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History of electron microscopy for materials at the Weizmann Institute

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Following three years as a postdoc in Battelle Geneva, I joined the Department of Plastics Research of the Weizmann Insitute (WIS) as a researcher in the summer of 1979. My research was funded by a Minerva (Germany) grant given to the photoelectrochemistry group in this department. This group, consisting of Prof. Joost Manassen z"l, Dr. David Cahen (from the Structural Chemistry Department) and Dr. Gary Hodes, had already made a name for itself in the mid-seventies by pioneering research on solar energy conversion using photoelectrochemical cells, based on cadmium sulfide and cadmium selenide electrodes immersed in polysulfide electrolyte. **Fig. 1a** shows one of the group meetings *circa* 1981 in the seminar room/library of the department in the basement of the Levine building (used now for genomic research). The Levine building and the two huts at the rear of the building, which hosted the department, were somewhat remote and isolated from the main Faculty of Chemistry premises, i.e. the Perlman and Bergman buildings. The research conditions were far from ideal, to say the least. However, the department staff was scientifically motivated and enthusiastic. At one point around 1983 we organized a football team and played once a week (see **Fig. 1b**). The team lasted for several years, but I stopped one day in 1985 after a painful fall.

Figure 1a. Meeting of the photoelectrochemistry group in the seminar room of the Levine building ca. 1980. Standing from left: Baruch Vaines, Dr. Reshef Tenne, Prof. Joost Manassen, Dr. Gary Hodes, Dr. David Cahen, Menashe Lev, Harvey Flaisher and Stuart Licht; Sitting: Tina Engelhard and Geula Dagan.

Figure 1b. Soccer team of the Department of Plastics Research. Standing from left: Eyal Sabatani, Israel Rubinstein, Shlomo Margel, Yves Tricot, Dan Frenkel; kneeling from left: Zelu Itzikovitz, Daniel Wagner, Reshef Tenne, Baruch Ittah.

Prior to my appointment at the Weizmann Institute, I had little experience with electron microscopy. Electron microscopy, however, was not new at the Weizmann Institute. In fact, Prof. David Danon z"l and Dr. Yehuda Marikovsky z"l had already established the first transmission electron microscopy lab for life science research in 1955. **Fig. 2** shows the tranmission electron microscope being moved on a horse wagon in 1963 to the then new Ullman building. Also, some work with scanning electron microcopy of semiconductor surfaces had been done by Dr. Gary Hodes and Dr. David Cahen in the late 1970s, based on instruments available at the Hebrew University of Jerusalem, both on the Givat Ram campus and the Faculty of Agriculture campus across the road from the WIS.

Figure 2. The transmission electron microscope is moved to a new lab in the Ullman building in 1963. See Weizmann Wonder and Wander report- https://wis-wander.weizmann.ac.il/life-sciences/someone-operate-it-and-place-put-it

As soon as I joined the Institute, I started working on the modification of semiconductor surfaces and in particular CdSe, for application in photoelectrochemical solar cells. Observing that upon light-induced acid-etching the semiconductor surface becomes very opaque and highly responsive to light, I took it for a scanning electron microscopy (SEM) analysis. Since there was no electron microscopy (EM) facility for studying materials at the WIS, I made extensive use of the SEM facility of the Faculty of Agriculture of the Hebrew University across the road, which was operated by Mrs. Naomy Bahat (under the supervision of Prof. Avraham Shahar z"l). Unfortunately, this SEM did not have an energy dispersive X-ray spectroscopy (EDS) detector and I was obliged to go elsewhere to perform chemical analysis of the CdSe-etched surfaces. I decided to try to convince the management of the institute to buy an SEM/EDS set-up. I talked frequently with my department head – Prof. Moshe Levy z"l and Prof. Joost Manassen z"l on this issue, but since I was a young investigator without tenure, my influence on the decision-making process was not high. After a few refusals, the President of the Institute – Prof. Michael Sela graciously agreed to contribute money for this undertaking. Then one day in 1983 I was invited to the cramped (mini)office of Prof. Mordechai Avron z"l, the VP for Scientific Affairs (Rector) in the Ullman building. He gave me permission to buy an instrument and to hire a person to run this system, with the strict condition that it would be placed in the existing electron microscopy (EM) unit dedicated to research in life sciences. Subsequently, I went to the head of this unit, Dr. Victor Ben-Giat, and while approaching his small office in the basement of the old Wolfson building, I noticed a mouse watching me attentively – a most auspicious welcome to the EM unit, which was next to a mice-breeding unit. At that time the EM unit possessed only a few Philips TEMs. The most modern one there, the EM400 TEM, see **Fig. 3**, was equipped with a scanning transmission electron microscopy (STEM) console, which had rarely been used. It belonged to the Biological Services Department, supervised by Dr. Yoram Solomon z"l, who was very receptive to the idea of adding an SEM for materials research to this unit.

Figure 3. Dr. Victor Ben-Giat and Mr. Carol Bakalsh with the EM 400 TEM in the old Wolfson EM lab

Victor located a small dark room for the SEM in the EM unit. Since I was not an expert in the field, I was advised by Lia Addadi (now a professor in our faculty) to go to the TAMI Institute in the Haifa Bay, where Dr. Eugenia Klein operated one of the first SEMs with EDS in the country and learn from her experience. Once there, I met Eugenia who had graduated from the Department of Structural Chemistry in the WIS under the supervision of Prof. Mendel Cohen z"l. I was so impressed with her deep knowledge of SEM/EDS, that I told Victor that we must hire her for the job. Soon after, Eugenia and I found ourselves examining a few SEMs in various corners of the country. I recall a joint trip to the Degania B factory for cutting tools to study their set-up. We also visited the Jordan Valley company in Migdal Ha-Emek to see their line of SiLi drifted detectors for EDS. In the summer of 1983, I went to work in the CNRS in Meudon near Paris. Prior to that, I spent a few days with my family in Eindhoven, home of Philips, and it became apparent to me that the Philips SEM 505 (which was later upgraded to the 515 model) with EDS analyzer of Tracor-Noran would be the most suitable system for us – see **Fig. 4**. The EDS analyzer came with large (12 inch) red-color storage media and a computer of 32 or 64 k. This SEM/EDS served us for 15 years, if not longer, with a few upgrades of the software and the interface electronics.

Fig. 4. The Philips 505 SEM in the De-Leonesco EM lab

I started my journey into 2D materials (layered compounds) in 1984, after receiving a large bright crystal of WSe_2 from Prof. A. Wold z"l of Brown University, who visited the WIS at the invitation of Dr. David Cahen (now a professor at our faculty). In a short time I learned how to passivate the material surface, obtaining exceedingly good photoresponse and reporting record solar-to-electrical conversion efficiencies (> 13%) for solar cells based on 2D materials. Using the Philips 505 and EDAX analyzer, I could clearly see the beautiful pattern of hexagonal etch pits on the WSe_2 surface, which emerged from screw dislocations on the semiconductor surface (see **Fig. 5**).

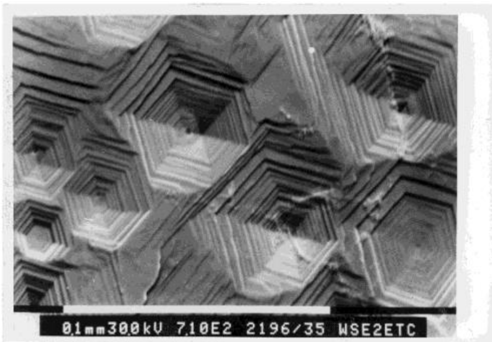


Figure 5. Etch pit pattern on the surface of surface-passivated WSe_2 crystal

In November 1987, at the initiative of the then President of the Institute – Prof. Aryeh Dvoretzky z”l, the EM unit was moved to a dedicated new facility in the de-Leonesco building. Around that time, the EM unit was transferred to the administrative responsibility of the Chemical Research Support Department, previously called Chemical Services, which was a blessing for the EM unit. I vividly recall the inauguration ceremony with Mrs. De-Leonesco z”l seated behind Prof. Dvoretzky (see **Fig. 6**). We were obviously delighted to have been moved from the “slums” in the basement of the old Wolfson building, with frequent visits from mice and the odor of their excrement, to a modern air-conditioned building.

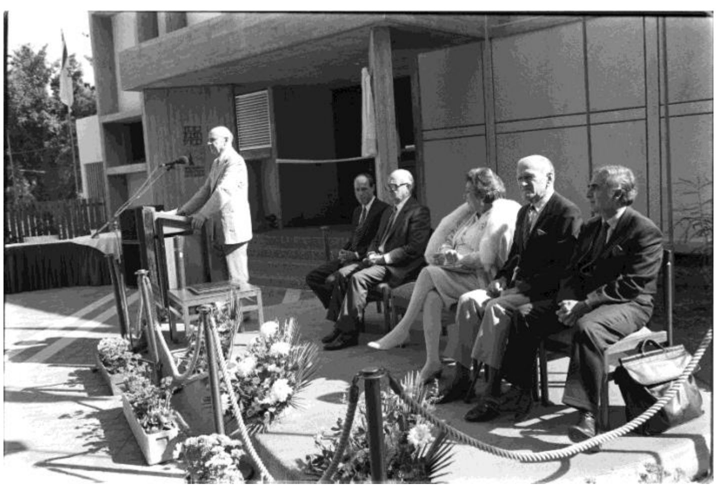
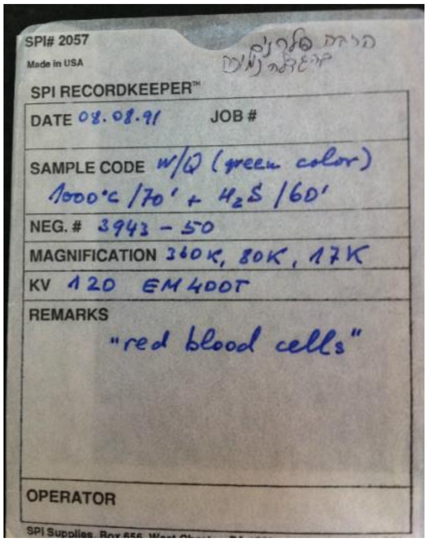


Figure 6. Inaguration ceremony of the De-Leonesco EM lab, 9.11.87. Speaking Prof. Aryeh Dvoretzky; sitting from the left: Prof. Yoram Groner, Adv. Moshe Porat, Mrs. De-Leonesco, Sir Marcus Sieff, Mr. Robert Parienty

In 1989 Prof. David Cahen and I were contacted by a newcomer from the Moscow Institute of Steel and Alloys – Dr. Lev Margulis z”l, who was an expert in TEM and electron diffraction (ED) of silicon wafers. At the first interview he told us his story. He had learned basic Hebrew in a clandestine site in Moscow and consequently was a Refusnik for several years and lost his job as a researcher. He suffered what appeared to us terrible anti-Semitic discrimination and hardships, but he never gave up his Zionistic dreams, and his perserverence eventually won out. We described to him our science where silicon had no role whatsoever. It took probably two more meetings to see that we had no common interests, and the three of us were heartbroken. On the one hand, both David and I did not have any interest in the TEM analysis of silicon dislocations, but we felt that here we had an expert in the TEM of materials, whom we could not afford to turn down. We developed a great empathy to Lev, which paid off handsomely in the years to come. We decided to hire him for a trial period of a few years. Our decision was greatly facilitated by granting him initially the Shapira Fellowship for immigrants, and subsequently the Gilaedi Fellowship from the Ministry of Absorption (Misrad Haklita). Already in 1987, one student of David, David Soltz, following a visit to Germany, built an early version of an electron beam induced current (EBIC) set-up, the first of its kind in the country, which permitted characterization of semiconductor junctions *in-situ* in the SEM. Later on using this set-up, David's post-doc Dr. Abraham Jakubovicz, who afterwards went to IBM Zurich, my student Diana Mahalu, and Lev Margulis jointly studied the charge transfer across WSe_2-gold interfaces and published a few remarkable works in *Phys. Rev. B* on this topic.

Sometime around that period, another immigrant from the former Soviet Union, Dr. Konstantin Gartsman started his career in David's group further upgrading the EBIC set-up. Together with a slew of excellent students – Leonid Chernyak (now a professor at Florida State University), Igor Lubomirsky (now a professor in our department at the WIS), they were able to obtain, using the EBIC/SEM, a series of groundbreaking results on ion migration in semiconducting lattices under the influence of electric field and light.

When I came back from my sabbatical in the laboratory of Prof. C. Levi-Clement in the CNRS Meudon (near Paris) in 1989, it became apparent to me that I wanted to stop etching semiconductor surfaces and instead start growing new materials. Having already worked with 2D materials for five years, I decided to try to study photoelectrochemical cells made of thin film MoS_2 and WS_2, which were prepared by chemical bath and electrochemical deposition techniques (jointly with Prof. Gary Hodes). While spending a few months in the laboratory of Prof. A. Fujishima in the University of Tokyo in the summer of 1991, I read the news of the discovery of carbon nanotubes by Dr. S. Iijima. I started questioning myself (and later on Prof. Gary Hodes) if it would be possible to prepare fullerenes and nanotubes from other 2D materials, such as WS_2 and MoS_2. Independently, during that summer (1991), Dr. Lev Margulis was using the EM400 TEM to study the structure of the WS_2 and MoS_2 films prepared by my post-doc Dr. Menachem Genut. He found strange nanostructures, which he designated as "red blood cells", because they appeared like donuts, i.e. circular nanoparticles with low contrast in the middle. **Fig. 7** left shows a picture of one of the original envelopes for the storage of TEM negatives with Lev's handwriting. Without going into too much detail, after a few months of pondering these results, I concluded that these nanoparticles, designated as inorganic fullerene-like (IF) and inorganic nanotubes (INT), are the multiwall analogues of carbon fullerenes and carbon nanotubes – see **Fig. 7** right for a typical TEM image of one such nanotube. After publishing a few joint papers in *Nature* and *Science* on these nanoparticles, Dr. Lev Margulis passed away unexpectedly in the summer of 1995. Earlier, Talmon Arad z"l, a TEM expert, who collaborated with Prof. Ada Yonath (Nobel Laureate) while at EMBL, Heidelberg, joined the Weizmann Institute. At his request, the Institute bought a new cryo-TEM the CM12, which had low contrast and no electron diffraction capability, but better resolution than the EM400. Talmon started working with Lev, too, and they got along very well until the tragic death of Lev (see **Fig. 8**).



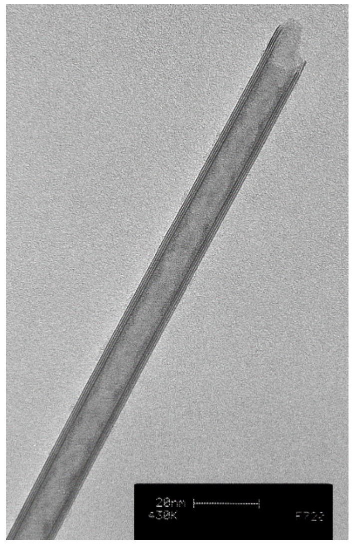


Figure 7. Left: Copy of an original envelope for storing TEM negatives with the hand-writing of Dr. Lev Margulis (the more recent comment written with pencile in Hebrew on the top is mine); Right: TEM image of a WS_2 nanotube

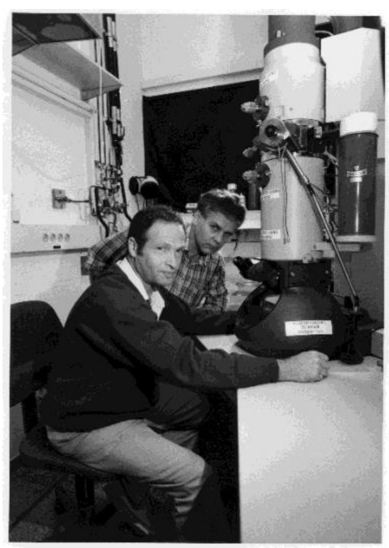


Figure 8. Dr. Lev Margulis (seated) and I (leaning) near the CN12 TEM (from 23.11.92).

Prof. Enrique Gruenbaum z"l, who had retired from Tel-Aviv University and made remarkable contributions to Lorentz microscopy of magnetic materials, joined us around 1995 as a consultant in my group. He helped Yaron Rosenfeld-Hacohen analyze his newly discovered $NiCl_2$ nanotubes and fullerene-like nanoparticles. Enrique was travelling via boats and trains to Oxford University almost every summer (he did not dare to fly). There he worked with Dr. John Hutchison, the foremost TEM of materials expert of that university at the time. John was using the high resolution JEOL 400 keV machine. He had several talented students with him – Jeremey Sloan (now a professor at Warwick University) and Rafal Dunin Borkowski (currently a professor at RWTH Aachen University and the director of the Ernst Ruske Center in Jülich – one of the foremost electron microscopy facilities in the world). With their help, we gained the first high resolution TEM images of WS_2 and MoS_2 nanotubes.

Following the tragic loss of Dr. Lev Margulis our research on IF and INT suffered from a lack of TEM expertise. Nonetheless, my research got a boost from a fortunate turn of events. Graciously, Prof. Meir Lahav, the department chair offered in 1997 to transfer Dr. Ronit Popovitz-Biro, a researcher in his group, to replace Lev. To our surprise, in a year or two, Ronit became fully versed with electron microscopy and started producing splendid results with the CM12 and later with the CM120. At one point in 1998 we submitted our first paper on $NiCl_2$ nanotubes to *Nature*. After some time the report came back from the journal. One of the referees argued, justifiably, that the data lacks an EDS (chemical) analysis of the nanotubes. Indeed none of the existing TEMs in the EM unit was earmarked for materials research and consequently we had no access to EDS/TEM set-up. I was extremely disappointed, because I believed that our $NiCl_2$ tubes and fullerenes were not sufficiently stable against humidity and they were scarce. At the advice of Prof. Meir Lahav, I went directly to the Vice-President Prof. Yoram Groner to complain. Under his supervision, it took no longer that two months to install the wonderful CM120 which was a boon to our research. The CM120 operated smoothly until five years ago when it was retired due to the arrival of the new JEOL2100. In the meantime, Dr. Ana Albu Yaron (Angie) who had just retired from her post in the Volcani Center and worked frequently with Dr. John Hutchison in Oxford, joined our group as a consultant. Angie was an extremely dedicated microscopist and I admired her tenacity and patience. Perhaps the culminating point of her work was the synthesis and analysis of IF-Cs_2O nanoparticles in 2005. These unique nanoparticles were inflammable in the ambient and therefore we built and installed a dedicated drybox and attached it to the CM120 – see **Fig. 9** (left). This add-on allowed us to transfer the inflammable nanoparticles without any exposure to the ambient atmosphere. One reason that these rare nanoparticles were incredibly difficult to find and analyze was the somewhat bizarre fact that the TEM column was contaminated with IF-WS_2 nanoparticles synthesized by my other students and the Cs_2O nanoparticles could not be easily discriminated and analyzed.

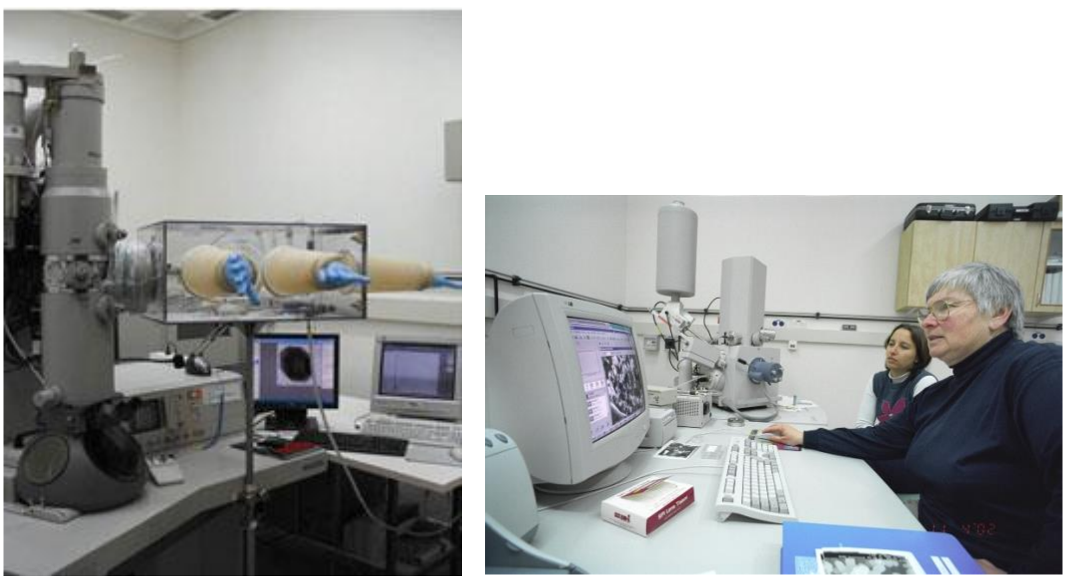


Figure 9. Left: The CM120 TEM with the “perspex” glovebox attached to the sample introduction chamber; right: Dr. Eugenia Kelin and Ifat Kaplan-Ashiri working with the E-SEM.

Prof. Lia Addadi and Prof. Steve Weiner did pioneering work on biomineralization at the WIS. Around 2000, FEI (successor to Philips) came up with an ingenious SEM, which can analyze samples under a moderate pressure of few mbars of water vapor. This development made it possible to image both biological samples under close to live conditions and highly insulating polymer specimens, saving the otherwise tedious coating process with a thin gold film. Using several hardware and software modifications, this microscope (**Fig. 9** right) was converted by Ifat Kaplan-Ashiri into a full nanomechanical testing set-up, during the preparation of her PhD thesis.

Around 2000, while Prof. David Cahen served as the academic head of the EM unit, discussions started about adding an NMR unit for brain research next to the EM unit. Following consultations with the EM manufacturer – Philips, it became clear that instalment of a nearby NMR unit would jeopardize the resolution of the electron microscopes due to interference with the strong magnetic fields. One day, the President of the Institute – Prof. Haim Harari contacted me and said that he was ready to offer the EM unit the two lower floors of the old Wolfson building, which was undergoing renovation. He asked me to go and visit the site and then call him back. I went there and other than smelling the nasty odor of the mice, I noticed that the ceiling was too low to accommodate a modern high-resolution TEM. I called back Haim and told him that the level of science there will not be higher than the height of the ceiling itself. He immediately recognized the problem and said he would build a room with an extra-high ceiling for the future high-resolution TEM (HRTEM). The next day he called me again and said that he had decided to build a whole new annex to the old Wolfson building with a room for six advanced microscopes. Obviously, I was enthusiastic and impressed by his far-sighted vision. **Fig. 10** shows an overall picture of the EM facility at that time. We of course know now that even the higher ceiling there is not adequate for the new generation of aberration (*Cs*)-corrected TEM, but at the time it was the greatest present he could possibly offer us. The new EM center was very well planned to allow cryo-microscopy with 20% humidity for biological specimens and also equipped with a very modern and quiet air-conditioning system. To verify that the acoustic noise would not exceed the specifications of the company for HRTEM, Prof. Mudi Sheves – the then Dean of the Faculty, hired a municipal garbage truck, which travelled back and forth along the road separating the EM center from the power center of the WIS, with no noticeable effect on the noise level, which could jeopardize the future TEM performance.

Figure 10. View of the current EM lab in the old Wolfson building and the annex hosting some of the high-performance SEMs/TEMs in the foreground. The Wolfson building is in the background.

Dr. Sharon Wolf, currently the director of the EM unit, joined the unit in 1998 and slowly geared her efforts towards electron tomography. Around 2004 it became clear that a new generation of microscopes was needed for both life sciences and materials research. In particular, the lack of high-resolution TEM (HRTEM) became a stumbling block for us and we desperately pleaded with the management to buy one for us. Luckily, the life scientists and, in particular, Dr. Sharon Wolf also needed a new cryo-HRTEM for their electron topography experiments. Under the leadership of our Dean, Prof. Mudi Sheves, we slowly crystallized our ideas and established a deal with FEI (the successor of Philips) to buy the Cryo F20 (200 keV) for the life sciences and the F30 HRTEM (300 keV) for materials research. **Fig. 11** shows Ronit working with the F30. Unfortunately, we lacked the expertise and did not buy the STEM unit and consequently HAADF experiments could not be done on this microscope. However, the quality of the HRTEM run by Dr. Ronit Popovitz-Biro was so high that at one point Dr. Lothar Houben, who later joined the EM unit to head the Titan Themis project, remarked that with Ronit and F30 we have 95% of the capacity of a *Cs*-corrected Titan, which although not completely accurate, was a great compliment to her.

Figure 11. Dr. Ronit Popovitz-Biro at work with the high-resolution F30 TEM. Note the acoustic noise shielding on the walls and the cylindrical power-supply tank delivering 300 keV

Some 18 years ago two excellent students joined my group, Ifat Kaplan-Ashiri and Maya Bar-Sadan. While Ifat made the first in-situ SEM measurements of the mechanical properties of WS_2 nanotubes, Maya became interested in the synthesis of MoS_2 nanooctahedra, which are considered to be the smallest hollow cage structures (IF) of that compound. Following a post-doctoral spell in Austin Texas, Ifat joined the EM lab becoming the head of the SEM section. At my encouragement, Maya started to look for a place where she could carry out detailed TEM analysis of the MoS_2 nanooctahedra. Finally, she ended up in the laboratory of Prof. Knut Urban, who headed the Ernst Ruske Center in Juelich, one of the largest TEM facilities in the world if not the largest one. Under his supervision, the first aberration (*Cs*) -corrected TEM was developed in 1998 demonstrating the first sub-Angström resolution. In fact, our first work using this revolutionary TEM technique (*PNAS*, 2008) was published as a result of this collaboration. Over the years, I collaborated with various laboratories, mostly in Europe, to gain access and analyze our nanotubes with the latest technology in *Cs*-corrected TEM. Sometime around 2013, I started to nag my department chair Prof. Leeor Kronik and the then Dean (Prof. Gilad Haran) that *Cs*-corrected TEM is a must on our campus. At their encouragement I sent a detailed letter to the then President (Prof. Daniel Zajfman). Coincidentally, Prof. Ada Yonath understood that the future of protein structural elucidation is in cryo-TEM. Unexpectedly, and to my delight, Maya became a life-partner with Dr. Lothar Houben who is one of the leading experts in *Cs*-corrected TEM/STEM. Upon returning to Israel in 2011 and joining the faculty of Ben-Gurion University, she convinced Lothar to join her in Rehovot in 2015 and he received an invitation to join the EM center and establish the *Cs*-corrected TEM unit at the WIS. It takes vision and courage to make a major decision, like the one taken by our former President Prof. Daniel Zajfman to upgrade the EM unit to its present status. In fact after 40 years that I have been preaching for electron microscopy in our campus, this is the first time that the WIS runs an electron microscopy facility which is state of the art. **Fig. 12** shows a global view of the new high-resolution TEM facility of the WIS, which operates in highly modern and well planned premises in the new Benoziyo building. This was of course not achieved through purchase of upgraded SEMs and TEMs, alone. Hiring experts to run the EM center is no less important and I wish to congratulate the new EM facility and especially the staff and hope they will go from strength to strength.

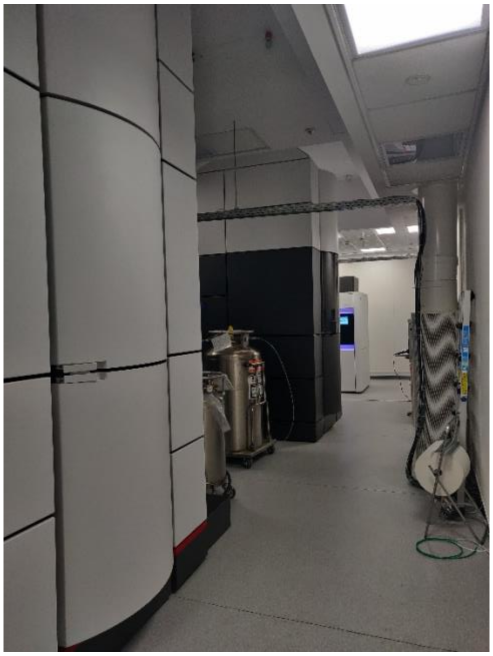


Figure 12. The new high-resolution TEM facility in the basement of the new Benoziyo building hosting the Titan Themis (left), Titan Kryos (middle) and the Talos Arctica (right) TEMs

I would like to conclude my personal account on the history of the EM-materials efforts by saying how grateful I am to the Weizmann Institute, which spared no effort or resources to make the entire EM unit a remarkable success story and thank all the current and past researchers and staff of the EM unit for their dedication. I wish to emphasize that this piece reflects my personal perspective of the historical development of the EM center, which is naturally focused on hard materials. I skipped important aspects of the EM center, which are dedicated to soft matter and biology or a combination of soft and hard matter and was pursued by other researchers at the WIS campus. I apologize if I missed any important aspect and people in my personal account of the contemporary history of the EM facility.