

On the positive correlation of the D and D' bands in the first-order Raman spectrum of graphite with XRD-coherence length in [-110] and [110] crystallographic directions.

E. Sanchez-Cortezon, M. Dieterle, Y. Uchida, G. Mestl, M. Schur, R. Schlögl

E-mail: emilio@fritz-haber-institut.mpg.de

Introduction

In the literature on graphite Raman spectra, two additional Raman bands at 1333 and 1620 cm^{-1} are often reported. There is still debate on the exact origin of these two Raman modes: either they may arise due to a size-effect¹ or due to distorted carbon structures. An explanation of the simultaneous appearance of these two modes is not given in the literature. To possibly find an explanation for this phenomenon, a polycrystalline powder of graphite was submitted to mechanical milling and studied by Raman spectroscopy, TEM, and XRD. A mathematical model was calculated to find a correlation between these characterisation techniques. The pure spectral components of the Raman spectra of the milled graphite samples were determined and compared to the calculated phonon dispersion curves of graphite as reported in the literature. The appearance of two Raman-forbidden modes at 1333 and 1620 cm^{-1} in the first-order Raman spectrum of graphite is explained by the effect exerted of a reduced of crystallite size.

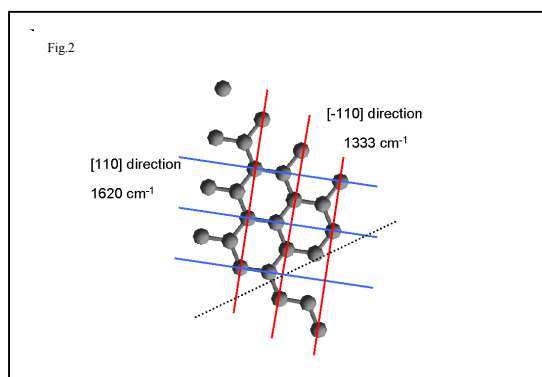
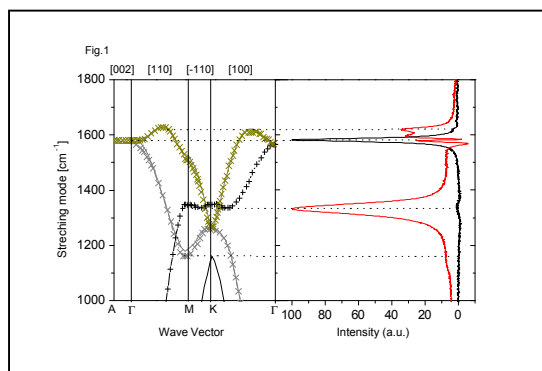
Experimental and Results

The samples were prepared from graphite AF-spezial (99.5 C % purity, Kropfmühl). The mechanical activation was conducted in an agate centrifugal ball mill. The milling variables under study were: the presence or absence of a nonpolar solvent, hexane, and the milling duration. The evolution of the structure was determined by X-ray diffraction in Debye-Scherrer geometry and by Raman spectroscopy with He-Ne-laser (632.8 nm) excitation. The mathematical model correlating Raman spectroscopic and XRD data was conducted by Partial Least Squares² (PLS) using MATLAB©. The identification of the pure spectral components in the Raman Spectra was done with the SIMPLISMA³ Toolbox running also under MATLAB©. With increasing milling time, the XRD coherence lengths of the [002] and [110] directions simultaneously decrease from 275 to 50 and 140 Å, respectively. This reduction in particle size is confirmed by TEM. The Raman spectra of the differently milled samples show the appearance of two additional bands at 1333 and 1620 cm^{-1} . PLS showed a positive correlation of the appearance of the Raman forbidden modes at 1333 and 1620 cm^{-1} with the decrease of XRD

¹ F. Tuinstra and J. L. Koenig. J. Chem. Phys. **53**, 1126 (1970).

² L. Eriksson, J. L. M. Hermens, E. Johansson, H. J. M. Verhaar and S. Wold. Aquatic. Sci. **57**, 3 (1995).

coherence lengths of the graphite structure. The SIMPLISMA analysis of the milled graphite samples revealed two pure spectral components: one associated with pristine graphite with one band at 1580 cm^{-1} and a second one with three main features at 1150 , 1333 , and 1620 cm^{-1} attributed to the decrease of XRD coherence lengths. The two spectral components are plotted together with the calculated phonon dispersion curves from graphite⁴, see Figure 1.



The size-induced Raman band at 1333 cm^{-1} of the second component is associated with a maximum phonon density of states on the dispersion branch in the $[-110]$ direction, and the size-induced Raman band at 1620 cm^{-1} is associated with a maximum phonon density of states on the dispersion branch in the $[110]$ direction. These two crystallographic directions are not similar and do not have similar d-spacing values. Figure 2 shows a scheme of a graphene sheet with these two crystal directions indicated which are related to these Raman-forbidden modes. Every disruption of a graphite layer will influence the coherence lengths in both directions as indicated by the dotted line.

³ W. Windig and S. Markel. J. Mol. Struct. **292**, 161 (1992).

⁴ R. Al-Jishi and G. Dresselhaus. Phys. Rev **B26**, 4514 (1982).



Conclusions

An explanation of the simultaneous appearance of the two Raman-forbidden modes at 1333 and 1620 cm^{-1} for disordered graphite was presented in this study. Raman measurements of disordered graphite showed the existence of two pure components: Pristine graphite which showed one Raman band located at 1580 cm^{-1} , and ill-defined graphite which showed two main bands located at 1333 and 1620 cm^{-1} , respectively. A positive correlation was found between the appearance of the Raman bands 1333 and 1620 cm^{-1} with the loss of long range periodicity of the graphite crystal reflections *002*, *100*, and *110*. The loss of long order periodicity in the [110] and in the [-110] direction occurs simultaneously and is positively correlated with the appearance of the 1333 and 1620 cm^{-1} bands. Hence, it can be concluded that the relaxation of the wave-selection rule due to the decrease of long order periodicity is responsible for the appearance of the two Raman-forbidden bands. These bands arise from nanocrystalline graphite and do not represent a new form of carbon. In contrast to the popular designation “disorder lines“, these bands indicate the presence of small but well-ordered graphite particles.