A study of intermixing in perovskite superlattices by simulation-supported \( c_s \)-corrected HAADF-STEM

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In this paper, we present and interpret high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrRuO}_3 \) superlattices. The images were taken in a probe-corrected (\( c_s = 0 \)) FEI microscope at 300 kV. We developed a simulation-based technique to evaluate possible intermixing at the interfaces via \( Z \)-contrast. The experimental and simulated image intensities across the interfaces are directly compared, where the gradients in the models are systematically varied. Different gradients in different sub-lattices at the interfaces can clearly be distinguished by a best fit criterion.

Coloured HAADF-STEM image (\( V = 300 \text{ kV}, c_s = 0 \)) of a \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrRuO}_3 \) layer structure.

1 Introduction Nowadays, functional oxides are one of the central topics in materials science. In particular, perovskite structures exhibit a broad spectrum of appealing and novel physical properties, like (anti)ferromagnetism, (anti)ferroelectricity, superconductivity and multiferroicity [1]. In this paper, we present results of a structural study of the interfaces in \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrRuO}_3 \) (LSMO/SRO) superlattices. These superlattices show an intriguingly strong antiferromagnetic interlayer coupling below 150 K, when both LSMO and SRO individual layers are ordered ferromagnetically. References [2, 3] describe in detail the magnetic properties of this kind of superlattices. The superlattices were fabricated by pulsed laser deposition, employing a KrF excimer laser. The growth was done on vicinal \( \text{TiO}_2 \)-terminated \( \text{SrTiO}_3(100) \) substrates, at \( T_g = 650 \text{ °C} \) and in an oxygen atmosphere with \( p(\text{O}_2) = 0.14 \text{ mbar} \). The sample under study in Figs. 1–5 has 30 layers of 1.6 nm LSMO and 5 nm SRO layer thickness. In Figs. 7 and 8, a superlattice with ultra-thin layers in the range of 1 nm is discussed. The STEM specimens were prepared by standard mechanical and ion-beam thinning procedures.

The interfaces are investigated by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) using a TITAN 80-300 FEI microscope with a spherical aberration corrected (\( c_s = 0 \)) probe forming system. In addition, electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (the latter not shown here) were utilised to characterise the LSMO/SRO specimens.

Figure 1 shows an experimental image of a LSMO/SRO interface inside the superlattice. The two layer types can clearly be distinguished on an atomic scale. A zoomed part of the pseudo-coloured micrograph (left) is given on the right, with the line of intensity evaluation being inserted (cf. Figs. 3–5). Intensity evaluation means that we are looking for the interface model, which fits best to the experimental status of intermixing. The line was arranged that way (Fig. 1, right) to cross all different types of atomic columns near the interface. The examination of intensity profiles across the
interfaces was performed for a diversity of composition
gradients to study possible intermixing, especially of the
magnetic Mn and Ru ions. Such chemical information may
help to explain the magnetic properties of SRO/LSMO and
SRO/SrTiO$_3$/LSMO/SrTiO$_3$ superlattices [2, 3].

2 Methods Before focusing on the characteristics of
HAADF-STEM some of the milestones in the field of
electron microscopy concerning ‘atomic resolution’ and
‘chemical imaging’ should be mentioned. The first paper
demonstrating the visibility of single heavy uranium atoms
in a high-resolution scanning electron micrograph was

Besides STEM, the availability of 400 kV electron
microscopes in the late 1980s considerably improved the
attainable resolution in high-resolution electron microscopy
(HREM). HREM ‘structure’ images became possible for
well-prepared thin samples and for imaging conditions that
provided correct phases for all diffracted beams contributing
to the image. That generation of microscopes allowed to
develop and apply chemical mapping techniques, which
were pioneered by the group of Ourmazd [5, 6]. Alternative
approaches are introduced in Refs. [7, 8]. For theoretical
studies, compositional variations in alloys and heterostruc-
tures were described by interpolating the crystal potentials in
a virtual crystal approximation (VCA approach) [9].

Questions of quantitatively matching simulations with
experimental HREM images are systematically studied in
Refs. [10, 11].

The availability of annular dark field scanning trans-
mision electron microscopes avoids most of the artefacts
known for HREM images, in particular phase distortions and
strong delocalisation. Substantial papers on theory and
simulation of annular dark field STEM images were
published around 1990 by Kirkland [12], Cowley [13], and
Pennycook [14, 15]. Beginning in those years, a lot of very
interesting applications of HAADF-STEM in materials
science were published studying a great variety of material
systems and their properties. Examples for different studies,
e.g. of layer structures, surfaces and interfaces, are given in
Refs. [16–24]. The possibilities of HAADF-STEM con-
siderably increased with the availability of spherical
aberration-corrected electron microscopes, which is, e.g.
demonstrated in the review of Urban [25] and in Ref. [26].
Specific physical properties of superlattice structures, e.g.
their electronic states or structural instabilities, are subject of
Refs. [27–29].

The book ‘Advanced Computing in Electron Microscopy’ [30], written by Kirkland, gives an overview
on theory and modelling. The effect of chromatic aberration
on $c_s$-corrected STEM images is explored in detail in Ref.
[31]. Numerical aspects of HAADF-STEM simulations of
very large nanostructure models are studied in Ref. [32].

In 2009, Van Aert et al. [33] reported on HAADF-STEM
studies of intermixing in perovskite layer structures
fabricated by pulsed laser deposition. The authors focused
on the development and application of a direct quantitative
technique of $Z$-contrast analysis in experimental STEM
images. The methodology is supported by convincing
statistical arguments. In the paper, the authors assume that
the specimen has a constant thickness, and that the intensity
of each imaged atomic column is directly proportional to the
averaged $Z$-value (cf. Fig. 2b). The possible influence of
the sample thickness on the $Z$-contrast is not considered. The
chemical composition in columns of unknown type is then
interpolated on the basis of measured intensities of known
columnar composition. The attainable accuracy may be
controlled via selective tolerance intervals. The authors
demonstrated the quantitative mapping of interface profiles
in the layer system La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$.

Contrary to that purely experimental-based interface
analysis, our procedure focuses on HAADF-STEM image
simulations, in which we systematically varied a crystal
model of the interface as well as the significant image
parameters to identify the best fit to the experimental images

![Figure 1](online color at: www.pss-a.com) Experimental
HAADF-STEM image of a LSMO/SRO interface inside a super-
lattice. Coloured micrograph (left), zoomed section (right) with the
red line of numbered peaks.

![Figure 2](online color at: www.pss-a.com) Example of a SRO/
LSMO interface model. (a) Atomic occupancy factors in the sub-
lattice planes, (b) averaged $Z$-values. The interface region is marked
by vertical dotted lines.
via the least square criterion. Starting from [110]-oriented tetragonal unit cells (equivalent to [100]-oriented pseudo-cubic unit cells), the different interface models were coded in super cells containing up to 1688 atoms. For the super cell generation and modelling the software package CrystalMaker [34] was used.

Figure 2 illustrates the generation of the crystallographic interface models used for the STEM image simulations. We assume that the two different types of sub-lattices, namely the A-sites (La/Sr, dark blue) and the B-sites (Ru/Mn, light gray), show intermixing at the interface. Within the A- and B-sites, the two different atomic species are distinguished by square and diamond symbols. It is the goal of this paper to identify the extent of the intermixing zone, i.e. to determine the number of mixing lattice planes and the steepness of the composition changes. In Fig. 2b, we display the averaged Z-contrast to be expected for the interface region. It should be mentioned that any amount of intermixing and sub-lattice stoichiometry may be modelled with the VCA approach adapting the occupancy factors of the single atomic species [9].

The simulation scheme used for the HAADF-STEM image simulations was developed by Ishizuka [35]. The related software package WinHREM™ is available via internet. Its algorithm is based on an FFT multislice algorithm, assuming that the specimen is divided into thin crystal slices. A focused electron beam (probe), which is corrected in our case, scans the specimen area under study. The multi-slicing is then executed for each sample point contributing to the STEM image. It has to be noted that the numerous convolutions ⊗ are carried out via FFT/FFT⁻¹, which makes the algorithm fast. The wave function Ψ in the slice n + 1 is calculated as follows:

\[ \Psi_{n+1}(r) = \{ \Psi_n(r) \cdot q(r) \} \otimes p(r), \] (1)

where p(r) is the propagator, q(r) the crystal phase grating, and r is the position.

The electrons scattered into high angles are registered and form the HAADF-STEM image signal. For appropriate crystalline specimens the intensity registered for single atomic columns may be interpreted in terms of the averaged Z-values. We applied Weikenmeier-Kohl scattering factors and thermal diffuse scattering absorption [36]. The half-angle of the electron probe is \( \alpha_{\text{probe}} < 0.75 \) 1/Å, and the detector utilizes a band from 1.5 1/Å to 5.0 1/Å (half-angles). The STEM computations showed that the Z-contrast decreases with increasing crystal thickness \( t \), e.g. the ratio of \( I_{0.8}/I_{0.5} \) is 1.4 for \( t = 8 \) nm, and 1.1 for \( t = 48 \) nm. In the following, we denote La\(_{0.7}\)-Sr\(_{0.3}\) as La\(^+\).

Figure 3 presents an example of image simulation of a LSMO/SRO interface. Figure 3a shows a CrystalMaker picture of the six-plane intermixing model (inclined top view). In Fig. 3b a simulated micrograph is given for \( V = 300 \) kV and \( c_s = 0 \), where the intensities for the matching procedure shown in Fig. 5 are taken along the red line. For the focus \( \Delta = 0 \), the over-all aberrations are minimum, the Z-contrast is best, and the atomic columns can clearly be resolved. We changed stepwise the occupancy of both the A-site (La/Sr) and B-site (Ru/Mn) atoms in the lattice planes of the variably extended intermixing zone.

The results of the STEM simulations are usually given as 8-bit grey images, which is also the case for the experimental micrographs taken with the TITAN 80-300 STEM. The intensity values of the atomic columns to be analysed were extracted using the program DigitalMicrograph [37]. We performed a relative fitting of the HAADF detector raw data, assuming the intensities distant from the interface being those of LSMO and SRO, respectively.

The data acquisition procedure allows the integration of the intensities over a trace with an adjustable width (see yellow marked area). In Fig. 4, we compare an intensity profile of 1 pixel width (a) with intensity values integrated...
A number of 5–10 parallel lines allows to evaluate the complete peak intensities in a proper way, with the signal/noise ratio being improved (Fig. 4b). After finishing the data acquisition in the experimental and simulated LSMO/SRO images, the mean values of the $I_i(r)_\text{C1N}$ atomic column intensities are adapted by a constant normalisation factor $f$ for all $I_i(r)_\text{exp}$ values. Then the standard deviation is calculated. To evaluate the quality of the fit we use:

$$I_i(r)_\text{diff} = f \cdot I_i(r)_\text{exp} - I_i(r)_\text{sim},$$

$$I_{\text{mean}} = \frac{1}{N} \sum_{i=1}^{N} I_i(r)_\text{diff},$$

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (I_i(r)_\text{diff} - I_{\text{mean}})^2}.$$  

The standard deviation values $\sigma$ used in practice are translated into [%]-values.

Figure 5 shows the quantitative comparison of the experimental STEM profile from Fig. 1 (green) with different simulated intensity curves. The chemical composition within one column may be interpreted in terms of “summed-up” $Z$-values. As marked by yellow bars in the left part of Fig. 5, two (model 1), six (model 2) and eight (model 3) atom planes intermix in the corresponding examples.

It is possible to identify unequivocally the interface model, which fits best to the experimental results. Model 2, which yielded the peak profile with best intensity agreement, has an intermixing zone of six $(2 \times 3, \text{cf. Fig. 2a})$ atom planes:

- La$^+$ mixing steps of $25\% \rightarrow$ Sr,
- Mn $\leftrightarrow$ Ru.

The numerical comparison of the 8-bit normalised peak intensities of models 1, 2 and 3 with the experimental peak intensities shows that model 2 provides the minimum standard deviation of $\sigma = 5.6\%$ for the considered eight peaks in Fig. 5 (cf. vertically dotted limits). One ought to keep in mind that the experimental STEM images contain additional unavoidable noise. It should be noted that a model without any intermixing in the range considered in Fig. 5, leads to $42.9\%$ deviation from the experimental intensity values.

In order to corroborate with the above HAADF-STEM analysis, and with the performed image simulations as well, we investigated the intermixing between SRO and LSMO by EELS line scans, employing a Gatan TRIDIEM energy filter.

The EELS results are shown in Fig. 6. We display the core loss intensities of the Ru-M$_{4,5}$, the Mn-L$_{2,3}$ and of the La-M$_{4,5}$ edges. The measurements were performed along a line of 6 nm length crossing three layers of SRO/LSMO/SRO in analogy to the one shown in Fig. 1. The intensities, indicated as number of counts, are calculated by integrating the background subtracted EEL spectra within windows set at the related edge energies. From Fig. 6 an intermixing of the elements Ru/Mn and La/Sr can be deduced to range over a distance of about 1 nm (or 5–6 atomic planes), which is
comparable to the findings by the introduced Z-contrast method.

3 Results and discussion  The quality of experimental images is always limited by the sample preparation, the imaging device itself and experimental noise. Figure 7 shows an experimental HAADF-STEM image of a SRO/LSMO interface taken at the TITAN 80-300 FEI microscope.

For statistical analysis and in order to check the homogeneity within the single perovskite components, we selected two different sub-lattices, namely La$_{0.7}$Sr$_{0.3}$ (top, yellow) and Sr (bottom, light blue). The peak intensities are extracted in both cases for 3 $\times$ 14 atomic columns. The mean value of the intensity for La$_{0.7}$Sr$_{0.3}$ reads as 243.7 ($Z_{La}: 57$). The value for Sr is 160.6 ($Z_{Sr}: 38$), both being scaled to 8-bit during the experimental registration procedure. The calculation of the standard deviation provided $\sigma$ = 4.8% for La$_{0.7}$Sr$_{0.3}$ and $\sigma$ = 4.2% for Sr. These accuracy values strengthen our opinion that there are narrow intensity distributions of congeneric atomic columns.

A superlattice with ultra-thin layers of LSMO and SRO is shown in Fig. 8. It was reported [38, 39] that very thin layers become insulating and non-ferromagnetic for a critical thickness being around 4-unit cells for LSMO and 3-unit cells for SRO. We, however, have strong experimental indication that our LSMO/SRO superlattices of nominally 3-unit cell thin individual LSMO and SRO layers are ferromagnetic. In addition to the related magnetic measurements (to be published somewhere else), HAADF-STEM images support the structural studies. The experimental peak profiles (green) taken along A-sites (La/Sr) and B-sites (Ru/Mn) are given in an 8-bit scale. The blue dotted marks help to recognise the typical shapes of the two profiles in the sub-lattices. Obviously, this STEM image allows to distinguish between box-shaped (Ru/Mn) and rounded (La/Sr) composition profiles.

Applying the methodology, which we introduced in Figs. 1–5, we may evaluate the intermixing in the multilayer system shown in Fig. 8. The HAADF-STEM simulations shown in Fig. 9 were carried out for a superlattice model with six layers containing 960 atoms ($a: 6.5$ nm, $b: 2.8$ nm, $c: 1.4$ nm). The six layers are stacked in the direction of the $a$-axis. According to the experimental findings, the Ru/Mn interface was assumed to be sharp. In the case of the La/Sr interface, we numerically proved that two intermixing lattice planes with

$$Sr \xrightarrow{\text{La/Sr}} La_{0.25}^{x}Sr_{0.75}, La_{0.75}^{x}Sr_{0.25} \rightarrow La^{x}$$

Figure 7 (online color at: www.pss-a.com) Statistical analysis of sub-lattice intensities in a STEM image of SRO/LSMO. The peak intensities are taken from 3 $\times$ 14 atomic columns marked by yellow and light blue lines.

Figure 8 (online color at: www.pss-a.com) Experimental HAADF-STEM image of a LSMO/SRO multilayer structure (middle). The peak profiles along the A-sites (La/Sr, bottom) and along the B-sites (Ru/Mn, top) were taken at the yellow and red lines, respectively. The A-site and B-site profiles look very different.

Figure 9 (online color at: www.pss-a.com) HAADF-STEM image simulation of a LSMO/SRO multilayer structure. Middle: Simulated micrograph ($V = 300$ kV, $c_{s} = 0$, grid: 512 $\times$ 512). The peak profiles along the A-sites (La/Sr, bottom) and along the B-sites (Ru/Mn, top) were taken at the yellow and red lines, respectively.
provide the best fit to the experimentally determined profile of the Z-contrast (cf. Figs. 8, 9 bottom parts). The Z-contrast is optimum for thin specimens (<10 slices of thickness c) and attenuates for increasing thickness.

The differences between the profiles of the La/Sr-(rounded) and Ru/Mn- (box-shaped) sublattices are surprising experimental findings. For the LSMO/SRO superlattices with thicker layers, we did not observe a similar behaviour. We suppose, it has to do with the considerably shorter deposition/growth time of these ultra-thin layers in the related superlattices.

4 Summary The microstructure of superlattices combining La0.7Sr0.3MnO3 and SrRuO3 and the atomic structure of their interfaces were studied by means of HAADF-STEM. The interfaces were proven to be affected by intermixing over 1–3 unit cells. This finding is in good agreement with our EELS studies, documented by the line scans of the La, Mn and Ru EELS edge intensities across the interfaces. Atomically resolved Z-dependent HAADF-STEM images offer a fairly good insight into interface diffusion/intermixing phenomena, if the experimental micrographs are quantitatively interpreted by simulated images of interface model structures.

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