# ATOMIC MATCHING ACROSS INTERNAL INTERFACES*

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## ABSTRACT

The atomic structure of internal interfaces in dense-packed systems has been investigated by high-resolution electron microscopy (HREM). Similarities between the atomic relaxations in heterophase interfaces and certain large-angle grain boundaries have been observed. In both types of interfaces localization of misfit leads to regions of good atomic matching within the interface separated by misfit dislocation-like defects. It appears that, whenever possible, the GB structures assume configurations in which the atomic coordination is not too much different from the ideal lattice. It is suggested that these kinds of relaxations primarily occur whenever the translational periods along the GB are large or when the interatomic distances are incommensurate. Incorporation of low index planes into the GB appears to lead to preferred, i.e. low energy structures, that can be quite dense with good atomic matching across a large fraction of the interface.

## INTRODUCTION

Internal interfaces accommodate the differences in the geometry between the two atomic lattices that are joined at the interface. On an atomic scale the interface structure depends on the atomic interactions near the interface and is also expected to be a strong function of the macroscopic geometric parameters describing the interface. The question can be asked, to what extend common structural features arise as a result of the atomic relaxations in different kinds of interfaces. Utilizing the atomic structure information available by studies employing the new generation of high-resolution electron microscopes we examine atomic matching in close-packed systems, including metal/metal-oxide interfaces and grain boundaries (GBs) in NiO and Au. We shall see that there are obvious similarities in the way atoms arrange themselves in a range of different interfaces. Evidence for coherence across interfaces will be discussed, particularly in cases where the misfit between the interatomic distances at the interface is large. It appears that good atomic matching can be obtained in local regions for many interfaces.

## MISFIT ACCOMMODATION AT INTERNAL INTERFACES

### Heterophase boundaries

It has been known for a long time that dense-packed planes are often preferred in nature as interfaces in precipitate formation or in epitaxial growth. The misfit between the lattices can be localized in the form of misfit dislocations as first discussed by van der Merwe [1] and experimentally observed by TEM techniques for numerous heterophase systems [2-4]. An indication for misfit localization can be found in Fig.1, which shows a (111) NiO/Cu interface viewed along $<0\bar{1}1>$. It appears that the interface is semi-coherent, with regions where coherence across the interface is maintained (see

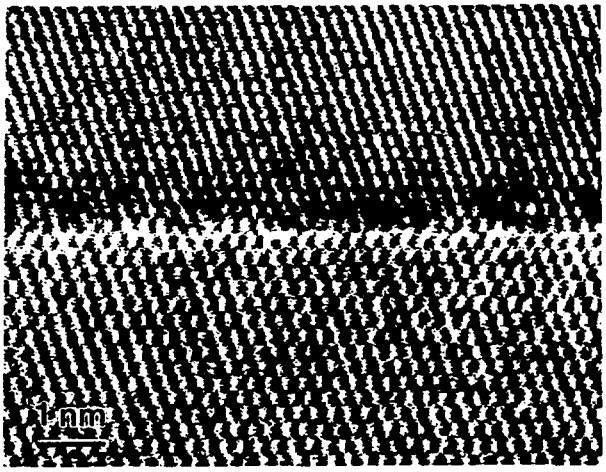

Fig. 1. NiO/Cu interface between NiO and Cu precipitates formed by internal reduction.

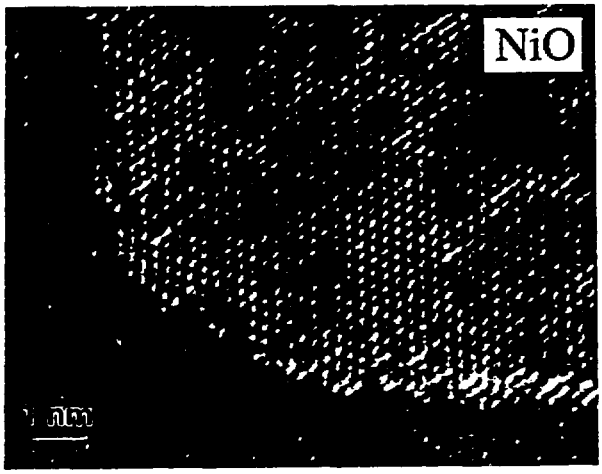


Fig. 2. NiO precipitate in Pd, formed by internal oxidation.

also Fig. 2) followed by regions of poor match. In this case it is difficult to apply HREM for the determination of the interface atomic structure, since a closely spaced hexagonal network of misfit dislocations is expected on (111) planes, which will disturb the atomic column contrast in the immediate vicinity of the interface. Nevertheless, a tendency towards coherence is frequently present in heterophase systems, even when the misfit is large as is also the case in NiO/Pd imaged in Fig. 2.

Grain Boundaries

For small-angle GBs, coherence between the two lattices is enforced in between primary GB dislocations and is accompanied by lattice strains, as seen in Fig 3. While small-angle GBs are well described by the Read-Shockley model, it is much less clear to what extend, if at all, atomic matching across large-angle GBs plays a role. In fact, large-angle GBs are generally considered incoherent. The geometric match between certain atomic sites in the GB, which is established for coincident site lattice (CSL) orientations, is generally destroyed when the bicrystal undergoes a rigid-body translation [5]. Atomic matching for the sake of the discussions in this paper is understood as having a GB region in which the relaxed atomic structures form a smooth transition between Lattice 1 and Lattice 2, while maintaining an environment for most atoms in the GB which is similar to the bulk. More specifically, such GBs can be considered semicoherent and may have one or more sets of major crystallographic planes that appear elastically continuous across the interface. A well-known example of this is the case of the small-angle GB which is demonstrated in Fig. 3. Of great importance for the structure and properties of GBs in general is the question concerning the role such matching regions play in the large-angle regime. To what extend are such structures possible

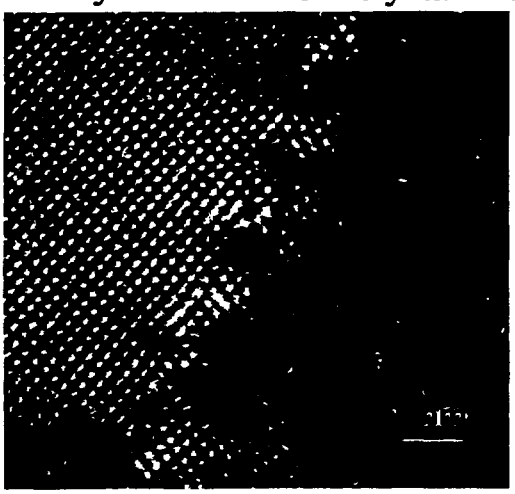

Fig. 3. Low-angle <001> tilt GB in NiO. Contrast variations around dislocation cores are due to elastic distortions.

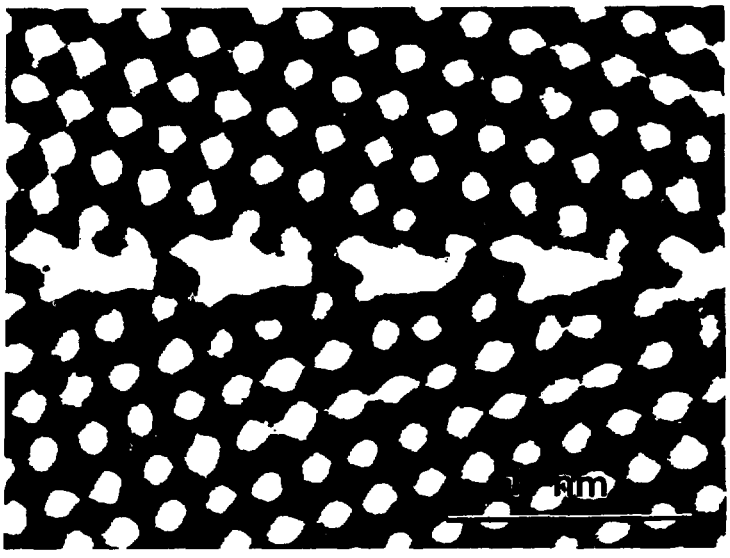

Fig. 4. $\Sigma = 5$, (310) tilt GB in NiO. The HREM image represents one of two variations which have been observed for this boundary [14].

and influence properties? An obvious criterion for the pervasiveness of such structures is the interfacial energy associated with them. It would appear that well-matched regions should be accompanied by low interfacial energies. Recent embedded atom calculations on metal GBs have indeed indicated a general correlation between the average degree of atomic coordination in the boundary and GB energy [6].

The idea that large-angle GBs may consist of regions of good match, followed by regions of poor match goes back to a suggestion by Mott [7] and is a common feature of most geometrical GB models, such as the CSL, O-lattice [8,9] and "planar matching" [10,11] models. While such models have been useful in the small-angle regime or for describing small deviations from special orientations, they have not for example been able to predict which GBs are of low energy [12]. Computer simulations are now increasingly being employed to determine structure and properties of GB model systems . Such calculations typically involve periodic boundary conditions, where the atomic relaxations are evaluated within a region defined by a GB planar unit cell [13].

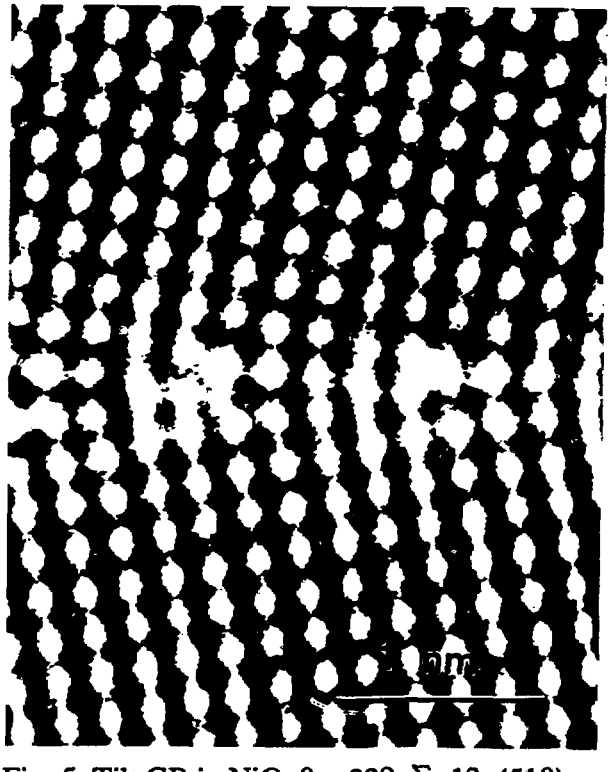

Fig. 5. Tilt GB in NiO, $\theta = 22^{o}$, $\Sigma$=13, (510).

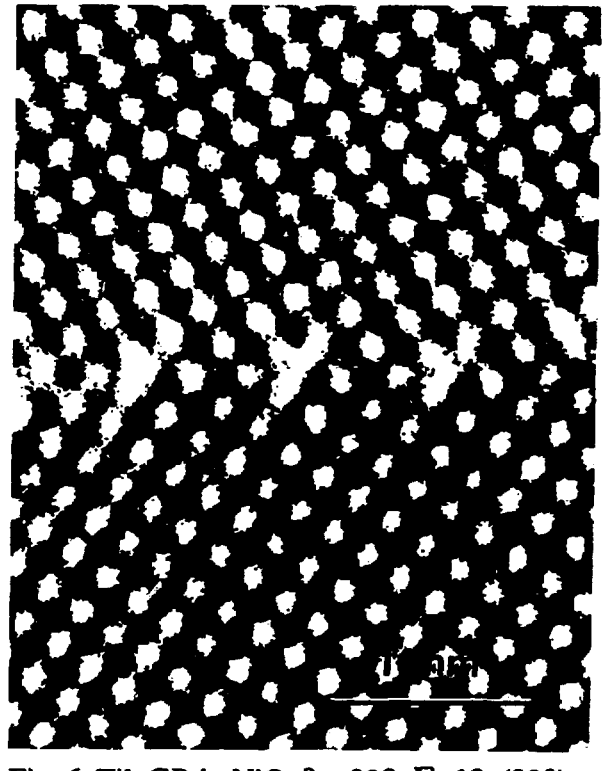

Fig. 6. Tilt GB in NiO, $\theta = 22^{o}$, $\Sigma$=13, (320).

When the planar unit cell is small, the structural units of the GB have a small period, which is accomplished for example by a low $\Sigma$ CSL boundary, where $\Sigma$ is the reciprocal volume density of coincident sites. Figure 4 shows a (310), $\Sigma$=5 symmetric <001> tilt GB in NiO [14,15] with quite small structural units. Such a boundary must be considered incoherent. The GB includes a rigid-body translation parallel and perpendicular to the GB plane and there is no continuation of low index lattice planes across the GB in the sense discussed above. Among the symmetric GBs there are additional low $\Sigma$ interfaces that appear incoherent, such as the $\theta = 28^{\circ}$, $\Sigma$=17, (530) GB . However others, such as the $\Sigma$ = 13, (510) GB shown in Fig. 5 clearly include regions with good atomic match in between regions of poor match. This GB, at $\theta = 22^{\circ}$ may be close enough to the small-angle regime, to preserve the coherence of (200) planes across the GB and to retain a semblance to dislocation cores without however-- due to cancellation of overlapping strain fields-- the associated long range elastic distortions typical for small-angle GBs (as seen in Fig.3). Figure 6 illustrates another such case for the (320) GB which has the same misorientation angle as the (510) GB. In this case we find closely spaced, well matched regions for which a good continuation of (220) planes across the GB can be observed by HREM.

Closely spaced structural units are mostly typical for low $\Sigma$ symmetric GBs. Such boundaries obviously constitute only a very small fraction of possible geometries and may in fact be atypical for general large-angle GBs for several reasons. First, there are many large-angle GBs which are not close to a low $\Sigma$ orientation. Second, it has been noted that asymmetric GBs, and notably those with a low index plane on one side of the GB, occur in abundance in tilt bicrystals of NiO, when the GB has a certain freedom to choose its inclination [16,17]. This suggests that such GBs have a low free energy. There are also theoretical reasons for this to be true [18]. It is also well known that dense-packed planes are often preferred in nature as free surfaces or interfaces in heterophase systems. Explicit GB energy calculations have indeed indicated, compared to symmetric GBs, lower energies for many asymmetric configurations [19-20].

An immediate consequence of considering not only low $\Sigma$ symmetric, but also asymmetric GBs and large $\Sigma$ symmetric GBs, is that the size of the structural GB unit cell increases. In the case of a GB for which the interatomic distances along the GB are irrational, the interface becomes incommensurate and the planar unit cell size infinite. Obviously, increased unit cell sizes call for different atomic relaxations at the GB which are not dictated by the short period inherent to the geometry of Fig. 3 for example.

Figure 7 shows a $<0\bar{1}1>$ , $\theta = 55^{\circ}$ tilt GB in Au. This boundary is both close to the misorientation $\theta = 54.74^{\circ}$ for which the planes $(111)_1$ and $(100)_2$ between the two crystals can be exactly parallel, and close to the $\Sigma$ = 41, $\theta = 55.88^{\circ}$ orientation. Long, extended (111)(100) facets are observed for this misorientation, suggesting that this GB is associated with a low free energy of formation. The GB is well structured and shows an amazing degree of atomic matching over most of the GB area as can be clearly seen in the enlarged section shown in Fig.7 b. The well matched regions are separated by tight regions that contain misfit-dislocation-like defects. Slight elastic distortions are centered around these defects. The spacing between the regions of misfit is 19 Å which corresponds to the average distance $\lambda = d_1 d_2/(d_1 - d_2)$ along the GB for

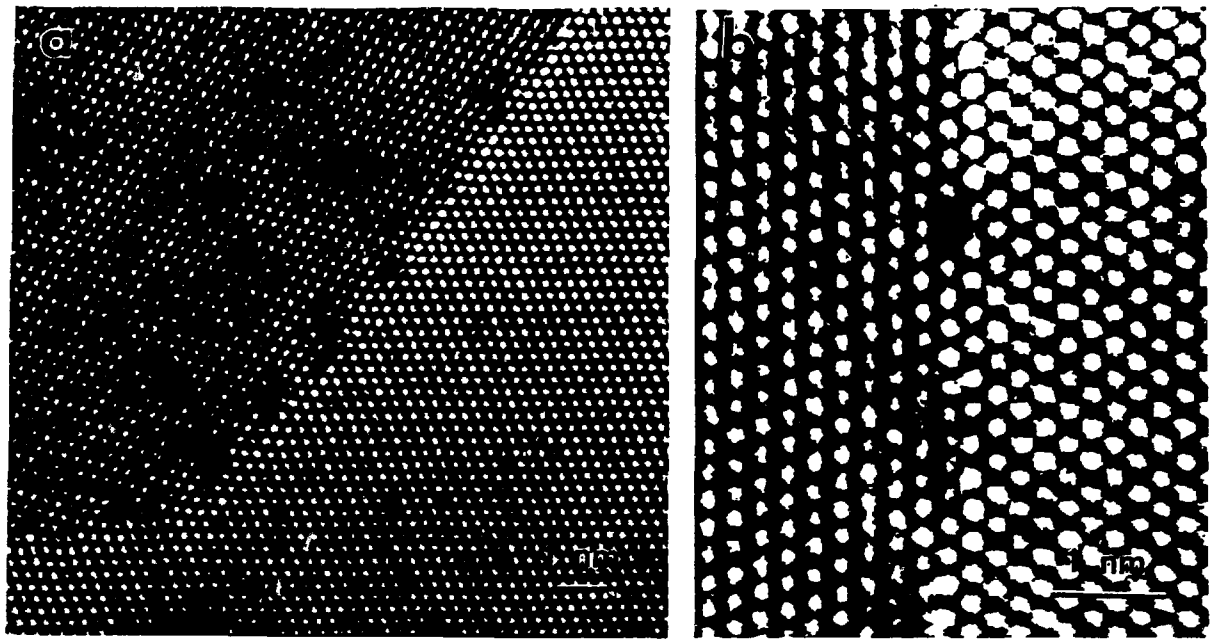

Fig. 7. Tilt GB in Au, misorientation axis <0$\bar{1}$1>, $\theta = 55^{o}$, near $\Sigma$=41. b) Enlarged section of (111)(100) interface. Atomic columns appear bright.

which one extra (200) plane is inserted to match the (111) planes on the other side of the interface ( $d_1$, $d_2$ are the interatomic distances along the GB). In the well-matched regions $(111)_1$ and $(\bar{1}11)_1$ planes appear linked to the $(200)_2$ and $(111)_2$ planes respectively. The relaxations in this GB are typical of the behavior in semicoherent interphase boundaries as first discussed by van der Merwe and observed by Matthews [1,2]. In contrast to this, if this GB is approximated by the $\Sigma$ = 41 GB, the CSL description would require a planar unit cell corresponding to the (100)(23 24 24 ) GB which is more than six times as long as the observed repeat distances for the misfit-dislocation-like defects in this GB.

We have observed evidence for atomic matching in a number of large-angle GBs. Such boundaries typically have regions of good atomic match followed by regions in which the environment of each atom strongly deviates from the ideal lattice. These regions, that are necessary for the accommodation of misfit, can take on different forms. The relaxations that are possible must depend on the particular geometry and the interatomic interactions which then lead to a minimum energy configuration. As indicated above, when the size of the planar unit cell of the GB becomes reasonably large, there may be a tendency to distribute the misfit to quite local regions within the planar unit cell with a concomitant generation of interspersed sections which have atomic coordi-

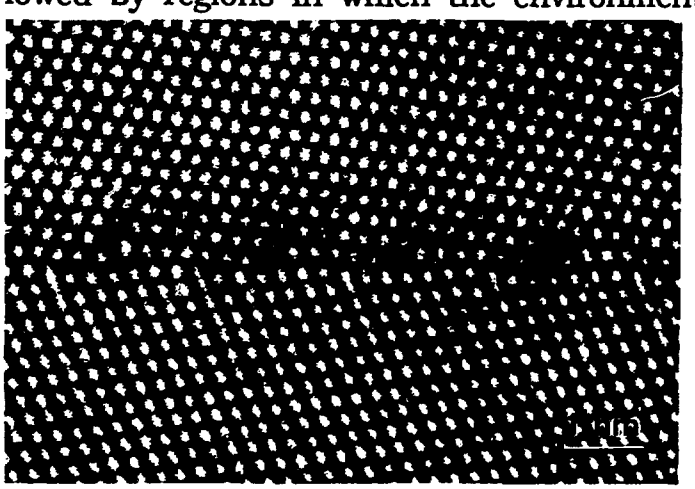

Fig. 8. Tilt GB in Au, misorientation axis <0$\bar{1}$1>, $\theta = 55^{o}$, near $\Sigma$=41. Symmetric (344) GB.

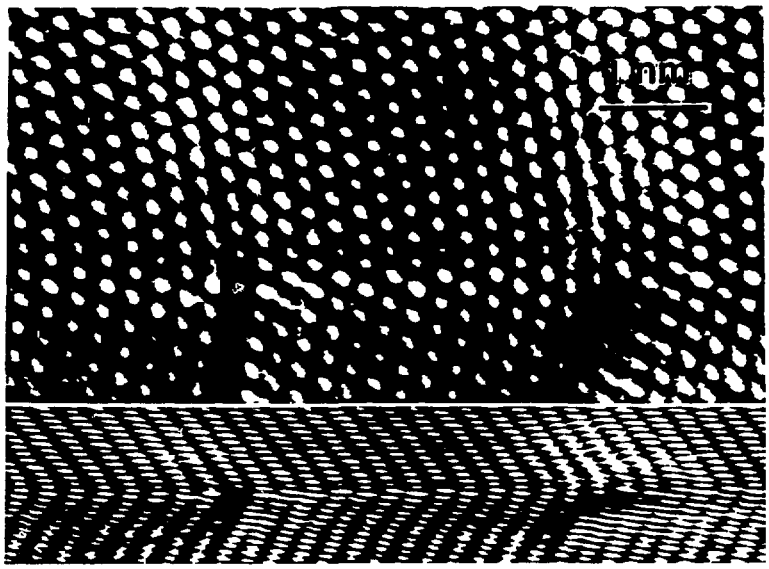

Fig. 9. Tilt GB in Au, misorientation axis <0$\bar{1}$1>, $\theta = 55^{o}$, near $\Sigma$=41. Symmetric (833) GB. Bottom:vertical dimension compressed.

nations similar to the bulk.

Such well-matched areas are not limited to asymmetric GBs but can also be recognized in large $\Sigma$ symmetric GBs, such as shown in Figs. 8 and 9. Figure 8 is an image of the (344) symmetric $\Sigma$=41 GB. Here the planar unit cell has a length of 17 Å and contains two cores. In between these regions of misfit there is a strong tendency to form well matched regions. This is apparent in several different ways: First, there is a good continuation of $(111)_{1,2}$ planes to $(200)_{2,1}$ planes across the GB. In addition the $(111)_1$ and $(111)_2$ planes, which meet under an angle of 14.6° degrees at the GB, appear to form strings of elastically well connected atomic columns in the immediate vicinity of the boundary. The GB clearly is not confined to a single plane, but appears dissociated due to the staggered arrangement of cores. An even more interesting structure is the (833) symmetric $\Sigma$41 GB of Fig.9. Here the $(111)_{1,2}$ planes, which make angle of 7.2° to the GB normal, are perfectly coherent across the GB. Another pair of $(111)_{1,2}$ planes is coherent with $(200)_{2,1}$ planes on the other side of the GB respectively. The misfit is taken up by the creation of stacking faults, which emanate on those $(111)_{1,2}$ planes that are close to the GB normal. This produces a three-dimensional structure which is very well matched on an atomic scale. The stacking faults give however rise to an extended strain field which is somewhat longer ranged than what is typical for a large-angle GB.

These observations of atomic matching in a number of different kinds of GBs indicate that this may be a general phenomenon in large-angle GBs and particularly in those with large planar unit cells. Recent computer simulations of a wide range of GBs, which revealed a correlation between the average atomic miscoordination in the GB and boundary energy, directly support such a view [6].

## CONCLUSIONS

The examples of atomic structures of interfaces which have been presented here emphasize the importance of the local arrangement of atoms in the interface. The strong tendency for establishing coherence and good atomic matching in a range of different interfaces are an indication that such configurations are low in energy. It seems almost trivial that atomic structures that approach configurations similar to their environment in the bulk would be pre-

ferred energetically. Direct observation by HREM has shown that such structures are favored in asymmetric GBs bounded by dense-packed planes and in interfaces that have large structural units. Therefore, although small GB periods have for a long time been almost considered synonymous with low energy boundaries, it should be emphasized that there are many relaxation paths for large angle-GBs which can give low energy structures. The degree of atomic matching and the incorporation of dense-packed planes are of major importance in the generation of internal interfaces.

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