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Distributions of atomic wire lengths

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Controlled growth of metal monatomic wires would enable on-demand tuning of electronic and magnetic properties in this new class of materials. Prior to this work, it was believed that the binding energy can be determined from the distribution of the lengths of the wires. Another misconception was that the antiripening mechanism or quantum effects are responsible for the growth of wires during postdeposition annealing. Combining kinetic Monte Carlo and first-principles density-functional theory calculations, we study the growth of one-dimensional atomic wires on the steps of vicinal surfaces. We show that for a large value of the bond energy, the antiripening mechanism and quantum effects do not affect the length of metal monatomic wires. The conditions under which wires with magic length appear are determined. The observed mechanism of wire growth will be useful both for explaining the experimental data and for creating atomic wires with a given length.

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I. INTRODUCTION

Metal monatomic wires of a small number of atoms or more are of great interest to various branches of nanoscience and nanotechnology because their properties usually differ considerably from those of the corresponding bulk or surface material. The characteristic properties of atomic wires include quantized conductance [1–3], electronic "end" states [4,5], charge-/spin-density waves [6], potential non-Fermi-liquid behavior [7,8], and giant Rashba split bands [9]. Efforts on atomic wires have been focused mainly on two categories, those that are extended between two contacts [1–3], and those supported on different substrates [10–14]. Atomic contacts and wires have their own challenges and opportunities in discovering new physical processes and concepts. However, supported atomic wires are thermodynamically more stable than freestanding ones. Therefore, in this study we focus on supported atomic wires.

Understanding the mechanisms that govern the growth of metal monatomic wires will be critical for engineering more advanced atomic structures with controlled properties. For example, many of the atomic wire physical properties—notably the electronic structure [4,15,16], optical properties [17], and magnetic behavior [18–20]—also depend on their finite dimensions, therefore it is desirable to understand and possibly control the factors determining the wire length. The simplest and cheapest way of forming atomic wires is deposition onto vicinal surfaces with a narrow terrace-size distribution [10,11] or semiconductor surface with low index [12–14].

The length of the wires generally depends on many parameters of the experiment. In the literature we found three types of histograms of the length distribution of metal wires, shown in Fig. 1. The first length distribution [21] [see Fig. 1(a)] has a clearly expressed maximum, and it is successfully approximated by the normal distribution. The second one [11] [see Fig. 1(b)] exponentially decays and has two maxima. It should be noted that Zaki *et al.* [11] do not claim that the measured distribution is double-peaked. Therefore, the double-peaked distribution for Co atomic wires on a Cu(775) is more hypothetical than experimentally proven. The third length distribution [see Fig. 1(c)] shows unequivocally an intriguing oscillation of the length of the wire [13]. This effect is called the magic size effect. Some experimental studies claim that kinetic factors do not play a dominant role in determining the wire length distribution and use a one-dimensional lattice gas model to determine the bond energy [11,21]. In this approach, the experimental values of the bond energy are much less than the theoretical values. For example, in the case of Co atomic wires on a Cu(775) the bond energy is 0.13 eV [11], while density functional theory (DFT) calculation gives 0.56 eV [22]. Another extraordinary statement is that quantum size effects are responsible for preferred lengths of self-assembled metallic nanowires grown on a germanium surface after annealing at temperatures ranging from 450 to 650 K [13].

Since metal monatomic wires can be utilized as building blocks of electrical devices or logic and memory circuits, it becomes topical to explore the mechanism of their formations. So far, despite a number of theoretical studies [21–24] of the formation of monatomic wires, there has not yet been a systematic study that investigates the influence of external factors on the wire length distribution. Such an investigation of the growth of metallic wires is indispensable not only for understanding the underlying mechanism of growth, but also

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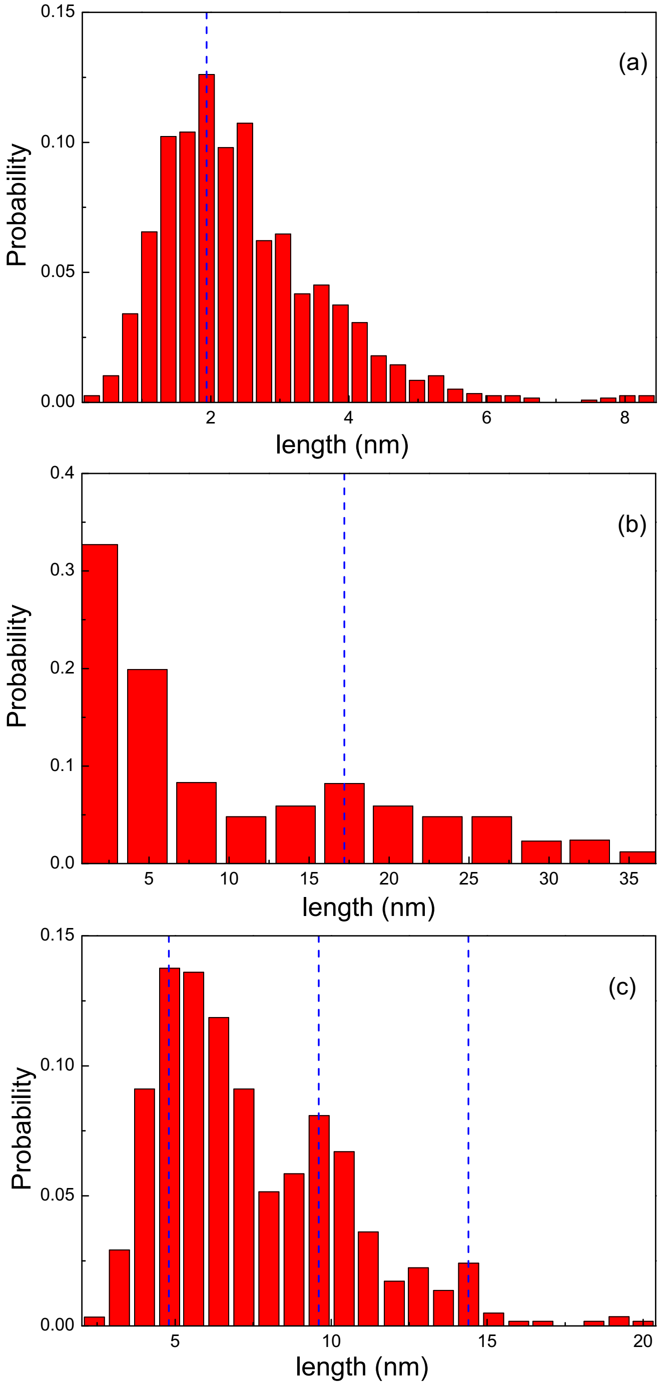

FIG. 1. Three types of experimental distributions of atomic wire lengths. (a) Ag (0.04 ML) deposited on Pt(997) at 400 K [21]. (b) Co (0.12 ML) deposited on Cu(775) at 165 K [11]. (c) Ir (0.3 ML) deposited on Ge(001) at 300 K and annealed at 650 K [13].

for designing future electrical devices. In this paper, we present comprehensive atomic-scale simulations of Co monatomic wire formation on a Cu(775). The first goal of our work is to understand the epitaxial growth of Co wires on a stepped Cu surface at the atomic scale. We perform kinetic Monte Carlo (kMC) simulations and reveal that the formation of monatomic Co wires on a Cu(775) at the bottom step edge can be explained qualitatively by the energy difference in interactions of adatoms with the surface step at the upper and lower terraces of the surface. The second goal is to demonstrate that the dependence of bond energy on the length of the wires does not affect the wire length distribution. More importantly, we reveal that the magic size effect in the growth of supported metallic nanowires is probably caused by the difference in the size of the terraces.

II. METHODS

To simulate the growth of Co on Cu(775), we apply the two-dimensional kinetic Monte Carlo (kMC) model using diffusion barriers for many atomic events calculated by the Vienna Ab initio Simulation Package (VASP) code [25,26]. The details of our VASP calculations are similar to those reported in Refs. [27,28]. The kMC model describes the elementary stochastic processes (deposition and atomic diffusion) in terms of reaction rates to avoid unnecessary calculations of potentially unsuccessful attempts. In this model, the rate of an atomic process is calculated using the Arrhenius expression, and prefactors for all events are set to 10^{12} Hz [29]. The length of the terrace of the stepped Cu(775) surface is set to 100 nm, the number of terraces is set to 10, and periodic boundary conditions are applied along the surface plane. The size effect calculations are performed using the Korringa-Kohn-Rostoker Green's function method [30,31] in the framework of the density functional theory.

III. MECHANISMS OF GROWTH OF ATOMIC WIRES

Before discussing our results, we will briefly describe the results of previous DFT calculations. For example, the theoretical study by Mo *et al.* [23] determined a mechanism of nanowire formation on vicinal surfaces consisting of three steps: (i) formation of a single-atom-thick Co wire located one row behind the Cu step edge, (ii) formation of a subsequent Co wire behind the first row, and (iii) formation of a Co wire on top of these two rows. However, nonencapsulated one- and two-atom-thick wires are observed in the experiment [11], in contrast to the encapsulated wires predicted by DFT calculations [23]. To resolve this contradiction and to enhance our understanding of the growth process of Co on a stepped Cu(775) surface at low temperatures, DFT calculations were performed.

At first, we need to understand how Co adatoms can approach the surface step. In Fig. 2, we depict a map of potential energy for the Co adatom approaching the surface step to illustrate four different cases. The repulsive area on the surface is clearly seen in all cases. If the surface is clean [see Fig. 2(a)], the adatom moving toward the step is repelled by the repulsive potential. The strength of this repulsive potential on the upper terrace (136 meV) is significantly larger than that on the lower terrace (69 meV). This difference is produced by the charge redistribution at step edges. Previous studies [32,33] have shown that the charge redistribution at step sites, with a flow of electron density from the upper step edge to the step base, is the main factor governing the different properties between the adatom-step interaction on the upper and lower terraces near the step edge. The reduction of the electron density at the edge of the upper terrace reduces the screening

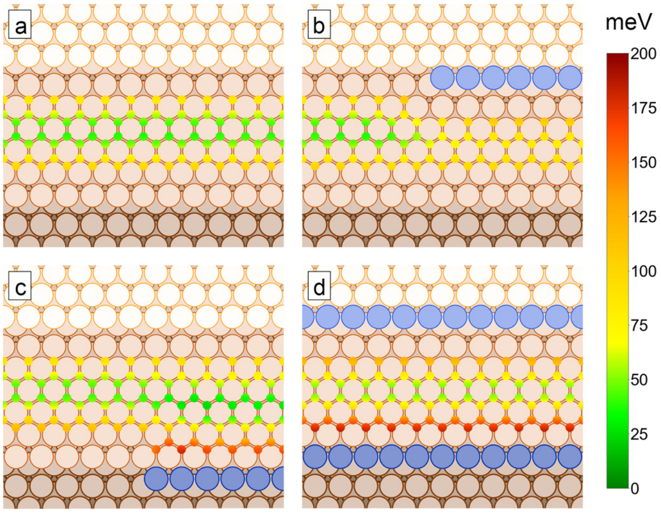

FIG. 2. Map of the potential energy for the Co adatom on Cu(775). (a) Clean surface. (b),(c) The surface has Co atomic wire on different terraces. (d) The vicinal surface is decorated with Co atomic wires.

of the direct Coulomb repulsive interaction between the Co adatom and the step atoms. For a step decorated with wires [see Figs. 2(b)–2(d)], the values of the repulsive barriers are 227 and 118 meV, respectively. Consequently, the repulsion between the adatoms and the step could prevent adatom diffusion toward the step edge.

Furthermore, we found an interesting effect. The wire located near the step increases the interaction energy between the adatom and the surface in the middle of the lower terrace [see Fig. 2(b)] and reduces it in the middle on the upper terrace [see Fig. 2(c)]. This way, the Co wire will block the diffusion for the adatoms located along the wire on the lower terrace and unlock the diffusion on the upper terrace. In this phenomenon, the Co wire is a "nano traffic light" for adatoms rushing along the terrace.

For a clear understanding of the mechanisms of self-organization, we carried out the kMC simulations of the growth process of Co on a stepped Cu(775) surface. Our kMC simulations are closely related to the experimental conditions [11]. The effect of charge redistribution at the step edges on adatom diffusion is included in our simulations. The results of kMC simulations convincingly demonstrate the self-organization of Co adatoms into atomic wires at the edge of the lower terraces. Figure 3 shows a schematic of the proposed growth process for Co atoms. The possible growth scenario is the following. After evaporation, the Co adatoms randomly diffuse along the terrace with a barrier of 40 meV and then get attached to the step edges. As noted above, the repulsive barrier of a step for a Co adatom at the upper terrace is larger than that at the lower terrace. For this reason, at temperatures from 150 to 170 K, adatoms can fairly easily reflect off ascending step edges and diffuse back onto the terrace. It should be noted that only a few (two to three) adatoms per thousand approach a step from ascending step edges. Then these atoms are incorporated into the brim via step fluctuations and vacancy mediated diffusion or via an exchange mechanism occurring at kink sites (250 meV) [27]. The existence of such a barrier was originally discussed by Schwoebel and Shipsey [34] and quantified for tungsten by Ehrlich and Hudda [35]. Ehrlich and Hudda found a direct observation in the ion microscope reveals that at low temperatures atoms do not roll over the edge of a plane; instead they are reflected [35]. Then Schwoebel and Shipsey proposed a very simple model explaining the experiment of Ehrlich and Hudda [34]. However, our results show that the reflection from the step on the surface is due not only to the large Ehrlich-Schwoebel barrier, but also to the dipole-dipole repulsion between the adatom and the step. The rest of the atoms approach step edges from the lower terrace. Sometimes, when two adatoms diffusing on the terrace meet each other, the formation of a dimer takes place. The probability of a dimer forming on the terrace decreases as the width of the terrace and the temperature increases. Dimers do not dissociate at temperatures below room temperature since the barrier for dimer decomposition exceeds 0.9 eV. The first stage ends when most of the adatoms approach the step. The formation of monatomic wires on a vicinal surface proceeds via the coalescence of step-trapped adatoms and dimers in the next stage.

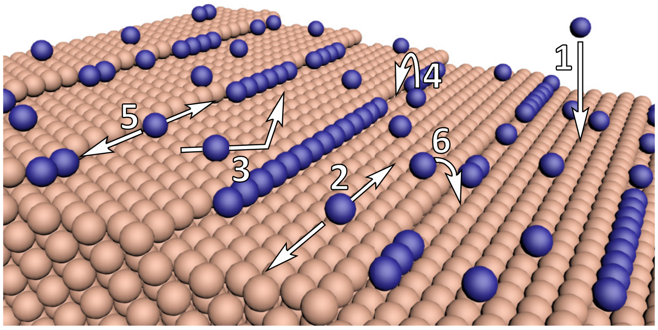

FIG. 3. Behavior of adatoms in the surface deposition process (deposition 1; diffusion along the terrace 2; reflection 3; diffusion to step 4; diffusion along the step 5; Ehrlich-Schwoebel diffusion 6).

IV. DISTRIBUTIONS OF ATOMIC WIRE LENGTHS

To compare the results of our simulations with the experiment, we plotted the distribution of atomic wire lengths. Figure 4 shows results for wire length distribution for different temperatures. In these calculations, we carefully took into account all the events except the formation of dimers and their diffusion. As can be easily seen, the average wire length increases with increasing temperature, and the distribution becomes more spread. Monomodal distribution refers to the first type of distribution shown in Fig. 1(a). It should be noted that if the annealing time significantly increases or decreases, then the distribution does not change. If we include the existence of dimers in the calculations, the peak in monomodal distribution narrows and shifts to a smaller value.

However, the Co/Cu(775) system has a bimodal distribution [see Fig. 1(b)]. In a recent paper [24], the following explanation was proposed. When the average length of the epitaxial wires exceeds the average wire length corresponding to the equilibrium length at the temperature of the substrate, during the annealing the majority of wires will lose atoms to reduce their size. These atoms will nucleate into small monatomic

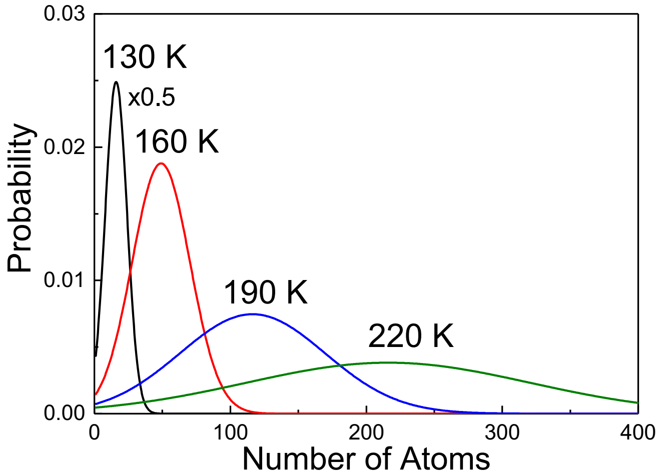

FIG. 4. Distributions of atomic wire lengths for four different temperatures (130, 160, 190, and 220 K). The distribution for 130 K was multiplied by 0.5.

wires, which, in contrast to large wires, should grow to attain the equilibrium length. Thus, during one of the stages of the evolution, there will be two peaks in the distribution: one corresponding to the shrinking large wires, and another that would describe the growing newly nucleated wires.

To verify the antiripening mechanism [24], we calculated the bond energy for monatomic wires as a function of wire length. Figure 5 displays the results of monatomic Co wires on Cu(775) up to the length of 12 atoms. One can see that the bond energy decreases with the growth of the wire. Thereby, edge atoms are more easily detached from large wires than from small ones. It is to be expected that the distribution of atomic wire lengths will be bimodal after annealing. We included the size effect in the kMC model, but the distribution of atomic wire lengths remained monomodal. This is due to the fact that the barrier for detachment of an atom from a wire or a dimer is large (0.7–0.9 eV). Only a very small number of atoms can be detached from wires at room temperature.

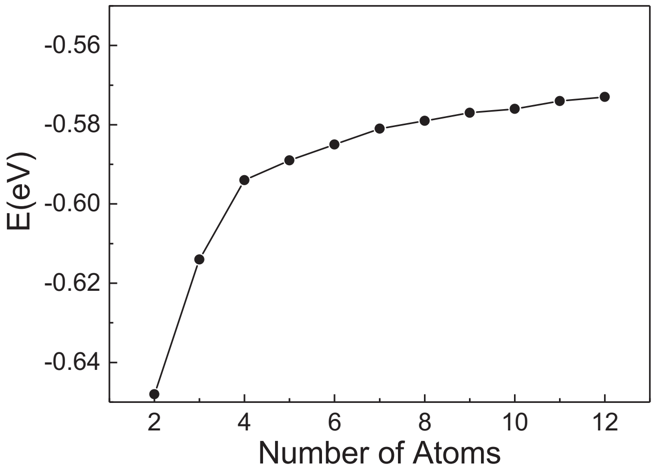

FIG. 5. Calculated bond energy for Co single-atom wires as a function of wire length.

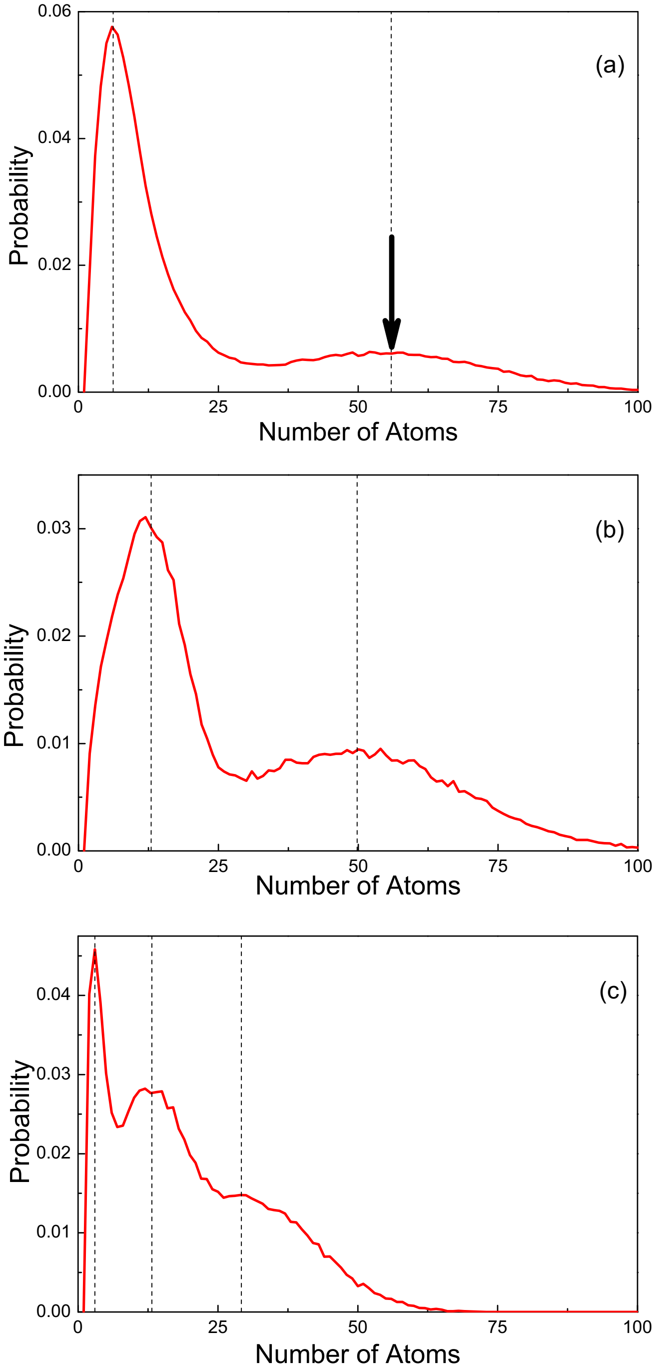

FIG. 6. Distributions of atomic wire lengths (160 K). The average width of the terrace corresponds to Cu(775). (a) The widths of the terraces are slightly different from each other as in the experiment. (b) The surface has terraces with two characteristic widths. (c) The surface has terraces with three characteristic widths. (b),(c) The widths of the terraces are significantly different from each other.

We analyzed the experimental work [11] repeatedly and thoroughly and found that the vicinal surface in real experiment was not ideal. The surface had both narrow and wide terraces. The results of our kMC simulation show that the distribution of atomic wire lengths should be bimodal in this case (see Fig. 6). The peak marked in Fig. 6(a) with the arrow appears in the distribution due to the presence of wide terraces. It appears only when the experimental parameters (coverage, flux, temperature) are above the critical values. The explanation for this phenomenon is the following. During the deposition, not all atoms approach the edge of the step. Many of the atoms remain on the terrace and form dimers. Then these dimers and atoms will increase the length of the wires on wide terraces and will form new growth centers on narrow terraces during annealing. The second peak in the distribution is larger if the difference in width between the wide and narrow terraces is significant [see Fig. 6(b)]. If the experimental parameters are below critical values or the vicinal surface is close to ideal, the distribution will be monomodal. If we assume that the surface has three or more characteristic widths, then the distribution of atomic wire lengths can be multimodal. This case is shown in Fig. 6(c). It is worth noting that the distribution is very similar to the experimental distribution shown in Fig. 1(c).

V. CONCLUSION

We performed a systematic theoretical study of the growth of metal atomic wires on a vicinal surface using first-principles DFT calculations and kMC simulations. We showed that the bond energy depends on the length of the atomic wire. This energy is considerably higher than the bond energy obtained experimentally [11]. The difference between the value of the bond energy obtained experimentally and the calculated one is typical for metal wires on vicinal surfaces [11,21]. This is due to the fact that the wires are metastable structures. It is not bond energy but diffusion barriers that determine the length of metal atomic wires. Therefore, bond energy cannot be determined from the distribution of atomic wire lengths. Perhaps bond energy can be estimated from the melting point or the temperature at which the wires are destroyed.

We found that so-called wires with magical lengths will be formed on the surface with different sizes of terraces. The quantum size effect does not affect the distribution of atomic wire lengths in the case when the bond energy is large. It depends mainly on the size of the terraces of the surface, the diffusion barriers of dimers and adatoms along the step, and such experimental parameters as temperature, coverage, and flux. Our results show that antiripening kinetics proposed in the work [24] is not suitable for describing the growth of metal atomic wires on vicinal surfaces.

We believe that our study will be very useful to understand the mechanisms that govern the growth of metal monatomic wires and will initiate the creation of a new, more realistic theoretical model describing the length distribution of atomic wires.

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