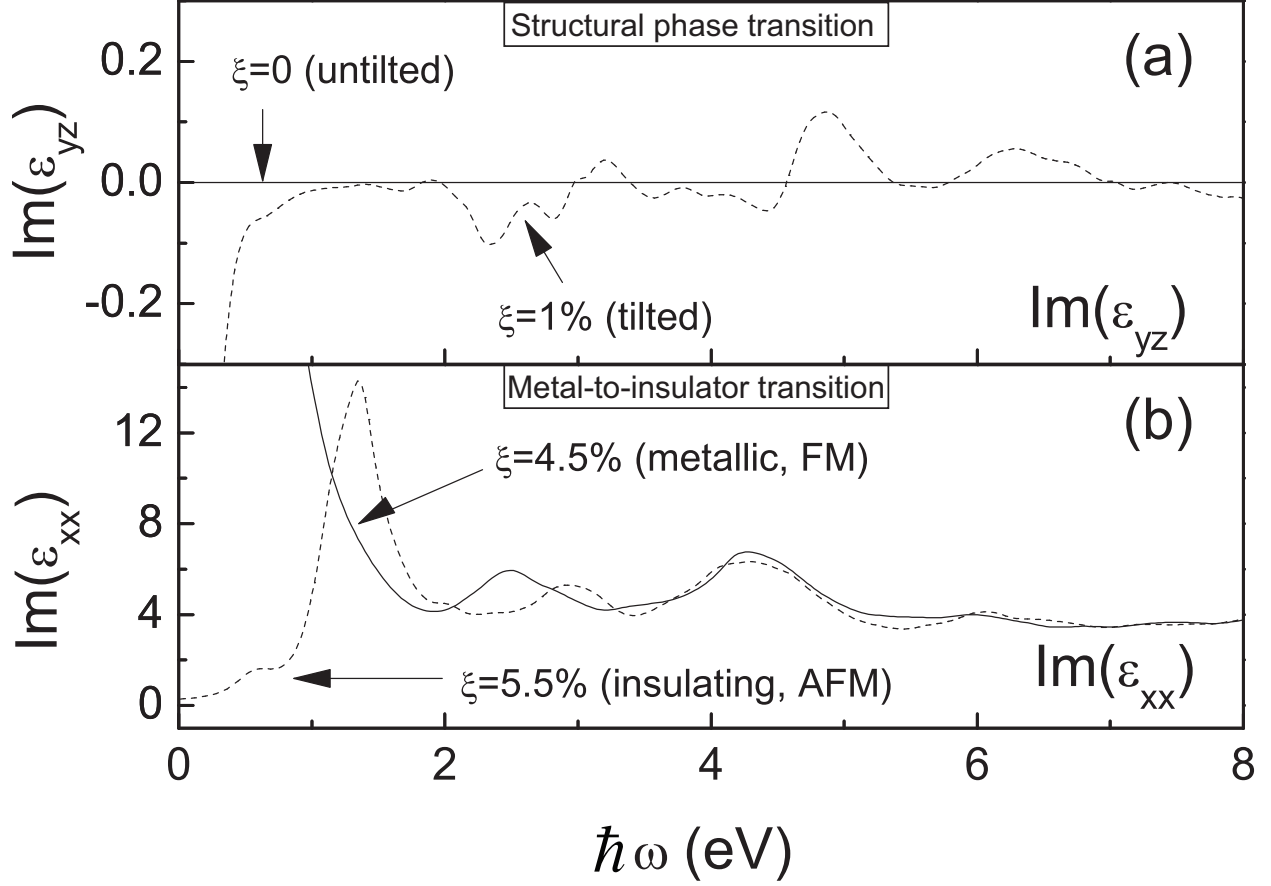


FIG. 3: Different optical tensor elements are used to monitor structural phase transition (from an untilted to a tilted structure), and the metal-to-insulator transition (from a metallic FM phase to an insulating AFM phase). (a) Off-diagonal element, $\text{Im}(\epsilon_{yz})$, as a function of photon energy $\hbar\omega$. The untilted structure has a null signal, while the tilted one has a signal. (b) Diagonal elements, $\text{Im}(\epsilon_{xx})$, as a function of $\hbar\omega$. The focus is on the lower energy side. In the metallic phase the $\text{Im}(\epsilon_{xx})$ diverges, while no divergence exists in the insulating phase.