PHONONS IN GRAPHITE INTERCALATION COMPOUNDS

S.A. Solin

Department of Physics, Michigan State University, East Lansing, Michigan 48824, U.S.A.

Abstract. - Vibrational excitations in pristine graphite and in graphite intercalation compounds are discussed. Modes associated with carbon atom intralayer motions and with the internal excitations of guest molecular species are emphasized.

1. Introduction. - The study of phonons in graphite intercalation compounds (GIC's) is by now a relatively mature subject.^{1,2,3} The road towards this maturity is characterized by recent spurts in the growth of our knowledge of GIC's in general and of phonons in GIC's in particular. Not surprisingly, our understanding of phonons in-GIC's is intimately coupled to an understanding of phonons in pristine graphite itself.^{4,5}

During the past several years research efforts on vibrations in GIC's have focused on five sub-areas: phonons in pristine graphite,⁵ phonons associated with the intralayer motions of carbon atoms in GIC's,¹⁻³ internal molecular modes of guest species in GIC's,^{6,7} interlayer c-axis modes involving both guest and host layers,^{8,9} and intercalate intralayer modes.¹⁰ In this brief manuscript, I would like to address the first three of the above mentioned areas. Thus, this paper constitutes an introductory setting for the latter two topics which are under active investigation and are considered in other papers in this proceedings. Space limitations also preclude the presentation of introductory material on GIC's, staging, sample preparation techniques, etc. Readers unfamiliar with those topics are referred to recent review articles.^{11,12}

2. Pristine Graphite. - Hexagonal graphite crystallizes in the D_{6h}^{14} space group with four atoms in the primitive cell.¹³ The zone center optic modes can be group theoretically decomposed into the following irreducible representation¹⁴

$$\Gamma_{\text{opt}} = 2 E_{2g} + E_{1u} + A_{2u} + 2 B_{2g}$$

of which the E_{2g} modes and the E_{1u} and A_{2u} modes are respectively Raman and infrared active in first order. All of the optically active modes have now been observed experimentally.^{5,1} They are shown in Figs. 1 and 2 which also show the eigenvectors

Fig. 1: The Raman spectra obtained from a cleaved surface of graphite and the atomic displacements of the Raman active E_{2g} modes.

Fig. 2: The $E_{\perp C}$ and $E_{\parallel C}$ reflectance of graphite and the atomic displacements of the IR active modes. The $E_{\parallel C}$ spectrum has been normalized for surface damage.

Fig. 3: Phonon dispersion curves for graphite in the $[001]$, $[100]$ and $[110]$ direction. From ref. 16.

associated with each mode.

Of particular importance is the A_{2u} mode at 848 cm^{-1} . Prior to its observation, the available Raman, IR and neutron scattering data (the latter of which were limited to $< 500\text{ cm}^{-1}$) had been used to test several models for the phonon dispersion curves of graphite.¹⁵ Although each of the available theoretical models "fit" the available data, their calculated values for the A_{2u} frequency ranged from 800 cm^{-1} to 1400 cm^{-1} . Armed with the crucial A_{2u} frequency, Horie and coworkers¹⁶ constructed an axially asymmetric Born-von Karman model which provides phonon dispersion curves that are in excellent agreement with all the available experimental data. The results of their calculations are shown in Fig. 3. Note, in particular, that the maximum phonon energy is not at the Γ point, but occurs along the line between Γ and M.

This feature is consistent with, indeed required by, the second order Raman spectrum of pristine graphite.¹⁷

In more recent calculations¹⁸ G. Dresselhaus and coworkers using a similar model to that of Horie and coworkers have improved the fit of the lower most branches to the neutron data of Nicklow et. al.⁴ Thus, it is reasonable to assert now that the phonon dispersion curves of pristine graphite are well understood and can be accurately calculated.

3. Intralayer Modes in GIC's. - The initial approach to intralayer carbon modes in GIC's was the nearest layer model.¹⁹ In this model it was noted that in an n^{th} stage GIC $n \geq 3$, the E_{2g} 1580 cm^{-1} intralayer mode would develop a satellite caused by the small perturbation of the bounding intercalate layers. Thus for $n \geq 3$ the Raman spectra of GIC's will contain a pair of lines at $\approx 1580 \text{ cm}^{-1}$. One of these is associated with interior carbon layers which have a nearest layer environment identical to that in pristine graphite. One is associated with bounding carbon layers perturbed by the intercalated layer. In stages 1 and 2 GIC's there exists only one type of nearest layer environment and thus only a single line should be observed in the 1580 cm^{-1} region. The above statements are verified by the Raman spectra of potassium graphite GIC's²⁰ which are shown in Fig. 4. These spectra are characteristic of the stage dependence of the Raman spectra of all GIC's studied to date.¹ Moreover, the stage dependence of the relative intensities of the members of the 1580 cm^{-1} doublet can be quantitatively accounted for by the nearest layer model.¹

Fig. 4: Raman spectra of stage n , $n \geq 2$ K-GIC's with compositions $C_{12n}K$.

Stage 1 alkali GIC's exhibit a Raman spectrum which is characteristically different from those of Fig. 4, but which provide an elegant verification of the calculated dispersion curves of Fig. 3.¹ Note from the Raman spectrum of stage 1 RbC_8 and CsC_8 ²¹ shown in Fig. 5 the polarized members of a triplet of modes in the 580 cm^{-1} region.²⁰ This triplet is quantitatively accounted for by the dispersion curves of Fig. 2 and is associated with M point out of plane motions of the carbon atoms.¹ These M point modes which are first order Raman inactive in pristine

Fig. 5: Polarized Raman spectra of the triplet region for the stage 1 (a) Cs; and (b) Rb GIC's with the incident polarization perpendicular and the scattered polarization parallel to the scattering plane. Polarized modes (A_g or A_1) are forbidden in this configuration?

Fig. 6: Polarized Raman spectra of the intercalant intralayer modes of stage 1 FeCl_3 -graphite.

graphite are activated by both disorder induced scattering²² and Brillouin zone folding effects³ in the 3-D relatively ordered structures of stage 1 RbC_8 and CsC_8 .²³ The stage 1 alkali GIC's also exhibit a broad Fano resonance at $\approx 1500 \text{ cm}^{-1}$ (not shown) which arises from electron-phonon coupling between Raman active phonons in the $800\text{--}1600 \text{ cm}^{-1}$ range and what appears to be an electronic continuum background.²⁴

4. Internal Molecular Modes. - To date there is very little data on internal molecular modes of guest species in GIC's. This lack of data is not for want of serious efforts to observe such modes since several groups have made serious attempts in this regard.

The first observation of molecular modes in a GIC was that of Br_2 molecular modes in bromine graphite.⁶ However, the Raman spectrum of that material exhibits the multiple intense overtone peaks which are characteristic of strong resonance Raman scattering. The classic example of this phenomena is given in the Raman resonance spectrum of CdS .²⁵ To my knowledge the only other system in which internal modes of the guest species have been observed from a GIC is FeCl_3 graphite.⁷ The low frequency polarized Raman spectra of stage 1 FeCl_3 graphite is shown in Fig. 6.

The modes observed in that figure can be accounted for group theoretically and correspond to modes of the FeCl_3 sandwich layers from which pure FeCl_3 is constructed.

There is evidence that the Raman spectrum of FeCl_3 graphite was also obtained under resonance enhanced conditions.²⁶ Thus it appears that resonance enhancement is required in order to observe molecular modes in the Raman spectra of GIC's. A lack of such enhancement would account for the failure to observe molecular modes in GIC's prepared with HNO_3 , metal-ammonia solutions, AsF_5 , SbCl_5 and other intercalants.

5. Concluding Remarks. - This paper briefly touches upon some developments in our understanding of vibrational excitations in GIC's. For GIC's the molecular modes and carbon atom intralayer modes can only be conveniently probed using optical techniques, e.g. Raman scattering and IR spectroscopy. During the past year new and exciting neutron scattering results on interlayer guest-host modes in GIC's⁹ and on intralayer intercalate modes in monionic guest species¹⁰ have been reported. In addition the former have also been observed in the Raman spectra of several stages of alkali GIC's.⁸ These new neutron and Raman results are the subjects of other papers in this conference.^{8,10}

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