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Preliminary results of the Italian neutron experimental station INES at ISIS: Archaeometric applications(*)

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Summary. — The INES project was sponsored by the CNR *Neutron Spectroscopy Advisory Committee*, stressing the importance of realizing an Italian Neutron Experimental Station (INES) at the world most powerful pulsed neutron source (ISIS, Rutherford Appleton Laboratory, UK) and evidencing the strategic value that such a test station would assume in the field of applied sciences like, for example, chemistry, material science, Earth science, crystallography, and last, but not least, in the field of science applied to the study of *cultural-heritage artifacts*.

PACS `07.90.+c` – Other topics in instruments, apparatus, and components common to several branches of physics and astronomy.
PACS `61.12.-q` – Neutron diffraction and scattering.
PACS `81.90.+c` – Other topics in materials science.

1. – Introduction

Neutron Scattering is one of the most powerful diagnostic techniques available for scientific and technological research in material science. This technique, even though widely employed among the technologically most advanced countries, is not as much widespread within the Italian scientific community, as the level of the GDP (*Gross Domestic Product*) and the political and social weight of the country would deserve. Among the various reasons responsible for the present situation, the most important is the absence of national neutron sources available to the scientific community. Indeed, the beginning of the 70's witnessed an absolute minimum, in Italy, of the neutron scattering activities. Followed

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by an almost total disengagement from any research activity in the nuclear energy field, after the Chernobyl accident.

In spite of this unfortunate situation, the role of CNR (*Consiglio Nazionale delle Ricerche*) has been of fundamental importance to partially compensate for this handicap. Since the mid 80's, a collaboration was started with the Rutherford Appleton Laboratory (RAL, UK), where a new generation pulsed neutron source (ISIS) was under construction. The building of the PRISMA spectrometer, by ISM-CNR during the period 1985-1995, and the following realization of the TOSCA spectrometer, by IEQ-CNR in the period 1996-2002, has witnessed a steady growth, both in qualitative and quantitative terms, of the Italian neutron scattering community. Today, thanks to the joint efforts of CNR and the former INFM (now merged into CNR) the Italian neutron community has reached a level of maturity that compares well with other countries in the European Union.

The idea of realizing an Italian experimental station at the world most powerful pulsed neutron source (ISIS, UK) is rather old and has been circulating among the members of the CNR *Neutron Spectroscopy Advisory Committee* for several years. However, it was only after the realization of the TOSCA spectrometer that this project could be finalized on a more concrete ground. The Italian Neutron Experimental Station (INES) was planned as a general-purpose facility, to be mainly used for testing of equipment, training, and development of neutron scattering techniques. It is worthwhile mentioning that the Committee, evidencing the importance that such a Test Station would assume in the applied sciences (Chemistry and Materials Science, Earth Sciences, Crystallography, etc.), had explicitly required that INES should be equipped with a neutron diffraction instrument. The project has been totally financed by the Italian *Consiglio Nazionale delle Ricerche* and was developed by a team of CNR researchers, in strict cooperation with several academic experts. At present, the construction and testing activity is concluded and the Italian Neutron Experimental Station is available for the whole Italian scientific community.

It is widely recognized that neutron diffraction is a very important tool for solving problems in condensed matter physics, chemistry and materials science. In particular, neutron diffraction plays an important role in technological problems where the localization and the quantitative measurement of residual stresses and strains can influence the performances of manufacts. In addition, the most recent techniques of data analysis (*e.g.*, Rietveld refinement applied to quantitative phase analysis and microstructure solution using the MAUD package) allow for a generalized qualitative and quantitative investigation of the samples. Finally, we should never forget that neutrons are characterized by a weak cross-section, at the atomic level, and therefore their penetration depth can easily reach several cm in almost all materials, including metals. This makes neutrons an almost ideal probe for *non-invasive*, *non-destructive* evaluation of the microscopic bulk features of almost any material. In this field, apart from the obvious *technological applications*, and the well-known diagnostic techniques in material science, another very important use of neutron diffraction is in the field of science applied to the study of *cultural-heritage artefacts.*

In general, the discovery and the detailed study of an ancient object or manufact originates a variety of problems that can be broadly grouped in two categories. First, one should determine the cultural and historical framework in which the object was produced. Second, it is crucial to determine the best conservation and/or restoration method. In this context, a careful material characterization analysis is of fundamental importance. In addition, this can be of great help in understanding the ancient manufacturing techniques, as well as the commercial and human exchanges between contemporary cultures. Several chemical, physical, and microstructural analysis techniques are available, with some of them less invasive than others. Among these, spectroscopic techniques using photons (*e.g.*, X-rays) or elementary particles (*e.g.*, neutrons) assume a relevant role thanks to their intrinsically non-destructive character. While the use of X-ray diffraction is quite diffuse in research laboratories, neutron diffraction is a relatively new technique that only recently has been applied to volume analysis of cultural-heritage manufacts [1, 2].

2. – Instrument description

INES is located on the N8 neutron beamline of ISIS, 22.8 m apart from the water moderator, downstream the inelastic spectrometer TOSCA. The neutron beam emerging from TOSCA is collimated to give a uniform square cross-section, of $\simeq 38$ mm size, at the INES sample position. The station is equipped with its own beam shutter so that the two instruments can operate almost independently from each other. On average, the samples measured on TOSCA remove between 5 and 10% of the neutron beam. Thus, INES can use between 90 and 95% of the nominal beam. The instrument is equipped with a time-of-flight (TOF) neutron diffractometer. In the actual configuration (see fig. 1), the diffractometer is equipped with 144 ^{3}He squashed detectors, grouped in 9 banks, each composed by 16 detectors, covering a range of about 160° on the horizontal scattering plane. The sample container is such that any ISIS standard sample environment equipment (*i.e.* furnaces and cryostats) can be placed in the instrument. That is made by a large vacuum tank (80 cm diameter and $\simeq 0.5$ m^3 effective volume) that allows the study of large objects, *including bulky archaeological artifacts*. In addition, this is equipped with four optical windows, where web cameras can be adapted for a visual inspection of the sample during the experiment. A diode laser device is also available, to visualize the center of the incident neutron beam, when using irregular samples [3]. Test measurements have shown that the instrumental features, in terms of counting efficiency and resolution, are extremely appealing and in full agreement with the design characteristics.

In table I, the main features of the TOF diffractometer are summarized. As we mentioned before, the primary flight path is rather long ($L_0 = 22.8$ m) and determines the good resolving power of the instrument. The minimum and maximum neutron wavelengths available on INES (λ_{min} and λ_{max}) are reported in the table caption. The resulting interval is mainly determined by the aperture and closure times of the nimonic chopper that is placed upstream the TOSCA spectrometer to reduce the noise effects produced by the fast neutrons. However, the actual selection of the recording TOF interval is chosen taking also into account the frame-overlap effect at the sample position of INES. The interval of momentum transfer (and d-spacing) that is available for each detector is also determined by the scattering angle 2θ according to the relations

$$Q = \frac{4\pi}{\lambda}\sin\theta, \tag{1}$$

$$d = \frac{2\pi}{Q}\,. \tag{2}$$

A selected sample of these intervals is illustrated in the table. We observe that a wide extension of momentum transfer ($\hbar Q$) and inter-plane spacing (d) is available using the whole set of 144 detectors. As we mentioned before, these are grouped in 9 banks and, usually, data analysis would produce 9 independent diffraction patterns at different

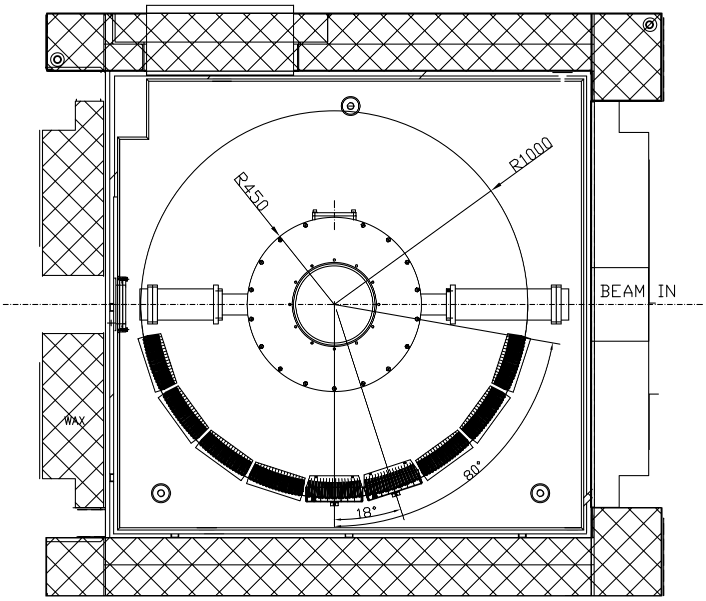

Fig. 1. – Schematic drawing of INES. The neutron beam enters from the right and the sample position is placed in the center of the figure. The nine detector banks are placed on a 100 cm radial position, covering an interval of scattering angles from 10° to 170°. The 80 cm diameter sample tank is also sketched. The upper half of the available space, on the right of the neutron beam, has been left free for testing of equipment and development of neutron instrumentation.

(nominal) scattering angles. This would allow to make texture analysis quick and easy. However, it is also possible to analyze the 144 patterns separately, at the expenses of a much longer acquisition time.

3. – Preliminary results

During the commissioning of the instrument, a careful calibration was carried out using a silicon powder sample (Si 640 C) in a vanadium container of 8 mm diameter. The Bragg peaks of silicon were reproduced with an accuracy better than 0.1%, on each detector, thus allowing for a very precise calibration of the secondary path and the scattering angles. The overall scattering throughput was measured using a cylindrical vanadium sample (10 mm diameter) and compared to a calculation based on the input monitor counting rate. For the calculation, we have taken into account all the geometric and technical characteristics of the instrument as well as the dimensions and shape of the sample. The results are shown in fig. 2 and evidence the good accuracy in the definition of all the instrumental parameters.

A polycrystal sample, characterized by a random and uniform distribution of preferred orientation regions is said to be free of texture. On the contrary, when regions showing preferred orientation of crystallites are observed, the sample is said to be textured. Texture is an important characteristics of metals, alloys, and ceramics. This is the result of the solidification process and therefore represents an important signature of the sample manufacturing history.

A preliminary test, aiming to evidence the possibility of performing texture analysis

TABLE I. – *INES main parameters: The neutron beam originates from the water moderator of ISIS. A NIMONIC chopper is located at 9.60 m from the moderator, to filter out the high-energy neutrons. This opens at* $t_{\min} = 724$ *µs and closes at* $t_{\max} = 10,339$ *µs (time is measured assuming that the proton beam hits the spallation target at* $t = 0$*) and selects the neutron wavelength interval (*$\lambda_{\min} = 0.17$ *Å,* $\lambda_{\max} = 3.24$ *Å). The primary neutron path at sample position is* $L_0 = 22.804$ *m, while the secondary path is* $L_1 = 1.000$ *m. In the table we report the data relative to the first detector of each bank (A-1, B-1, ⋯ , I-1) plus the last detector of the last bank (I-16). The resolution* $\Delta d/d$ *(HWHM) has been measured on the Bragg peak at* $d = 1.6375$ *Å of the silicon powder sample.*

Detector label	2θ (°)	$Q_{\min}$ (Å^{-1})	$Q_{\max}$ (Å^{-1})	$d_{\max}$ (Å)	$d_{\min}$ (Å)	$\Delta d/d$
A-1	170.6	3.85	62.62	1.63	0.10	0.0012
B-1	152.6	3.76	61.04	1.67	0.10	0.0012
C-1	134.6	3.57	57.96	1.76	0.11	0.0013
D-1	116.6	3.29	53.45	1.91	0.12	0.0015
E-1	98.6	2.93	47.62	2.14	0.13	0.0017
F-1	80.6	2.50	40.62	2.51	0.15	0.0020
G-1	62.6	2.01	32.63	3.13	0.19	0.0025
H-1	44.6	1.47	23.82	4.29	0.26	0.0035
I-1	26.6	0.89	14.44	7.07	0.44	0.0056
I-16	11.6	0.39	6.33	16.13	0.99	0.0130

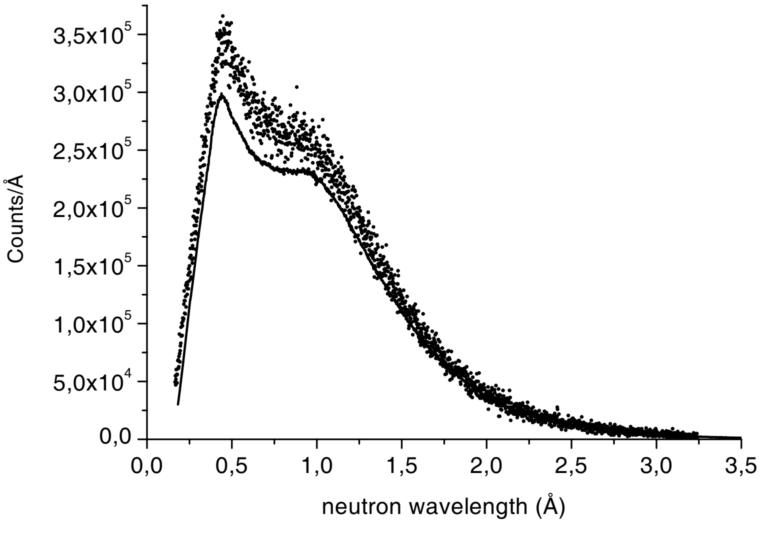

Fig. 2. – Comparison between measured spectrum N.16 (dots), and the one calculated using the geometric and technical characteristics of the instrument (line). The sample is a vanadium rod (10 mm diameter) while the distribution of the incident neutron flux is obtained from the calibrated input monitor.

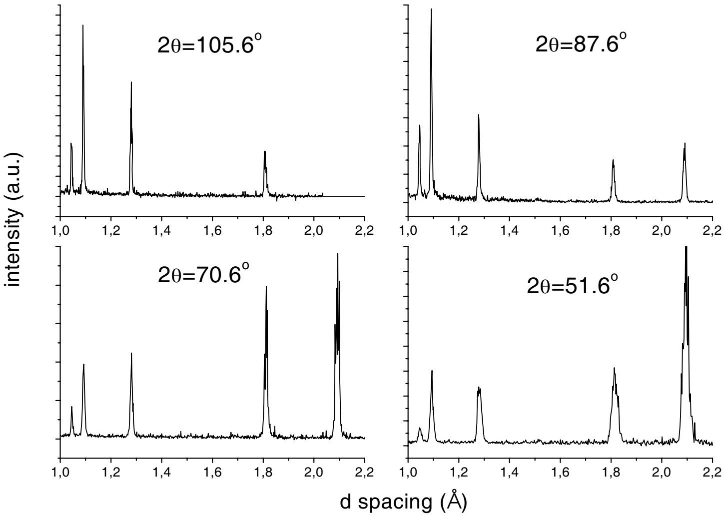

Fig. 3. – Measured texture of a Roman age bronze coin (average acquisition time $\simeq$ 1 hour). In the figure, we show four diffraction patterns, taken by four different detectors chosen at selected scattering angles. The large intensity variation of the various Bragg peaks is clearly visible.

of the samples, has been carried out on two different bronze sheets containing 2% and 4% (weight) tin, respectively. The sheets were prepared by mechanical rolling and straining along one axis. This produces a forced preferential orientation of the surface crystallites along the rolling direction. Measurements were performed with the beam axis perpendicular to the rolling plane and rotating the samples along the beam axis (ϕ). In spite of the weak texture level produced by this sample preparation method, we were able to observe, on both samples, a clear effect in the measured diffraction patterns both along the detector angle (θ) and along the sample rotation angle (ϕ).

A critical test of the instrument was performed using a Roman age bronze coin. This was oriented perpendicular to the beam and spectra were taken applying several rotations to the sample, around the beam axis, up to a final angle $\phi = 180°$. Thus, we were able to obtain a rather satisfactory mapping of the whole solid angle in less than 4 hours, with the possibility to obtain a full range of polar figures for all the peaks of interest. As an example, the potentials of the INES diffractometer are shown in fig. 3, where the high texture level of the Roman coin is clearly visible on four different diffraction patterns taken at various angular positions. In order to speed up measurement time and to obtain a more precise control on the sample rotation, a new automatic rotating device is under construction. This will permit to rotate small samples around the neutron beam axis and to obtain a full polar figure in a relatively short time (between 3 and 10 hours, depending on the scattering power of the sample).

The polar figure of a textured object represents the map of the crystallites domain orientation. This is a fingerprint of the production technique and can be of great help in following the historical evolution of the manufacturing techniques. Last, but not least, a good polar figure could be potentially used to distinguish a genuine archaeological object from a copy.

4. – Conclusions

The high penetration power of thermal neutrons into dense objects makes neutron diffraction a non-invasive, non-destructive, technique allowing one to obtain microscopic structural information, integrated over the scattering volume of the sample. This feature is particularly important for bulky metal manufacts of archaeological origin. The position of Bragg peaks gives a detailed information on the interplane distance at the atomic level which can provide information on residual stresses and strains and represent a signature of thermal history of the sample. In addition, texture analysis provides information on the preferred orientation distribution of crystal domains in the material. This knowledge can be of fundamental importance in corroborating or invalidating proposed manufacturing techniques.

At present, the INES experimental neutron station is equipped with a general purposes diffraction instrument allowing to measure any kind of standard samples, in an extended range of temperatures, with a very good resolution (see table). The wide sample chamber permits measurements on almost any kind of objects, even rather large and with irregular shapes such as, for example, industrial specimens and artefacts of historical interest. These can be carefully positioned into the neutron beam by visual inspection of the target position using a laser beam and a web camera. The scattered neutrons are collected by nine detector banks, each composed by sixteen elements of squashed ^{3}He tubes. The possibility of analyzing the signal from each single detector, coupled with the planned rotating device, will permit to obtain a full coverage of the scattering solid angle and the reconstruction of polar figures for almost any kind of samples. Thanks to these characteristics, INES can candidate itself as one of the most interesting neutron diffraction instruments for cultural-heritage samples.

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