# Quantitative measurement of structural fluctuation at LaNiO<sub>3</sub>/LaAlO<sub>3</sub> interfaces as a function of thickness

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It has been well documented that oxide films thinner than a few unit cells (u.c.) are often insulating, and the Anderson localization supported by the low dimensionality is one of the major mechanisms of such insulating behavior. To discriminate the effect of randomness from that of dimensionality, we examined structural fluctuation as well as the average structure of LaNiO<sub>3</sub> thin films on LaAlO<sub>3</sub> substrates as a function of thickness. The surface x-ray diffraction experiment revealed that there is little difference in average atomic position and atomic occupancy among 2 to 5 u.c. thick samples. The main difference occurs in the atomic displacement parameters. 4 and 5 u.c. thick samples have significantly smaller atomic displacement parameters than 2 and 3 u.c. thick samples. This result suggests that structural fluctuation plays some role in the interfacial transport properties although it is often neglected in the discussion of oxide interface physics.

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# I. INTRODUCTION

Fluctuation makes electrons localized. This effect, Anderson localization, is enhanced under lower dimensionality. Although there is interfacial free electron gas [1] or interfacial superconductivity [2] at the oxide interfaces, the interfaces tend to make the electrons immobile [3]. For example, the electron conduction of two-dimensional electron gas at the interface between LaAlO<sub>3</sub> (LAO) and SrTiO<sub>3</sub> (STO) is suffered by the Anderson localization when the STO channel is thinner than six unit cells (u.c.) [4]; a 3 nm thick  $SrIrO_3$ film shows Anderson type metal-insulator transition whereas 35 nm thick samples show metallic behavior [5], etc. [6]. Any kind of spatial fluctuations that interact with carriers, such as structural, electronic, magnetic, or orbital fluctuations, have an ability to make carriers localized. In the case of the interfaces of strongly correlated materials, electron correlation may cause a further unexpected type of fluctuation.

Interfaces between transition metal oxides exhibit various phenomena. For example, charge transfer across the interface induces many characteristic phenomena [7,8]. It is also reported in various systems that electric resistivity increases in very thin films, typically  $\sim 3$  u.c. thick or thinner, whereas metallic conduction appears in thicker films [3,5,6,9– 11]. The thickness-induced metal-insulator transition may be caused by various mechanisms. Atomic interdiffusion at the interface and interfacial cation/anion deficiency cause strong randomness, as well as the formation of different materials, at the interface. The reduction of the bandwidth happens due to dimension lowering. Spontaneous electron migration and electron correlation can induce inhomogeneous doping as well as inhomogeneous electric field. Under such a complicated situation, detailed structure information including spatial fluctuation is required to clarify the origin of the carrier localization at the interface.

Every static fluctuation in materials is either induced by or reflected in the structural fluctuation. The degree of structural fluctuation is measured by the isotropic atomic displacement parameter  $B_{iso} = 8\pi^2 \langle u^2 \rangle$  for each atom, where *u* denotes the atomic displacement from the equilibrium atomic position in the crystal lattice along a certain direction. The crystallographically defined  $B_{iso}$  parameter for each site is easily measured for crystalline samples by performing x-ray structure analysis. Although they are interpreted as the measure of the thermal vibration in the most cases,  $B_{iso}$  reflects both dynamical and static displacements from their equilibrium position. For the interfaces, it can be derived through a detailed analysis of the crystal truncation rod (CTR) scattering data, which is one of the methods of surface x-ray diffraction. Since the analysis involves many parameters, reliable  $B_{iso}$  parameters for oxide interfaces are rarely reported so far. One of the examples of such observations is the large  $B_{iso}$  parameters for oxygens at the hydrophilic  $TiO_2$  surface [12]. For the epitaxial interfaces of metal oxides, the number of structural parameters to be determined is increased, which makes a reliable analysis difficult. In particular, the  $B_{iso}$  parameters cannot be extracted from the model-free electron density analysis, although such an analysis is a powerful tool for determining atomic positions in complicated structures [13,14]. To obtain the values of

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 $B_{iso}$  parameters, one needs to perform structure refinement with proper estimation of experimental uncertainty. For this requirement, we utilized Bayesian inference of the interfacial structure [15] on the basis of the CTR data with the aid of the idea of effective number of observations [16].

In this study, we have examined the structural fluctuation as well as the average structure of LNO thin films grown on pseudocubic LAO (001) surfaces, one of the most well studied oxide interfaces. The *c*-lattice parameter of thick LNO films on LAO is  $3.901 \pm 0.006$  Å [9,17]. When the oxygen partial pressure during film growth was decreased from 0.2 to 0.02 mbar, an increase of the *c*-lattice parameter by 0.05 Å is reported for LNO films on STO [18], which is a result of the introduction of oxygen vacancies. Around the surface of LNO ultrathin films, outward Ni displacement from the oxygen layer by  $\sim 0.1$  Å occurred within the range of a few u.c. from the surface [19], in accordance with their theoretical calculation. The effect of an LAO cap layer on top of LNO/LAO films was reported in [20]. The Ni-O-Ni bond angle at the surface, which is related to the transfer integral, was strongly affected by the cap layer. Our result shows that the interplane distance in the LNO ultrathin films is constant regardless of the carrier mobility, whereas the positional fluctuation shows a noticeable difference between the metallic and insulating interfaces.

# **II. EXPERIMENT**

LNO thin films with a thickness of n u.c. were grown on atomically flat (001) surfaces of LAO (n = 1 to 5) by pulsed laser deposition; we denote these samples as  $(LNO)_n/LAO$ . The samples were grown by the same group with the same condition with Ref. [9], in which the transport property and the density of states of the films as a function of the thickness were reported. (LNO)<sub>5</sub>/LAO has finite density of state at the Fermi energy,  $n \leq 3$  shows soft-gap behavior, and n = 4 is the transient thickness [9]. Eight pieces of samples were prepared: two pieces each for n = 2, 3, and 5 samples and one piece each for n = 1 and 4 samples. During deposition, the substrate temperature was maintained at 450 °C under an oxygen pressure of  $10^{-3}$  Torr. The film thickness was precisely controlled on the atomic scale by monitoring the intensity oscillation of reflection high-energy electron diffraction. The films were subsequently annealed at 400 °C for 45 min under oxygen at atmospheric pressure to fill residual oxygen vacancies.

The CTR scattering measurements were performed with the four-circle diffractometers installed at BL-3A at the Photon Factory, KEK, Japan, and the six-circle diffractometer at BL13XU [21,22] of SPring-8, Japan. The x-ray energies were 12 and 25 keV, respectively. During the measurements, the samples were kept in a vacuum chamber at  $10^{-5}$  Torr. The scattering intensity from LNO/LAO samples was detected by a two-dimensional pixel array detector. Illumination area and Lorentz factor corrections were applied following the formula provided in [23]. The scattering vectors ( $hk\zeta$ ) were expressed with the basis vector of the reciprocal lattice vectors corresponding to the pseudocubic LAO lattice.

For each of the samples of each thickness, measurements along hk = 00, 01, 02, 11, and 12 rods up to  $\zeta = 4$  were performed. We call the samples  $n\alpha$ , where  $n = \{1, 2, ..., 5\}$ 

denotes the designed thickness. The original image data for them are identical with the result reported in [24]. For this study, we have improved the image data processing to evaluate precise scattering vector for the observed signal using the position sensitivity of the detector. In addition, the Monte Carlo (MC) sampling procedures were improved to the exchange MC method [16] to increase the searching power of the global minimum solution. The other samples were newly grown and measured. The samples  $n\beta$ , where *n* denotes the designed thickness, were measured in a wide range in the reciprocal space.

Structure refinement and estimation of the uncertainty of the refined parameters were performed using the maximum *a posteriori* estimation via the software CTR-structure [15,16]. We considered the intensity on the rods having only integers *h* and *k* in our analysis. The occupancy parameters *occ*, isotropic atomic displacement parameter  $B_{iso}$ , and out-of-plane atomic displacements *dz* with respect to the substrate lattice were refined. In addition, the O2 site, the oxygen site on the BO<sub>2</sub>plane parallel to the surface, was assumed to be split by  $2\Delta z$ along the surface normal direction for the analyses for samples  $2\beta$ ,  $3\beta$ , and  $5\beta$ .

## **III. RESULTS AND ANALYSIS**

CTR scattering data for samples  $2\beta$ ,  $5\alpha$ , and  $5\beta$  are presented in Fig. 1, together with the result of the fitting. The typical *R* value ( $R = \frac{\sum |\sqrt{I_{exp}} - \sqrt{I_{cal}}|}{\sum \sqrt{I_{exp}}}$ , where  $I_{exp}$  and  $I_{cal}$  denote the measured and calculated intensity, respectively) for the analyses of all eight samples was 10%. Figure 2 shows the depth profiles of *occ*, dz, and  $B_{iso}$  for the three samples. The midpanels show that the dz values for the B site ions are larger than those for the La sites around the surface, meaning that the B site ions displace outward with respect to the La ions for all samples. The  $B_{iso}$  parameters for sample 5 $\alpha$  were averaged over the unit cell; i.e., the  $B_{iso}$  parameters for La, B, O1, and O2 site atoms within a unit cell were assumed to have the same value, to reduce the number of fitting parameters. The depth profile of the averaged  $B_{iso}$  represents the positional fluctuation caused by the distance from the interface. For the samples  $2\beta$ ,  $3\beta$  (not shown in Figs. 1 and 2; see Supplemental Material [25]), and  $5\beta$ , wider range within the reciprocal space was measured, which allows us to extract the  $B_{iso}$  parameters for the La separately from those for the other parts in the unit cell. The increased  $B_{iso}$  at the interface for n = 5 sample is attributed only to the A site.

For better comparison between metallic (n > 4) and insulating (n < 4) LNO samples, the depth profiles of the dz of La and B sites are plotted in Figs. 3(a) and 3(b). We can see slight downturn around the surface in dz for the La site [panel (a)] and a slight upturn for the B site [panel (b)], which shows the abovementioned outward B site displacement with respect to the La ions. The closed symbols show the results for the insulating samples, and the open symbols show those for the metallic samples. As can be seen, there is no clear difference in the slope of the dz parameter, which shows the lattice spacing between the insulating and metallic films. This result differs from our previous study [24], in which we reported the different lattice spacing for insulating  $(2\beta$ 



FIG. 1. CTR scattering profiles along the  $hk\zeta$  rods for samples (a)  $2\beta$ , (b)  $5\alpha$ , and (c)  $5\beta$ . The open symbols show the experimental results. The solid curves show the results of fitting, indicating the calculated intensity derived from the refined structure. The error bars, which are shorter than the symbol size for most of the plots, show the statistical error.

and  $3\beta$ ) and metallic ( $5\beta$ ) LNO films on LAO substrate. The experimental data for the samples  $1\alpha-5\alpha$  are identical with those used in [24], and the difference is therefore caused by the improvement of the data analysis.

In contrast, there is a clear difference in the  $B_{iso}$  parameter between the metallic and insulating samples as shown in Fig. 3(c). Although n = 1, 2, and 3 samples show large  $B_{iso}$  parameters in the entire LNO region, n = 4 and 5 samples have small  $B_{iso}$  parameters in the middle of the LNO region. The site dependence of the  $B_{iso}$  parameter is exhibited by Fig. 3(d). For the sample  $2\beta$ , La and BO<sub>6</sub> octahedra have similar values of  $B_{iso}$  parameters, which show monotonic increase from the interface to the surface. This result means the positional fluctuated layer has larger fluctuation. For the sample  $3\beta$ , the buildup of the fluctuation for BO<sub>6</sub> octahedra is suppressed compared with that for La. This tendency is more prominent in the sample  $5\beta$ . In the metallic n = 5 sample, the BO<sub>6</sub> sublattice has little structural fluctuation.

According to Fig. 3(d), La site has larger  $B_{iso}$  parameter than the octahedron network. The magnitude of  $B_{iso}$  induced by the thermal vibration for ordinary oxides at the room temperature is less than 1 Å<sup>2</sup>. The atomic displacement indicated by the  $B_{\rm iso} \simeq 3$  Å<sup>2</sup> is 0.15 to 0.2 Å, which cannot originate from thermal vibration. One possible source of this increase in  $B_{iso}$  parameter is the spontaneous alternating A-site ion displacement, which is commonly observed in bulk RNiO<sub>3</sub> crystals for R=Pr, Nd, Sm, or Eu. In order to examine this possibility, we measured the intensity profile along  $(\frac{1}{2}\frac{3}{2}\zeta)$  and  $(\frac{1}{2}1\zeta)$  rods as shown in Fig. 4. The twofold structure of La induces new Bragg reflections characterized by the wave vectors of  $(\frac{1}{2}00)$ ,  $(\frac{1}{2}\frac{1}{2}0)$ , or  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  in the pseudocubic cell. There is no additional Bragg reflection except for the ones characterized by the wave vector  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ , which is the same wave vector with the LAO. The closed symbols in Fig. 4 show the measured intensity for samples  $2\beta$  and  $5\alpha$ . Red curves show the calculated intensity from the structure having the same NiO<sub>6</sub> octahedral rotation as that reported in [17] for thick films. The calculated intensities were derived with an assumption of the equidistribution of the possible structural domains corresponding to the symmetry breaking from the  $Pm\bar{3}m$  pseudocubic lattice. As can be seen, the intensity around  $\frac{1}{2}\frac{3}{2}\zeta$  for  $\zeta \sim \frac{3}{2}$  and  $\frac{5}{2}$ is well reproduced by the structural model without the La displacement. Therefore, the increased  $B_{iso}$  parameters of La sites in the LNO ultrathin films are not induced by the formation of the twofold structure. They are rather induced by



FIG. 2. Extracted structure parameters *occ*, dz, and  $B_{iso}$  for samples (a)  $2\beta$ , (b)  $5\alpha$ , and (c)  $5\beta$ .



FIG. 3. (a) Depth profiles of the La displacement with respect to the substrate lattice for samples having various thicknesses. (b) Depth profiles of the B site (Ti and Ni). (c) Depth profiles of the atomic displacement parameters averaged over the unit cell for samples  $1\alpha-5\alpha$ . (d) Depth profiles for the La site and BO<sub>6</sub> octahedra for samples  $2\beta$ ,  $3\beta$ , and  $5\beta$ . (e) Schematic of the atomic fluctuation for samples  $5\beta$  and  $2\beta$ .



FIG. 4. Intensity profiles measured along  $\frac{1}{2}\frac{3}{2}\zeta$  for samples (a)  $2\beta$  and (b)  $5\alpha$ . Red solid curves show the calculated intensity assuming the same NiO<sub>6</sub> octahedral rotation as that reported in [17] for thick films. (c) Selected x-ray photography taken on  $\frac{1}{2}\frac{3}{2}\zeta$  line (top panels) and  $\frac{1}{2}1\zeta$  line (bottom panels). The split peaks on the top panels are caused by the twin structure of pseudocubic LAO substrate.

the static structural inhomogeneity. Our structure refinement is summarized in Fig. 3(e).

#### **IV. DISCUSSION**

## A. Average structure at the surface/interface

Local polarization of the interior of thin films has been studied experimentally for some perovskite oxide heterostructures [26–29]. As expected, films having high electric conductivity exhibit no polarization, and the overall polarization within the film is well explained by the band alignment at the interface [30]. The typical magnitude of the local polarization inside of the films that are a few nanometers thick is ~GV/m [29,31]. In the present case, we found no clear polarization in the interior of the metallic samples  $5\alpha$  and  $5\beta$ , as shown in Figs. 2(b) and 2(c); insulating films are too thin to have the interior region.

At the oxide surfaces, we often observe local polarization. In the present result, Fig. 2 shows that the B site ions around the surface displace outward with respect to the La ions for all samples. This result supports a previous structural report for LaNiO<sub>3</sub> films [32]. Similar surface polarization was also found in (La,Sr)MnO<sub>3</sub> ultrathin films (4 u.c. thick or thinner) on STO [33]. However, such a surface relaxation is not a general tendency of the (001) plane of perovskite oxides. For example, no such relative displacement is observed at the surface of LAO film on top of STO (A site displaces outward [28], or there is no relative displacement [34,35]). Surface polarization is sensitive to the surface contamination or adsorbate atoms; this feature is used to control the surface activity for the chemical reactions [36].

Interfacial volumetric expansion is often observed (LAO/STO [28,34,35]; (La,Sr)MnO<sub>3</sub>/STO [37]; LNO/STO [24,38]; and LNO/LSAT [32]), whereas no volumetric

expansion is reported for some cases (LAO/STO [13]; (La,Sr)MnO<sub>3</sub>/STO [33]; LaMnO<sub>3</sub>/LaNiO<sub>3</sub> interface [29]). There is no simple rule for predicting the interfacial expansion only from the chemical composition. To the best of our knowledge, there is no interfacial contraction in the interfaces between two perovskite oxides. Since the oxygen deficiency or excess oxygens make the cell volume larger, the magnitude of the expansion can be a measure of the defects. In our case, no interfacial expansion was observed in any of the eight pieces of LNO/LAO samples, which implies a small amount of the oxygen deficiency. Nevertheless, there is a large atomic fluctuation around the average positions at the interface, which is indicated by the large  $B_{iso}$  parameters.

#### B. Structural fluctuation at the interface

Figure 3(c) shows the depth dependence of the  $B_{iso}$  parameters. It may be treated as a three-layer structure, i.e., an interfacial large  $B_{iso}$  layer (~2 u.c. thick), a surface large  $B_{iso}$ layer (~2 u.c. thick), and a midfilm small  $B_{iso}$  layer. The idea of three-layer structure of thin films is instinctive and is often used for interpretation of the film properties [29,39– 41], whereas the characteristic features of the interfacial and surface layers are different. The layers can be characterized by octahedral rotation [40,42,43], *c*-lattice parameter [29,40], magnetization [39,41], or valence [29,44,45]. Here, we add a new class of layer characterization, the magnitude of the atomic positional fluctuation. The chemical transient layer is likely to involve positional fluctuation. All the samples have large  $B_{iso}$  parameter in the surface transient atomic occupancy region, at which the atom has its neighbor on one side, while it does not on the other side. Similarly, at the interface,  $\sim 1.6\%$ difference in average B-O bond length between LNO and LAO [46,47] causes fluctuations, while the effect should be weaker than that at the surface. The La ions having AlO<sub>6</sub> on one side and NiO<sub>6</sub> on the other side should be pushed away from the NiO<sub>6</sub> side. Therefore, it is natural to have a large  $B_{iso}$  parameter in the transient atomic occupancy region. Similarly, some increase in  $B_{iso}$ -parameter at the interface between LNO and STO, whose cell volumes are very different, and little increase in B at the interface between LaMnO<sub>3</sub> (LMO) and STO, whose cell volumes are quite close, were found in our previous report [29]. In this subsection, let us focus our attention on the interface.

The thickness of the interface is stable for all samples. Here, we examine the thickness of the transient layer from the point of view of Landau free energy  $F[c(z)] = \int [\frac{E_s}{2} (\frac{dc}{dz})^2 + E_b(-c^2 + \frac{1}{2}c^4)]dz$ , where *F* denotes the free energy as a functional of c(z), which represents the occupancy difference of Ni and Al, and  $E_s$  is the excess energy of the interface. The bulk energy term  $E_b(-c^2 + \frac{1}{2}c^4)$  provides energy minima at  $c = \pm 1$ , meaning that LNO tends to separate from LAO. In order to examine the interface, let us use the boundary condition c(z) = -1 for  $z \to -\infty$ , c(z) = +1 for  $z \to +\infty$ , and c(0) = 0. The solution is  $c(z) = \tanh(\sqrt{E_b/E_s} \cdot z)$ , showing that the thickness of the transient layer for occupancy is  $\sqrt{E_s/E_b}$ .

In the sample  $2\beta$ , both La and BO<sub>6</sub> octahedra have increasing  $B_{iso}$  from the interface to the surface. The sample  $5\beta$  shows little increase in  $B_{iso}$  around the interface for BO<sub>6</sub> octahedra and some increase in  $B_{iso}$  for La ions. The sample  $3\beta$  appears intermediately between them. This behavior shows that the interior of the thick film forms its stable structure and the structural deformation caused by the interface is limited to a-few-unit-cell thickness from the nominal interface. As mentioned above, one expects a large  $B_{iso}$  at the interface, and therefore little increase in  $B_{iso}$  around the interface for  $BO_6$  octahedra is intriguing. We interpret this as a result of the ionic packing around La and B site ions. Perovskite oxides having a tolerance factor less than one have a small A site ionic radius, which results in octahedral rotation. LNO is classified in this type. The structural framework is defined by the BO<sub>6</sub> octahedra, and small A site ions have wide room around them. Therefore, one can expect larger fluctuation in La sites. Electron conduction happens in the BO<sub>6</sub> cages, thus the structure of octahedral network is relevant for the discussion of transport property. Let us discuss the relation between the octahedral network and the transport property.

Anderson localization at the interface is usually explained by the interfacial fluctuation supported by low dimensionality [9,48–52]. The low dimensionality effect is often emphasized as the key to the localization [53] in the modern studies. Most of the previous studies assumed that the structural fluctuation is constant. In our study, the only difference between conductive LNO and insulating LNO is the degree of the structural inhomogeneity. In particular, the  $B_{iso}$  for BO<sub>6</sub> octahedra in the interior of the metallic LNO film is as small as that in the bulk substrate. This suggests that the insulating behavior in the LNO ultrathin films is due to enhanced structural fluctuations. Oxygen vacancies in the ultrathin films are proposed to be the cause of the insulating behavior [54]. Although we did not see oxygen vacancies around the interface, the large positional fluctuation of La can be caused by the vacancy at the neighboring oxygen site. Another possibility is that the atomic fluctuation is a result of the localization. The Coulomb interaction in an Anderson insulator causes the band structure to have a soft gap [50,51], which in turn modulates the atomic arrangement.

#### V. CONCLUSION

Thickness variation of the structure of LNO thin films was examined by a surface x-ray diffraction technique. The result was analyzed by the Bayesian inference to derive the atomic displacement parameters  $B_{iso}s$  as well as atomic occupancies and positions as functions of the depth. The result shows that the  $B_{iso}$  parameters are significantly large in the insulating films, which are thinner than 3 unit cells. When the film thickness is increased, the fluctuation is decreased to make a better connection of the BO<sub>6</sub> octahedra, which can break the localization of the electrons.

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## APPENDIX: EXAMINATION OF THE UNCERTAINTY OF ANALYSIS

Figure 2 shows the extracted structure parameters for samples  $5\alpha$  and  $5\beta$ . The diffraction data for the two results were taken from different pieces of samples and different measured Q range (here, Q stands for the length of the scattering vector). In addition, the parameter set used for the fitting was also different. In order to examine the sample dependence of the structure, we present the result of the analysis on sample  $5\beta$  with the same parameter set based on the similar Q range with sample  $5\alpha$  in Fig. 5. Figure 5 shows the data used for the analysis; the range is limited to  $\zeta < 4.2$ , which is the same as the data taken for sample  $5\alpha$ . The resulting parameter presented in Fig. 5(b) is very similar to Fig. 2(b), demonstrating the structure of the films were well controlled.

Occupancy and the  $B_{iso}$ -parameter often have strong correlation. This is because both the reduction of the occupancy and the increase of the  $B_{iso}$ -parameter results in a decrease of the amplitude of the scattered x-ray. Nevertheless, their different Q dependence allows us to observe the two parameters simultaneously when we measure sufficiently large Q range. Our MC analysis provides not only the uncertainty of the resulting parameters but also the correlation between the parameters. Figures 5(c) and 5(d) show the 40 000 MC samples of the occupancy for La and Ni vs unitcell averaged  $B_{iso}$  for z=4 position, i.e., at the surface region. As can be



FIG. 5. (a) The dataset for sample  $5\beta$  in the range of  $\zeta < 4.2$  together with the result of fitting. (b) The extracted structure parameters using the same parameter set with sample  $5\alpha$  shown in Fig. 2(b). (c) and (d) show the 40 000 MC samples of the occupancy for (c) La and (d) Ni vs unitcell averaged  $B_{iso}$  for z = 4 position, i.e., at the surface region.

seen, there are little parameter correlation between the  $B_{iso}$  and the occupancy parameters for this case. The error bars in

Figs. 2 and 5 show the distribution of the MC samples for each parameter.

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