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Evaluation of Anharmonicity in Nature of Homo- to Heterogeneous Adsorbed clusters on Ag (111) Surface for the Application of Thin Film Engineering

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Abstract: Molecular dynamics methods along with Embedded-Atom-Method potentials are used to investigate the relative variation in the surface diffusion of homo (Ag_6), hetero (Cu_6), binary heterogeneous (Zr_3-Cu_3) and ternary heterogeneous (Zr_2-Cu_2-Ag_2) adatoms clusters on Ag(111) surface. The work is the extension of the calculations for hetero diffusion Hayat *et al.* [Mod. Phys. Let. B 82 (2017) 1750316] and for heterogeneous diffusion Imran *et al.* [Chin. Phys. B 25(7) (2016) 076601; Surf. Interface Anal. (2019) 1-9]. This study of homo, hetero, and heterogeneous adatoms clusters can be significant to study the thin film growth on the surface and highlights the issues generated when someone shifts epitaxial layer growth from metals to binary and ternary alloys. At 300 K, while for these hexamers, the rate of diffusion is small; and influenced by anchoring, breathing and shearing motion. The diffusion rate boosts with the rise in temperature for all types of clusters. The Cu hexamer cluster diffusion rate on Ag(111) is enormously high relative to others. For the heterogeneous cluster diffusion, the anharmonic behavior increases with the species of element increase due to lattice discrepancy which contributes to decrease the collective atoms diffusion rate of the cluster. At high temperatures (500 and 700 K), the different types of atomic diffusion are noticed such as the exchange of cluster adatoms with the substrate silver atoms and pop-up of the surface atom over the cluster.

Keywords: adatoms clusters, molecular dynamics, surface diffusion

1. Introduction

The Surface phenomenon of all natures such as; crystal growth, thin film formation, catalysis, and surface reconstruction, diffusion on the surface is the most key phenomena. Therefore, surface diffusion is the most important pillar to understand the various domains, i.e, chemical reactions, catalytic application, and electronic device formation though thin film growth. It is already recognized that for the quality and the topology of growing films, the diffusion is an event controlling [1]. The issues are generated when somebody shifted from homo to hetero and finally heterogeneous film growth on the surface of materials. In order to understand nanostructures with mandatory exact properties, there is a factual need to endorse heterogeneous-epitaxy, which is a field of special interest.

It is interesting to see the important atomic procedures involved in epitaxial growth, which are mostly operated by the surface diffusion of the single adatom or atomic clusters on metallic surfaces. The diffusion of small clusters on surface plays an important part in the development of epitaxial nanostructures and its structural control, in thin film growth and deposition. It provides a convincing understanding of surface dynamical processes, such as, chemical reactions and the growth of clusters and epitaxial layers. Processes involving the motion of single-adatom and small clusters on surfaces lead to the roughing and leveling of the surface. To get a deep vision into the thin film growth and kinetics film, it is of crucial importance to visualize the interaction of adatoms-surface and adatoms-adatoms on the surfaces. These diffusion properties are closely related to the macroscopic pattern like nano-structuring and epitaxial layer growth on the surfaces. The identified diffusion processes at the microscopic level are expected to predict the properties of the materials and their structures at the atomic level. It also enables one to comprehend experimentally the observed diffusion mechanisms. The

results of the geometrical features of the *fcc* (111) surface can be used as a support for the experiments of reliable homogeneous- and heterogeneous-epitaxial growth and deposition process.

It is notable that the role of variation in size and a mismatch of lattice in the case of the small island's atoms like Cu and Zr relative to Ag atoms and surface energy disparity lead to enhance the dynamics [2-4]. The Embedded Atom Method potentials (EAM) are well known in the simulation field which provides the bonding of the atoms [5]. These potentials already confirmed for the surface study and bulk properties such as thermal properties of metals, crystal defects in crystals and surface anharmonicity using molecular dynamics techniques [6-12].

In the next sections, we discussed the computational details in Sec. 2. Section 3 contains the results of hexamer clusters of four types at three different temperatures. Homo-cluster case is studied first time in detail using molecular dynamic (MD) technique; center of mass, mean square displacement, diffusion coefficient and the effective energy barrier are calculated for the case Ag_6/Ag(111), while, hetero- and heterogeneous-clusters [Cu_6/Ag(111); Zr_3-Cu_3/Ag(111) and Zr_2-Cu_2-Ag_2/Ag(111)] are reported for comparison only. Finally, the conclusion and summary are drawn in Section 4.

2. Computational details

For MD simulation "LAMMPS" [13] package, which contains mainly "*Dynamo*" routine, is used to do the calculations for this work. The total energy E_t for the interaction is calculated by

$$E_t = \sum_{i,j} \varphi(r_{ij}) + \sum_i F(n_i)$$
$$n_i = \sum_j \rho(r_{ij})$$

here $\varphi(r_{ij})$, $\rho(r_{ij})$ and $F(n_i)$ are the pair interaction, density, and embedded functions, respectively.

The substrate material is comprises of silver atoms which have *fcc* lattice and the lattice constant of 4.09 Å at 0 K. We had reported the simulated lattice constant of Ag at different temperatures [14] along with the experimental values [15]. Simulation block which contains 14986 silver atoms of the substrate is modeled such that with mutually perpendicular axes; 80 Å along both directions [1 1 $\bar{2}$] and [1 $\bar{1}$ 0]; and 40 Å along the direction [1 1 1]. Although, the periodic boundaries are imposed along the [1 1 $\bar{2}$] and [1 $\bar{1}$ 0] directions, while, third direction is kept fixed so that (1 1 1) surface obtained. In the first step, the simulation cell is relaxed to obtain lower energy configuration using NVE Ensemble. The temperature of the cell is raised using NPT ensemble. Here the time steps of 0.5 *fs* are taken for the integration of newton's equation of motions. Finally, the system is thermalized using NVE ensemble at a constant temperature. For visualization and snapshots VMD software is used [16].

The trajectory of the cluster when diffused at the surface can be found by the trace of center of mass (CM). After the estimation of CM the diffusion coefficient of the addatoms clusters can be calculated using the expression

$$D = lim_{t\to\infty} \frac{([R_c(t) - R_c(0)]^2)}{2dt}$$

Where D is the diffusion coefficient $R_c(t)$ is the CM of the adatoms cluster at time t, $R_c(0)$ is the CM of cluster at time 0, 2 are the dimensions of the system, and dt is the time interval.

3. Results and discussion

To investigate the homo- and hetero-cluster diffusion mechanism, the four combinations of six adatom clusters on silver surface are chosen such as Ag_6/Ag(111), Cu_6/Ag(111), Zr_3-Cu_3/Ag(111) and Zr_2-Cu_2-Ag_2/Ag(111). The adatoms clusters are placed on the Ag(111) surface at initially *fcc* sites on (111)surface and their mechanisms of motion are observed.

3.1 Homo-diffusion

For the study of homo-diffusion 6-Ag atoms cluster is adsorbed on Ag(111) surface. We carried out simulation at 300 K, then at 500 K, and finally at 700 K. All possible movements for Silver hexamer are seen at the said temperatures. At high temperature (700 K), diffusion is observed more effective and instantly changes the island into sub-islands frequently, one having 4-atoms and other having 2-atoms, for the very short time interval of simulation (2 to 3 ps). The process of hexamer diffusion in the form of snapshots is given in the Fig. 1.

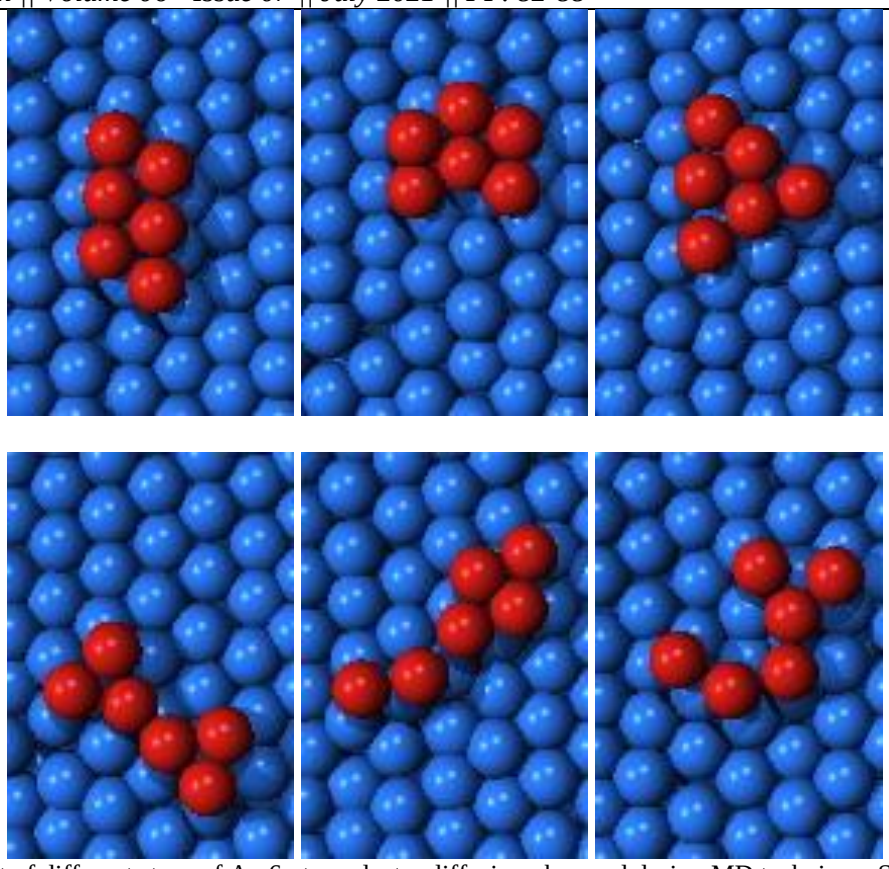

Figure 1: Report of different steps of Ag 6-atom cluster diffusion observed during MD technique. Snapshots are representing selective orientations during diffusion at different temperatures.

The CM at 500 K temperature is represented in Fig. 2. It travels ~ 25 Å along x-axis and ~ 20 Å along y-axis. Dark spots in plot represent the stay of cluster at that position. The diffusion coefficient at 300 K is 4.6×10^{8} Å^2/s. While, with the increase in temperature at 500 K the diffusion coefficient is 3.51×10^{10} Å^2/s, and gradually at 700 K the value of diffusion coefficient is 1.33×10^{11} Å^2/s. The Arrhenius plot for diffusion coefficient is given in Fig. 3. The effective energy limit for the Ag hexamer is 262 meV, which is deduced from the Arrhenius plot. The value of diffusion prefector is found 1.48×10^{13} Å^2/s. The diffusion coefficient and energy barriers for Ag_6/Ag(111) are high in molecular dynamics techniques as compared to Self-Learning Kinetic Monte Carlo (SLKMC) calculations given by A. Karim [17], although, for the diffusion coefficient at different temperatures the trend is same. The reason seems to be that there are some processes which are not appearing in the SLKMC calculations such as: separation of single atom from rest of the island and pop-up of the atom from the island. On the other hand, theoretical values using *ab-initio* density-functional theory supplemented with an embedded-atom method for $Ag_{1\text{-}5}$/Ag(111) [18] are in agreement with our MD results [14].

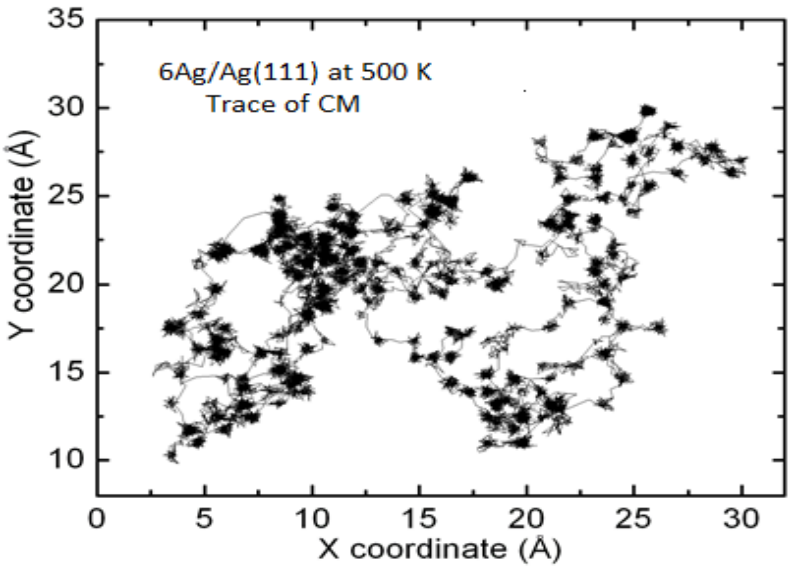

Figure 2: CM for Ag haxamer at 500 K on Ag(111) surface.

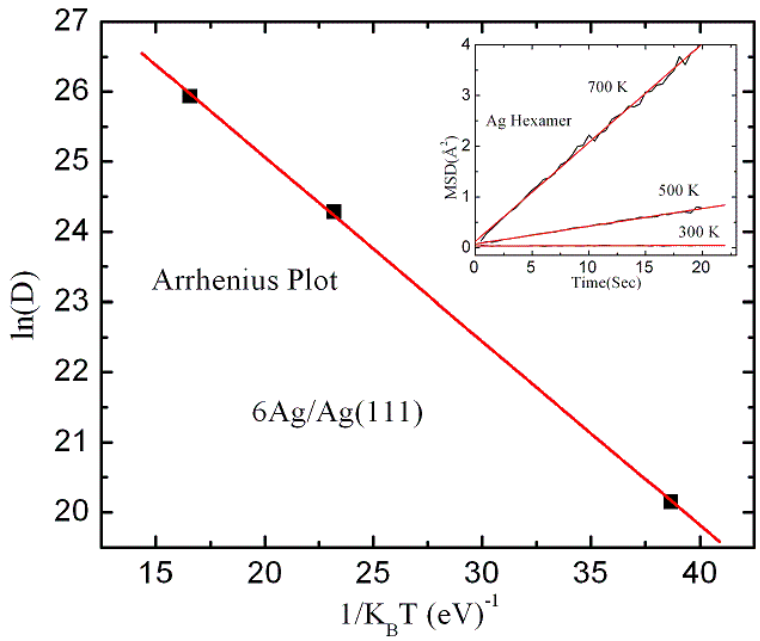

Figure 3: Arrhenius plot of the diffusion coefficient of Ag hexamer. The inset displays of mean square displacement for Ag_6 cluster on Ag(111), as a function of time at 300, 500 and 700 K.

3.2. Hetero-diffusion

To study the hetero-diffusion, Cu hexamer is adsorbed at Ag(111) surface. Initially, the cluster adatoms are positioned at *fcc* sites on (111) surface. Due to the change in size of Cu and Ag adatoms, it gets interesting dynamics to search the minimum energy configurations at the same time for all six atoms, which increases the instability and rate of diffusion dynamics increased. Processes of 6-atom Cu cluster behavior on Ag(111) surface is summarized in Fig. 4 based on pictures, which is observed during molecular dynamics simulation. From left to right in Fig. 4: five-atoms circled around one-atom; pop-ups of one-atom among six-atoms; at high temperature, dynamics of cluster restricted in two groups of three atoms. Last picture of Fig. 4 represents that during diffusion Cu cluster gets organized in two groups of trimer, one trimer in triangle shape attached to a line of trimer, nevertheless, restricted in the same cluster. It moves ~ 5 Å along the x- and y-axes in 2 ns. The diffusion rate of Cu_6/Ag(111) is high, because of the Cu adatoms are smaller in size than that of Ag atoms and bond length difference is 13.5%, therefore, it is difficult for all the 6-Cu cluster adatoms to get a minimum energy position at once. Hence, for 6-adatoms, so does instability, the competition to get minima is increased on the surface, in conclusion, the rate of diffusion increases. The detailed hetero-diffusion phenomenon is discussed

in previous studies [19, 20].

The strange phenomenon of pop-up of the cluster atom, which unfolds a fundamental feature of hetero-epitaxy, gives a deep insight into the vibrational dynamics of the cluster atoms and substrate [21]. Reason for this behavior is the slight bond-strength disparity and bond length difference between Ag (2.89 Å) and Cu (2.55 Å), which boost the kinetics of the cluster. An Cu cluster adatom when positioned on an *fcc* (or *hcp*) site on (111) surface, may obtain optimized the Cu-Ag bond lengths [22]. These bond lengths may obtain elasticity and become equal to the Ag bond length of bulk. These may get shortened almost equal to that of bulk Cu, by breaking the Cu-Ag bonds [23].

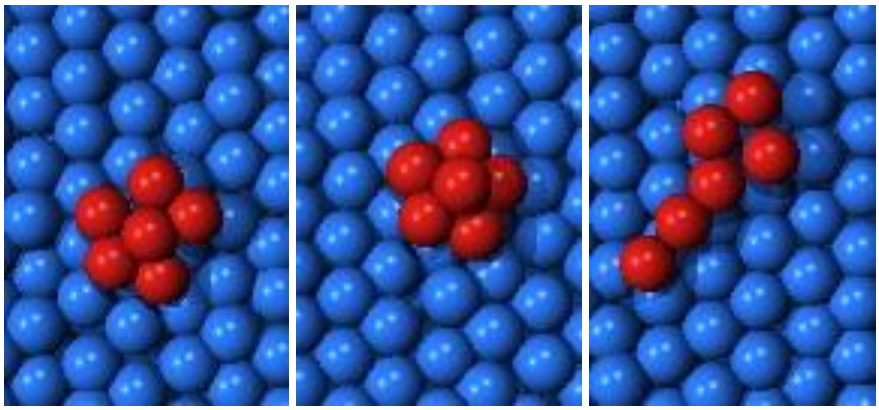

Figure 4: Images of the six-atom Cu cluster configuration during the MD diffusion on Ag(111). Blue color atoms represent the silver surface atoms and red color atoms represent the copper adsorbed adatoms.

3.3. Heterogeneous-diffusion

To study the heterogeneous diffusion we have taken the two cases binary alloy hexamer and ternary alloy hexamer

A. Binary Hexamer

We observed diffusion of binary heterogeneous haxamer (Zr_3-Cu_3) adatoms cluster on the Ag(111) substrates at 300, 500 and 700 K. The following snapshots explained the diffusion process of haxamer taken at some critical points and are shown in Fig. 5. Here is the representation of the exchange process for Zr adatom with silver Ag substrate atoms. Silver knocked-atom becomes the part of the heterogeneous cluster. Silver atom pop-up over the cluster and exhibits the anharmonicity of cluster dynamics and mixing of surface atoms with adatoms (see Fig. 5)

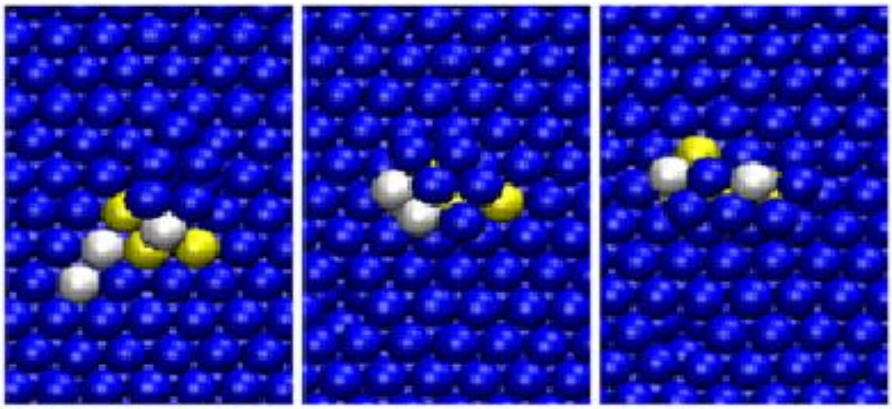

Figure 5: Complete report of diffusion process for binary Zr_3-Cu_3 cluster at sliver (111) surface. Blue color, yellow color, and white color represent Ag(surface), Zr (adatoms) and Copper (adatoms), respectively.

It is noticed that at 700 K diffusion is based on hopping, long jumps, more rapid rotational motion and occurrence of the atomic exchange phenomenon as exposed in Fig. 5. As one expect, one of the Zr adatom removes the surface atom, being small size and relatively more energetic, occupy that empty site and the surface popped-atom joins the adatoms cluster. With the passage of short time, that newly guest-atom (Ag-atom), popup of over the island which is shown in Fig. 5. The detailed binary heterogeneous cluster diffusion is discussed in

our previous work [24].

B. Ternary Hexamer

Here 2Zr, 2Cu, and 2Ag adatoms develop the ternary hexamer, those are placed initially at *fcc* chosen sites over the substrate Ag(111). The diffusion path can be soundly observed by visualization the paths of the islands of the cluster. Images are taken during the diffusion procedure are given in Fig. 6.

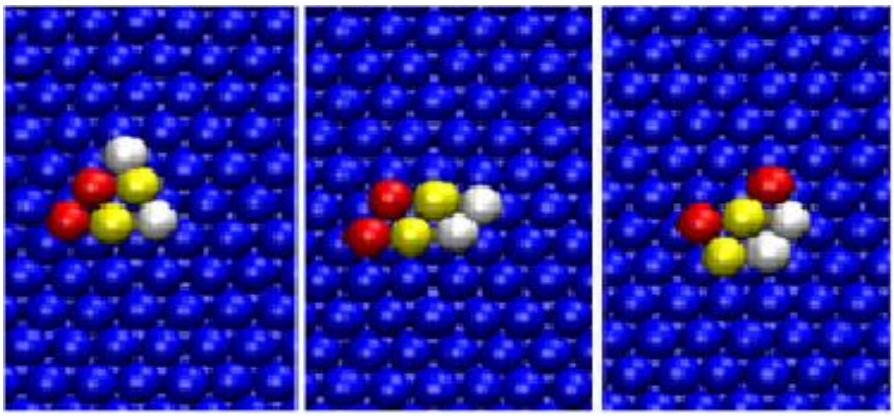

Figure 6: Ternary heterogeneous (Zr_2-Cu_2-Ag_2) adatoms cluster dynamics on silver surface are given. Blue, yellow, white, and red color atoms represent the silver surface, Zr(adatoms), Cu(adatoms) and Ag(adatoms), respectively.

It is found that the dynamics are ignorable at 300 K, nonetheless, practical diffusion is found at 500 and 700 K. The ternary island can take place different sites at the surface i.e. *fcc* or *hcp* sites as shown in Fig. 6. At 700 K, it is observed that Zr-adatom replaced by the substitution of silver atom of surface. The diffusion behavior of ternary cluster is similar to binary hexamer i.e. the motion is mainly concentrated or localized at different sites over the surface. However, the coefficient of diffusion is slightly lower relative to the binary cluster due to the presence of silver adatoms in the cluster. The diffusion coefficient of the cluster is 1.69×10^{10} $Å^2$/sec. The detailed discussion about the ternary heterogeneous adatoms cluster is studied in recent work [25]. It is observed that with the increase of species of the cluster the anharmonicity in the nature of diffusion is increased.

4. Summary and Conclusion

The MD simulation technique is applied based on the Embedded-atom Method (EAM) to study the relative change in behavior, for six-atom cluster, from homo- to hetero-diffusion and finally heterogeneous-diffusion on Ag(111). Four cases are studied such as: homo-hexamer adatoms cluster Ag_6, hetero-hexamer cluster adatoms Cu_6, binary heterogeneous adatoms cluster Zr_3-Cu_3, and ternary heterogeneous adatoms clusters Zr_2-Cu_2-Ag_2 (having the same number of atoms) to analyze the effect of change cluster element and size of cluster atoms on the diffusion phenomena. The diffusion process for these clusters having the same number of atoms studies on the basis processes observed in snapshots, diffusion constant, energy barriers and CM variation during the simulation process at different temperatures. Conclusion developed that the rate of diffusion has increased with the temperature rise. It is concluded that diffusion mechanisms is based on hopping, shearing, sliding and concentrated motion for all these different clusters at low temperature. While, binary and ternary hexamer exhibits atomic exchange process at high temperature say 500 and 700 K, where a surface layer Ag atoms exchange itself with zirconium adatoms. At 700 K, these dynamics process, enhanced and the adatoms cluster's diffusion is dominant. The reason for the exchange of Zr atom with surface atom, which is not found frequently for other adatoms, is that the Zr adatoms carry/show strong interactions with the substrate silver atoms.

The Zr adatoms dynamics found almost in the form of a group, showing the Zr-Zr atomic interaction is strong relative to other adatoms. Silver adsorbed atoms perform dynamics being the part of a cluster. However, sliver adatom, for a very short time of the interval, popped-up over the remaining cluster very rarely. Breakage and rejoining of single and more atoms from the cluster are also viewed.

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