

Formulas for Shapes

*Some metals have a memory: They can be bent and, if subject to the right treatment, can reassume their original shape. **STEFAN MÜLLER**, Director at the **MAX PLANCK INSTITUTE FOR MATHEMATICS IN THE SCIENCES**, and his colleague **ANJA SCHLÖMERKEMPER** are exploring the mathematical laws on which this memory is based, and through which it may be improved.*

Anja Schlömerkemper often sits at her desk and ponders geometric structures, formulas and proofs. When she plays with a paper clip while doing this, and bends the small organizational tool out of shape, it will not necessarily have outlived its usefulness. If immersed in hot water, it quickly reassumes its original form – if it is made of a shape-memory alloy. Such a paper clip can be found in the scientist’s office at the Max Planck Institute for Mathematics in Leipzig – to demonstrate what she is pondering: the mathematical models for such materials and how to use these models to improve the materials.

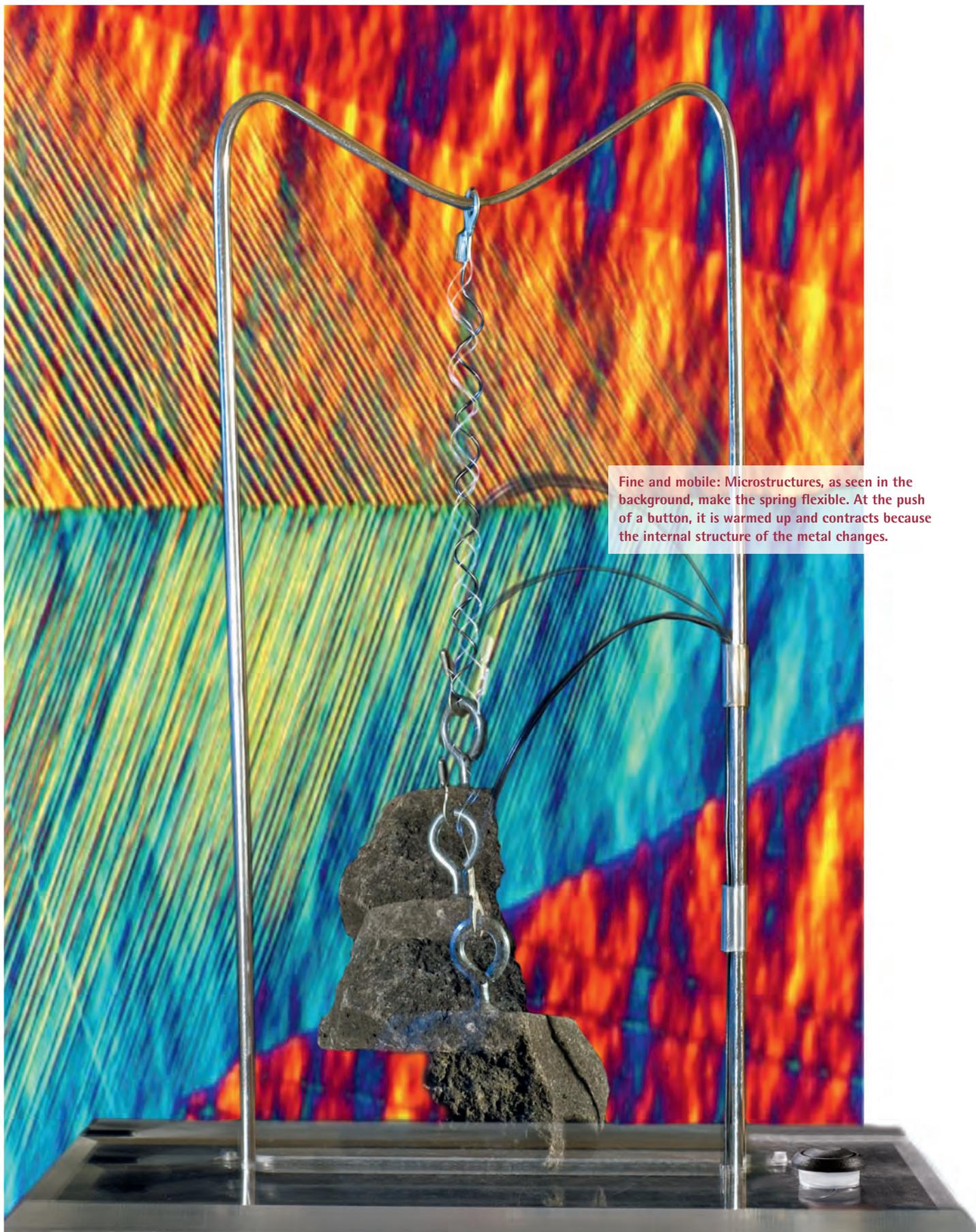
The metals are used in the field of medicine, for example, for stents, which widen constricted blood vessels, and for artificial cardiac valves. Doctors guide the compact, folded implants, which are made of a nickel-titanium alloy, through the blood

vessels to the required location. When heated to body temperature, the stents open up – a method that is less complicated than getting a traditional steel stent to work using an inflated balloon.

Materials scientists do not fully understand why memory alloys behave in this way, so developing similar materials for other applications requires laborious tests. The Leipzig-based mathematicians want to change this. And that is not all they want: the mathematical methods they are searching for can also be used to describe, for example, how magnetic materials are used in storage media. They also help us understand how bubbles form in a layer of paint. The scientists are ultimately solving mathematical problems that are impeding progress in other, completely different areas of the sciences.

“Whereas engineers look for formulas that apply to the data from

specific measurements, we try to find generally applicable mathematical models,” says Anja Schlömerkemper, who heads a research group at the institute in Leipzig. This assertion touches on a philosophical question: Do people impose mathematics on the world, or does the world have a mathematical structure that merely awaits revelation? In any case, mathematicians penetrated into curved spaces, apparently with no specific purpose in mind, when they developed non-Euclidian geometry. Barely a century later, in his general theory of relativity, Albert Einstein discovered that space is actually curved. “It is ultimately impossible to say whether the laws we use to describe the world are universally applicable,” says Stefan Müller, Director of the department in which Anja Schlömerkemper works: “But a certain degree of regularity in the world would appear to be a precondition of our understanding.”



Fine and mobile: Microstructures, as seen in the background, make the spring flexible. At the push of a button, it is warmed up and contracts because the internal structure of the metal changes.

PHOTO: BASTIAN EHL (FRONT)/C. CHU, R. D. JAMES



PHOTOS: BASTIAN EHL (4)

Hard at work: Anja Schlömerkemper and Stefan Müller try to find a calculation to express the allowed microstructures in memory metals. Paper models help them in their search.

Stefan Müller and Anja Schlömerkemper rarely deal with such large-scale questions, however; the problems they tackle are usually much smaller – even microscopic in nature. They are looking for the laws that can be used to describe microstructures. “Microstructures are responsible for the special characteristics of memory alloys,” explains Anja Schlömerkemper. Materials scientists understand microstructures as structures that exist in the microscopic range. These include the scales on shark skin and trabeculae in human bones, as well as the structure formed by data points in a magnetic memory.

In the microstructure of memory alloys, the regions where the alloy atoms are differently oriented alternate. These differently oriented regions can also be found in Anja Schlömerkemper’s paper clip, but only at room temperature. They disappear at higher temperatures, and with them, the mi-

crostructure: the material is then left with only one order. Because the paper clip experiences this structural change in warm water, it “remembers” its original form.

To explain what happens when metals remember their structure, Anja Schlömerkemper uses a simple example and a sketch: she draws a square lattice. This is what the structure looks like at high temperatures – in a two-dimensional model, at least. In three-dimensional space, the squares become cubes. There is an atom at each point in the lattice, and each square or cube corresponds to an elementary cell in the crystal. This is the structural unit on which the composition of a crystal is based – and metals are crystals, too.

NATURE WANTS TO CONSERVE ENERGY

The technical term for the cubic structure is austenite, coined in honor of the British metallurgist Sir Wil-

liam Chandler Roberts-Austen. Any attempt to bend something in the square lattice would deform the elementary cells, which the material does not like at all. The alteration of the atoms from their usual state costs energy, and nature avoids any process that costs energy.

At high temperatures, at which the material forms only a square lattice, the paper clip springs back into its original, fully functional shape. The material is actually trained into this shape: the paper clip with the capacity to remember actually originates from a piece of wire. It is bent into the shape of a paper clip when cold, clamped this way and then heated until the atoms have changed into the new state. Some memory alloys are also trained through several heating and cooling cycles. While all this effort is worthwhile for cardiac valves, it is less so for mass-produced goods like paper clips – Anja Schlömerkem-

per's paper clip is ultimately for demonstration purposes only.

The fact that memory alloys can easily be bent at room temperature is due to the structure their atoms form at this temperature. Materials scientists refer to the arrangement as the martensite phase. To demonstrate this, Anja Schlömerkemper draws two lattices based on rectangles with two sides of different lengths. In one case, the longer sides are horizontally aligned; in the second, they are vertically aligned. In a three-dimensional memory alloy, the rectangles expand to form

possible; the greater the number of possible microstructures, the more flexible the material. If the material is forced to accept a prohibited microstructure, it may tear or break.

The reason why not all microstructures are possible can be clearly illustrated, at least for the model of differently oriented rectangles: the lattices must match up where the two orientations meet. This means that they must share lattice points. The atoms located at the boundary actually belong to both lattices and must be at home in both. This is possible only if they fit quite precisely into the struc-

ture for a function of functions. In other words, unlike a function, a functional is not evaluated at a number – for example, a number taken from physical measurements. Instead, it is evaluated at a function, such as a function that describes the deformation of the crystal.

BRANCHING OUT TO RESOLVE A DILEMMA

Second, the quest for the energy minimum is also rendered difficult by the fact that, in nature, many effects that have an impact on energy compete with each other. At least



Live wire: Immersion in warm water enables the bent paper clips to return to their fully functional shape. The extent to which they can be bent while cold is determined by the number of possible microstructures.

cuboids, and instead of two orientations, there are three, corresponding to a tetragonal structure. In the cold shape-memory alloy, the regions with the differently oriented cuboids form the microstructure. Or, to be more precise, the microstructures, since the way in which the regions orient themselves depends on whether the wire forms a paper clip or a twisted fantasy shape.

CONFLICTS AT THE LATTICE BOUNDARY

If the process ended there, the mathematicians in Leipzig would not have much more to do. However, this is not the case, as only certain microstructures are allowed. “What we would like to discover mathematically is precisely which microstructures are allowed,” says Anja Schlömerkemper. The mathematicians would like to determine, among other things, when the number of allowed microstructures is as high as

possible. Anything else would, again, cost too much energy.

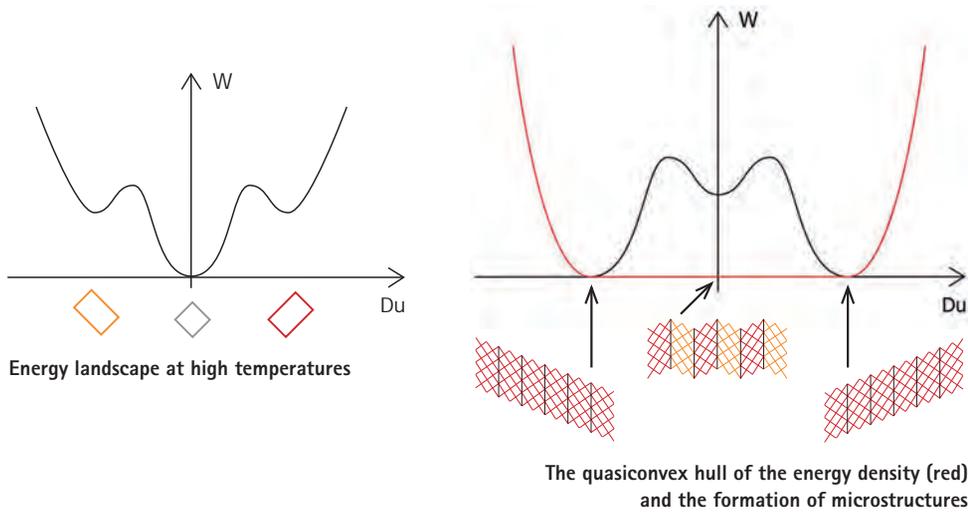
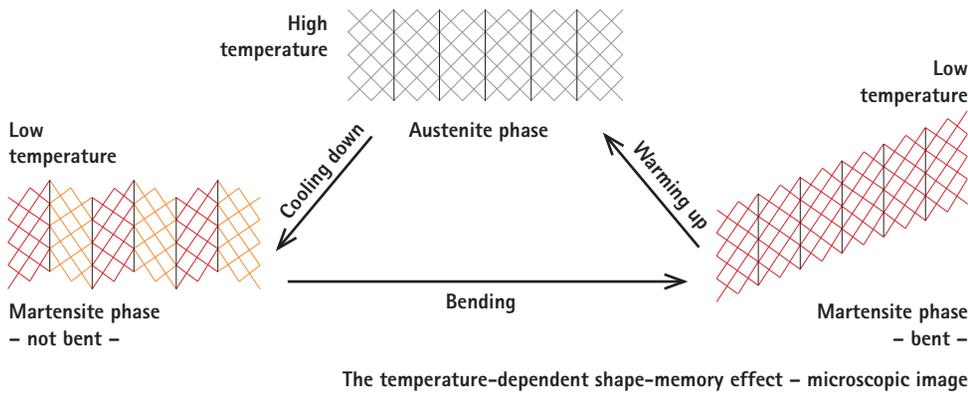
“I like to begin by imagining the geometric appearance of the possible structures,” says Stefan Müller: “Only when we have done this do we try to develop a calculation.” However, the end product must constitute a mathematical statement or formula and, if possible, a formulation that provides materials scientists with an indication of suitable materials. In other words, one that contains easily quantifiable parameters. “Energy provides a starting point here,” says Stefan Müller.

As the energy level of the allowed microstructures must be as low as possible, a problem arises that mathematicians can generally manage well: the search for an energy function minimum. However, the energy function of a shape-memory alloy is in no way as simple as a discussion of curves at school. First, the energy is a functional – the mathematical

two influences vie with each other in a microstructure: elastic energy and interfacial energy. The less the preferred structure of the atoms is deformed in the bent paper clip, the lower the elastic energy. If the microstructure is as fine as possible, the regions with differently oriented atoms are as small as possible and the structure is very flexible. This is very similar to a game with building blocks: the smaller the stones, the more varied the structures that can be built with them.

However, a fine microstructure also has a disadvantage: there are a lot of interfaces in it at which the differently oriented lattices must align themselves. This costs energy, as the atoms must shift somewhat from their preferred positions. Thus, from this perspective, the fewer interfaces there are, the coarser the structure and the better the energy balance. The compromise formula for obtaining the optimum of elastic energy

THE MATHEMATICS OF SHAPE MEMORY



At high temperatures, the atoms of a shape-memory alloy form a cubic structure (above, austenite phase). If the material is bent to form, for example, a paper clip and then cooled down, the atoms arrange themselves in cuboids and form a microstructure (martensite phase), thus the external form of the paper clip is maintained. It is possible to bend the wire thanks to the variety of possible microstructures. The reasons for this behavior are energetic (below): At high temperatures, there is an exact minimum for energy W , which is due to the cubic structure. At low temperatures, there are two variants that can connect with each other with different orientations Du . This explains why a large number of microstructures are energetically favored (red line between the two minima).

and interfacial energy was developed by Stefan Müller and Robert V. Kohn from Courant Institute in New York.

Using this calculation, the Leipzig-based mathematicians can also understand what happens when some regions of a material are formed by cuboids and some by cubes. This usually occurs while the material is adapting to a change in temperature. Where cuboids and cubes come into contact with each other, they must somehow cope with each other structurally.

The square lattice has virtually no scope for concessions, but the rectangular one does. It can ultimately

form a microstructure with different orientations, albeit with energy-intensive interfaces. In the striving for the energetic minimum, this dilemma leads to a complex delicate structure: the two differently oriented tetragonal structures form layers of a few micrometers in thickness around ten micrometers away from the boundary of the two structures. In this way, the material saves interfacial energy. In order to adapt flexibly to the cubic lattice structure close to the interface, the layers branch out until the individual layers measure significantly less than one micrometer.

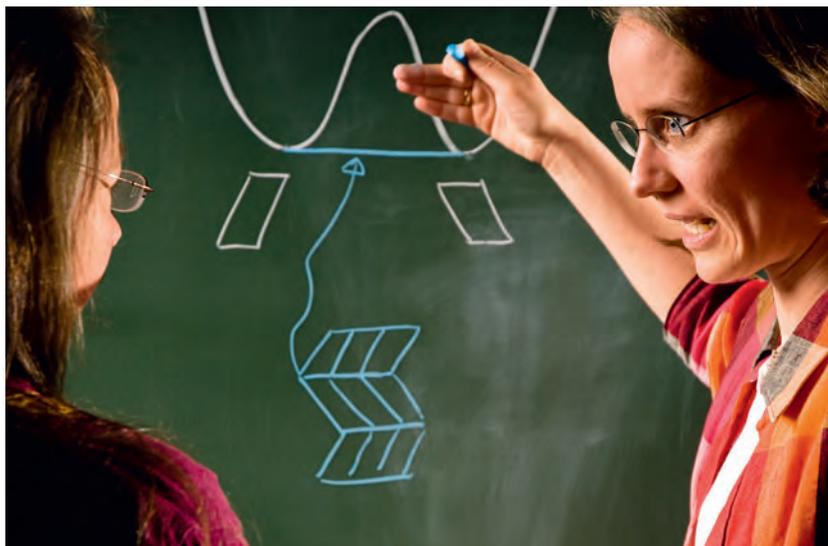
ILLUSTRATION: MPI FOR MATHEMATICS IN THE SCIENCES

“This helps us explain why microstructures can be found so frequently in nature,” says Stefan Müller. Using methods very similar to those that led to this insight, it is possible to calculate the state that is particularly favorable in energy terms for many other applications. Thus, the formulas explain why the electrons amble around in orbitals. Or why the roofs of the Olympic Stadium in Munich are curved - this subjects the membrane supports to the least possible strain.

Mathematicians usually turn to elliptic partial differential equations when they wish to determine a minimum energy state. Differential equations are mathematical workhorses and are widely used by scientists. They help in the quest for functions with which varied natural phenomena can be defined, including the development of biological populations or the climate. Partial differential equations describe phenomena that, like most natural processes, are influenced by several factors. And the use of the attribute “elliptic” often expresses the search for the minimum energy level. With their work on memory alloys, Stefan Müller and his team have come closer to their goal of systematically understanding such equations. This is helpful because, to date, computers have generally had to test all possible solutions and, as a result, are hopelessly overburdened when faced with the task of, for example, predicting microstructures.

However, the search for the energetic compromise formula that can help with this task is not exactly easy and, what is more, it is rendered significantly more complex by the fact that the microstructure is three-dimensional. In order to describe the spatial orientations of the elementa-

PHOTO: BASTIAN EHL



At the energy low point: Anja Schlömerkemper explains the quasiconvex hull (blue) for microstructures. This describes combinations of the two variants of the parallelogram (right and left).

ry cells, the scientists must work with matrices. These tables, with which mathematicians feed their equations, consist of three lines and columns and span a nine-dimensional space within which the mathematicians must operate.

A HULL FOR ALLOWED STRUCTURES

Moreover, there are more variants for interesting memory metals, such as the easily deformed version of nickel and titanium alloys, than for tetragonal structures. Anja Schlömerkemper is working, for example, on the microstructures of monoclinic lattices. Their elementary cells consist of a deformed cuboid and resemble an unstable shelf that has ended up tilting to one side: “For such materials, we are looking for the quasiconvex hull,” says Schlömerkemper – which means that the researchers can discover how strongly a wire can be bent and still be completely filled out by microstructures. If this is not possible, the wire deforms plastically – that is, like a traditional paper clip.

The term “convex” as used here has little to do with the corresponding lens form. “The convex hull of a set includes all mean values between the elements of the set,” explains Stefan Müller: “Therefore, all shades

of gray are found in the convex hull of black and white.” In the memory alloys, the usual convex hull contains more elements than are found in crystals, as only those microstructures in which the lattices fit together are possible – the state expressed by the term quasiconvex.

In any case, this is far more complicated for the microstructure of monoclinic lattices than for the case that Anja Schlömerkemper illustrates using square and rectangular lattices. In fact, there are twelve variants of the monoclinic structure in which the elementary cells are differently oriented. It is not possible to combine all of the orientations with each other because, with the best will in the world, the lattices on the edge often do not fit together. However, Anja Schlömerkemper and her colleague Isaac V. Chenchiah, who previously carried out work as a post-doctoral researcher at the Max Planck Institute in Leipzig and now teaches at the University of Bristol, are not only looking for the ways of combining the different variants.

The scientists started by identifying groups among the twelve different orientations in which four of the differently oriented lattices connect with each other in a way that involves as little strain as possible.

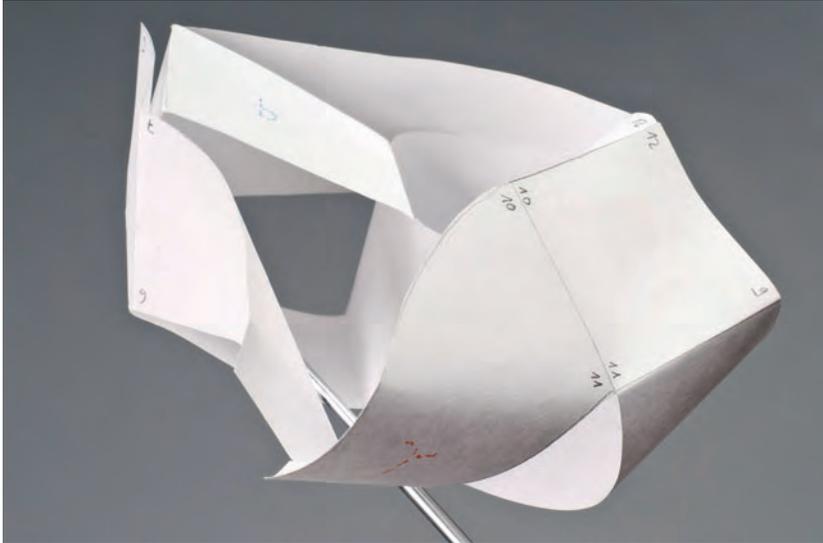
However, zones can also be found beside each other in the microstructure of such a material whose orientation does not belong to one and the same group. There thus exist between these groups geometric relationships that Anja Schlömerkemper also wants to get a handle on mathematically. Instead of keeping her hands busy with a paper clip while pondering this problem, she constructs a paper model of the intergroup law: she sticks nine paper triangles together to form an unusual structure.

THE SEARCH FOR THE ESSENTIAL

Each rectangle stands for a group of differently oriented structures that are compatible with each other. The corners of the pieces of paper have numbers on them that correspond to the twelve variants of the elementary cells. Wherever the variants from different groups match, the triangles are connected. This gives rise to a structure around which the intertwined bands of paper wind.

“Sometimes it helps to change the perspective,” says Anja Schlömerkemper: “We project the problem in three dimensions to obtain a geometric impression.” Anja Schlömerkemper and Isaac Chenchiah then have to express this in a formula. This also means that they must focus on the essential. “It is always a question of understanding the really essential information and not all of the details,” says Stefan Müller.

This is a problem that Anja Schlömerkemper must overcome in another project, as well. Together with Kaushik Bhattacharya from Caltech in Pasadena in the US, she is looking for the allowed microstructures that can form in polycrystalline memory alloys. Polycrystalline ma-



Arts and crafts in the service of mathematics: Using a paper model, the Leipzig mathematicians show how the variants of a monoclinic lattice can be combined to form microstructures.

materials make up the bulk of the natural minerals and everyday materials we encounter: cast-iron frying pans, automotive sheet metal, roof tiles and artery-widening stents. Unlike monocrystals, as considered by Anja Schlömerkemper in model form for monoclinic structures, they consist of a myriad of densely packed crystal grains. Materials scientists refer to the way these crystallites align themselves as texture. It is a function of the manufacturing process and is often a matter of chance, yet sometimes it also follows certain

rules. In most cases, the texture limits the shape memory of the corresponding alloys. Anja Schlömerkemper and Kaushik Bhattacharya want to find out how the grains least obstruct themselves and thus display good shape memory.

The mathematicians ultimately want to predict the characteristics of the material with a law that takes into account both the microstructure and the order of the crystallites. Furthermore, the long-term objective is a law that requires the input of nothing more than the crystal data – the

dimensions of the elementary cells and information on the texture – and that can then calculate the possible microstructures. Based on this, they want to make it easier for materials scientists to find suitable alloys for all applications.

This law, on which the Leipzig scientists are working together with Dierk Raabe's department at the Max Planck Institute for Iron Research in Düsseldorf, creates something very big from something very small. Mathematicians call this "multi-scale". Predicting the microstructure from an unlimited number of elementary cells that can be more complicated than that of a stretched cube or distorted cuboid is only a first step toward the fulfillment of this objective. "But we are just starting out with this," says Stefan Müller. And this provides so much material to ruminate over that the scientists are sure to bend some more paper clips while deep in thought. They will definitely be happy then to have paper clips that can remember their functional shape.

PETER HERGERSBERG



PHOTOS: BASTIAN EHL (4)

Memory at the push of a button: In the cold spring, the atoms form cuboids that can be oriented in different ways – the stone expands the spring. In the heated metal, the atoms group together to form an inflexible lattice of cubes: the spring contracts.