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SOME EXAMPLES OF APPLICATIONS OF LASER MICRO RAMAN SPECTROSCOPY

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INTRODUCTION

Laser Raman spectroscopy has been recognized as a powerful technique for the determination and analysis of different compounds because of sharp and characteristic spectra which may be observed from a large variety of samples. The entry of Raman spectroscopy into the field of microanalysis can provide information which up to now has not been available from any other micro-analytical technique, such as electron or ion microprobing techniques. The goal of the present work is to estimate the possibility of experimental applications of laser micro Raman spectroscopy in the field of condensed matter physics.

EXPERIMENT

The Rudjer Bošković Institute in Zagreb is equipped with the Z 24 - DILOR Raman spectrometer. The basic configuration of this instrument (Fig. 1) results from the coupling of a conventional light microscope (Olympus BH-2) to a triple additive monochromator and photon counting detection followed by a data processing system. The 488 and 514.5 nm excitation light (Ar^+ laser) is focussed on a selected position of

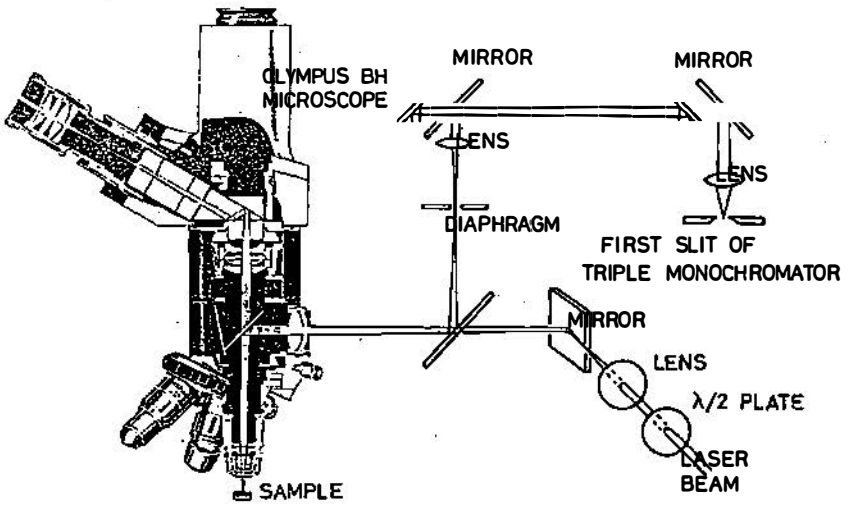

Fig. 1. Basic configuration of micro Raman spectrometer

the sample through an objective. The diameter of the laser spot in the focal point depends on the numerical aperture (NA) or the magnification of the objective.

The NA used in all experiments, as will be desoribed below, was 0.95 in vacuo (or 100x objective was used). In these conditions, using the laser line 514.5 nm, the diameter of the spot at the focal point is 0.6 μm. The depth of the focal point, measured from the surface, can be adjusted with a micro gauge with precision of 1 μm. The backward scattered light is collected by the same objective, passes through a beamsplitter, and enters the first monochromator through a system of three lenses (Fig. 1).

RESULTS

a) Identifications of ancient artists paint

The micro Raman spectroscopy, as a relatively new analytical method, has not yet been widely applied in art. Only several examples of its application have been published so far /1,2/.

A project of study of the colorants and pigments used in Croatian painting from XII to XVI century is under way. The obtained analytical data can give much useful informatior on the provenance of the painting, the origin of pigments that had been used, etc. We joined this project by applying micro Raman technique. The spectra presented show the presence of azurite ($Cu_2(OH)_2(CO_3)_2$) in the blue paint (Fig. 2) taken from the old crucifix (XIV century) situated in the church of St. Andrew on the island Čiovo near Trogir and gypsum ($CaSO_4 \cdot 2H_2O$) in the underlying ground layer (Fig. 3).

b) Investigations of the impurities in crystalline silicon

In general, impurities perturb phonon states. It results in changing of integral intensity and the FWHM of the phonon bends. The results presented in Fig. 4 show rapid increasing of the integral intensity and decreasing of FWHM for the phonon transition bend 520 cm^{-1} in silicon.

The observed increase of the integral intensity (Fig. 4 a) splits in several peaks when better spatial resolution is applyed (Fig. 4 b). Assuming that perturbation is caused by the presence of impurities, the observed phenomena could indicate the presence of different kind of impurities.

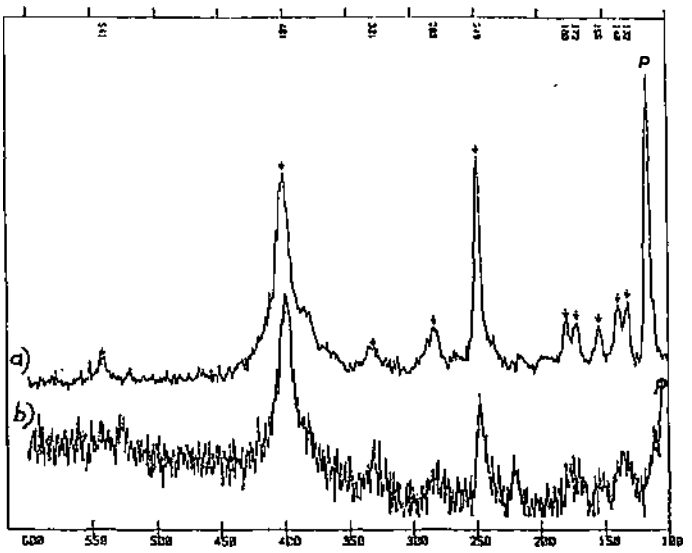

Fig. 2

a) Reference spectrum (mineral azurite - macro crystal); exciting line: 514.5 nm; 10 mW power at sample; step: 1 cm^{-1}; accumulation time: 1 s; slits width: 600 µm; P: plasma line.

b) Spectrum of the blue pigment (mineral azurite - micro crystal, 10 µm across); exciting line: 488 nm; 3 mW power at sample; step: 0.5 cm^{-1}; accumulation time: 1 s; slits width: 400 µm; P: plasma line.

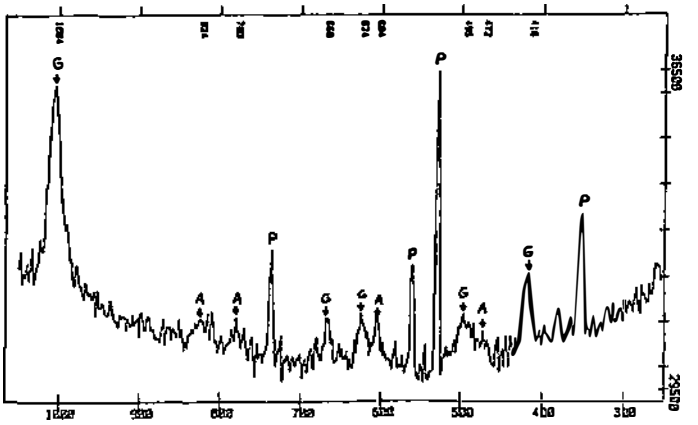

Fig. 3. Spectrum of undelying ground layer (gypsum - micro crystals, 3 µm across); exciting line: 488 nm; 6 mW power at sample; step: 1 cm^{-1}; accumulation time: 1 s; slits width: 600 µm; P: plasma line; G: gypsum line; A: lines of unknown compound.

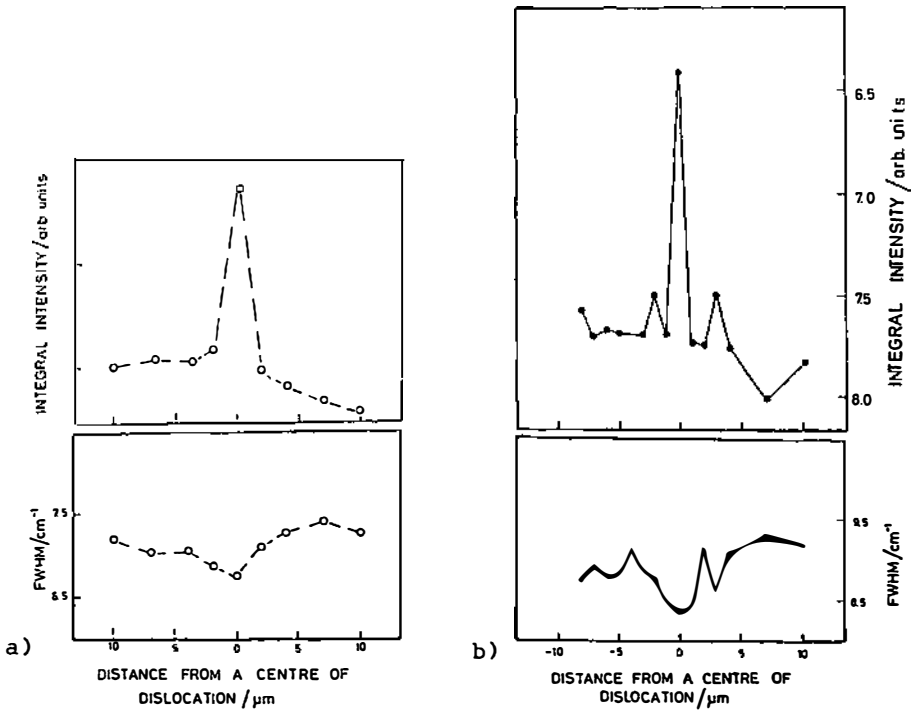

Fig. 4 Integral intensity and FWHM dependence on distance from the dislocation centre (μm); exciting line: 488 nm; 60 mW power at sample.

a) spatial resolution of the laser spot was 3 μm
b) spatial resolution of the laser spot was 0.6 μm

This conclusion is consistent with the results obtained at the grain boundary by secondary ion mass spectrometry /3/ which indicated the presence of oxygen and carbon in silicon.

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