Ar-loaded and N_2-loaded crystal structures (in CIF format) have been deposited as CCDC 277428-277437. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax, (+44)1223-336-033; or deposit@ccdc.cam.ac.uk].

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High Frictional Anisotropy of Periodic and Aperiodic Directions on a Quasicrystal Surface

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Strong friction anisotropy is found when the twofold surface of an atomically clean aluminum-nickel-cobalt quasicrystal slides against a thiol-passivated titanium-nitride tip. Friction along the aperiodic direction is one-eighth as much as that along the periodic direction. This anisotropy, which is about three times as large as the highest value observed in anisotropic crystalline surfaces, disappears after the surface is oxidized in air. These results reveal a strong connection between interface atomic structure and the mechanisms by which energy is dissipated, which likely include electronic or phononic contributions, or both.

The origin of friction and the energy dissipation mechanisms that underlie it are still being explored in fundamental studies. To this day, simple ideas from the times of Leonardo da Vinci, such as the existence of a strong connection between the geometric corrugation profiles (even at the atomic scale) of two contacting surfaces, are still invoked to explain friction (*1*). The idea is that commensurability leads to intimate interlocking and high friction, whereas incommensurability leads to low friction, because the two materials do not come into registry at any length scale. Some of these ideas have been verified recently by rubbing two surfaces of graphite or mica against each other (*2, 3*) under conditions where wear and plastic deformation are minimized, so that fundamental dissipation forces can be explored. Friction was found to be largest when the crystallographic orientation of the two identical surfaces coincided. Commensurability, however, is only one aspect of the friction problem and does not apply to most interfaces, because the contacting materials are different and therefore almost always incommensurate. Friction anisotropy between incommensurate surfaces has been observed when at least one of the surfaces is crystalline and anisotropic, i.e., when the periodicity changes in different directions. This anisotropy is typically less than a factor of 2 (*4*), although in the case of some organic monolayers on mica, a factor of 3 was observed (*5*).

A different question is whether the existence of periodicity itself is important in friction. For example, it is in periodic systems that the highest thermal and electrical conductivities are found. To explore this question, one could compare the friction properties of a material prepared in crystalline and amorphous forms. This, however, is very difficult, because the two surfaces of the material are likely to be chemically different, which would change the friction properties. As we discuss below, our quasicrystal surface provides a unique example of a material where the periodicity exists only in one direction.

Quasicrystal intermetallics (*6, 7*), which have long-range atomic order but no periodicity, are ideal samples for exploring this idea, because in two-dimensional quasicrystals, such as decagonal Al-Ni-Co, certain surface terminations exhibit periodic as well as aperiodic atomic ordering along different directions. Quasicrystal surfaces, which are oxidized under ambient conditions, are already known for their high hardness and low friction (*8–12*), although these results were obtained under conditions where plastic deformation occurred during sliding. To investigate fundamental aspects of friction on quasicrystals, we cut an Al-Ni-Co single quasicrystal perpendicular to its 10-fold rotational axis to produce a surface

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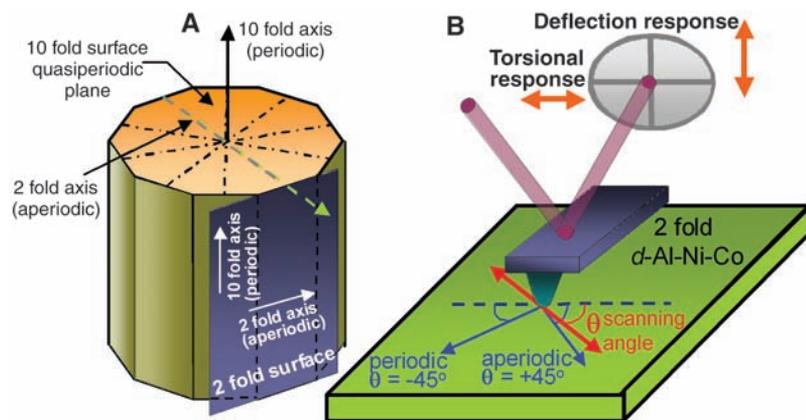*To whom correspondence should be addressed. E-mail: mbsalmeron@lbl.gov

Fig. 1. (A) Schematic model of a decagonal Al-Ni-Co quasicrystal, showing the orientation of decagonal and twofold planes. The 2-fold plane is periodic along the 10-fold direction and aperiodic along the 2-fold direction. (B) Schematic of the cantilever and the scanning geometry during friction studies.

with one periodic and one aperiodic axis separated by 90°. The clean, oxide-free surface was prepared and studied under ultrahigh-vacuum (UHV) conditions (*13*).

We used a combined atomic force–scanning tunneling microscope (AFM-STM) to probe the atomic structure of the surface and to perform tribological measurements (*14*). When a clean metal surface and a clean tip come into contact, the adhesion force may be very strong, and surface damage can be unavoidable. This is the case for the TiN/quasicrystal contact (*15, 16*). Therefore, we passivated the TiN tip with a molecular layer of hexadecane thiol, which substantially reduced the adhesion force. This treatment, coupled with low loads, yielded stable and reproducible contacts that obeyed the Derjaguin-Müller-Toporov (DMT) classical elastic model without hysteresis (*17*). Absence of wear was also confirmed through repetitive imaging.

Figure 1A shows the high-symmetry axes of the quasicrystal superimposed on the typical growth habit. Earlier studies of decagonal Al-Ni-Co (*18, 19*) indicated that the structure consists of two types of atomic layers stacked in a periodic sequence along the 10-fold direction, with a spacing of 0.2 nm. Each layer has pentagonal (quasicrystalline) symmetry. Thus, the periodicity along the 10-fold direction is 0.4 nm. The twofold plane contains both periodic and aperiodic axes (Fig. 1A).

STM images, such as the one in Fig. 2, confirmed the periodic and aperiodic nature of this surface. On a larger scale, the surface exhibited a terrace-step structure, and the terraces contained rows of protrusions. The protrusions inside the rows were periodically spaced by 0.4 nm, which is consistent with a bulk termination model. The rows, however, are not periodically spaced. The rows with highest contrast, marked by lines, are separated by 0.8 and 1.3 nm. The rows are arranged such that their spacings form a Fibonacci sequence, which is often observed in quasicrystalline materials (*6*). Other features of the rows, such as arrangements of less-prominent rows relative to the main ones and their spacing, are also related to the Fibonacci sequence.

sequence, which confirms quasicrystallinity in the direction perpendicular to the rows.

The torsional response of the AFM cantilever is proportional to the component of in-plane frictional force perpendicular to the lever axis, whereas the deflection response depends on both the tip-sample force perpendicular to the surface (normal load) and the component of in-plane (frictional) force parallel to the projected lever axis. The angle θ defines the scanning direction relative to the axis of the cantilever (Fig. 1B). In a typical AFM friction experiment, a scanning angle of zero is chosen, so that frictional and normal forces are decoupled. In our experiments, the sample was deliberately oriented such that the 10-fold and 2-fold axes were at θ = ± 45°, and the lever torsional response was measured as a function of normal load and scanning angle. Because the mechanical response of the AFM lever should be identical for the two directions, an observed asymmetry in torsional response reflects a tip-sample frictional anisotropy. The 2-fold Al-Ni-Co decagonal quasicrystal surface showed high torsional response along the 10-fold (periodic) direction, and low torsional response along the 2-fold (aperiodic) direction (Fig. 3A). The ratio was 7.8 ± 1.3, based on data at θ = −45° and +45°, measured in five different sets of experiments with independent sample and tip preparations. The measured torsional response remained anisotropic for all applied loads (Fig. 3B) throughout the wearless regime. The tip-sample electrical conductance was measured simultaneously and found to be independent of scanning angle, which indicates that the contact area did not change with direction (*20*). The friction curves can be fit well with the DMT elastic model (*17*), which contains only one adjustable parameter. The ratio of the parameters for each curve gives a value of 8.2 ± 0.4 for the friction-force ratio in the periodic and aperiodic directions.

The torsional response of the cantilever is proportional to the product of the frictional force and the cosine of the scanning angle. The component of frictional force along the lever

axis causes buckling, which changes the deflection response. If AFM feedback is active, this will cause a change in the normal load, so the measurements of scanning angle–dependent torsional response were carried out with the feedback loop disabled. The sample slope was compensated so that the tip-sample distance, and therefore the applied load, were independent of lateral displacement. Even in open-loop conditions, the buckling component of frictional force modulates the effective normal load, because the tilt of the cantilever relative to the sample surface projects a component of the buckling force normal to the surface. Because the torsional response was measured experimentally by taking the dif-

Fig. 3. (**A**) Torsional response of the cantilever measured as a function of scanning angle on the twofold surface of the Al-Ni-Co decagonal quasicrystal. The torsional response was higher along the periodic direction than it was along the aperiodic direction. The solid line shows the calculated torsional response with scanning angle for an anisotropy factor (ratio of friction forces) of 8. The data points are normalized averages of five independent measurements each. (**B**) Torsional response as a function of applied load in both periodic and aperiodic directions. The lines are fits to the DMT model (*17*). The ratio of shear stress in each direction derived from the fits is 8.2 ± 0.4. (**C**) Plot of the torsional response as a function of scanning angle on an isotropic silicon oxide surface with a roughness of <0.3 nm. The solid line shows the calculated torsional response.

Fig. 2. Collage of two STM images (sample voltage V_s = 1.2 V, current I = 0.1 nA) of the twofold Al-Ni-Co surface. The surface showed a 0.4-nm periodicity along the 10-fold direction. In the direction perpendicular to the atomic rows (twofold direction) a quasiperiodic sequence of 0.8 and 1.3 nm distances was observed.
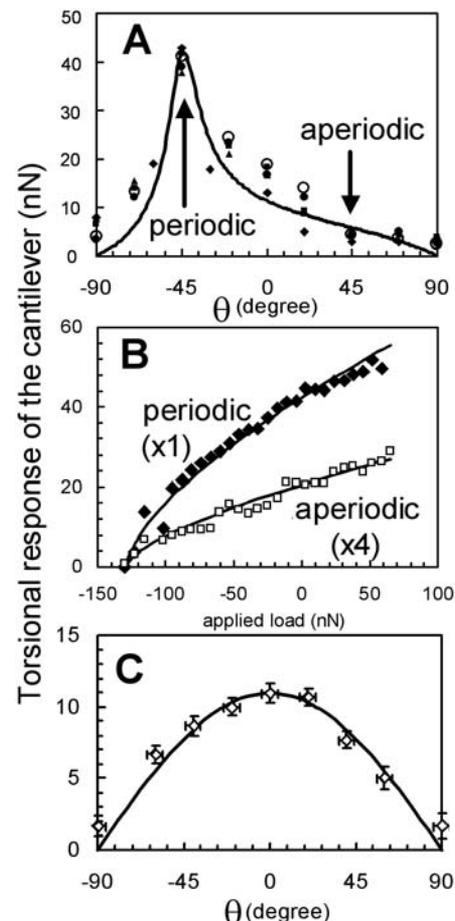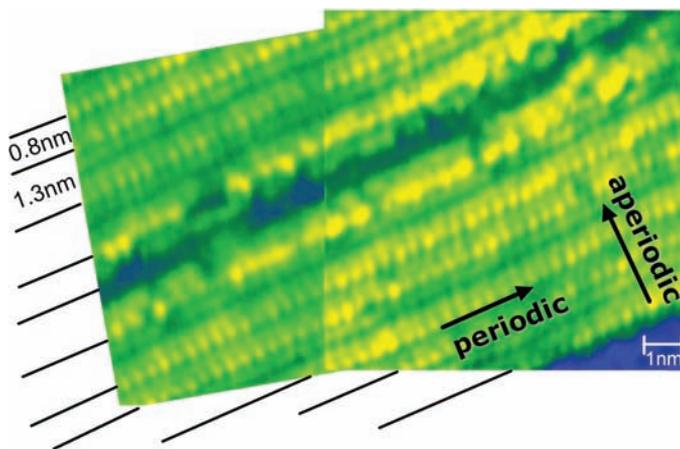
Fig. 4. (**A**) Plot of the torsional response as a function of load along periodic and aperiodic directions after oxidizing the Al-Ni-Co quasicrystal by exposure to air. The anisotropy shown by the clean sample is lost. (**B**) Contact AFM topographical image at an applied load of 0 nN, revealing an amorphous granular oxide film with grain dimensions of 10 to 20 nm. The directions of the atomic rows of the underlying clean substrate are still recognizable.
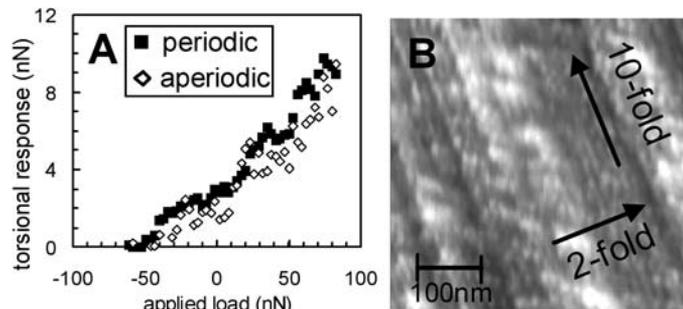
ference between the signal in the forward and reverse scan directions, the buckling effects cancel out to first order (*21*).

The solid line in Fig. 3A was calculated by assuming an elliptical dependence of friction on scanning direction, with the major axis along the high-friction periodic direction and the minor axis along the low-friction aperiodic direction. The ratio of the major and minor axes corresponds to the friction anisotropy. The magnitude and anisotropy ratio were fit to the experimental torsional response data, giving a reasonable fit for all scanning angles. The experimental procedure was validated by comparing simulation results and torsional response data for an isotropic amorphous silicon-oxide surface, with a root mean square roughness of 0.25 ± 0.06 nm. The squares in Fig. 3C show the measured friction force as a function of θ. It decreases as θ deviates from zero, as expected. The agreement between the experimental data and the simulation (solid line) is excellent.

The friction anisotropy against the thiol-passivated TiN tip disappeared when the surface was oxidized (Fig. 4A) by exposure to air. Extrapolating from studies of icosahedral Al-rich quasicrystals (*22, 23*), exposure to air at room temperature should form a surface layer of nearly-pure aluminum oxide, 2 to 3 nm thick (Fig. 4B). Hence, the friction anisotropy in Fig. 3B must arise from a short-range interaction between the tip and the surface, which depends on the atomic structure of the clean surface.

Previous macroscopic studies of quasicrystal friction have used two factors to explain the unique tribological properties of these materials: high hardness, which controls the plastic contact area and hence influences friction, and oxide formation (*9–12*). Neither factor applies to our study, because oxide-free surfaces were studied under elastic conditions.

Several other factors could account for the observed friction anisotropy. One is an anisotropic response of the hexadecane thiol molecules that coat the tip. The hydrocarbon chains might bend and align parallel to the atomic rows as the tip sweeps along the periodic direction but not when the tip scans perpendicular to the rows. However, the vertical corrugations along periodic and aperiodic directions are only slightly different

(0.03 versus 0.04 nm, peak-to-peak) and very small compared with the size of the alkyl chains, which are 0.4 nm in diameter and 2 nm long, so this explanation seems unlikely. Incommensurability between the probe and the surface (*24*) cannot be invoked either, because in our experiments, the TiN tip is amorphous and is covered by alkanethiol molecules, meaning that registry is unlikely in any scan direction.

Two final factors are dissipation by electronic and phononic contributions, where energy is dissipated via excitation and propagation of electron hole pairs and phonons, respectively. These contributions play an important role in bulk electrical and thermal conductivities, which are known to be highly anisotropic in the decagonal phases (*25, 26*). The transport properties are "normal" along the periodic direction, but anomalous within the aperiodic planes for the decagonal phases. For instance, the bulk thermal conductivity along the periodic direction is larger than it is along the twofold direction by an order of magnitude at room temperature in Al-Ni-Co. The unusual aspects of electron transport in quasicrystals are often associated with electron localization and with the existence of a pseudogap in the electronic density of states at the Fermi level. Phononic friction is also a candidate explanation, because the excitation and propagation of surface phonons along the aperiodic direction could be inhibited by phonon energy gaps (*27, 28*) predicted theoretically, leading to low energy dissipation. We note that phononic friction is intertwined with the issue of incommensurability, because registry affects the efficiency of phonon excitation (*29*).

It is likely that electronic and/or phononic contributions play an essential role in determining the friction anisotropy caused by the existence of electron and phonon gaps in the aperiodic direction. Our results call for a detailed modeling of the generation and propagation mode of electronic and phonon excitations for this well-defined surface structure.

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