

2023 lab report about the JEOL JEM-F200 Multipurpose HR-TEM

1. General overview and management

The HR-TEM lab operated rather continuously during the year with only two stops due to failures, one in January related with water leakage and another in September related with an accidental interruption of electrical supply. The first failure required in-place service by JEOL, while the second was settled by phone assistance.

The non-stop operativity was also ensured by the increased number of users and by the employment of Dr. Michele Alderighi, a CISUP technician whose activity was mainly related with the HR-TEM lab.

The Management Committee is still composed by Prof. Enrico Mugnaioli (UniPI-DST, responsible for the HR-TEM lab), Prof. Vincenzo De Tata (UniPI- DRTNTMC), Prof. Leonardo Rossi (UniPI-DMCS), Prof. Renzo Valentini (UniPI-DICI) and Dr. Letizia Modeo (UniPI-DB).

2. Users

The current habilitated users of the HR-TEM lab are:

- Dr. Maria Concetta Scavuzzo, Technical personnel at UniPI-DRTNTMC;
- Dr. Sofia Lorenzon, Post-doc at UniPI-DST;
- Dr. Roberto Borriello, PhD at UniPI-DST;
- Dr. Daniele Sonaglioni, PhD at UniPI-DF and at IIT@SSSA Pontedera;
- Dr. Mauro Gemmi, PI at IIT@SSSA Pontedera;
- Dr. Paola Parlanti, Post-doc at IIT@SSSA Pontedera;
- Dr. Iryna Andrusenko, Post-doc at IIT@SSSA Pontedera;
- Dr. Valentina Zannier, Researcher at CNR-Istituto Nanoscienze Pisa.

These users are supported and coordinated by three super-users:

- Prof. Enrico Mugnaioli, PA at UniPI-DST (responsible for the HR-TEM lab);
- Dr. Paolo Lucchesi, Technical personnel at UniPI-DMCS;
- Dr. Michele Alderighi, Technical personnel at UniPI-CISUP.

3. Use of the laboratory

In 2023, the HR-TEM lab has operated for 165 days, roughly equivalent to 1320 hours. The machine time was used as shown in the following table and graphs.

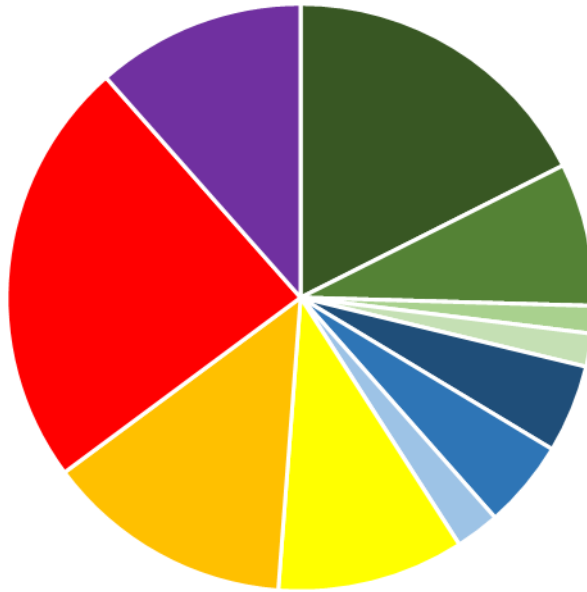
Days	Type of activity	Operator	Description
13.0	Lab management	Alderighi M., Lorenzon S.	Calibration and optimization of EDS - Collaboration with Prof. Capitani (University of Milan Bicocca)
4.0	Lab management	Lucchesi P.	Tests of TEM imaging on biological and bio-related samples
3.0	Lab management	Mugnaioli E., Alderighi M.	Electron diffraction calibration

2.0	Lab management	Alderighi M., Mugnaioli E.	Test of samples prepared by ion milling
2.0	Lab management	Andrusenko I.	Test on beam-sensitive MOF - Collaboration with Prof. Taddei (UniPI-DCCI)
2.0	Lab management	external	ASTAR training by Nanomegas experts
1.5	Lab management	external	EDS and HR-STEM training by JEOL experts
1.0	Lab management	Mugnaioli E., Alderighi M.	Test of samples prepared by FIB
0.5	Lab management	Mugnaioli E., Sonaglioni D.	Setting of low-dose conditions for ED experiments on beam sensitive organic samples
4.0	User training	Mugnaioli E.	Training of Dr. Lorenzon and Dr. Borriello (UniPI-DST)
3.0	User training	Lucchesi P.	Training of Dr. Galgani (UniPI-DRTNTMC)
3.0	User training	Mugnaioli E.	Training of Dr. Alderighi (UniPI-CISUP)
2.0	User training	Lucchesi P.	Training of Dr. Scotto (UniPI-DRTNTMC)
1.0	User training	Lucchesi P.	Training of Dr. Scavuzzo (UniPI-DRTNTMC)
1.5	Company demo	Mugnaioli E.	ASTAR Nanomegas demo
1.0	Company demo	external	JEOL demo for Acciaierie d'Italia
3.0	Company service	Mugnaioli E.	JEOL service
3.0	Education	Mugnaioli E.	Activities for PhD's (Geoscienze e Ambiente)
2.0	Education	Mugnaioli E.	Bruno Freitas Pio de Azevedo's thesis, Master Degree in Scienze Ambientali
2.0	Education	Mugnaioli E.	Abdur Rahman's internship, Biopham Erasmus Mundus Joint Master Degrees
1.0	Education	Gemmi M.	Practical lessons for the course Electron microscopy of nanomaterials (Materials and Nanotechnology)
8.0	PhD projects	Sonaglioni D.	Daniele Sonaglioni, PhD in Fisica
1.5	Dissemination	Lucchesi P.	Dissemination activities organized by CIME
1.0	Dissemination	Lucchesi P., Mugnaioli E.	Bright 2023
1.0	Dissemination	Mugnaioli E., Alderighi M.	Electron Crystallography School organized by Associazione Italiana di Cristallografia
0.5	Dissemination	Mugnaioli E., Alderighi M., Lorenzon S.	Open Day of the Dipartimento di Scienze della Terra of UniPI

8.0	In-house measurements	Lucchesi P.	Analysis of ultrathin sections of embedded tissues
6.0	In-house measurements	Lorenzon S., Borriello R., Mugnaioli E.	Analysis of ultra-reduced phases from Luobusa suture zone and from the Bohemian massif
1.5	In-house measurements	Mugnaioli E.	Structural investigation of pseudo-gibbsite
1.5	In-house measurements	Mugnaioli E.	Structural investigation of thorikosite
11.0	Free-of-charge measurements	Parlanti P., Gemmi M.	Collaboration with IIT@SSSA (Pontedera) for the development of advanced TEM-related applications involving mainly ASTAR and 3D ED on impactites.
4.0	Free-of-charge measurements	Mugnaioli E.	Analysis of asbestiform minerals - Collaboration with Prof. Gualtieri (University of Modena e Reggio Emilia)
2.0	Free-of-charge measurements	Alderighi M., Mugnaioli E.	Analysis of euglena light receptors - Collaboration with Dr. Gualtieri (CNR-Istituto di Biofisica)
1.0	Free-of-charge measurements	Alderighi M.	Preliminary investigation for Virgo Collaboration
1.0	Free-of-charge measurements	Borriello R.	Analysis of shocked Moon meteorite - Collaboration with Dr. Pittarello (Naturhistorisches Museum Wien, Austria)
1.0	Free-of-charge measurements	Mugnaioli E.	Analysis of REE-carbonates - Collaboration with Prof. Capitani (University of Milan Bicocca)
1.0	Free-of-charge measurements	Mugnaioli E.	Analysis of Ryugu asteroid return samples - Collaboration with Dr. Ferrari (Istituto Nazionale di Astrofisica)
0.5	Free-of-charge measurements	Mugnaioli E.	Analysis of bubbles in impact materials - Collaboration with Dr. Di Vincenzo (CNR-Istituto di Geoscienze e Georisorse)
0.5	Free-of-charge measurements	Mugnaioli E.	Analysis of core-shell heterostructures for medical applications - Collaboration with Dr. Voliani (University of Genoa)
0.5	Free-of-charge measurements	Mugnaioli E.	Analysis of NP obtained by explosion - Collaboration with Dr. Caposciutti (UniPI-DIESTC)
19.5	Financed project / collaborations	Zannier V., Mugnaioli E.	Collaboration with CNR-Istituto Nanoscienze for the study of semiconductor nanostructures for optoelectronic devices

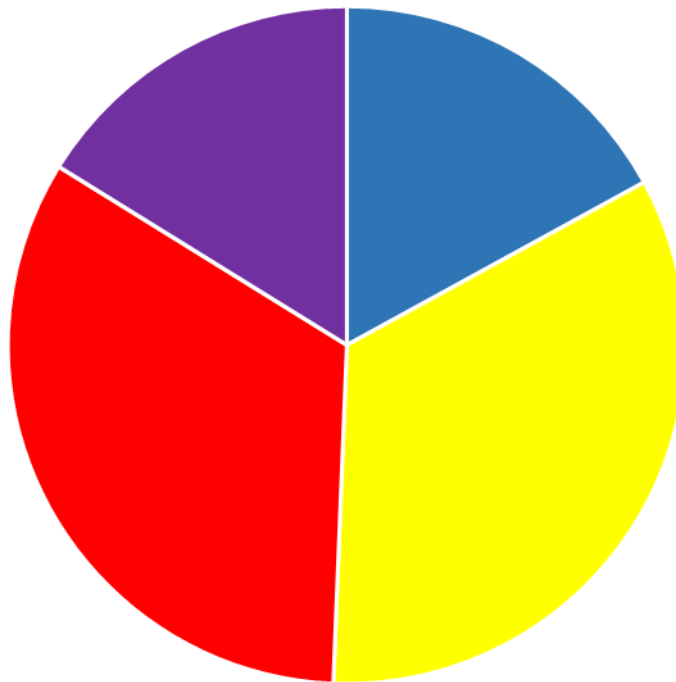
3.5	Financed project / collaborations	Alderighi M.	Nanoparticles in organic substrate - Prof. Antonetti (UniPI-DCCI)
3.0	Financed project / collaborations	Mugnaioli E., Lorenzon S.	PRIN project on birifrangent garnets - Prof. Mugnaioli (UniPI-DST)
2.0	Financed project / collaborations	Alderighi M., Mugnaioli E.	Collaboration with CNR-Istituto Nanoscienze for the study of electric wafer heterostructures
2.0	Financed project / collaborations	Mugnaioli E.	Analysis of calcite/aragonite interface - Collaboration with Dr. Németh (Institute for Geological and Geochemical Research, Hungary)
2.0	Financed project / collaborations	Mugnaioli E.	Analysis of nano-precipitates (oxides and carbides) - Collaboration with Dr. Nazzareni (University of Perugia)
1.5	Financed project / collaborations	Alderighi M.	Nanoparticles in water – Collaboration with Prof. Pucci (UniPI-DCCI)
1.5	Financed project / collaborations	Lucchesi P.	Cellular analyses - Collaboration with Dr. Levantini (CNR-Istituto di Tecnologie Biomediche)
1.5	Financed project / collaborations	Mugnaioli E.	Analysis of keu - Collaboration with Prof. Petrini (UniPI-DST)
1.5	Financed project / collaborations	Mugnaioli E.	Investigation of hydrothermal products of experimental mineralogy - Collaboration with Prof. Pignatelli (University of Nancy, France)
1.0	Financed project / collaborations	Mugnaioli E.	Investigation of Nakhla meteorite - Collaboration with Prof. Pignatelli (University of Nancy, France)
12.0	Third-party measurements	Scavuzzo M.C., Lucchesi P.	Analysis of pathological samples - Collaboration with AOUP
7.0	Third-party measurements	Mugnaioli E., Alderighi M.	Electron diffraction studies of nano-compounds - Nanomegas (Belgium)

Type of activities

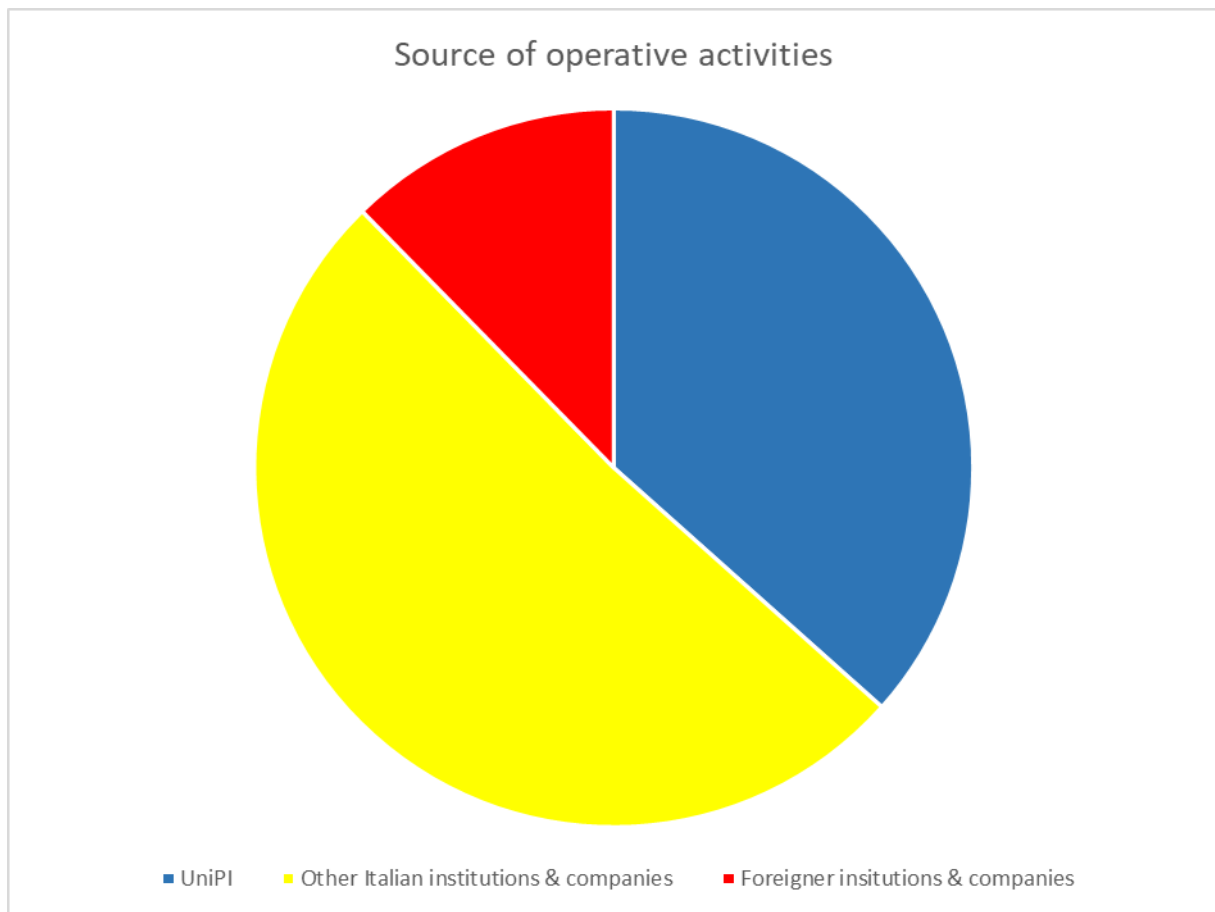


- Lab management
- User training
- Company demos
- Company service
- Education
- PhD projects
- Dissemination
- In-house measurements
- Free-of-charge measurements
- Financed project / collaborations
- Third-party measurements

Operative activities (excluding lab management)



- Education & Dissemination
- Free-of-charge measurements
- Financed project / collaborations
- Third-party measurements



Lab management. Lab management was mostly managed by the three super-users.

Beside routine and extraordinary activities connected with the functionality of TEM, the most relevant action was the quantitative calibration of EDS in collaboration with Prof. Capitani's group (University of Milan Bicocca). The procedure required the measurement of a number of standards and an exhaustive testing on hydrated and non-hydrated samples. The calibration is still on-going, but hopefully shall allow chemical measurements with errors below 0.5%wt and spot size of few nanometers. The possibility to perform such kind of measurements with a FEG-TEM is unique in Italy (and arguably worldwide), and will be relevant for establishing scientific collaborations and obtain funds through projects and third-party measurements.

Also, a calibration for low-dose experiments was created for measuring beam-sensitive materials, like pharmaceutical compounds and metal-organic frameworks.

The HR-TEM lab was also used for two demo sessions by JEOL and Nanomegas, respectively. These activities were 'repaid' by two advanced training sessions with in-presence foreigner experts.

The training of Dr. Scavuzzo was finalized. Three more new users were successfully trained: Dr. Alderighi, Dr. Lorenzon and Dr. Borriello. Two more users are being currently trained: Dr. Galgani and Dr. Scotto.

Only one technical intervention by JEOL was required at the beginning of the year. A second technical failure in September was solved by remote assistance by JEOL.

Education & Dissemination. HR-TEM lab was used for the following education activities within UniPI:

- demonstrations for the students of the course of "Electron microscopy of nanomaterials" held by M. Gemmi for the Master degree in Materials and Nanotechnology.
- practical sessions of the course "Principi ed applicazioni pratiche del microscopio a trasmissione elettronica (TEM)", activated by the PhD School in Geoscienze e Ambiente;

- internship of Abdur Rahman in the framework of the Biopham Erasmus Mundus Joint Master Degrees;
- part of the experimental activity related with the final product of Bruno Freitas Pio de Azevedo, master student of Scienze Ambientali;

Moreover, TEM was used in the framework of two PhD projects.

The HR-TEM lab took part to Bright 2023 and the Open Day of the Dipartimento di Scienze della Terra. It also hosted few practical sessions of the Winter School and the Summer School organized yearly by the Centro per la Microscopia Elettronica (CIME) of UniPI.

Finally, the HR-TEM lab was involved in the practical sessions of the Electron Crystallography school organized in Pisa by the Associazione Italiana di Cristallografia, which gathered some of the most renown European experts on the topic of electron diffraction and students from all around the world. The presence of the HR-TEM lab was one of the reason Pisa was selected as location for the school.

No cost was claimed for education and (no-profit) dissemination activities.

Free-of-charge measurements. Free-of-charge measurements comprised both in-house sessions and test/preliminary measurements that may favor the establishment of future financed collaborations or projects.

In-house measurements were performed by the two super-users Prof. Mugnaioli and Dr. Lucchesi. These sessions partially compensate the time super-users dedicate for the lab management and third-party measurements. None of these in-house measurements interfere with the other activities of HR-TEM lab.

Other free-of-charge sessions were used for testing the performances of the HR-TEM lab in view of future financed collaborations and common projects. Most of these sessions involved activities in collaboration with researchers external from UniPI, either Italian or foreigner. Fruitful outcomes of these activities are expected in the year 2024.

Finally, a special free-of-charge collaboration is still active between CISUP and Dr. Gemmi's group (IIT@SSSA Pontedera), for sharing expertise and instrument capabilities. The collaboration mostly involved application of Nanomegas ASTAR package.

Financed projects / collaborations. A number of short collaborations and one-day measurements were accomplished during the year, both with personnel of UniPI and with external researchers.

Moreover, a year-long scientific collaboration has been active with Dr. Zannier (CNR-Istituto Nanoscienze) for the study of semiconductor nano-heterostructures for optoelectronic applications. This collaboration comprised part of the scientific results used for two Master Degree theses at UniPI: Neri D. (Laurea Magistrale in Fisica) and Sorodoc R. A. (Master Degree in Materials and Nanotechnology). This collaboration is expected to be renewed in 2024.

Finally, the PRIN 2022 project "Nano-focus on metamorphic garnet" was granted in 2023. Prof. Enrico Mugnaioli is RU responsible for this project, which largely involves the HR-TEM lab. Indeed, the existence of the HR-TEM lab was an essential requisite of the project and was functional of its successful founding.

Third-party measurements. There are two long-lasting agreements for measurement services with the Azienda Ospedaliera Universitaria Pisana (AOUP) and with the Belgian company Nanomegas.

4. Products

Data collected by the TEM are reported in the following products published in the year 2023.

Papers in peer reviewed international journals:

- 1) Ermini M. L., Summa M., Zamborlin A., Frusca, Mapanao A. K., Mugnaioli E., Bertorelli R., Voliani V.: **Copper nano-architecture topical cream for the accelerated recovery of burnt skin.** *Nanoscale Advances*, **5**, 1212–1219 (2023).
- 2) Ghezzi L., Mugnaioli E., Perchiazzi N., Duce C., Pelosi C., Zamponi E., Pollastri S., Campanella B., Onor M., Abdellatif M., Franceschini F., Petrini R.: **Hexavalent chromium release over time from a pyrolyzed Cr-bearing tannery sludge.** *Scientific Reports*, **13**, 16283 (2023).
- 3) Goudjil M., Lepore G. O., Bindi L., Mugnaioli E., Baroni T., Mezaoui D., Bonazzi P.: **Synthesis and characterization of $\text{AsO}[(\text{W},\text{Mo})\text{O}_3]_{13}$, a new (6)-intergrowth tungsten bronze (ITB).** *Journal of Solid State Chemistry*, **322**, 123987 (2023).
- 4) Gualtieri A. F., Malferrari D., Di Giuseppe D., Scognamiglio V., Sala O., Lassinantti Gualtieri M., Bersani D., Fornasini L., Mugnaioli E.: **There is plenty of asbestos at the bottom. The case of magnesite raw material contaminated with asbestos fibres.** *Science of Total Environment*, **898**, 166275 (2023).

Communications in national and international meetings:

- 1) Petrini R., Ghezzi L., Mugnaioli E., Perchiazzi N., Franceschini F.: **Chromium oxidation in the time-dependent response of the pyrolyzed tannery waste KEU: environmental implications.** *The Geoscience paradigm Resources, Risk and future perspectives*, Potenza (Italy), September 2023
- 2) Sonaglioni D., Mugnaioli E., Andrusenko I., Capaccioli S., Gemmi M.: **Electron diffraction and fast calorimetry of molecular compounds of pharmaceutical interest.** *109° Congresso Nazionale SIF*, Salerno (Italy), September 2023.
- 3) Sonaglioni D., Mugnaioli E., Andrusenko I., Capaccioli S., Gemmi M.: **An unusual case of polymorphism: vemurafenib.** *Crystal Forms @ Bologna 12th*, Bologna (Italy), September 2023.
- 4) Ferrari M., Folco L., De Angelis S., Masotta M., Raponi A., De Sanctis M. C., Mugnaioli E., Ciarniello M., Ammannito E., La Francesca E., Rossi L., Pedone M.: **Investigating the ammonium-bearing phase in Ryugu samples.** *Hayabusa Symposium 2023*, Sagamihara (Japan), November 2023.

Discovery of new minerals:

- 1) Borriello R., Xiong F., Ma C., Lorenzon S., Mugnaioli E., Yang J., Xu X., Grew E. S.: **Jianmuite, IMA 2023-057.** *CNMNC Newsletter 75; Mineralogical Magazine*, **87**, (2023).

Master degree theses:

- 1) Freitas Pio De Azevedo B.: **Iron-modified natural zeolites: innovative solutions for the removal of hexavalent chromium from contaminated waters.** *Tesi di Laurea Magistrale in Scienze Ambientali*, Università di Pisa. Tutors: Petrini R., Mugnaioli E., discussion: 15/12/2023.
- 2) Nieri D., **Nanowire dots as quantum radiation detectors.** *Laurea Magistrale in Fisica*, Università di Pisa. Tutors: Tredicucci A., Zannier V., discussion: 27/03/2023.
- 3) Sorodoc R. A., **Growth and characterization of GaAsP quantum dot nanowires.** *Tesi di Laurea Magistrale in Materials and Nanotechnology*, Università di Pisa. Tutors: Sorba L., Zannier V., discussion: 24/11/2023.

Granted projects involving the HR-TEM facility:

- 1) Cesare B., Mugnaioli E.: **Nano-focus on metamorphic garnet. PRIN 2022.**

5. Open issues and future perspectives

The HR-TEM can now be considered fully operative. In 2023 it worked more than double the days it worked in 2022. This target was accomplished thanks to the employment of the new technical personnel CISUP Dr. Alderighi, mostly working for the HR-TEM lab management, and thanks to the increased number of users, some affiliated to research institutions external to UniPI but connected to the HR-TEM by scientific collaborations. We also stress the fact that the activities of the HR-TEM lab involve a number of different Departments of UniPI, related with both Life Sciences and Physical Sciences.

Roughly half of the working time of the HR-TEM was dedicated to not financed activities (among which education and dissemination), and half to financed activities (scientific collaborations and third-party measurements). Notably, the latter appear already consistent with the self-support of the laboratory. The budget connected with long-lasting collaborations and agreements is greater than the one connected with stand-alone measurements, and the HR-TEM lab is active in searching new collaborations that may guarantee a reliable source of income over the time.

Still, there is space for more measuring time. At least 50 more days of measurement per year are still available. Moreover, we point out that the majority of collaborations and third-party measurements involve counterparts that are external to UniPI. We therefore invite CISUP to go on advertising within UniPI the possibilities offered by the HR-TEM lab. We hope that in future the HR-TEM lab will be functional for UniPI in opening new collaborations and getting extra-funding for research activities. The formation of new users belonging to different Departments of UniPI is also welcome.