

(groupe d'espace D_{6h}^4 avec $Z = 4$ atomes par maille), la théorie des groupes permet de prévoir le nombre et l'activité des phonons optiques du graphite à $\vec{K} = 0$:

$$\Gamma = 2 B_{2g} + 2 E_{2g} + A_{2u} + E_{1u}$$

Seuls sont actifs en Raman les deux modes E_{2g} , ce qui est en parfait accord avec l'expérience. Ils correspondent à des vibrations en phase (42 cm^{-1}) et en opposition de phase (1581 cm^{-1}) des atomes de carbone dans les plans graphitiques (1, 2). Les bandes observées sur le spectre Raman à plus hautes fréquences, entre 2400 et 3300 cm^{-1} , sont attribuées à des processus multiphonons (spectre Raman du deuxième ordre), correspondant à des harmoniques et combinaisons (2).

Lorsqu'on examine des carbones moins organisés, on note sur les spectres Raman la présence de la raie à 1581 cm^{-1} du graphite cristallisé, plus ou moins élargie et déplacée vers les hautes fréquences, mais aussi celle de nouvelles bandes vers 1350 et 1620 cm^{-1} , dont l'intensité augmente avec le désordre de la structure (2, 3). Nous retrouvons ces caractéristiques sur les spectres des composites carbone-carbone (figure 1). L'interprétation, actuellement admise, est que ces nouvelles raies sont dues à un effet Raman du premier ordre, induit par le désordre, et correspondraient aux maximums de la densité d'états à un phonon. Ainsi, dans les graphites mal organisés, les dimensions des cristallites ne peuvent plus être considérées comme étant infinies devant celles de la maille élémentaire, et l'on a une relaxation des règles de sélection. Maintenant sont actifs en Raman non seulement les modes de centre de zone correspondant à un vecteur d'onde nul, mais aussi des phonons à $\vec{K} \neq 0$, de sorte que le spectre Raman reflète la distribution de fréquence des phonons sur toute la zone de Brillouin (2, 3).

D'autre part, une relation empirique (3) a été établie entre la valeur du rapport d'intensité des raies à 1350 et 1580 cm^{-1} , et la dimension des cristallites constituant le carbone. Il faut noter, toutefois, que

cette relation n'exploite que très partiellement les données fournies par le spectre Raman puisqu'elle est basée sur l'intensité d'une seule raie nouvelle. Or, d'autres informations telles que les largeurs de raies, l'observation de vibrations harmoniques, etc., n'ont pu encore être exploitées. Par exemple, on peut noter que certains carbones très mal organisés (carbones vitreux) présentent des raies très nettes entre 2400 et 3300 cm^{-1} (2, 3) alors qu'elles sont complètement absentes pour d'autres échantillons (3). Ces observations n'ont pas encore trouvé d'explication et n'ont donc pu être exploitées.

Conclusion

Si l'on revient à nos résultats présentés sur la figure 1, on peut dire d'ores et déjà que la sonde Raman est un outil précieux pour la caractérisation *in situ* des carbones de matériaux composites. D'après nos spectres et les données antérieures tirées de la littérature, on peut, dans le cas présent (figures 1 b et 1 c), conclure que le carbone de la matrice est moins bien graphité que celui des fibres. Les dimensions des cristallites constituant ces carbones peuvent aussi être évaluées à partir de la relation empirique précédemment établie (3). On constate, d'autre part, qu'un traitement de la surface du composite dégrade considérablement l'organisation superficielle des carbones le constituant. Il est donc clair que les techniques d'analyse nécessitant un tel traitement vont donner des renseignements erronés quant à la texture des carbones de ces matériaux. Il apparaît enfin qu'une étude systématique des spectres Raman des carbones est nécessaire afin d'aboutir à une meilleure interprétation de ces spectres et par conséquent à une caractérisation plus précise des composites carbone-carbone.

Bibliographie

- (1) R. J. Nemanich, G. Lucovsky et S. A. Solin, « Lattice Dynamics », M. Balkanski Ed., Flammarion, Paris 1977, p. 619.
- (2) R. J. Nemanich et S. A. Solin, *Phys. Rev. B*, 1979, **20**, 392.
- (3) F. Tuinstra et J. L. Koenig, *J. Chem. Phys.*, 1970, **53**, 1126.
- (4) R. Vidano et D. B. Fischbach, *J. Amer. Ceram. Soc.*, 1978, **61**, 13.

Sample preparation and handling techniques for microanalysis with the Raman microprobe

by Mark E. Andersen (Walter C. McCrone Associates, Inc., Chicago, Illinois)

Techniques de préparation et de maniement des échantillons pour la microanalyse à l'aide de la microsonde Raman

Avec la venue du micro-Raman, une nouvelle technique pour l'analyse de petites particules nous est offerte. Le maniement de particules dont la taille se situe dans la gamme de 1 à 100 μm exige une précision rendue possible par les techniques développées pour d'autres instruments de microanalyse. Avec ces techniques, des particules de

dimensions inférieures à un micron peuvent être extraites de n'importe quel substrat et examinées, par exemple, au microscope polarisant, à la Mole, au SEM, au microscope électronique et à la microsonde ionique. Des adaptations spécifiques de cette technique, et d'autres, à la Mole, seront discutées.

With the introduction of micro-Raman instruments, Raman spectroscopists now have the capability of analyzing micrometer sized particles. Particle handling techniques and microscopy in general have not been widely utilized by most Raman are applicable to micro-Raman instruments especially the Mole. The purpose of this paper is to discuss microscopic techniques which are applicable to micro-Raman instruments especially the Mole.

Microscope illumination

The Leitz Orthoplan microscope, which is used in the Mole for focusing the laser beam and collecting the Raman scattered light, is a

flexible high quality instrument in itself. For analysis of small ($< 2 \mu\text{m}$) particles, high magnification and resolution are necessary to identify and position a particle with respect to the focused laser. Proper Köhler illumination of the specimen is necessary in order to achieve optimum resolution and contrast. This illumination set up is achieved by following a few simple alignment procedures specified in the Leitz User's Manual or standard references (McCrone and Delly, 1973).

Among the advantages of this illumination is an evenly illuminated field of view with variable depth of field. This is particularly useful when studying thick samples.

The incident illuminator of the microscope has been altered to allow

the laser beam to be focused on the sample. During the alteration the aperture diaphragm was discarded resulting in a loss of contrast. Reinstallation of this diaphragm will allow for greatly improved image quality.

Another potentially useful feature of the Leitz Orthoplan is its capacity for conversion to a polarized light microscope. Determination of optical properties such as pleochroism, birefringence, or optic sign may aid in the identification or orientation of small particles. Laser induced changes in the particles not visible in non-polarized light may be revealed by polarized light. In some circumstances darkground, phase contrast or interference methods may be useful in identifying particles or regions of interest for Mole analysis.

Particle handling techniques

Frequently it is necessary to identify single particles as small as 1 μm or even less. In order to do this various microanalytical tools must be employed either singly or in combination, including electron and ion microprobes, scanning electron microscopes (SEM) and transmission electron microscopes (TEM), micro x-ray diffraction cameras, polarized light microscope, and now Mole.

The key to utilizing these tools is particle handling capability. Using a few simple tools and techniques (McCrone and Delly, 1973; Teetsov, 1977), particles as small as 5 μm may be manipulated routinely and with a bit more care these same techniques may be extended to 1 μm sized particles. Although mechanical manipulators are useful in some circumstances such as when particles are being removed from small flat substrates, they are not nearly as flexible nor as rapid as direct handling of the tools. The Mole is useful in analyzing particles *in situ*, but substrate size, geometry, fluorescence, Raman emissions or particle thermal properties may favor removal to alternative substrates. The residual rubber cement or collodion used for particle handling is not detected during Raman analysis of the particles.

Once isolated a sample may be mounted upon any substrate convenient for analysis. If elemental data are needed, it is often convenient to use the Mole upon a particle mounted on a beryllium plate suitable for electron microprobe so that only one particle mount is necessary.

Substrate choice for Mole

The ideal substrate for Mole analysis is one which yields no fluorescence or Raman scattered peaks which interfere with the spectrum due to the particle of interest. Additionally the substrate should be colorless, transparent, optically isotropic (if polarized light is used for illumination), flat and clean. Thermal stability and chemical inertness are required. The substrate should also be capable of conducting laser generated heat away from the sample (Bennett and Rosasco, 1978).

Two substrates have been recommended in the past (Rosasco and Etz, 1977), corundum and lithium fluoride (LiF). Corundum has good thermal and chemical properties, but it yields an interfering spectrum and is optically anisotropic, *i.e.*, birefringent. LiF yields no first order spectrum but it is chemically reactive.

For most samples a glass microscope slide is an appropriate substrate although many slides show birefringence due to strain. For small particles the Raman bands due to the glass substrate begin to interfere. These particles may be mounted upon periclase (MgO). Cleavage fragments of periclase single crystals fulfill every requirement listed above. Where chemical inertness is not a requirement cleavage fragments of single crystal halite (NaCl) are readily available.

Immersion techniques

Two of the main problems confronting the micro-Raman spectroscopist are sample fluorescence and sample reaction or degradation induced by the laser beam. Exposure of the particle to

various solvents before or during analysis may reduce these problems.

Particles removed from some substrate or from suspension may have their surfaces contaminated with a small amount of fluorescent material which can interfere with the spectrum of the particle. Washing of the particle with various solvents (with which the particle does not react) using techniques mentioned above may remove the contaminant.

Immersion of particles in a liquid medium to inhibit their reaction was first proposed by Rosasco and Etz (1977), who coated ammonium sulphate crystals with oil to prevent reaction with water vapor in air. No evidence of spectral interference due this oil was reported.

The thermal properties of the substrate upon which a sample is mounted may aid in the dissipation of heat generated by the laser in the particle (Bennett and Rosasco, 1978). Cooling of the substrate and particle before and during probing may protect the particle from thermal decomposition, although condensation of may create problems. This technique depends upon the thermal conductivity of the sample itself. The rate of heat generation induced by the laser in a particle may exceed the rate of dissipation to the substrate and the particle will be destroyed no matter what the properties of the substrate are.

For a strongly light absorbing particle, the heat is generated very near its surface. The thermal properties of air in which the particle is immersed are not sufficient in many cases to remove this heat rapidly enough to protect the sample. One potential way of protecting the particle may be through the use of a cold dry gas stream passed over the particle. The gas would cool the sample surface yet not induce condensation upon the objective.

Water is widely used as a heat sink and its thermal properties are useful for Mole analysis. A particle of interest is first attached to the substrate using a very thin film of collodion or simply by suspending it in a non-reacting solvent (water) and allowing the solvent to completely evaporate. If the sample is a complete unknown there is obviously some danger of destroying it due to reaction with the solvent. Rapid use of very small droplets will minimize these dangers (Teetsov, 1977). For use with high power, short working distance objectives a very thin coverslip is prepared. After blowing a glass bubble with thin (5-20 μm) walls, an appropriately sized fragment is broken off to serve as a coverslip. Water is then introduced as an immersion medium and a spectrum may be recorded.

When a small (< 5 μm) crystal of naphthalene is examined in air, the laser induces sublimation and the crystal disappears before a complete spectrum is obtained. If very low power levels (< 20 mW laser output) are used the spectrum is too weak to record. Figure 1 shows the spectrum obtained from a 2 μm particle of naphthalene immersed in water with a glass substrate and coverslip. At least seven Raman lines are apparent and no interference due to glass or water is apparent.

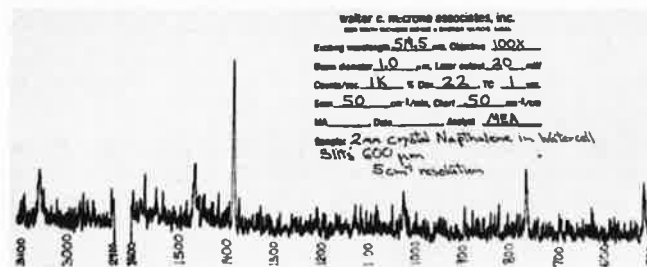


Figure 1.

Figure 2 shows the spectrum of a 2 μm crystal of goethite ($\alpha\text{-FeOOH}$) immersed in a water-glass cell. The crystal was orange colored and induced convection in the surrounding water when exposed to the 514.5 nm laser. The water was not observed to boil

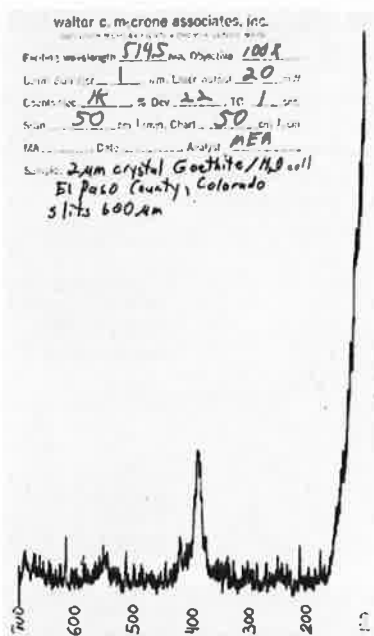


Figure 2.

and the crystal did not decompose. When a similar crystal was examined in air, decomposition occurred rapidly under the same conditions.

Within the same sample of goethite were many very small ($< 1 \mu\text{m}$) crystals of goethite in suspension. When exposed to the laser, the crystals appeared to become « trapped » within the laser beam presumably due to convection currents. These crystals remained in motion which likely enhanced their thermal stability. This effect may be useful in analyzing suspensions.

For particles which react with water, a low fluorescent immersion oil may be used instead of water. Figure 3 is the spectrum of a $20 \mu\text{m}$ crystal of ammonium carbonate immersed in an oil-glass cell. Comparison with the spectrum of the oil (figure 4) reveals distinct peaks at $180, 1030$ and 1045 cm^{-1} due to the crystal. In air the sample rapidly decomposes during analysis. The spectral interferences of the oil become more of a problem when the sample produces a weaker spectrum. Fortunately, the oil itself is a fairly weak Raman scatterer and « windows » are also present in the spectrum where no interfering oil peaks exist.

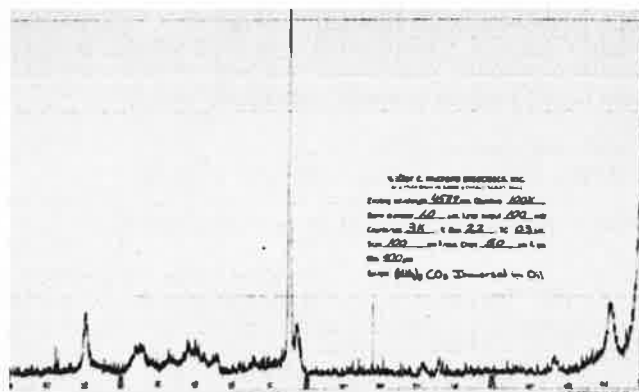


Figure 3.

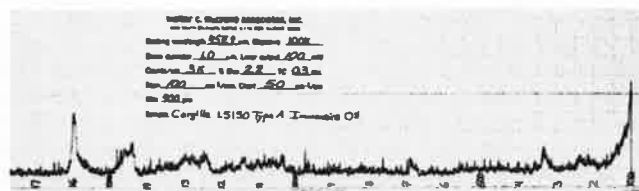


Figure 4.

This immersion technique may be used with the objectives which are supplied with the Mole. Oil and water immersion objectives are also available for this type of analysis eliminating the need of a coverslip.

Acknowledgments

The author wishes to thank Bob Muggli and Howard Humecki for many fruitful discussions and for reviewing this manuscript.

Bibliography

- H. S. Bennett and G. J. Rosasco, Heating microscopic particles with laser beams, *J. Appl. Phys.*, 1978, **49**, 640.
- W. C. McCrone and J. G. Delly, Particle Atlas Vol. I, Edition 2, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1973).
- G. J. Rosasco and E. S. Etz, The Raman Microprobe: a new analytical tool, *Research/Development*, 1977, **28**, 20.
- A. S. Teetsov, Techniques of Small Particle Manipulation, *Microscope*, 1977, **25**, 103.

Réactions en phase solide

par M^{me} M. C. Dhamelincourt-Deneufeglise, (C.N.R.S, Université des Sciences et Techniques de Lille, U.E.R. de Chimie, Laboratoire de spectrochimie infrarouge et Raman, 59650 Villeneuve d'Ascq, France)

Solid phase reactions

Numerous reactions between solids were studied using vibrational spectroscopy. Up to the present, this technique provided only a net indication of the total reaction. The Raman microprobe permits precise

observation of the reaction products formed at the interface due to the spatial resolution of the technique.

The reaction between copper sulphate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) and lead oxide (PbO) at ambient temperature is used as an illustration.

Les réactions solide-solide suivies par spectrométrie Raman sont habituellement réalisées par contact intime des réactifs sous forme de poudres. Les spectres obtenus ne donnent alors qu'un résultat global et ne permettent pas de suivre le développement des produits de la réaction à l'interface même des réactifs.

La microsonde Mole, de par sa capacité à analyser de très petits volumes d'échantillons, nous a paru particulièrement bien adaptée pour suivre les réactions au niveau de cet interface.

Nous avons suivi la réaction à température ambiante de l'oxyde de