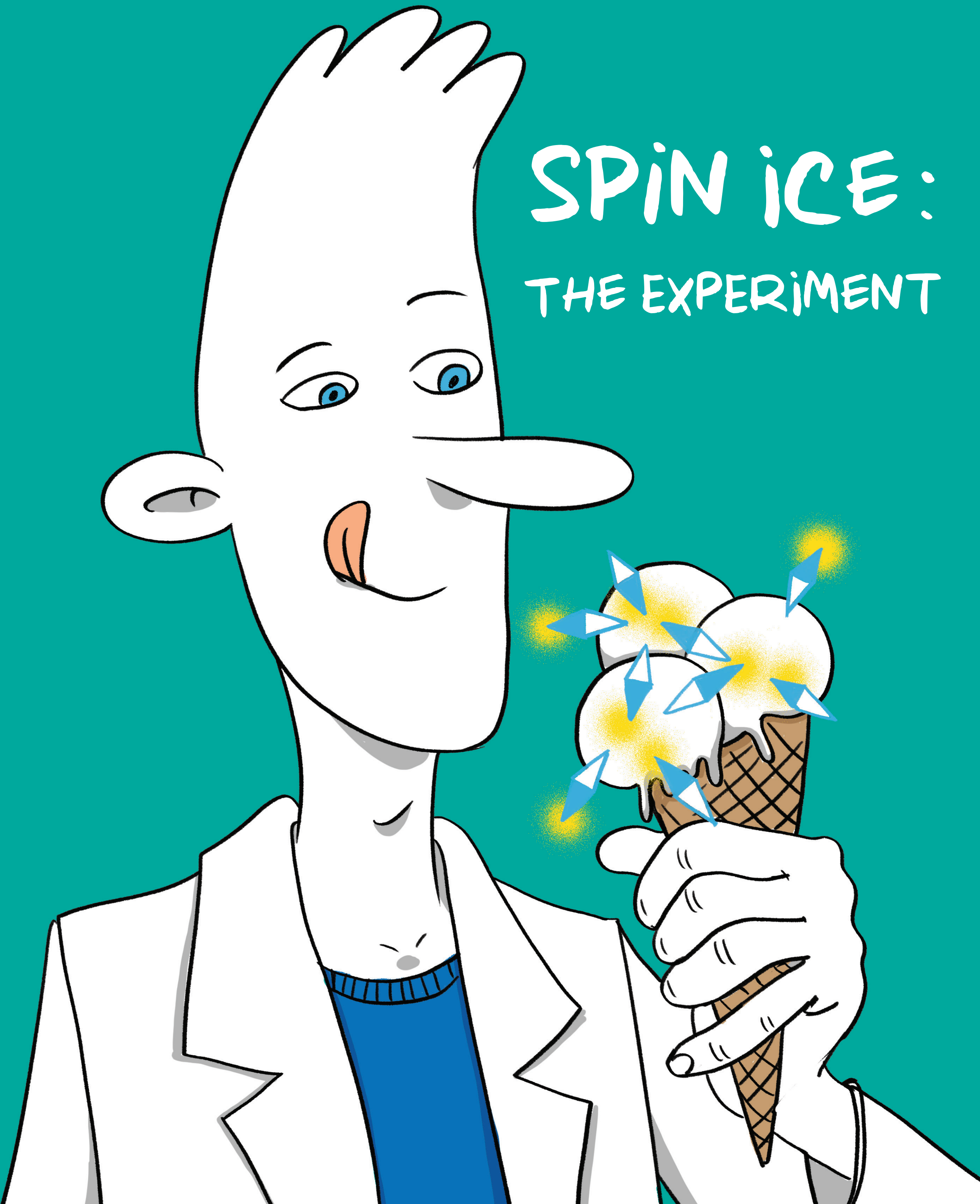
Léon Brillouin Laboratory and Paris-Saclay University

ISABELLE MIREBEAU - CLAUDIA DECORSE

DESIGNED BY AURÉLIE BORDENAVE

SPIN ICE: THE EXPERIMENT



Introduction

What does the work of a researcher consist of? What is a research experiment? How does it go from day to day? These questions are of concern to students and also to members of the general public interested in science "in the making", and not simply in the results, the vast majority of which remain unknown to the public.

A scientific adventure is first and foremost a human adventure, with its share of surprises, trials and errors, interactions between different skills and between different environments. A mixture, sometimes explosive, always fascinating, of questions and answers that are mutually inspiring, from concepts of variable geometry, where nothing is ever completely acquired, in a constant dynamic. An adventure that sometimes unfolds like a rambling path, rather than the linear and logical progression shown in publications.

In particular, research in the physics of condensed matter (solids and liquids), such as that taking such as takes place on the plateau de Saclay, calls for multiple skills and collaboration between chemists and physicists, university laboratories and very large research facilities, nuclear reactors, synchrotrons, lasers, etc.

We have chosen to illustrate such a research experiment by means of a comic book. The chosen subject, spin ices, is an example of these couplings, these surprises, which add spice to our profession. It is also a real challenge, because the study of condensed matter and the study of magnetism are difficult to popularise, even if their applications have transformed our daily life, from mobile phones to computers.

Up against a wall (or faced with a blank page) in an attempt to make the subject accessible, we are using the story of a fictitious experiment, inspired by some early research. The story is based on collaboration between the plateau teams, along with results provided by our colleagues in France and overseas. The main publications are referenced at the end of the comic book.

We tried to combine the vision of the cartoonist, Aurélie Bordenave, full of humour and fantasy, with scientific rigour. We have also chosen to show all the stages of the approach, from A (the basic question, the synthesis of the material) to Z (the thesis defence or the publication).

Using the viewpoint of the student who discovers the subject and gets involved in it, allows us to present some of the characteristics of a happy researcher: enthusiasm, imagination, hard work, rigour, the desire to understand, a critical eye, modesty and honesty, plus a dash of luck, on a route that is anything but nothing like a smooth ride.

We hope that comic books will contribute to making the reality of our profession known, and who knows, to attracting new recruits?

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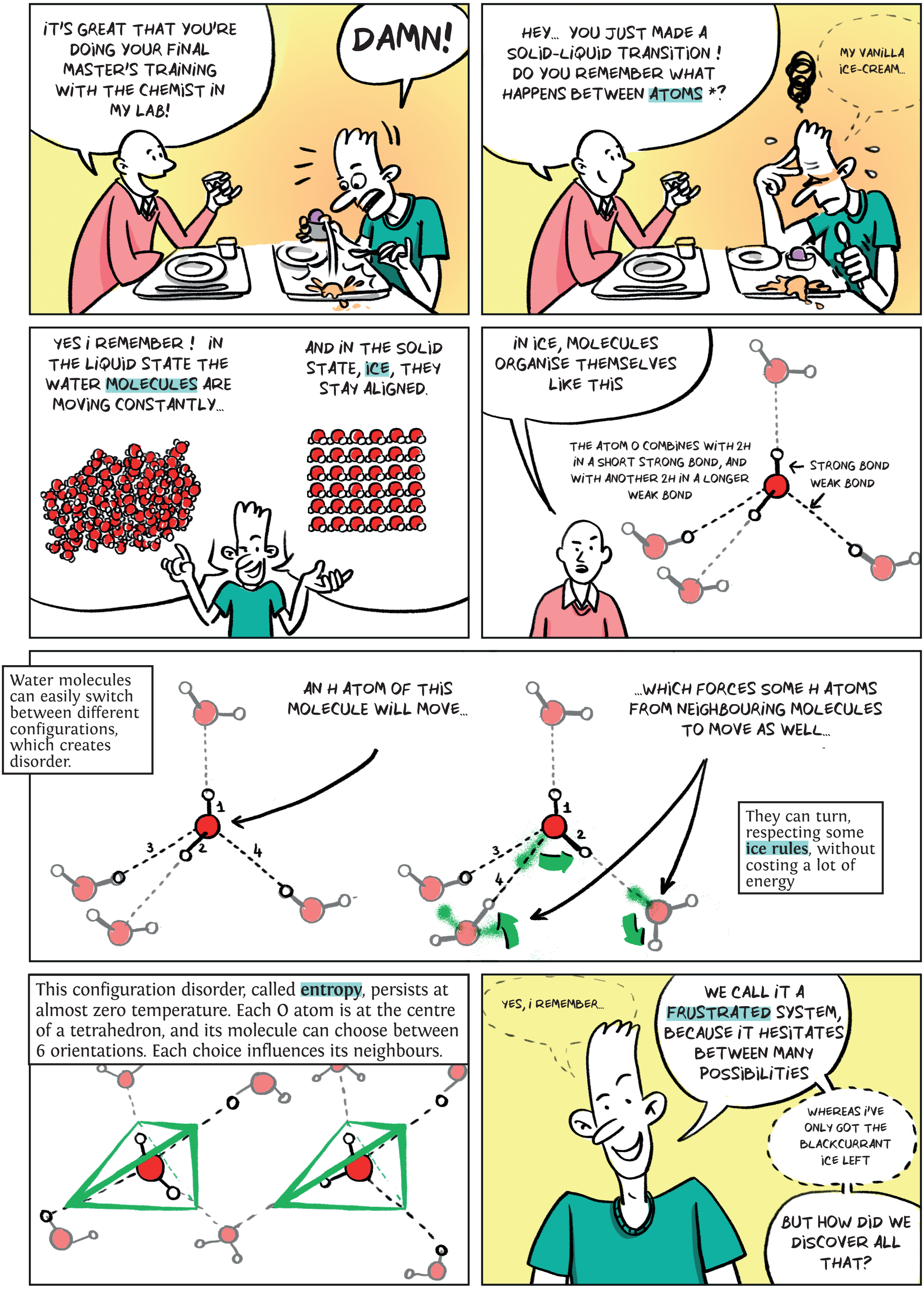
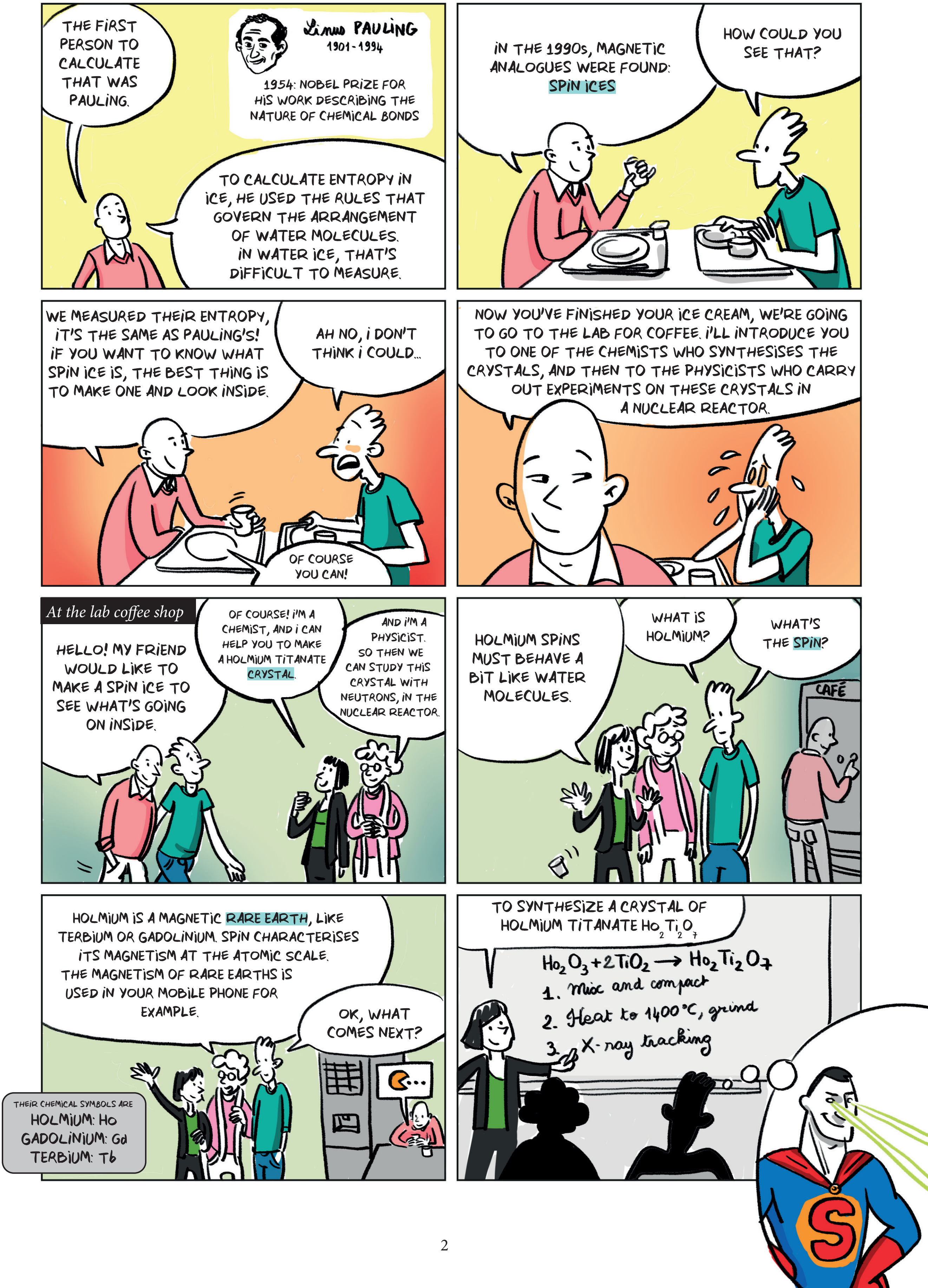
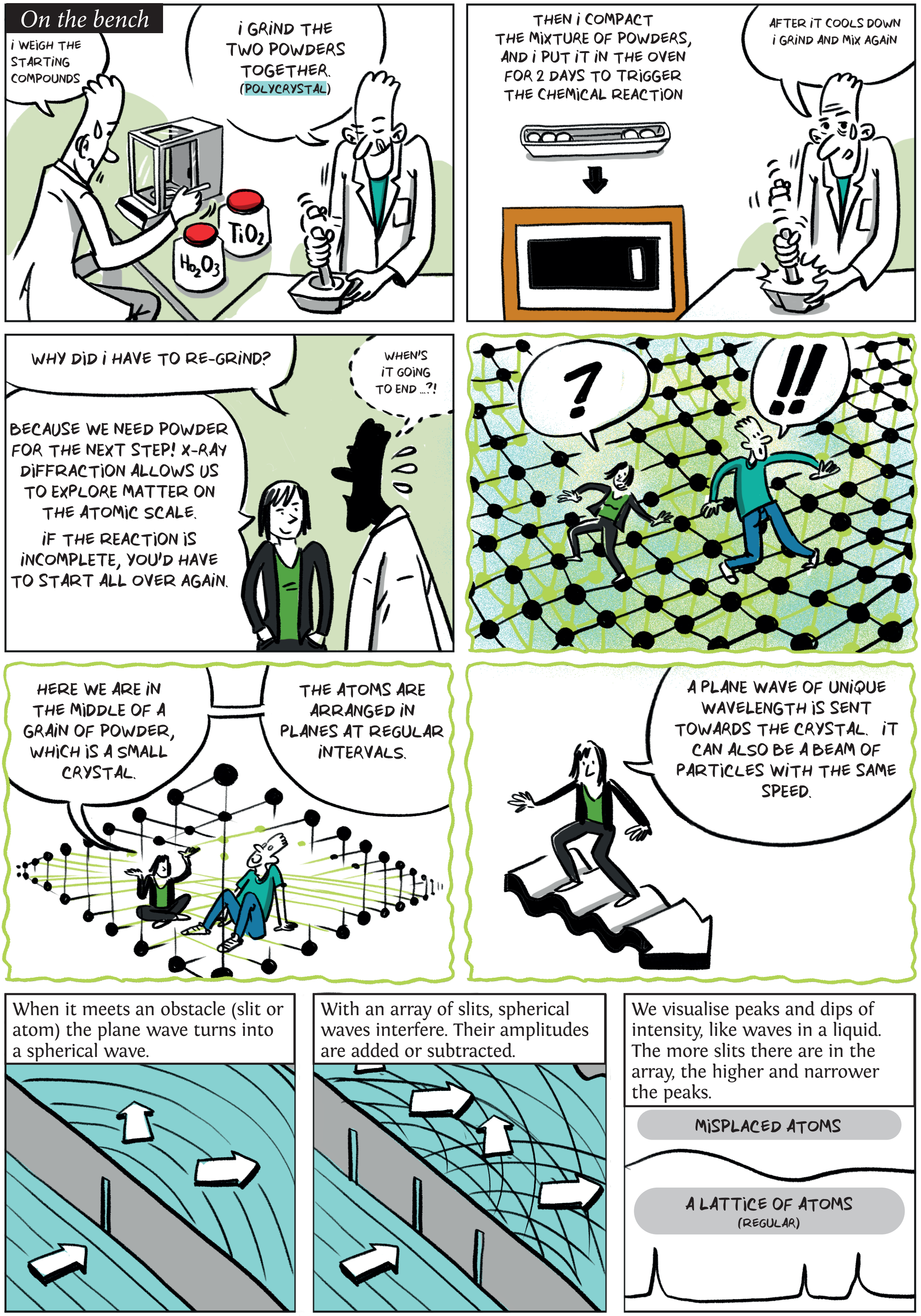
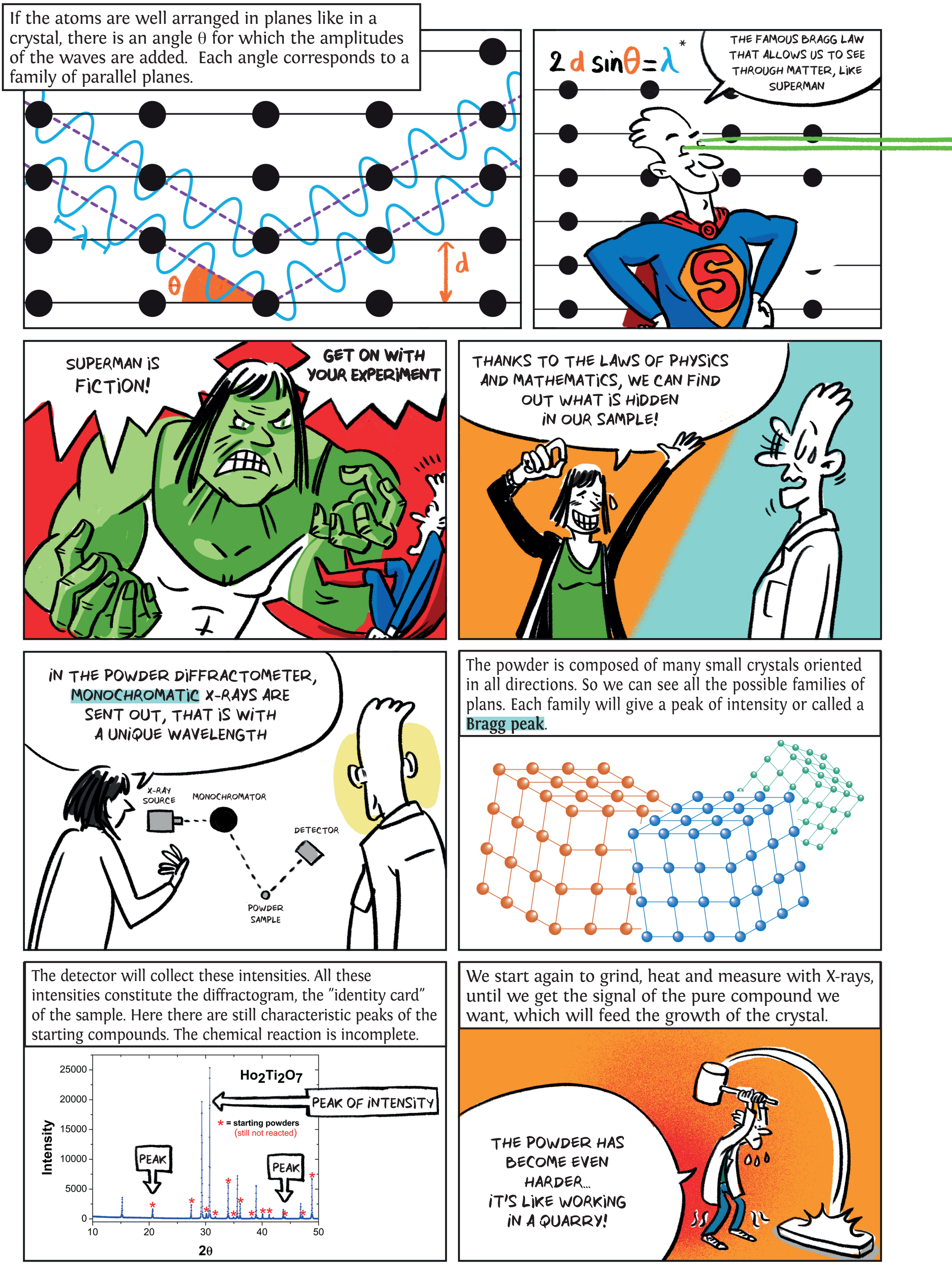


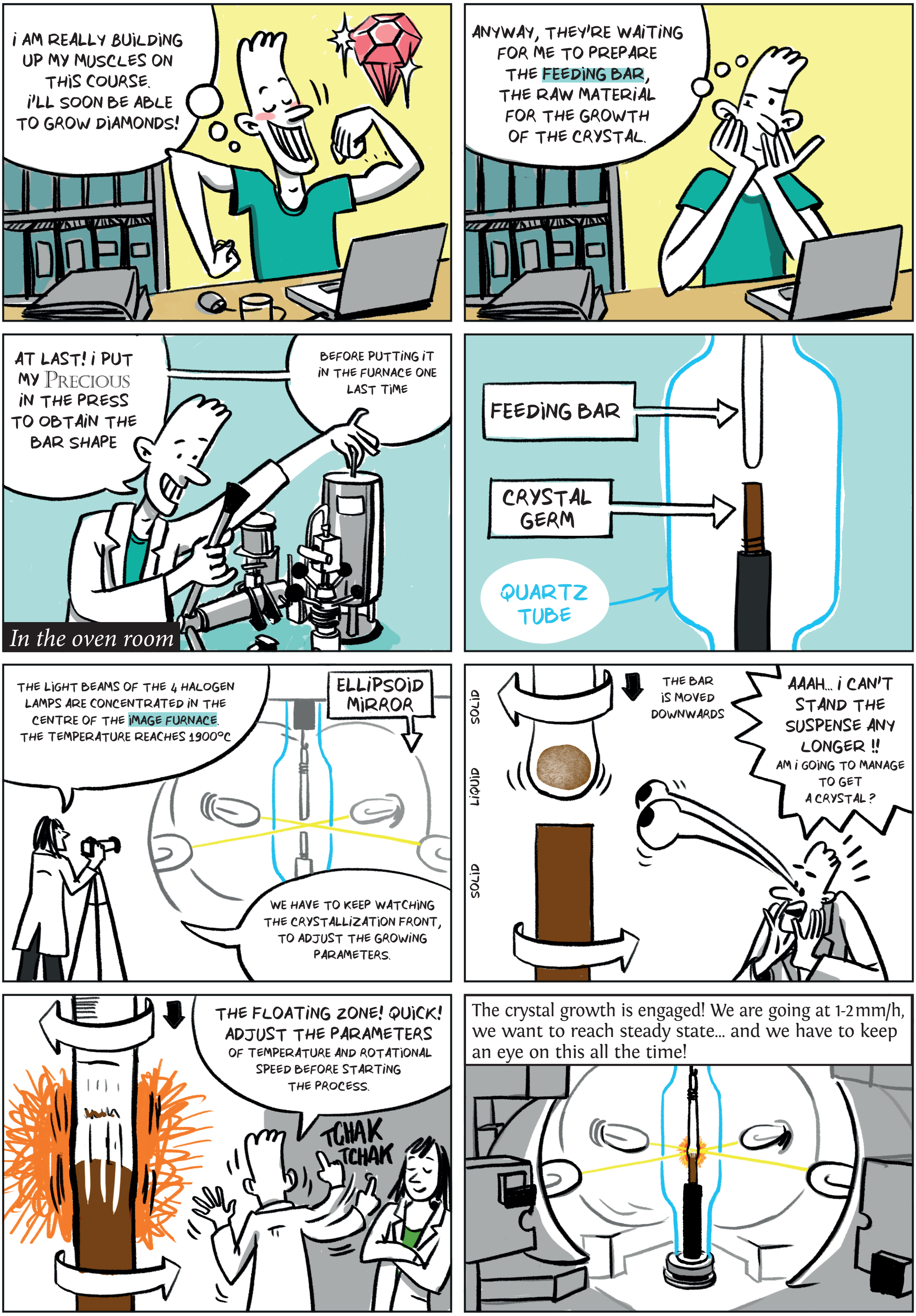
* *Words from the glossary are* **highlighted** *the first time they appear in the text. The glossary can be found on the inside back cover.*


THE FIRST PERSON TO CALCULATE THAT WAS PAULING.
Linus PAULING 1901-1994
1954: NOBEL PRIZE FOR HIS WORK DESCRIBING THE NATURE OF CHEMICAL BONDS
TO CALCULATE ENTROPY IN ICE, HE USED THE RULES THAT GOVERN THE ARRANGEMENT OF WATER MOLECULES. IN WATER ICE, THAT'S DIFFICULT TO MEASURE.
IN THE 1990s, MAGNETIC ANALOGUES WERE FOUND: SPIN ICES
HOW COULD YOU SEE THAT?
WE MEASURED THEIR ENTROPY, IT'S THE SAME AS PAULING'S! IF YOU WANT TO KNOW WHAT SPIN ICE IS, THE BEST THING IS TO MAKE ONE AND LOOK INSIDE.
AH NO, I DON'T THINK I COULD...
OF COURSE YOU CAN!
NOW YOU'VE FINISHED YOUR ICE CREAM, WE'RE GOING TO GO TO THE LAB FOR COFFEE. I'LL INTRODUCE YOU TO ONE OF THE CHEMISTS WHO SYNTHESISES THE CRYSTALS, AND THEN TO THE PHYSICISTS WHO CARRY OUT EXPERIMENTS ON THESE CRYSTALS IN A NUCLEAR REACTOR.
At the lab coffee shop
HELLO! MY FRIEND WOULD LIKE TO MAKE A SPIN ICE TO SEE WHAT'S GOING ON INSIDE.
OF COURSE! I'M A CHEMIST, AND I CAN HELP YOU TO MAKE A HOLMIUM TITANATE CRYSTAL.
AND I'M A PHYSICIST. SO THEN WE CAN STUDY THIS CRYSTAL WITH NEUTRONS, IN THE NUCLEAR REACTOR.
HOLMIUM SPINS MUST BEHAVE A BIT LIKE WATER MOLECULES.
WHAT IS HOLMIUM?
WHAT'S THE SPIN?
CAFÉ
HOLMIUM IS A MAGNETIC RARE EARTH, LIKE TERBIUM OR GADOLINIUM. SPIN CHARACTERISES ITS MAGNETISM AT THE ATOMIC SCALE. THE MAGNETISM OF RARE EARTHS IS USED IN YOUR MOBILE PHONE FOR EXAMPLE.
OK, WHAT COMES NEXT?
THEIR CHEMICAL SYMBOLS ARE HOLMIUM: Ho GADOLINIUM: Gd TERBIUM: Tb
TO SYNTHESIZE A CRYSTAL OF HOLMIUM TITANATE $Ho_2Ti_2O_7$
$Ho_2O_3 + 2TiO_2 \rightarrow Ho_2Ti_2O_7$
1. Mix and compact
2. Heat to 1400°C, grind
3. X-ray tracking

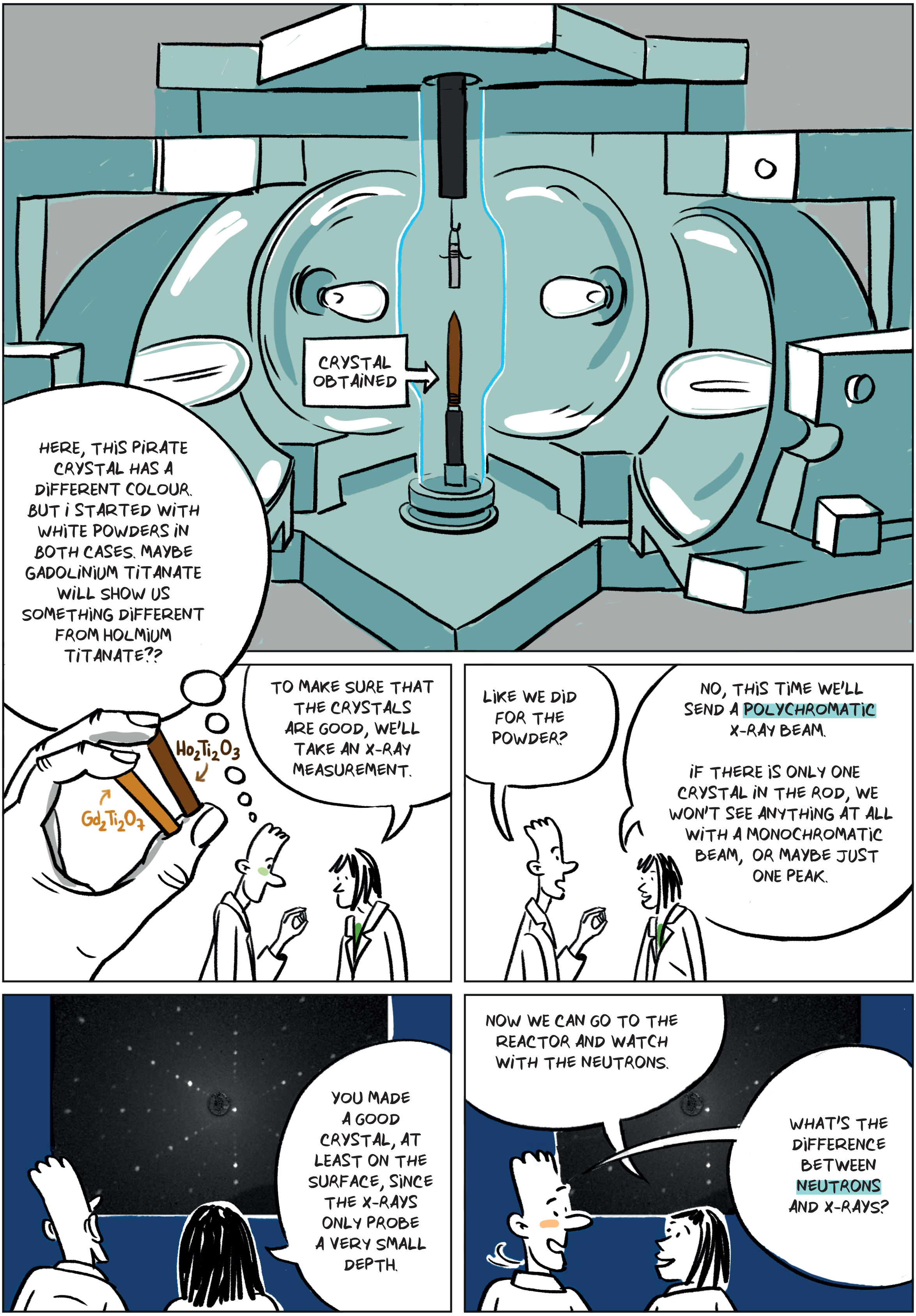

On the bench
I WEIGH THE STARTING COMPOUNDS
Ho_2O_3
TiO_2
I GRIND THE TWO POWDERS TOGETHER. (POLYCRYSTAL)
THEN I COMPACT THE MIXTURE OF POWDERS, AND I PUT IT IN THE OVEN FOR 2 DAYS TO TRIGGER THE CHEMICAL REACTION
AFTER IT COOLS DOWN I GRIND AND MIX AGAIN
WHY DID I HAVE TO RE-GRIND?
WHEN'S IT GOING TO END ...?!
BECAUSE WE NEED POWDER FOR THE NEXT STEP! X-RAY DIFFRACTION ALLOWS US TO EXPLORE MATTER ON THE ATOMIC SCALE.
IF THE REACTION IS INCOMPLETE, YOU'D HAVE TO START ALL OVER AGAIN.
?
!!
HERE WE ARE IN THE MIDDLE OF A GRAIN OF POWDER, WHICH IS A SMALL CRYSTAL.
THE ATOMS ARE ARRANGED IN PLANES AT REGULAR INTERVALS.
A PLANE WAVE OF UNIQUE WAVELENGTH IS SENT TOWARDS THE CRYSTAL. IT CAN ALSO BE A BEAM OF PARTICLES WITH THE SAME SPEED.
When it meets an obstacle (slit or atom) the plane wave turns into a spherical wave.
With an array of slits, spherical waves interfere. Their amplitudes are added or subtracted.
We visualise peaks and dips of intensity, like waves in a liquid. The more slits there are in the array, the higher and narrower the peaks.
MISPLACED ATOMS
A LATTICE OF ATOMS (REGULAR)



*the Bragg law

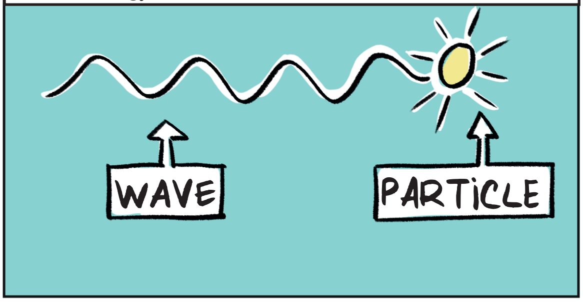

I AM REALLY BUILDING UP MY MUSCLES ON THIS COURSE. I'LL SOON BE ABLE TO GROW DIAMONDS!
ANYWAY, THEY'RE WAITING FOR ME TO PREPARE THE FEEDING BAR, THE RAW MATERIAL FOR THE GROWTH OF THE CRYSTAL.
AT LAST! I PUT MY PRECIOUS IN THE PRESS TO OBTAIN THE BAR SHAPE
BEFORE PUTTING IT IN THE FURNACE ONE LAST TIME
In the oven room
FEEDING BAR
CRYSTAL GERM
QUARTZ TUBE
THE LIGHT BEAMS OF THE 4 HALOGEN LAMPS ARE CONCENTRATED IN THE CENTRE OF THE IMAGE FURNACE. THE TEMPERATURE REACHES 1900°C
ELLIPSOID MIRROR
WE HAVE TO KEEP WATCHING THE CRYSTALLIZATION FRONT, TO ADJUST THE GROWING PARAMETERS.
SOLID
LIQUID
SOLID
THE BAR IS MOVED DOWNWARDS
AAAH... I CAN'T STAND THE SUSPENSE ANY LONGER !!
AM I GOING TO MANAGE TO GET A CRYSTAL ?
THE FLOATING ZONE! QUICK! ADJUST THE PARAMETERS OF TEMPERATURE AND ROTATIONAL SPEED BEFORE STARTING THE PROCESS.
TCHAK TCHAK
The crystal growth is engaged! We are going at 1-2 mm/h, we want to reach steady state... and we have to keep an eye on this all the time!


ADJUSTMENTS HAVE TO BE MADE ALL THE TIME. YOU HAVE TO RECTIFY THE TRANSLATION SPEEDS TO TRANSFER THE MATTER FROM THE BAR TO THE CRYSTAL IN A REGULAR WAY IN ORDER TO MAINTAIN A STABLE FLOATING ZONE AT THE CENTER OF THE FURNACE.
ARE WE GOING TO FIND OUT SOON WHETHER THE CRYSTAL IS OK?
YES, EVENTUALLY... IN 3 DAYS
WHAT?!!
YES THE GROWTH TAKES TWO DAYS AND THE CRYSTAL HAS TO COOL DOWN ON THE THIRD DAY!
PATIENCE YOUNG PADAWAN, ACQUIRE YOU MUST
It's finished growing
WITH THE LIQUID AREA CUT OFF, THE HOLMIUM TITANATE CRYSTAL WILL NOW COOL DOWN SLOWLY FOR ONE DAY
So the crystal cools down...
ZZZZ
I AM PROUD OF YOU, YOUNG PADAWAN, THIS CRYSTAL MAGNIFICENT PROMISES TO BE
THANK YOU MASTER
YOU CAN TRY TO MAKE ANOTHER CRYSTAL ALL BY YOURSELF.
I WILL MAKE A GADOLINIUM CRYSTAL TO SEE THE DIFFERENCE.
MAYBE NO ONE'S THOUGHT OF IT BEFORE?

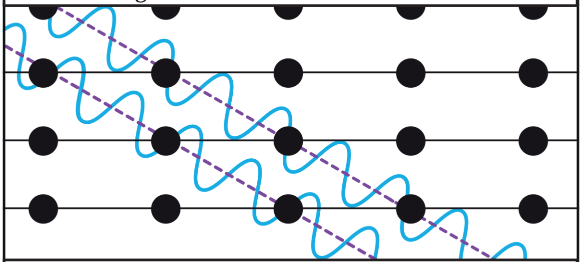


CRYSTAL OBTAINED
HERE, THIS PIRATE CRYSTAL HAS A DIFFERENT COLOUR. BUT I STARTED WITH WHITE POWDERS IN BOTH CASES. MAYBE GADOLINIUM TITANATE WILL SHOW US SOMETHING DIFFERENT FROM HOLMIUM TITANATE??
$Ho_2Ti_2O_3$
$Gd_2Ti_2O_7$
TO MAKE SURE THAT THE CRYSTALS ARE GOOD, WE'LL TAKE AN X-RAY MEASUREMENT.
LIKE WE DID FOR THE POWDER?
NO, THIS TIME WE'LL SEND A POLYCHROMATIC X-RAY BEAM.
IF THERE IS ONLY ONE CRYSTAL IN THE ROD, WE WON'T SEE ANYTHING AT ALL WITH A MONOCHROMATIC BEAM, OR MAYBE JUST ONE PEAK.
YOU MADE A GOOD CRYSTAL, AT LEAST ON THE SURFACE, SINCE THE X-RAYS ONLY PROBE A VERY SMALL DEPTH.
NOW WE CAN GO TO THE REACTOR AND WATCH WITH THE NEUTRONS.
WHAT'S THE DIFFERENCE BETWEEN NEUTRONS AND X-RAYS?

The neutron is a wave, like X-rays. It is also a particle, so we can visualise the trajectory. If we know the wavelength of this particle, we can deduce its velocity and its energy.

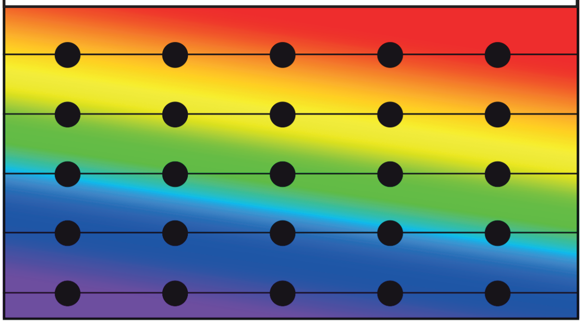


Neutrons and X-rays are complementary probes of matter. They both have wavelengths of the same order of magnitude as the distances between atoms.

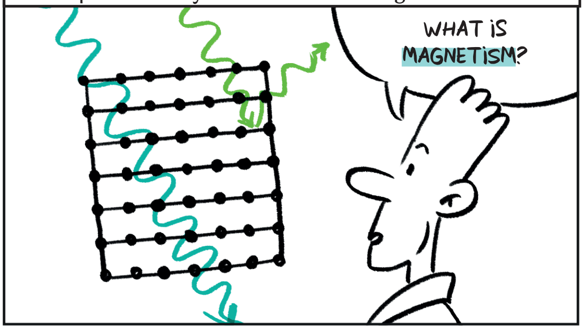


This is why we can measure these distances by sending these radiations.

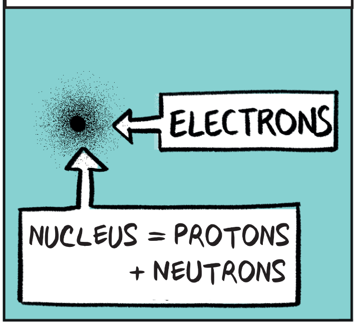
It wouldn't work with visible light for example, because wavelengths are far too big, and there wouldn't be any diffraction at all.



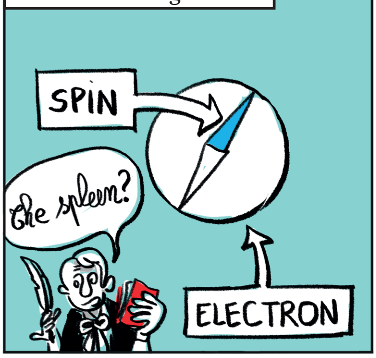
In addition, neutrons allow the whole crystal to be explored, not just the surface. And especially the neutron has a spin. It is very sensitive to the magnetism of atoms.



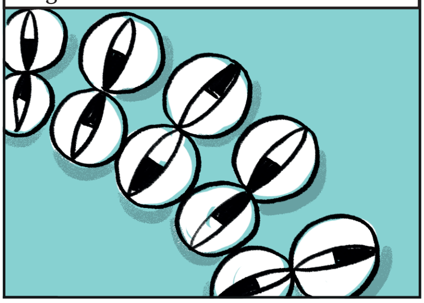
An atom is composed of a nucleus (protons + neutrons) and electrons in orbit.



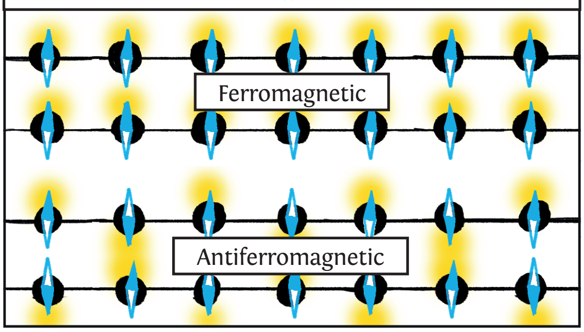
Electrons have a spin, like a small magnet.



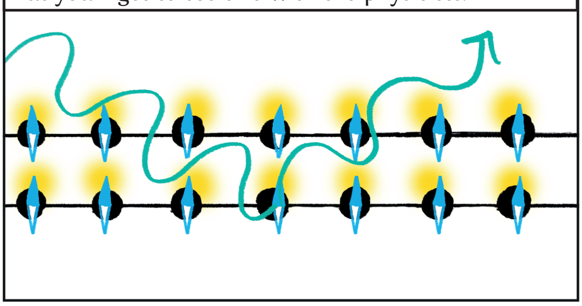
The electrons of the atomic layers are arranged in pairs of opposite spins, so they cancel out each other's magnetism.

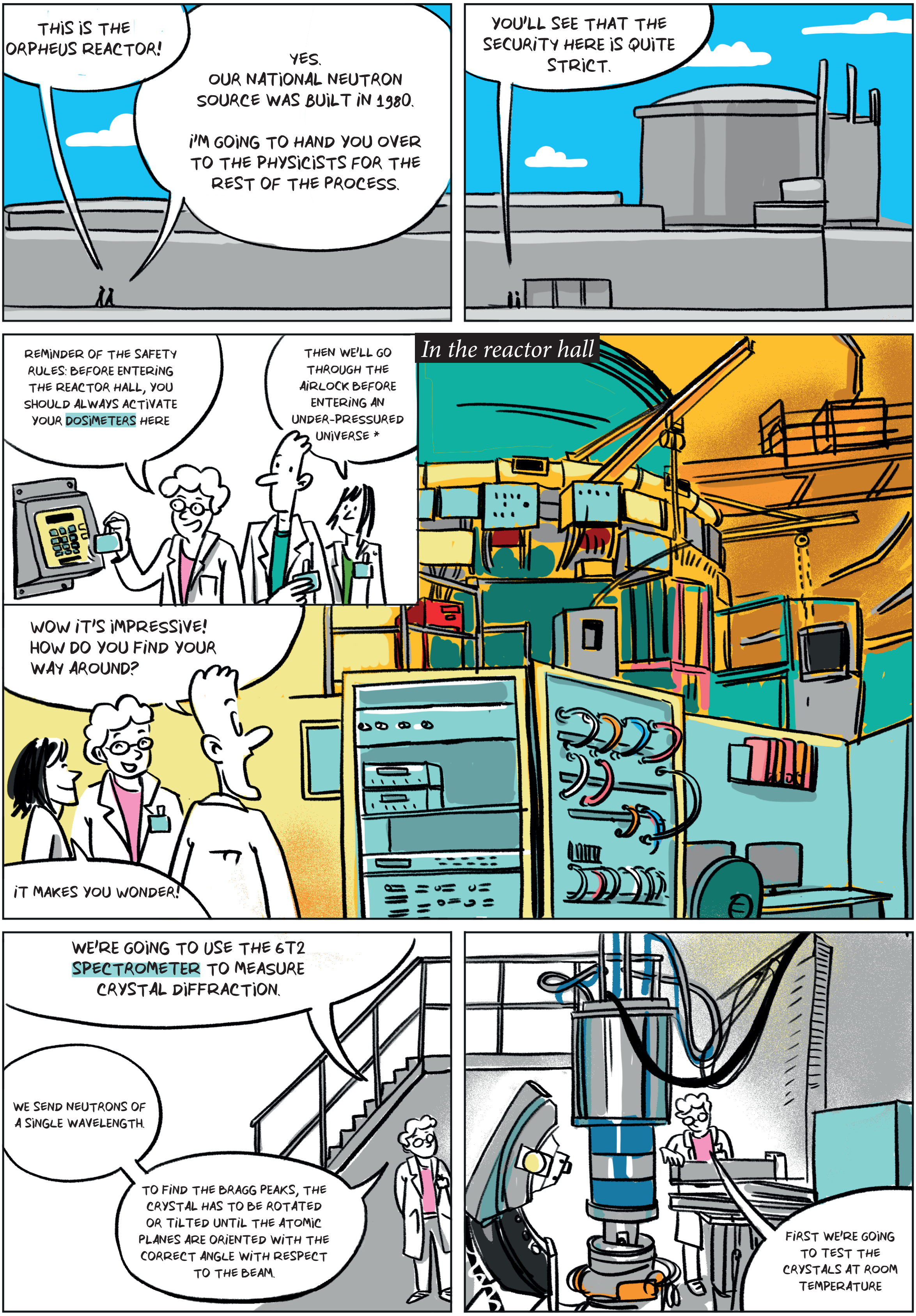


In magnetic atoms, there are still single electrons, whose spins do not compensate each other. The spins of these electrons can network.

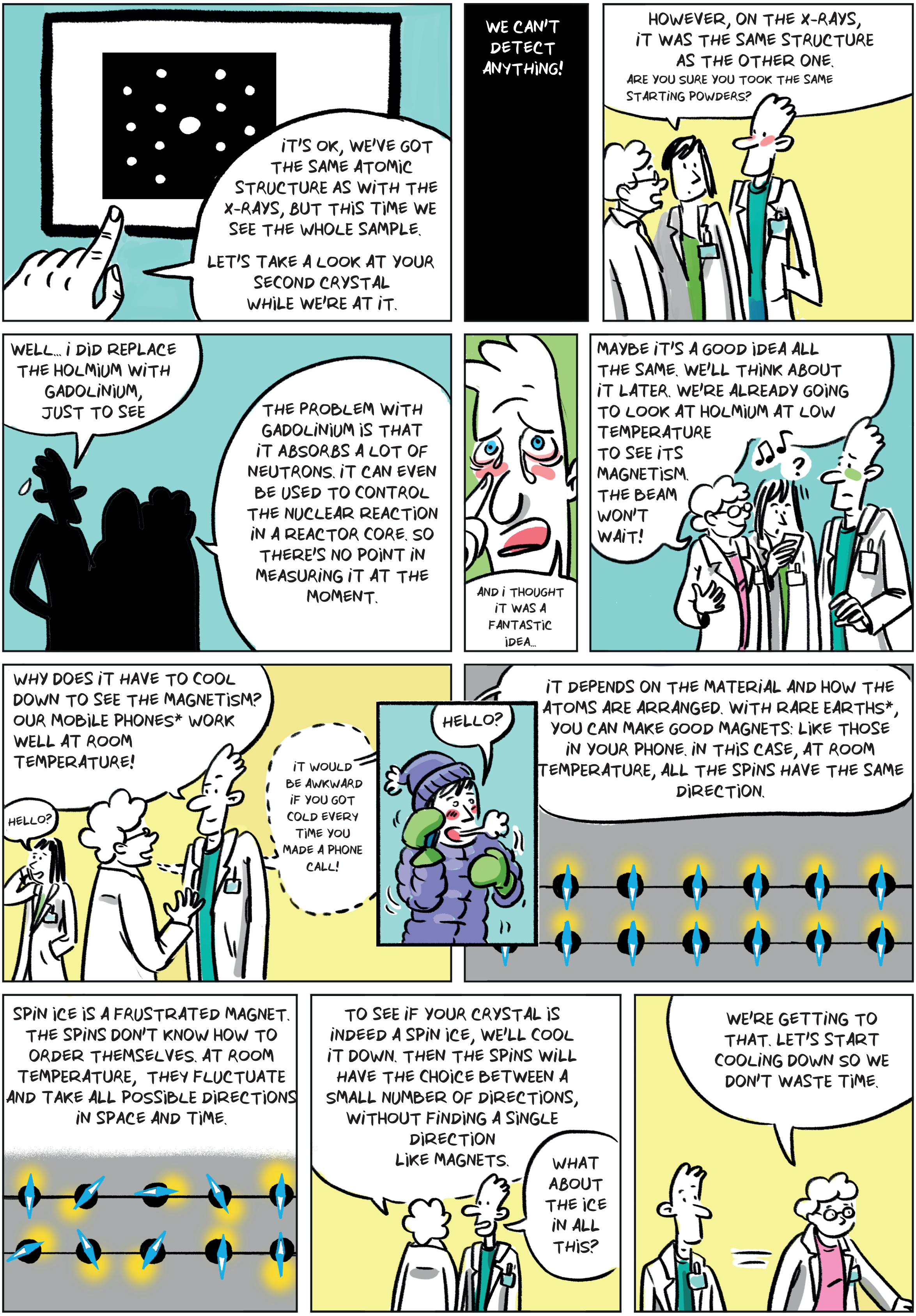


The spin of neutrons interacts with the spin of magnetic atoms. This allows us to see how the atomic spins are organised from atom to atom. But you'll get to see this with the physicists.

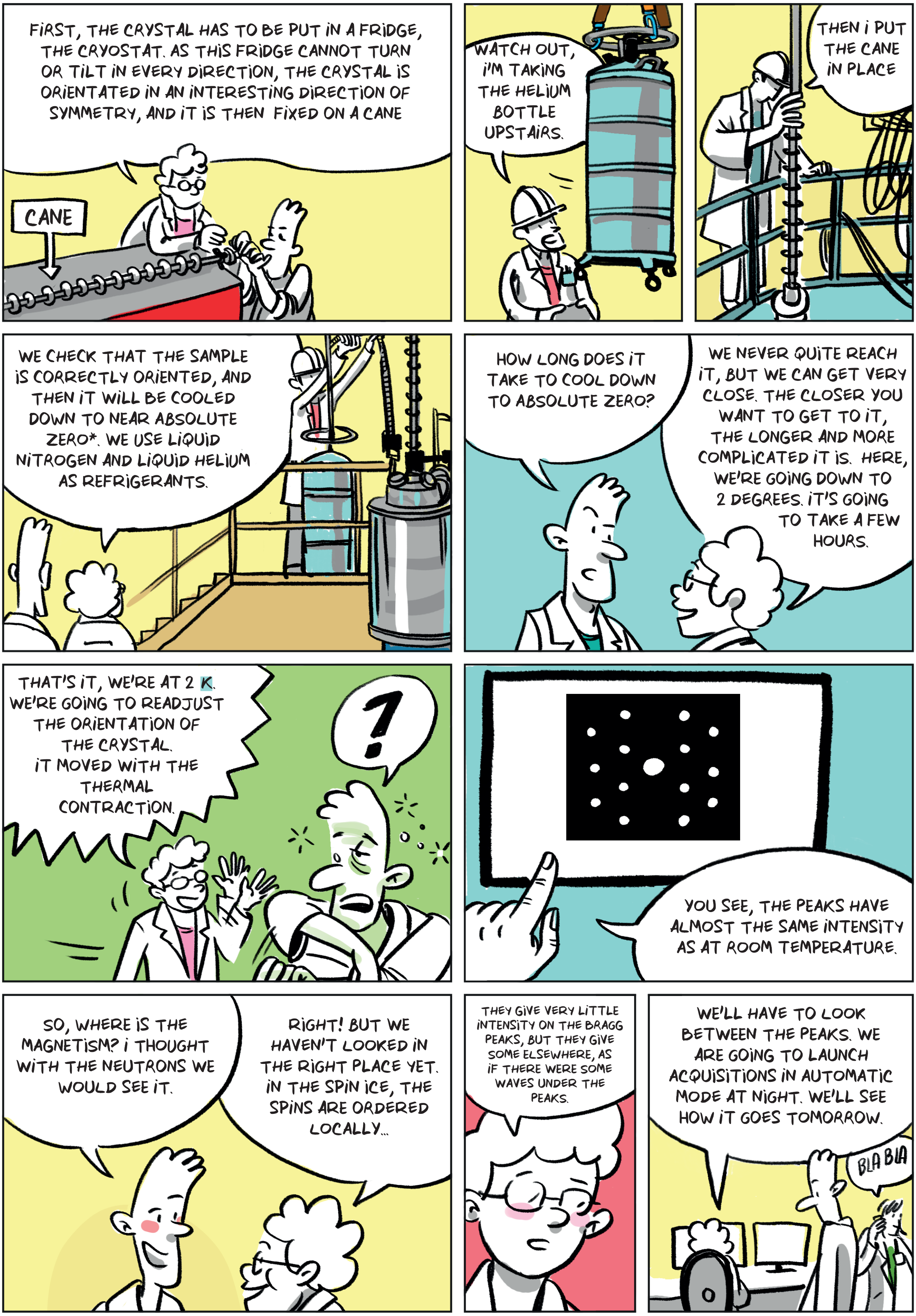




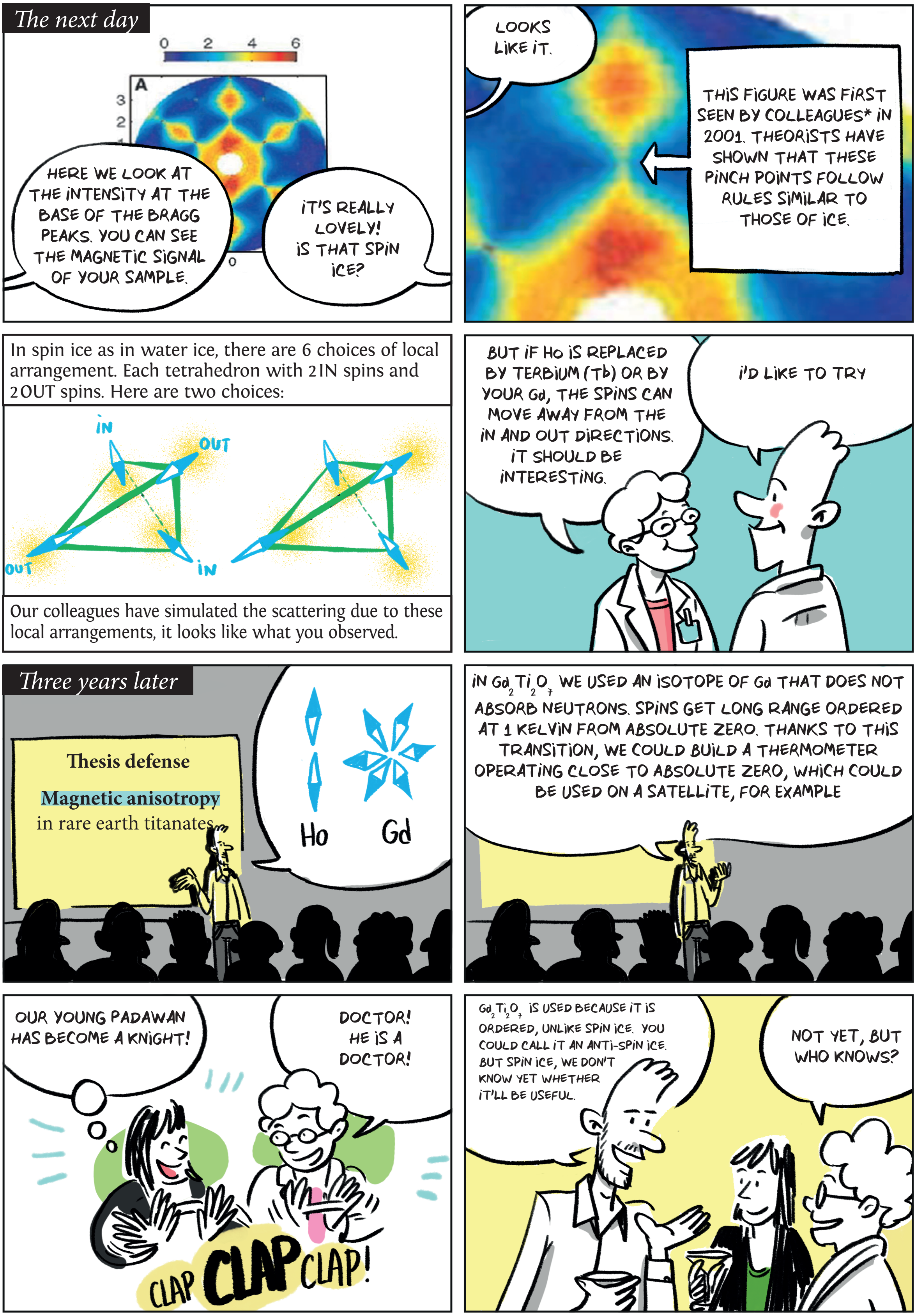
*The experimental hall is kept at reduced pressure so that in the event of a radioactive incident, the contaminated air does not escape to the outside. (Here, we don't want anything to come out, unlike in a clean room where nothing must get in)



* *Rare earth magnets make very powerful and very small magnets, used in microphones, loudspeakers and mobile phone vibrators.*



* *Absolute zero (zero **Kelvin**) corresponds to -273.15 degrees Celsius.*



* *Spin correlations in $Ho_2Ti_2O_7$: a dipolar spin ice model,* S. T. Bramwell *et al,* Phys. Rev. Lett, **87**, 047205, (2001).

Glossary

Atom - An elementary constituent of matter, (solid, liquid or gas). The atom is made of a nucleus comprising protons and neutrons, and a cloud of electrons.

Bragg peak - When a monochromatic neutron or X-ray beam is diffracted by a crystal, its intensity is strongly increased in certain directions - these are the Bragg peaks, characteristics of crystalline material.

Condensed Matter - The atoms of matter, in solid or liquid state.

Crystal (single crystal) - A material in which the atoms are arranged in a regular and periodic manner. The cell characterises the arrangement of atoms in a unit that is repeated in space. The lattice characterizes the periodicity.

Crystal (polycrystal - powder or ceramic) - Material composed of a multitude of small crystals. It is in the form of a powder or a solid called ceramic (compressed powder that has undergone a heat treatment).

Dosimeter - Worn on the chest, it is used to measure the radiation received.

Entropy - The term entropy was introduced by Clausius in 1865 from the Greek word meaning transformation. In statistical physics, it characterises the level of disorganisation of a set of particles. In ice, it is bound to the number of configurations of water molecules, which can orient themselves in different ways in relation to each other.

Feeding bar - Matter used to grow a single crystal in the image furnace. It is a ceramic cylinder made of the same chemical compound as that of the desired crystal.

Frustration - A frustrated system, such as ice or spin ice, has a multitude of possible configurations or states for the molecules or spins that make it up. The system "hesitates" between these different states. Frustration is often induced by the competition of interactions which cannot be satisfied simultaneously.

Ice - Water in a solid state. There are many types of ice. Here we consider ice in a crystalline solid state with a cubic lattice.

Kelvin (K) - Unit of temperature measurement written as K, it is also a microscopic unit of energy. Absolute zero corresponds to -273.15 degrees Celsius.

Ice (Rules of Ice) - Governs the arrangement of water molecules in cubic ice. Each oxygen O in an H_2O molecule occupies the centre of a tetrahedron and has 2 H "close" to it (those of its molecule) and 2 H "far" (belonging to neighbouring molecules). The molecules can reorient themselves by keeping these rules even close to absolute zero. The configurational disorder or entropy was calculated by Linus Pauling in 1935.

Image furnace - This is a vertical furnace, where the temperature rises in a very small area, the hot spot, by concentrating the light rays coming from halogen lamps by means of mirrors (a pocket-sized version of Odeillo's solar furnace!). It allows one to grow a crystal using the floating zone method. At the hot spot, the material is melted and then solidified very slowly to obtain the single crystal. Growth is controlled by translating the melted zone and monitoring with a camera.

Spin ice - Magnetic material whose disorder mimics that of water ice. The compounds $Ho_2Ti_2O_7$ et $Dy_2Ti_2O_7$ are the best known. The Ho or Dy atoms have a very anisotropic magnetism. They occupy the summits of tetrahedrons connected by the summits and their spins point either inwards (IN) or outwards (OUT). Each tetrahedron has 2 IN spins and two OUT spins. This analogy with water ice explains why the entropy of configuration is the same.

Magnetic anisotropy - At the atomic scale, property of the electronic cloud of the magnetic atom which has a preferred direction or plane. On a macroscopic scale, property of a material with preferred directions of magnetisation.

Magnetism - In an atom, the spins of the electrons often group together in pairs of opposite spins. If the atom is magnetic, the spins of its electrons do not all compensate each other. The spins of these magnetic atoms can be arranged in several ways. The best known is the ferromagnetism, where all the spins are oriented the same and form a large magnet.

Molecule - An electrically neutral assembly of atoms, connected to each other by chemical bonds. Example the water molecule H_2O.

Monochromatic - A property of radiation that has only one wavelength. Example - blue light.

Neutron - A constituent particle of the nucleus of atoms (along with the proton). Emitted during a nuclear reaction, neutron beams allow the study of condensed matter (solid or liquid).

Polychromatic - Radiation that includes several wavelengths (usually a continuous spectrum). Example - sunlight.

Rare Earths - Rare earths are a group of metals with similar properties. Their magnetism comes from their electron configuration and the unpaired electrons of the 4f layer. Contrary to what their name suggests, not all of them are rare.

Spectrometer - A device that sends radiation onto a material and collects the radiation scattered on a detector.

Spin - An intrinsic property of a particle, such as mass or electric charge, and characterising its magnetism. Spin is the intrinsic kinetic moment, as if the particle was a tiny rotating ball. It is a quantum quantity, but it is often represented by a vector, such as a compass or a small magnet. Neutron spin interacts with the spins of the atoms, which makes it possible to know their values, orientations, arrangements and vibrations in the material.

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WE DEDICATE THIS COMIC BOOK TO ALL RESEARCHERS, PHYSICISTS AND CHEMISTS, EXPERIMENTERS AND THEORISTS, WHO HAVE PLAYED WITH SPIN ICE, MAGNETISM AND CONDENSED MATTER; AND TO ALL THE STUDENTS WHO HAVE ALLOWED THEMSELVES TO BE CONTAMINATED BY RESEARCH.

IM. and CD.

SPIN ICE: THE EXPERIMENT

A Master's student discovers the world of research. He or she tackles a very specialised subject, spin ice, magnetic compounds endowed with a mysterious property, entropy, which offers them a multitude of possible states, like protons in ice.

He grows crystals, studies them with X-rays and then uses neutrons from a reactor to probe this exotic magnetism. He asks questions, takes initiatives, goes from surprises to disappointments, and let himself be won over by the discoverer's virus.

TO FIND OUT MORE

About spin ice

- *Spin ices in frustrated magnetic pyrochlores*
  S. T. Bramwell and M. J. P. Gingras,
  Science **294**, 1495 (2001).
- *Spin Liquids and Spin Ices, (Liquides et Glaces de spin)*
  R. Ballou et C. Lacroix,
  Pour la Science, **364** (2008).

About the Orphée reactor

- Comic book *Let's Scatter Neutrons* (in English, 2019)
- Booklet *Le LLB au quotidien* (2019) (*Daily Life at the LLB*) published by the Léon Brillouin Laboratory, and available on: www-llb.cea.fr

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