A survey of the Italian research in solid state physics by infrared spectroscopy with electron-beam sources

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Abstract. Two beamlines for the use of InfraRed Synchrotron Radiation (IRSR) are presently working in Italy, at the ELETTRA storage ring in Trieste, and at the collider DAFNE in Frascati. A third facility, SPARC in Frascati, has been equipped for the extraction of Terahertz radiation with the aim to perform pump-probe time-domain experiments. Here we describe those apparatus and we review the main results that the Italian groups have obtained therein, in recent years, in solid-state physics. We also describe the experiments performed in collaboration with the storage ring BESSY in Berlin, for the exploitation of Coherent Synchrotron Radiation, and the terahertz beam line recently implemented at SPARC, the Free Electron Laser of Laboratori Nazionali di Frascati.

1. The beamline SINBAD at DAFNE and the high-pressure measurements

SINBAD (Synchrotron Infrared Beamline At DAFNE) was the first InfraRed Synchrotron Radiation (IRSR) beamline built in Italy, under a collaboration between the Istituto Nazionale di Fisica Nucleare (INFN) and the Università di Roma La Sapienza. SINBAD collects in a parasitic regime the radiation emitted by a bending magnet of DAFNE, an electron-positron collider that is designed to work at 0.51 GeV with a beam current of more than 1 A in each ring. Due to such a high current, the infrared extracted from DAFNE is more brilliant than that of a black body by more than one order of magnitude at 100 cm⁻¹. The front end of SINBAD collects a solid angle of 18 x 45 mrad² and the plane extraction mirror is placed at about 4,5 m from the source located along the bending magnet arc. The
beamline layout, designed with the help of ray-tracing simulation, consists of six mirrors that first focus the radiation, and then transfer a collimated beam to the experimental area.

After the commissioning in 2003, two experimental stations have been built on SINBAD, both of which are equipped with Michelson interferometers. One of them includes an infrared microscope Hyperion 3000 coupled to a Focal Plane Array (FPA) detector and is devoted to chemical and biophysical studies. The other one, equipped with a cryogenic and a high-pressure apparatus, is specialized in solid-state physics. Both stations host every year numerous Italian and European groups under EU projects.

**Figure 1.** Comparison between the transmittance spectrum of a manganite in a diamond anvil cell (DAC) with use of the IRSR of SINBAD (solid line) and the internal Hg source of the interferometer (dashed line). The two intensities are plotted on the same scale. The arrows indicate the phonon lines.

IRSR displays all its potential in the far-infrared range and on samples of small size (Figure 1). For this reason, since the beginning the SINBAD radiation was applied to Diamond Anvil Cells (DAC) in order to study the insulator-to-metal (IMT) transitions induced by pressure in novel materials like the colossal-magnetoresistance manganites. Figure 2 shows indeed a IMT in a La-Ca manganite which is insulating at ambient pressure. Evidence for the IMT is provided by the weakening of the phonon peaks with pressure at room temperature, due to the shielding effect of the free carriers.

**Figure 2.** IMT in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, induced by pressure and observed in the FIR with IRSR [2].

**Figure 3.** P-T diagram of the charge-order/metal coexistence in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ [3].
Recently, similar measurements were extended to low temperatures at SPRING-8, with the collaboration of the group of the Kobe university. Data on a Nd-Sr manganite, which is insulating for charge order (CO), allowed some of us to obtain the P-T phase diagram shown in Figure 3, which is the first to our knowledge for the CO-metal coexistence. These measurements, like those in Figure 2, could never be performed with a sufficient signal-to-noise ratio without the use of IRSR.

2. The beamline SISSI at ELETTRA and the spectroscopy of strongly correlated systems

The SISSI beamline at ELETTRA was designed and built by the group of La Sapienza, with the technical and financial support of Sincrotrone Trieste, and is operating since 2005. Its layout is much simpler than that of SINBAD and is shown in Figure 4. The extraction mirror M1 collects the beam, 65x25 mrad wide, from the bending magnet. The radiation is then focused by the ellipsoid M2 beyond the shielding wall, reflected by the plane mirror M3, and refocused by the ellipsoid M4 on the entrance of the interferometer [4].

![Optical layout of the SISSI beamline at ELETTRA](image4)

**Figure 4.** Optical layout of the SISSI beamline at ELETTRA [4].

![Mid-IR reflectance spectra](image5)

**Figure 5.** Mid-IR reflectance spectra acquired with a linear scan (step 1 micron) in the z direction on a Si$_3$N$_4$ “flower” pattern over a gold background (visible image in the center). The value of the reflectance as a function of z and frequency is indicated by the color scale. The knife edge aperture was 4x4 micron, the resolution was 8 cm$^{-1}$ and 64 scans were accumulated using both the globar and the synchrotron.
The beamline feeds two experimental stations, both of which are equipped with a Michelson interferometer. As for SINBAD, one of them is devoted to chemistry and biophysics and includes an infrared microscope Hyperion 3000 with FPA detector. The other one, equipped with cryogenics and high-pressure cells, is devoted mainly to solid-state physics.

The advantage of using synchrotron radiation instead of conventional sources, when operating an infrared microscope in the mid infrared, can be appreciated in Figure 5. Therein, the spectra of a sample obtained by depositing a low-reflectance Si₃N₄ “flower” pattern on a gold substrate (shown in the middle) are measured with the microscope coupled to a MCT detector, by using either the globar (left) or the IRSR of SISSI (right). Not only the quality of the right image is much higher, but therein only one can resolve (at 2500 cm⁻¹ and above) the reflectivity gap between the "flowers".

The activity at SISSI in solid state physics has been focused mainly on the study of superconductors, of strongly correlated systems, and of the transport properties at interfaces.

![Figure 6. Far-infrared reflectivity (a) and optical conductivity (b) of undoped, polycrystalline, SmOFeAs. The inset of a) shows the reflectivity at 300 K between 50 and 20000 cm⁻¹, that of b) the difference Δσ₁=σ₁(ω,T)-σ₁(ω,150 K) [5].](image)

The former subject has been addressed, in recent years, by measuring the optical properties of the newly discovered superconductors of the Fe-As family. A complete Infrared-Raman study of the phonon spectrum has been performed on SmFeAsO polycrystalline samples, both doped and undoped, and compared with Density Functional Theory calculations within the pseudopotential approximation. In this way, the structural and dynamical lattice properties of both the SmFeAsO and the prototype LaFeAsO compounds have been obtained [5]. The good agreement between the data and the optical phonon frequencies computed at the Γ point showed the capability of the employed *ab-initio* methods to describe the dynamical properties of these novel superconductors.

Extended studies on strongly correlated systems have also been performed at SISSI, with focus on the Magnéli phases of vanadium oxide: VO₂, V₂O₅, and V₅O₇. A first study was carried out by combined Raman, IR transmittance and IR reflectivity measurements at room temperature, on monoclinic VO₂ over the 0–19 GPa and 0–14 GPa pressure ranges, respectively (figure 7). Both the lattice dynamics and the optical gap showed a remarkable stability up to $P^* \approx 10$ GPa, whereas subtle modifications in the V ion arrangements within the monoclinic lattice, together with the onset of a
metallization process via band gap filling, were observed for $P > P^*$. While at $P=0$ the VO$_2$ metallic phase is found only in conjunction with the rutile structure above 340 K, the study showed that a new metallic phase within a monoclinic structure is accessible in the high pressure regime at room temperature.

Figure 7. Mid-infrared reflectivity (a) and transmittance (b) of VO$_2$ at selected pressures. The arrows indicate increasing pressure. Dashed lines replace the data at the frequencies where the diamond-window absorption of the DAC is too high. Inset: corresponding low-frequency optical density [6].

The infrared study of VO$_2$ [7] was performed both on pure and on Cr-doped crystals. In this way one could monitor the transition from the antiferromagnetic (AF) to the paramagnetic (PM) state either when it is coupled to insulator-to-metal transition (MIT), as in the former case, or not (as Cr-doped samples). The opening of a large insulating gap at 100 K is clearly shown in Figure 8, together with an upturn in the low-frequency conductivity above 400 K which indicates the appearance of a pseudogap. This feature is probably related to the destruction of quasi-particles predicted by theory when, in correlated metals, the renormalized Fermi energy becomes comparable with the thermal energy.

In the same field, a recent work on ($V_{0.989}Cr_{0.011}$)$_2$O$_3$ [8] can illustrate the synergetic opportunities offered by the simultaneous presence of IR, UV, and X-ray beamlines in a facility like ELETTRA. ($V_{0.989}Cr_{0.011}$)$_2$O$_3$ provides the opportunity to span all phases of the vanadium oxide through two MITs. One, from the AF insulator to the PM metal, also shows a change of crystal symmetry, the other (from PM metal to PM insulator) is iso-structural and a prototype of the correlation-driven Mott transition. By combining three spectroscopies with different lateral resolution, IR, scanning photoemission microscopy (SPEM) and X-ray diffraction (XRD), with LDA + DMFT calculations, the authors could explore the phase diagram of Cr-doped V$_2$O$_3$ from macroscopic to microscopic scales, finding...
evidence of an electronic phase separation in the PM phase (Figure 9). The poor metallic behavior, which partially prevents the application of this material, is therefore explained in terms of a coexistence of metallic and insulating domains stabilized by structural defects. However, both IR and XRD measurements demonstrate that external pressure can drive the MIT much closer to a genuine Mott transition, leading eventually to the homogeneous metallic phase which is required for the applications.

Figure 9. Scanning photoemission microscopy images and spectra on (V$_{0.989}$Cr$_{0.011}$)$_2$O$_3$, collected at 27 eV photon energy and at different temperatures on a 50 x 50 μm sample area. The pictorial contrast between metallic and insulating zones is obtained from the photoemission intensity at the Fermi level from its minimum value, in violet, to its maximum, in red. Inhomogeneous properties are found within the PM phase at $T = 220$ K (a) and 260 K (b), where metallic (in red) and insulating (in blue) domains coexist. After heating the sample to 320 K (c) a homogenous insulating state is obtained. After a whole thermal cycle (d) the metallic regions can be found in the same position and shape as in (a).

Figure 10. The optical conductivity at 10 K of the (SrMnO$_3$)$_n$/LaMnO$_3$$_{2n}$ heterostructures, showing a metallic behavior (Drude term) for $n \leq 3$. 
A third solid-state subject investigated at SISSI concerns the electronic properties of the interfaces and their differences from those of bulk materials, with focus on the manganites. It is known from transport measurements that thin films made of \((\text{SrMnO}_3)/(\text{LaMnO}_3)_{2n}\) superlattices (SL), for small \(n\), become metallic even if the individual layers should be insulating. At SISSI the reflectivity of such SL was measured for \(n=1, 3, 5,\) and \(8\) and for \(10 < T < 400 \text{ K}\) [9]. The spectra showed a \(T\)-dependent IMT for \(n \leq 3\), driven by the softening of a polaronic mid-infrared (MIR) band which, in turn, built up a strong Drude term. At \(n = 5\) that softening is incomplete, while at the largest SL period \((n = 8)\) the MIR band was independent of \(T\) and the SL remained insulating. One could thus first observe the IMT in a manganite in the absence of the disorder, due to chemical doping, which affects the bulk transitions. Moreover, in no way the SL optical properties could be reconstructed from those of the original bulk materials. This suggests that the \((\text{SrMnO}_3)/(\text{LaMnO}_3)_{2n}\) heterostructures represent an original physical state of matter.

3. Sub-Terahertz coherent radiation at BESSY and the superconducting gap

A fruitful collaboration was established in 2005 between the group of Rome La Sapienza and U. Schade, who is responsible for the infrared beamline IRIS at BESSY (Berlin). This storage ring has the unique capability to work, routinely for users twice a year, in the so-called \(\alpha\)-mode [10]. In such a condition of the magnetic lattice, very short bunches carrying a total current of about 20 mA run along an ideal orbit. Under these conditions, coherent radiation is emitted at wavelengths larger than the bunch length (figure 11), namely, between 3-5 and 30 cm\(^{-1}\) (sub-Terahertz range). The collected radiation is more brilliant than the ordinary IRSR by orders of magnitude (figure 12) and is extraordinarily stable.

![Figure 11](image1.png)

**Figure 11.** The principle of CSR: at wavelengths smaller than the bunch length, all the \(N\) electrons in the bunch emit coherently, and the sub-Terahertz power becomes proportional to \(N^2\).

![Figure 12](image2.png)

**Figure 12.** The effective gain of CSR with respect to a mercury lamp measured in the sample compartment of the interferometer.

Those properties of CSR were exploited in a series of experiments devoted to study the superconducting optical gap \(2\Delta\) of novel superconductors [11-13], especially those where the low critical temperature, and the consequent low value of \(2\Delta\), prevented the use of conventional sources (including IRSR). Other phenomena related to superconductivity were also investigated, like the Josephson Plasma Resonance (JPR).
A 1% variation in the reflectivity ratio of CaAlSi between the superconducting and the normal phase allows one to measure the superconducting gap in this material by CSR radiation. The inset shows the stability of CSR within a few parts in $10^{-3}$ through the ratio of subsequent spectra (30 scans each) [11].

Figure 13. A 1% variation in the reflectivity ratio of CaAlSi between the superconducting and the normal phase allows one to measure the superconducting gap in this material by CSR radiation. The inset shows the stability of CSR within a few parts in $10^{-3}$ through the ratio of subsequent spectra (30 scans each) [11].

A first example, shown in Figure 13, is the determination of $2\Delta$ in the superconductor CaAlSi, whose structure is similar to that of MgB$_2$, from the peak in the ratio between the reflectivity measured below $T_c$ and that measured in the normal phase [12]. As shown in the inset, the overall variation of 1% can be detected thanks to the stability of CSR, which reaches a few parts per thousand between subsequent spectra. Figure 13 shows instead the JPR revealed by the CSR polarized along the $c$ axis of a superconducting anisotropic crystal, the cuprate La-Ba-Sr-Cu-O. JPR is a direct insulator-to-superconductor transition which is triggered in the $c$ axis by the superconducting transition in the orthogonal ab planes. In fact, the Cooper pairs of the Cu-O planes tunnel along the $c$ axis through the insulating La-Sr(Ba) planes. As one can see in figure 14, while the far-infrared reflectivity remains that typical of an insulator at all temperatures, as shown by the unshielded phonon peaks, the reflectivity in the sub-Terahertz region jumps to 1 below $T_c$ [13].

Figure 14. The Josephson plasma resonance observed by CSR radiation polarized along the $c$ axis of the superconducting crystal La-Ba-Sr-Cu-O [12].

4. The Terahertz radiation source at the SPARC facility.

All the work presented up to now has concerned frequency-domain spectroscopy, even if mainly based on the use of unconventional infrared sources. Presently, the opportunity to perform time-domain spectroscopy in the Terahertz spectral region, and in particular THz-pump/THz-probe experiments, is offered to the Italian spectroscopic community. Indeed, a dedicated beamline for coherent THz radiation has been built at SPARC [14] on the "dogleg" line (see Fig. 15) and is under characterization under the project TERASPARC.

The linac-driven THz radiation is produced at SPARC as pulsed Coherent Transition Radiation (CTR) generated by the highly relativistic electron beam (100 – 180 MeV, 10 Hz repetition rate) going through the interface between the vacuum and a silicon aluminated screen placed in the vacuum pipe at 45 deg with respect to the beam direction. The backward CTR radiation, reflected normally to the beam direction, is extracted from the vacuum pipe through a $z$-cut quartz window and collected by a
90° off-axis parabolic mirror, whose focal plane corresponds to the source plane. The parallel beam is then reflected vertically down towards an aluminium flat mirror, placed at 45° with respect to the horizontal plane. The radiation, reflected horizontally, finally enters the home-made Martin-Puplett interferometer [15].

**Figure 15.** Layout of the SPARC facility in Frascati, with the CTR target for the extraction of Terahertz radiation.

Either sub-ps high-brightness electron beams or longitudinally modulated beams can be used to generate high power coherent THz radiation, broadband or narrowband, respectively. The technique used at SPARC to manipulate such electron beam relies on low energy RF compression (the velocity bunching) [16] and on the use of properly shaped trains of UV laser pulses hitting the photo-cathode (comb laser beam) [17]. One of the interferograms measured starting from April 2011 is shown in figure 17. A 115 MeV, 200 pC longitudinally compressed beam, down to 720 (40) fs, has been measured.
Figure 17. One of the interferograms (blue dots) collected at SPARC by means of a Martin-Puplett interferometer. The interferogram has been fit with a three-Gaussian curve (red curve) [18] to take into account the high-pass filter behavior of the interferometer. A sub-ps, 200 pC, 115 MeV electron beam has been characterized.

The first experiment which will be performed with the new apparatus, coupled to the optical layout shown in figure 18, is the determination of the life time of the excited states in Ge-Si:Ge quantum wells. Both the pump and the probe will be in the THz range, thus reducing to a minimum the perturbation on the system. These measurements will be part of a research plan which is aimed at implementing a new class of Terahertz Quantum Cascade Lasers [19].

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