

Order-disorder phase transition in Au₂Fe on Ru(0001)J.-B. Marie,¹ A. Bellec,¹ C. Chacon,¹ Y. Girard,¹ J. Lagoute,¹ V. Repain,¹ S. Rousset,¹ Y. Garreau,¹ and A. Coati²¹Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot-Paris 7, UMR CNRS 7162, 75205 Paris Cedex 13, France²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin Boîte Postale 48, 91192 Gif-sur-Yvette Cedex, France

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Order-disorder transition of the epitaxial surface alloy of bulk immiscible elements Au_{1-x}Fe_x on Ru(0001) is studied using complementary experiments of scanning tunneling microscopy and grazing incidence x-ray diffraction. For $x \simeq 1/3$, we evidence an apparent continuous transition towards disorder with increasing temperature from 550 to 700 K. An ordered Au₂Fe two-dimensional alloy is found to be composed of nanometer size domains of the three variants that switch to a two-dimensional solid solution with temperature. A two-levels model is developed to analyze those results which conducts to interpret this phase transition as the result of an order-disorder transition within two dimensional uncorrelated grains, or domains, with nearly fixed size. This system is a good candidate in order to study two-dimensional phase transitions of surface alloy, a largely unexplored domain but crucial to understanding thermal stability of bimetallic nanoparticles.

DOI: [10.1103/PhysRevB.94.235440](https://doi.org/10.1103/PhysRevB.94.235440)**I. INTRODUCTION**

Studies of surface modifications induced by chemical species and/or thermal instabilities are very important subjects of applied and fundamental researches. For example, metallic nanoparticles have interesting properties because of the versatile coupling between chemical and physical properties. Their surfaces play the most important role concerning chemical reactions with their environment. It follows that their resilience against strong modifications (composition, structures, shapes) will determine if the particles will or will not be industrially used. For bimetallic nanoparticles, the composition of surfaces and their ordered or disordered states are essential. Effectively, in real situations, some extrinsic defects will destroy the prepared particles such as adsorbed impurities or contacts with a substrate. Moreover, it is known that thermal transitions (order/disorder and fusion) are strongly size dependent [1]. So, in order to obtain stable facets we can use either bulk immiscible elements or a strongly segregating species. From a fundamental point of view the question is: Can we extend what is known about surfaces of semi-infinite alloys or surface alloys to the facets of nanoparticles? Unfortunately, especially for immiscible elements, there is little reported on the alloying thermodynamics and phase stability of the nanoparticles surfaces [2,3]. In this paper we are focusing on supported two-dimensional alloys of immiscible elements where there is a clear lack of theoretical and experimental studies, especially concerning their order-disorder phase transitions [4].

Here, in order to be exclusively sensitive to two-dimensional size effects, we used two bulk immiscible species, Au and Fe, deposited on a Ru(0001) surface. Indeed, when two species form ordered alloys or a solid solution in the bulk, they often form ordered two-dimensional (2D) alloys on a third surface. For examples, CoFe on W(110) [5] or NiPd on Au(111) [6]. So, nanoparticles of this kind of system can be unstable against grain boundaries formations [7] or segregation [8]. Concerning immiscible elements, except for PbSn on Rh(111) [9], all pure *AB/C* two-dimensional metallic alloys observed at room temperature (the substrate *C* is often a refractory material) after an annealing process are either disordered [10,11] or demixed under the form of domains

which sizes around a few nanometers [12,13]. For the other 2D metallic alloys *AB/B* (the commonly called surface alloys), *A* species is mixed within the first plane (at least) of a *B* substrate which provides a reservoir of *B* atoms. These last surface alloys are of great interest but segregation effects are so important that thermal studies restricted to their surfaces are difficult (surface melting of alloys has been theoretically studied based on a Landau approach but is clearly out of the scope of our systems) [14].

II. EXPERIMENTS

Au and Fe codeposited on the clean (0001) surface of a ruthenium single-crystal under ultrahigh vacuum conditions mix together and form a two-dimensional ($\sqrt{3} \times \sqrt{3}$) R30° superstructure (called $\sqrt{3}$ in the text). Preparation and scanning tunneling microscopy (STM) characterizations can be found elsewhere [15] together with *ab initio* calculations explaining its stability against phase separation [16], i.e., a negative enthalpy of mixing, ΔH . Shortly, in order to synthesize this superstructure, gold is first evaporated on the clean Ru surface, then briefly annealed in order to form two-dimensional islands. Iron is then evaporated at room temperature, followed by a flash annealing around 700 K. Notice that one pure Au monolayer (ML) relaxes partially its compressive surface stress through the formation of a herringbone reconstruction. Comparatively, a pure Fe ML stays under tension and is fully commensurate with the substrate forming a $p(1 \times 1)$ structure. When Au and Fe are mixed (which need an annealing at sufficient high temperature in order to give enough mobility to the atomic species), tensile and compressive area are relaxed through the formation of the 2D commensurate $\sqrt{3}$. Moreover, theory explains the stability of this structure among others because it maximizes the magnetic moment per Fe atom [16].

A. Order-disorder phase transition observed by GIXD

Some experimental observations are, however, still unexplained. First, for $x = 1/3$, prolonged annealing around 700 K does not improve LEED patterns characteristic of the $\sqrt{3}$ long range order (LRO) observed at 300 K (RT) (see LEED

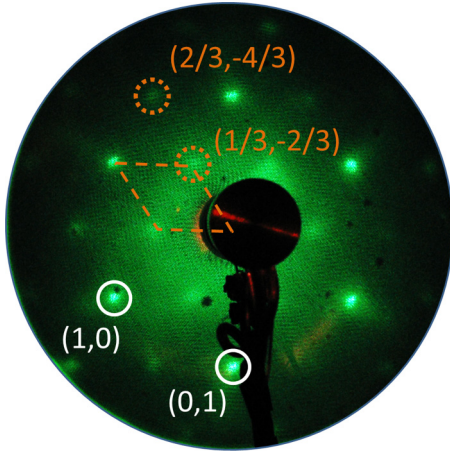


FIG. 1. A low energy electron diffraction (LEED) picture of a Au₂Fe ML on a Ru(0001) surface shows the threefold pattern of the $\sqrt{3}$ superstructure. First and second order peaks are indicated by dashed orange circles.

picture on Fig. 1). Second, for x between 0.2 to 0.5, we always observed large $\sqrt{3}$ superstructure peaks [see grazing incidence x-ray diffraction (GIXD) measurements on Fig. 2]. Third, whatever the stoichiometry, there is no signature of other ordered superstructure above RT. This point is in contradiction with previous theoretical calculations [15,16], where, depending on the stoichiometry, different small sized stable structures are predicted. We cannot exclude the existence of other larger sized superstructures at lower temperature, and similar experiments as the ones presented here could be performed to check this possibility. So, in this paper, we followed the growth and disappearance of the $\sqrt{3}$ above RT thanks to x-ray diffraction, and a scenario of continuous-order-disorder phase transition which involved defects is proposed thanks to complementary STM measurements presented in Sec. II B.

We performed GIXD experiments on the SIXS beamline in the SOLEIL synchrotron (see Fig. 1 for the peaks indexation in the reciprocal space). The best way to determine the

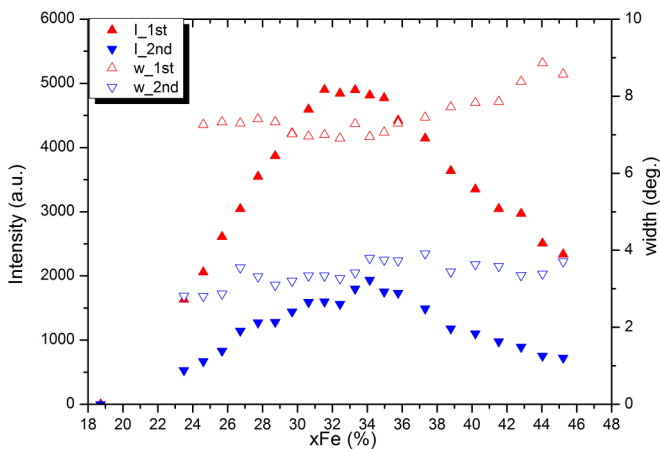


FIG. 2. Integrated intensities and widths at half maximum of diffracted $\bar{Q}_{1/3}$ and $\bar{Q}_{2/3}$ superstructure peaks as a function of Fe concentration x . First and second order peaks are indicated by up and down triangles, respectively.

order of the transition would be to follow some fractional Bragg peaks (BP) characteristic of the superstructure with increasing temperature until a complete disorder is established (no intensity). Fingerprints of the transition around the critical temperature are an abrupt (first order) or continuous (second order) decrease of the BP integrated intensity and a divergence of the width at half maximum. This is not what we observe.

After a standard cleaning procedure of the Ru surface and calibration of the two evaporators thanks to *in situ* STM measurements, we followed the x-ray diffracted intensity during heating and cooling of one Au₂Fe full monolayer. First, we annealed this sample from 530 to 690 K with a ramp rate of 1 K per min while recording in-plane ω scans (rocking scans) around fractional reciprocal space vectors of the $\sqrt{3}$ superstructure: $\bar{Q}_{1/3} = (1/3 - 2/3 \ 0.1)$ and $(2/3 - 4/3 \ 0.1)$. Once those peaks disappeared, we followed the cooling evolution by applying the same procedure. Those scans are presented in Fig. 3. The most striking results are: (i) those peaks are not sharp as BP should be; (ii) once rescaled, they exactly overlay each other, keeping constant the width at half maximum until complete disappearance. The first point (which is coherent with previous LEED studies) implies that the coherence length is small, i.e., superstructure domains are small. The correlation length derived from the width of the rocking curves according to the formula $L_c \simeq a\Delta\omega$ is around 3 nm ($a = 2.7 \text{ \AA}$). The second point is spectacular because we were expecting an enlargement due to an order-disorder phase transition, or direct melting (congruent phase transition). In order to be more quantitative, we adjusted the peaks by Lorentzian shape plus a continuous background (fits with Gaussian functions conduct to slightly worse results). We used the following fitting function:

$$y = y_0(T) + \frac{2A(T)}{\pi} \frac{\delta\omega(T)}{4(x - x_c)^2 + \delta\omega(T)^2}.$$

The peak integral $A(T)$ and the width at half maximum, $\delta\omega(T)$, are displayed on Fig. 5 for the heating and cooling procedures. First, there is no evolution between RT and $T_p \simeq 570 \text{ K}$. Then, the amplitude decreases continuously with temperature while the width at half maximum stays nearly constant until $T_e \simeq 700 \text{ K}$, above which the peaks become evanescent. Error bars reflect the precision of the measurements, essentially thermalization time and background subtraction.

How can this very peculiar behavior be understood? The Ru(0001) surface presents a triangular symmetry, so a $\sqrt{3}$ superstructure should follow a three-states Potts second order phase transition [17] between a perfect structure and a disordered $p(1 \times 1)$ (liquidlike or gaslike solid solution). Below the critical temperature, $T < T_c$, the long range order should conduct to a BP (convoluted by the instrumental width). Above T_c , the short range order (already present below T_c) should persist in the case of a second order phase transition (usually a broad Lorentzian). The temperature width of a second order transition is generally around 1 to 10 K. For a first order phase transition, there should be an abrupt disappearance of the BP with a lack of short range order and a more or less pronounced hysteresis behavior [18]. If the surface had contained “defects,” those evolutions

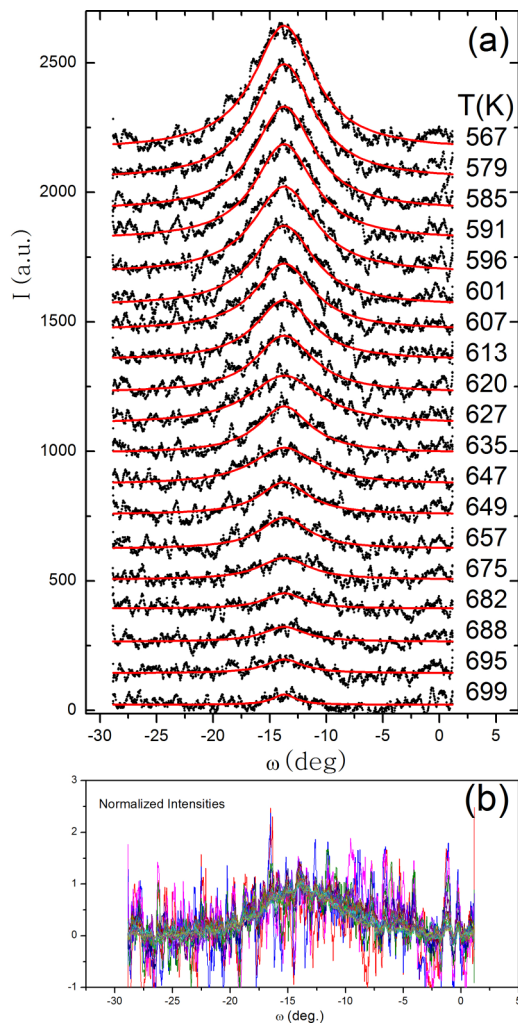


FIG. 3. Top: ω scan (rocking scan) dependence of the $\bar{Q}_{1/3} = (1/3 - 2/3 \ 0.1)$ superstructure peak intensity in a Au₂Fe ML on a Ru(0001) surface (background has been subtracted for clarity). Data were taken during a 1 K/min cooling rate from 700 to 550 K. A smoothing (black line, adjacent average on 10 points) has been applied. The red lines are Lorentzian fits of the data with a constant width at half maximum $\delta\omega(T) \simeq 6.5^\circ$ (similar fits can be obtained with Gaussian functions). Bottom: Same peaks normalized by the maxima of the corresponding Lorentzian fitting function. Those data show a collapse of the intensity without broadening indicating a sum of uncorrelated contributions from each domain.

should have been rounded and critical exponents consequently modified [19], but transitions should keep mainly their first or second order characteristics. All these reminders concern a reconstructed surface of pure elements or a commensurate adsorbed monolayer (ML). But, as previously said, much less is known about supported two-dimensional alloys. So we must answer three questions: (i) Why does the system seem blocked from RT to T_p ? (ii) Why is the peak width constant between RT and T_e ? How does one explain the decrease of the peak maxima with temperature?

Before answering, we must recall that diffraction peaks result from interferences due to correlated organization among objects. So, our GIXD measurements are essentially sensitive

to the in-plane ($l = 0$) $\sqrt{3}$ ordered part of the surface (an increasing background with temperature due to the diffuse intensity induced mainly by the Ru substrate that has been removed). Second, $\sqrt{3}$ superstructure develops in three equivalent domains separated by phase shift boundaries below the transition temperature. If the three domains are in equal proportion, which can be supposed because Ru is a hexagonal close packed (hcp) structure, and whatever if domain walls are periodically structured or not (we did not observe any splitting peaks), the intensities of fractional peaks are only due to atomic correlations inside domains [20]. So, we interpret our GIXD measurement by the addition of an incoherent contribution from each domain (see Sec. III).

To address the question of the pinning temperature, we first have to examine the thermal Debye-Waller factor (TDWF) of the Ru substrate and its influence on the surface's TDWF. It is known that the corrugation potential of a substrate could drastically limit the adatoms thermal oscillations [21]. So, below T_p , the alloyed film is trapped in the substrate potential, this temperature is called the freezing temperature [22,23], the system is kinetically blocked, and the fractional diffraction peak is nearly constant. Quantitatively, at RT, the mean bulk TDW factors of Ru, Au, and Fe are, respectively (in units of \AA^2), 0.14, 0.34, and 0.62 [24–26]. Then, it is clear that Au and Fe atoms on Ru are far from their own bulk environment and if we suppose that they are rigidly connected to the Ru, their oscillations are greatly reduced (the good comparisons should involve the surface's TDWF, which are around twice the bulk values, but the relative trend should be the same). With this crude hypothesis ($B_{\text{surf}} \simeq 2 \times 0.14 \text{\AA}^2$ for all the surface atoms), the intensity reduction around $\bar{Q}_{1/3}$ between $T_0 = 300$ and $T_e = 700$ K would be

$$I_{T_0}/I_{T_e} = \exp\left(\frac{Q_{1/3}^2 B_{\text{surf}}}{8\pi^2} \frac{T_e - T_0}{T_0}\right) \simeq 1.01.$$

Clearly, Ru TDWF does not affect intensities and has no direct influence on the Au and Fe vibrations. Moreover, we have to mention that it could be possible that the $\sqrt{3}$ is an intermediate structure between a more complex bigger unit cell sized superstructure [a $p(3 \times 3)$ for example] and the complete thermal disorder. This has been observed, for example, for Sn on Ge [27]. In that case, a possible solid-solid phase transition could exist and its critical temperature would be below RT. However, the temperature increase should be accompanied by a significant reduction of the surface TDWF. This is actually not the case, and even if we cannot reject this hypothesis, the study of this possible solid-solid phase transition should be studied specifically, which is beyond the scope of this actual chemical order-disorder phase transition. So, around T_p , Au and Fe atoms relax out of their potential wells and the system explores its phase diagram thanks to vacancies diffusion and direct atoms exchange between neighboring sites. We suppose that our measurements are realized at equilibrium and no decrease (or increase) of the intensity with time is expected. Then, above T_p , the system can be interpreted as an assembly of uncorrelated domains in which atoms move from site to site. Could we expect a demixing behavior? Three arguments are against this interpretation. As already explained, the alloy formation energy is negative, so for $T \neq 0$ entropic

contributions should increase the disorder, i.e., a random site occupancy. Second, recent *ab initio* calculations have shown [16] that a free-standing Au_2Fe 2D film (a plane between two vacuum slabs) can be ordered. So, this structure is extremely stable against demixing. Thirdly, kinetic Monte Carlo (KMC) results obtained for $\text{AgFe}/\text{Ru}(0001)$ [28] have shown that, indeed, this kind of system can present a demixed striped area until high temperatures. But the enthalpy of mixing of AgFe alloys are quasinull contrarily to AuFe alloys [15]. These three theoretical calculations act for the emergence of a completely disordered high temperature phase.

B. Medium range order: STM results

Now, we are addressing the intriguing issue of constant width at half maximum of the diffraction peaks whatever the temperature. As already evaluated, a rough estimation of a corresponding length scale is around 3 nm. This is very small compared to the size of domains limited by the Ru steps (around 50 to 200 nm in our case). So the system should be constrained by limiting factors such as kinetics which control the annihilation of domains walls, or a small amount of pinned defects. The first possibility could be ruled out because we verified the reproducibility of our measurements with time for a fixed temperature (the waiting time between two measurements was around 20 min). So, we retain the second possibility thanks to real space imaging of the superstructure obtained at room temperature after alloying.

A generic atomic arrangement at full coverage for an Fe $1/3$ ML is depicted on Fig. 4. The large size of the scanned area, $15 \times 15 \text{ nm}^2$, allows us to split the picture in two parts. The lower one represents the atomic organization where dark points are Fe atoms; the remaining part is gold [15]. Areas of $\sqrt{3}$ are clearly identified albeit some local defects as Fe dimers or small chains of three to six atoms, i.e., a succession of Fe atoms in the nearest neighbor positions. Notice that there is no Fe nor Au island. The bigger black dots are supposed to be impurities or local defects (their estimated density is around 0.1 to 1%); they are in the on-top positions relative to the substrate (there is strong evidence that they replaced Ru atoms). Oxygen or carbon are the possible ones because of the known reactivity of Ru with those elements. We may also suppose that iron atoms could be inserted in the very first plane of the ruthenium surface. Effectively, experiments [15,29] have shown that above 800 K, iron begins to insert in Ru. Actually, the samples have not been annealed above that temperature. But this hypothesis cannot be rejected. Whatever, it is known that defects located on-top of substrate sites do not break the symmetries of the elastic field around them [21]. So, they should not influence one type of domain compared to the others; all the domains react in the same way.

The upper part of the picture represents the three possible domains of the superstructure separated by extended antiphase boundaries (APB). This sketch has been obtained by pointing the Fe atoms positions and plotting a point at the nearest cross of the three dense directions. Each point belongs to one domain and is surrounded by six smaller open circles representing Au atoms. The characteristic lengths of domains are ~ 3 to 10 nm; they are separated by various boundaries made of more or less long Fe or Au chains (we cannot qualify these chains as light or

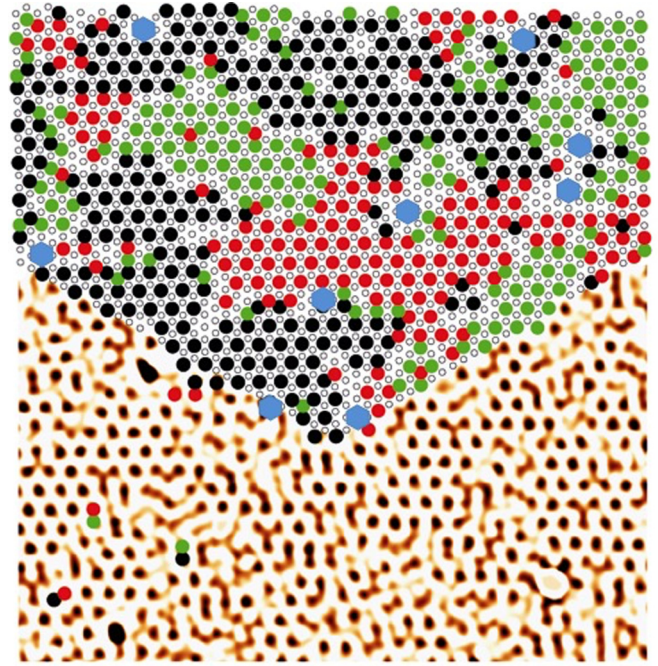


FIG. 4. STM image of a Au_2Fe full ML on a $\text{Ru}(0001)$ surface (at RT) after annealing to 800 K ($15 \times 15 \text{ nm}^2$). Fe atoms appear darker; Au atoms hardly appear. In the upper half of the image, three colored domains are separated by APB. Big plain (small open) circles depict Fe (Au) atoms. Blue hexagons correspond to embedded impurities or defects in “on top” positions. This picture has been processed by the WSXM software [33].

heavy as it is usually accepted because local atomic densities, the site occupation, are always equal to one) [30,31].

Knowing the starting point of the atoms configuration, we define the nearly constant width of the Lorentzian peak as the mean size of the domains; in other words, the correlation length between the $\sqrt{3}$ unit cells is limited by quenched APB. This is not understood at all and new experiments should be done with a fine control of the impurities density.

Finally, we must admit that during heating above T_p , ordered domains stabilized by a mesh of immobile defects, such as embedded impurities or local defects, must persist while keeping intact parts of the $\sqrt{3}$ superstructure. All domains are independent of each other, and during the transition, i.e., between T_p and T_e , each domain switches into a disordered state. In the following section we use a simple model to estimate the number of ordered domains and, consequently, our GIXD results.

III. TWO LEVELS MODEL AND ENTHALPY OF DISORDERED PHASE FORMATION

Now, we can address the issue of the decreasing integrated intensity of the $\sqrt{3}$ superstructure peaks as a function of the temperature for a one ML coverage at $x = 1/3$ (similar curves have been obtained for the stoichiometry $x = 1/2$). We suppose that the integrated diffracted intensity is proportional to the incoherent sum of all the intensities produced by each ordered domain. To get their number, we use an adaptation of a two-levels model [32]. Shortly, the system is seen as a full

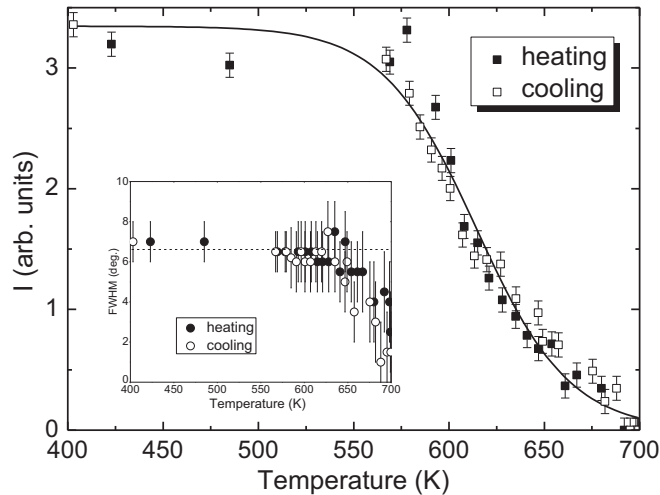


FIG. 5. Temperature dependence of the $\bar{Q}_{1/3}$ GIXD [integrated intensity $A(T)$] peak in a Au₂Fe ML on a Ru(0001) surface and width at half maximum $\delta\omega(T)$ (inset). The small 1% Debye-Waller factor correction has been ignored (see text). Heating (cooling), solid (hollow) symbols. The continuous fitting line is proportional to $1/(1 + \exp^{t/\bar{n}})$ where $t = \frac{T - T_c}{D}$. The order-disorder transition temperature T_c is around 610 K.

plane of $N\sqrt{3}$ unit cells (u.c) where sites are matching with the Ru substrate. This plane is divided in M (independent of the temperature) small areas belonging to four different families: three of which are ordered, and the fourth is disordered. All these domains are uncorrelated and their Fe composition is $x = 1/3$. A schema of the three ordered domains families would be very similar to the upper part of Fig. 4. In the last family, domains are composed of randomly occupied u.c. by 1/3 of Fe and 2/3 of Au atoms. There are N_{ord} (respectively N_{dis}) u.c. in ordered (respectively disordered) domains and $M_{\text{ord},n}$ ordered domains, where n is the size of a domain, i.e., the number of u.c. which compose this domain. As we suppose that the domain size is constant, we follow Ref. [32] by averaging over the domains sizes distribution and obtain the temperature dependence of the integrated intensity proportional to $M_{\text{ord},\bar{n}} \sim 1/(1 + \exp^{t/\bar{n}})$, the number of ordered domains.

$t = \frac{T - T_c}{D}$ is the reduced temperature and T_c , the critical temperature, is obtained when $N_{\text{ord}}(T_c) = N_{\text{dis}}(T_c)$. The

scaling parameter D is given by $D = k_B T_c^2 / \delta\Delta H$, where $\delta\Delta H$ is the difference between the enthalpy of formation (per atom) of the disordered phase relative to the ordered one.

We can remark that \bar{n} is not a free parameter; it is directly related to the width of the diffraction peak and then to the coherence length, from which we can estimate $\bar{n} \sim 40$ u.c. The fit reported in Fig. 5 conduct to the following mean estimations: $T_c \simeq 610$ K and $\delta\Delta H \approx 30$ meV/u.c (i.e., 10 meV/atom). A more precise knowledge of the domain size distribution could improve the fits, especially around T_p , and gives better values. Nevertheless, knowing the energy of formation of the ordered Au₂Fe phase, $\Delta H = -180$ meV/atom, we can estimate the energy of formation of the disordered phase at ~ -170 meV/atom. It would be interesting to compare this result to *ab initio* calculations [16].

Finally, because the $\sqrt{3}$ is the most stable superstructure above RT irrespective of the stoichiometry, the first alloy nuclei at equilibrium are constituted by iron atoms surrounded by six gold atoms. Impurities help to localize and stabilize these nuclei, as already known by standard thermodynamics. Then, when x increases, bigger $\sqrt{3}$ domains are formed until the creation of sharp APB. Above $x = 1/3$, for a fixed defects density, the domain size stays nearly constant, but more and more local defective u.c. are formed (the small Fe chains on Fig. 4) while keeping sharp APB (no thick iron domain walls). These local defective u.c. are gradually invading all $\sqrt{3}$ areas.

IV. CONCLUSION

In conclusion, we studied the Fe_xAu_{1-x} two-dimensional surface alloy (around $x = 1/3$) on Ru(0001) by STM at room temperature and GIXD at high temperature during *in situ* heating and cooling. The long range order does not exist due to local defects which stabilized a mean range order inside uncorrelated domains. A two-levels model allows us to estimate the formation energy of a disordered two-dimensional alloy of immiscible elements.

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- [1] W. H. Qi and M. P. Wang, *Mat. Chem. Phys.* **88**, 280 (2004).
- [2] S. Xiao, W. Hu, W. Luo, Y. Wu, X. Li, and H. Deng, *Phys. J. B* **54**, 479 (2006).
- [3] Y. Wang and M. Hou, *J. Phys. Chem. C* **116**, 10814 (2012).
- [4] J. Villain and J. G. Moreira, *J. Phys.: Condens. Matter* **3**, 4587 (1991).
- [5] M. Pratzner and H. J. Elmers, *Phys. Rev. Lett.* **90**, 077201 (2003).
- [6] A. Damian, I. Braems, F. Maroun, and P. Allongue, *Elect. Acta* **112**, 824 (2013).
- [7] F. Tournus, K. Sato, T. Epicier, T. J. Konno, and V. Dupuis, *Phys. Rev. Lett.* **110**, 055501 (2013).
- [8] M. Zhang, Z. Yan, Q. Sun, J. Xie, and J. Jing, *New J. Chem.* **36**, 2533 (2012).
- [9] J. Yuhara, M. Schmid, and P. Varga, *Phys. Rev. B* **67**, 195407 (2003).
- [10] B. Sadigh, M. Asta, V. Ozolins, A. K. Schmid, N. C. Bartelt, A. A. Quong, and R. Q. Hwang, *Phys. Rev. Lett.* **83**, 1379 (1999).
- [11] H. E. Hoster, E. Filonenko, B. Richter, and R. J. Behm, *Phys. Rev. B* **73**, 165413 (2006).
- [12] J. L. Stevens and R. Q. Hwang, *Phys. Rev. Lett.* **74**, 2078 (1995).
- [13] G. E. Thayer, N. C. Bartelt, V. Ozolins, A. K. Schmid, S. Chiang, and R. Q. Hwang, *Phys. Rev. Lett.* **89**, 036101 (2002).
- [14] R. Lipowsky, *Phys. Rev. Lett.* **49**, 1575 (1982).

- [15] S. Mehendale, Y. Girard, V. Repain, C. Chacon, J. Lagoute, S. Rousset, M. Marathe, and S. Narasimhan, *Phys. Rev. Lett.* **105**, 056101 (2010).
- [16] M. Marathe, A. Diaz-Ortiz, and S. Narasimhan, *Phys. Rev. B* **88**, 245442 (2013).
- [17] L. D. Roelofs, *Appl. Surf. Sci.* **11**, 425 (1982).
- [18] A. R. Kortan and R. L. Park, *Phys. Rev. B* **23**, 6340 (1981).
- [19] M. E. Fischer, *Phys. Rev.* **176**, 257 (1968).
- [20] E. Vlieg, J. F. Van Der Veen, S. J. Gurman, C. Norris, and J. E. Macdonald, *Surf. Sci.* **210**, 301 (1989).
- [21] I. Lyuksyutov, *Two-Dimensional Crystals* (Academic Press Inc., Boston, 1992).
- [22] A. Bergbreiter, H. E. Hoster, S. Sakong, A. Groß, and R. J. Behm, *Phys. Chem. Chem. Phys.* **9**, 5127 (2007).
- [23] A. K. Engstfeld, C. K. Jung, and R. J. Behm, *Surf. Sci.* **643**, 65 (2016).
- [24] M. S. Narayana, N. G. Krishna, and D. B. Sirdeshmukh, *Acta Cryst. A* **57**, 217 (2001).
- [25] E. Ferrari, L. Galli, E. Miniussi, M. Morri, M. Panighel, M. Ricci, P. Lacovig, S. Lizzit, and A. Baraldi, *Phys. Rev. B* **82**, 195420 (2010).
- [26] V. F. Sears and S. A. Shelley, *Acta Cryst. A* **47**, 441 (1991).
- [27] F. Ronci, S. Colonna, S. D. Thorpe, A. Cricenti, and G. Le Lay, *Phys. Rev. Lett.* **95**, 156101 (2005).
- [28] B. Yang, T. Muppidi, V. Ozolins, and M. Asta, *Phys. Rev. B* **77**, 205408 (2008).
- [29] X. P. Zhang, R. X. Cao, L. Sun, B. You, An Hu, and H. F. Ding, *Phys. Rev. B* **83**, 193402 (2011).
- [30] D. A. Huse and M. E. Fisher, *Phys. Rev. B* **29**, 239 (1984).
- [31] Y. Nakajima, C. Voges, T. Nagao, S. Hasegawa, G. Klos, and H. Pfnür, *Phys. Rev. B* **55**, 8129 (1997).
- [32] W. H. Kirchhoff and I. W. Levin, *J. Res. Natl. Bur. Stand.* **92**, 113 (1987).
- [33] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, *Rev. Sci. Instrum.* **78**, 013705 (2007).