

Raman scattering in graphite-lithium intercalation compounds

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The Raman spectra of stage-1 and -2 graphite-lithium intercalation compounds are reported. The spectra show a sharp line at $\sim 1600 \text{ cm}^{-1}$ near the position of the graphite optic mode and a broad continuum from ~ 1000 to $\sim 4000 \text{ cm}^{-1}$ which can be correlated with the two-phonon Raman spectrum of graphite. Particular emphasis is given to the similarities and differences of Raman spectra in graphite-lithium compounds as compared with other donor and acceptor intercalation compounds.

I. INTRODUCTION

In the past several years Raman scattering has been used extensively to study the zone-center vibrational modes of graphite intercalation compounds.¹ Raman-active modes have been identified with carbon²⁻¹¹ and intercalate layer^{2,12} vibrations. More recently, infrared-active modes have been studied, contributing complementary information about the odd-parity carbon layer vibrations.^{9,13,14} Previous work emphasized the difference in behavior of the lattice mode structure between acceptor compounds and alkali-metal donor compounds, particularly with regard to the unique behavior of the stage-1 compounds C_8K , C_8Rb , and C_8Cs .^{3-5,7}

In this paper we report results of a Raman-scattering study of the stage-1 and -2 graphite-lithium donor compounds. The Raman spectra were taken at 4, 77, and 300 K and cover the spectral range $300\text{--}4000 \text{ cm}^{-1}$. The present paper focuses on aspects of the Raman spectra that are common for all alkali-metal donor compounds and those aspects that are dependent on the intercalate species. In particular, the unique features of the Raman spectra for the stage-1 donor compounds C_8K , C_8Rb , and C_8Cs are not found in C_6Li , in agreement with previous room-temperature studies on C_6Li by Zanini *et al.*⁶ In contrast, C_6Li shows a sharp line feature superimposed on an intense broad Raman continuum, which is distinctly different from the Raman spectra for the C_8X ($X = \text{K}, \text{Rb}, \text{and Cs}$) compounds. The sharp

line feature observed for both stage-1 and stage-2 graphite-lithium is identified with the graphite bounding layer E_{2g_2} mode. The mode frequencies $\omega(E_{2g_2})$ for these compounds are consistent with results previously reported for the downshift of $\omega(E_{2g_2})$ with increasing reciprocal stage ($1/n$) for all alkali-metal donor compounds.^{7,14} This frequency downshift has been interpreted in terms of an in-plane lattice expansion introduced by the intercalation process.¹⁴ The spectrum for stage-2 graphite-lithium also exhibits a broad structure identified with second-order scattering processes. Results, based on a Lorentzian line-shape analysis, are presented for the peak frequencies and linewidths for the sharp line features at 4, 77, and 300 K. The behavior of the Raman spectra for the alkali-metal donor compounds is also contrasted with the behavior of acceptor compounds.^{8-10,13}

II. EXPERIMENTAL DETAILS

The samples (dimensions $\approx 1 \times 2 \times 0.3 \text{ cm}^3$) were prepared from highly oriented pyrolytic graphite (HOPG), and intercalated in stainless-steel crucibles containing molten alkali metal. The procedures used for the preparation of graphite-lithium samples suitable for Raman-scattering measurements have been described elsewhere.¹⁵ Proper staging of the samples was confirmed by x-ray-diffraction scans of the (00 l) reflections using $\text{MoK}\alpha$ radiation. Raman spectra

were taken on three stage-1 and one stage-2 samples. For each sample, spectra from several regions of each *c* face were taken.

For measurements below room temperature, the Pyrex-encapsulated samples were mounted on a cold finger inserted into a Janis Vari-Temp Dewar. The cold finger was partially submerged in the cryogenic liquid with the sample positioned just above the liquid level. Raman-scattering measurements were carried out in the Brewster-angle backscattering geometry using low laser power (~ 20 – 50 mW) to avoid irreversible laser heating effects. The scattered light was analyzed with a double holographic grating spectrometer. A signal averager was used to add the spectra from consecutive scans.

III. DISCUSSION OF RESULTS

We first discuss the spectra for stage-1 graphite lithium shown in Fig. 1. The Raman spectra were taken at 4, 77, and 300 K and cover the frequency range from $300 < \omega < 3800$ cm^{-1} . As can be seen

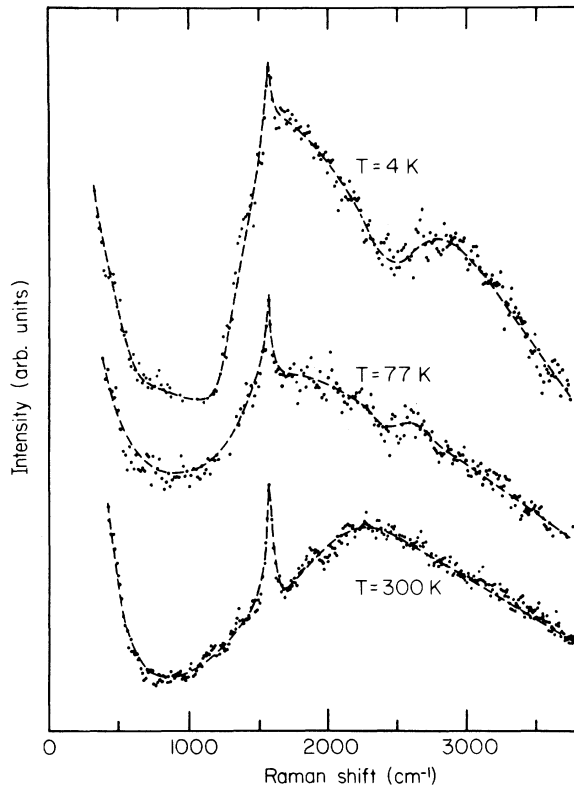


FIG. 1. Raman spectra for stage-1 graphite-lithium taken at 4, 77, and 300 K. A smooth curve has been drawn through the scattered experimental data points. The experimental parameters of the sharp E_{2g_2} bounding layer mode (see Table I) have been determined more accurately from other data involving a large number of scans and fitting to a Lorentzian line shape.

from the figure, the spectra consist of a broad continuum extending from ~ 1000 to 4000 cm^{-1} with a superimposed sharp peak at ~ 1600 cm^{-1} . The continuum scattering and the sharp peak both exhibit a significant temperature dependence. When the sample is cooled to liquid-helium temperatures, the continuum exhibits two distinct broad features, centered at ~ 1700 and ~ 2800 cm^{-1} . It is interesting to note that the position of the 1700-cm^{-1} maximum is near the peak in the one-phonon density of states for pristine graphite, while the 2800-cm^{-1} maximum is near the maximum in the two-phonon Raman spectrum of pristine graphite.¹⁶ Two distinct broad features are also found in the 77-K data, though the 300-K data show only a single broad peak. We identify the sharp feature with the zone-center (E_{2g_2}) intralayer mode associated with the bounding graphite layers.^{3,4} Values for the peak positions and linewidths for the sharp feature in Fig. 1 are given in Table I for the spectra at 4, 77, and 300 K based on a Lorentzian line-shape analysis.

The data for stage-2 graphite-lithium compounds (see Fig. 2) also exhibit a sharp feature peaked at ~ 1600 cm^{-1} , superimposed on a broad continuum extending to ~ 3800 cm^{-1} , as in the spectra for the stage-1 graphite-lithium compounds.

Some temperature dependence of the spectra is also observed for the stage-2 graphite-lithium compounds. By comparing the spectra in Figs. 1 and 2 we see that the intensity of the sharp feature is larger relative to the continuum for the stage-2 compound than for stage 1. In Table I are listed data for the peak positions and linewidths for the sharp feature observed in the stage-2 samples at the three temperatures indicated in Fig. 2.

The spectra in Figs. 1 and 2 for the graphite-lithium compounds differ from Raman spectra taken on other graphite intercalation compounds in several respects, though other features are similar to observations made on other intercalation compounds.

TABLE I. Graphite bounding layer mode frequency ω_0 and linewidth Γ for graphite-lithium compounds. Line-widths are given as full width at half maximum intensity.

Temperature (K)	Parameter	Values for stage 1 (cm^{-1})	Values for stage 2 (cm^{-1})
4	ω_0	1600 ± 3	1602 ± 4
	Γ	48 ± 4	28 ± 4
77	ω_0	1590 ± 3	1601 ± 4
	Γ	40 ± 4	27 ± 4
300	ω_0	1594 ± 3	1604 ± 4
	Γ	48 ± 4	33 ± 4

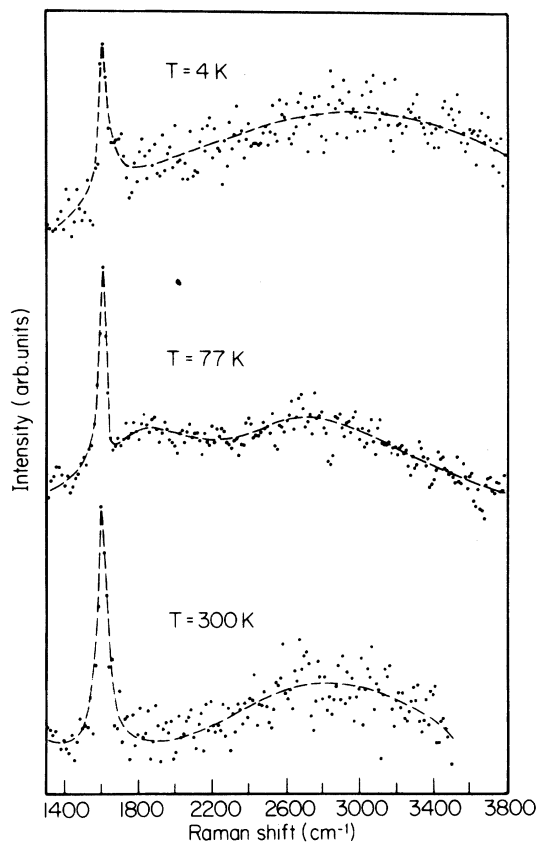


FIG. 2. Raman spectra for stage-2 graphite-lithium taken at 4, 77, and 300 K. (See caption to Fig. 1.)

Perhaps the most striking difference relates to the characteristics of the frequency-dependent continuum, which for the C_8X ($X = K, Rb, \text{ and } Cs$) alkali-metal donor compounds is strongly coupled to the E_{2g_2} zone-center mode,¹⁷ resulting in a broad asymmetric Breit-Wigner line shape^{3,4} for this coupled mode. In contrast, the frequency-dependent continuum in the graphite-lithium compounds does not couple to the E_{2g_2} zone-center mode, so that the resulting line shape is not of the Breit-Wigner form. Because of the similarities of the two-phonon spectrum in pristine graphite and in graphite-lithium, the continuum for the graphite-lithium compounds is identified with two-phonon processes, which at high frequencies ($\sim 2800 \text{ cm}^{-1}$) involves two optic phonons and at lower frequencies ($\sim 1700 \text{ cm}^{-1}$) an optic and an acoustic or low-frequency optic phonon. The frequency-dependent continuum in the case of the C_8X donor compounds can also be identified with a multiphonon process, but in this case the coupled phonons could include an optical graphite phonon with one or more intercalate phonons. These differences in behavior could be identified with a much

larger coupling between the graphite and intercalant for the case of the C_8X compounds which have much larger intercalate ionic radii than lithium in C_6Li . It is of interest to note that the two-phonon continuum is also observable for the stage-2 graphite-lithium samples, but has not been reported for stage-2 spectra with any other intercalants. Because of the low intensity of the sharp features near $\sim 1600 \text{ cm}^{-1}$, a high gain is used in taking the spectra in Fig. 2, favoring the observation of relatively weak second-order processes.

It should be also noted that no continuum features have been reported for the acceptor compounds. This is consistent with a weaker coupling between the graphite and intercalate layers for the acceptor compounds. Furthermore, the sharp graphitic features near 1600 cm^{-1} tend to be stronger for the acceptor compounds so that the lower gain used in taking typical spectra would deemphasize weak broad continuum structure, were such structures present.

Another contrasting feature between the spectra in first stage graphite-lithium and in first-stage C_8K , C_8Rb , and C_8Cs is the absence in C_6Li of the sharp feature observed near $\sim 560 \text{ cm}^{-1}$ in the C_8X compounds, in agreement with previous observations by Zanini *et al.*⁶ The 560 cm^{-1} structure, which has been identified with a zone folding of M_{1g} modes into the Γ point for the $p(2 \times 2)$ superlattice for C_8X ,³ would not be expected to occur in C_6Li , which exhibits a $p(\sqrt{3} \times \sqrt{3}) R 30^\circ$ superlattice^{18,19} that would fold K -point modes into the Γ point. Thus, as has previously been noted,^{6,11} the absence of a 560-cm^{-1} mode in C_6Li is consistent with the identification of this structure in the C_8X compounds with zone folding of the M_{1g} phonon mode.

The sharp feature in the stage-2 graphite-lithium compounds is associated with in-plane E_{2g_2} vibrations in the graphite bounding layers (E_{2g_2}) and exhibits the same behavior as in stage-2 compounds with the donor intercalants K, Rb, and Cs. In the case of graphite Rb, where Raman spectra have been taken on samples covering a range of intercalate concentrations,⁷ the mode frequencies $\omega(E_{2g_2})$ are found to soften as a function of increasing intercalate concentration or increasing reciprocal stage ($1/n$) as shown in Fig. 3. Also plotted on this figure are results for $\omega(E_{2g_2})$ for stage-2 graphite-lithium. These results are seen to be in good agreement with the results obtained for the other alkali-metal compounds. Little temperature dependence of the mode frequencies for the stage-2 compounds is found. We attribute the mode softening of $\omega(E_{2g_2})$ with increasing ($1/n$) to a lattice strain caused by the electron charge transfer to the graphite layers from the donor alkali-metal intercalants. The results of Fig. 3 indicate that the charge transferred to the graphite bounding layers for the lithium intercalant is comparable to that for other alkali-metal intercalants. It is also interesting to note

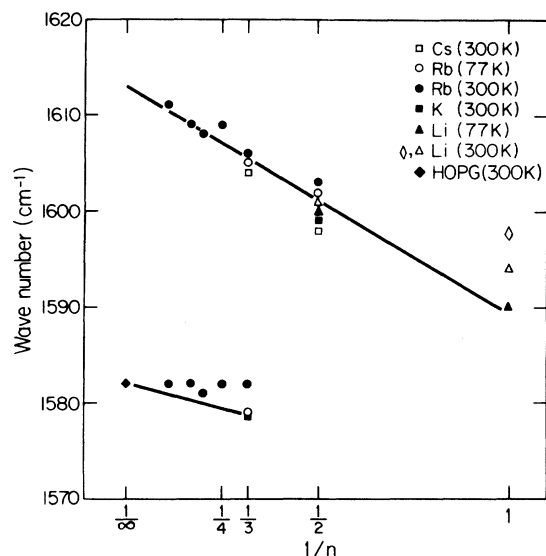


FIG. 3. Dependence of the frequency for the E_{2g_2} graphite bounding and interior layer modes vs reciprocal stage ($1/n$) for alkali-metal donor compounds. The results for graphite-lithium exhibit approximately the same linear dependence on ($1/n$) as do the other alkali-metal compounds. The results indicated by \bullet for Rb and \diamond for Li are taken, respectively, from Refs. 7 and 6.

that for the acceptor compounds with the intercalants FeCl_3 , AlCl_3 , and Br_2 ,^{9,10,13} the mode frequency $\omega(E_{2g_2})$ stiffens as a function of ($1/n$), which is opposite to the behavior observed in the donor compounds.

Also plotted in Fig. 3 are results for the stage-1 graphite-lithium samples. These results are seen to follow the ($1/n$) plot qualitatively and are consistent within the measured linewidth with previous results by Zanini *et al.*⁶ Departures from the ($1/n$) plot are generally expected for stage-1 compounds, since in this case the graphite bounding layer is surrounded by intercalate layers on either side, in contrast with higher stage compounds where the graphite bounding layer is surrounded by an intercalate layer on one side and a graphite layer on the other side. However, the departure of the stage-1 graphite-lithium data from the ($1/n$) plot is quite small, presumably because of the small size of the Li ion. On the other hand, for the alkali metals K, Rb, and Cs, the in-plane intercalate density is approximately 50% higher for stage 1 as compared with the higher-stage compounds. Furthermore, these stage-1 compounds exhibit a strong coupling of the E_{2g_2} mode to a frequency-dependent phonon continuum,¹⁷ and consequently a significant softening of the coupled mode is observed. Thus no attempt is made here to relate

the coupled-mode frequencies for C_8K , C_8Rb , and C_8Cs to the results plotted in Fig. 3. It should also be noted that the coupled-mode frequencies for these stage-1 compounds show little dependence on temperature.³ In contrast, a distinct stiffening of $\omega(E_{2g_2})$ is found in stage-1 C_6Li as T is lowered from 77 to 4 K (see Table I). This result is in contrast also with results for the stage-1 acceptor compound graphite AsF_5 for which $\omega(E_{2g_2})$ shows a small frequency upshift by about 3 cm^{-1} as the temperature is lowered from room temperature to 77 K.⁸ We note that Nemanich *et al.* have reported an increase of 2 cm^{-1} in the E_{2g_2} intralayer mode frequency of pyrolytic graphite in cooling from 300 to 12 K.⁴ As they point out, this stiffening would usually be expected to be associated with a decrease in the in-plane C-C bond length. However, a negative coefficient of linear expansion has been observed in the basal plane for single crystal²⁰ and pyrolytic graphite.²¹

The results in Table I for the magnitude and temperature dependence of the linewidth Γ (full width at half maximum intensity) for the stage-1 and -2 graphite-lithium sharp features are also of interest. The room-temperature value of Γ for C_6Li is ~ 9 times that for the stage-1 acceptor C_8AsF_5 and ~ 3 times that for pyrolytic graphite at 300 K. It is not understood why the linewidth for C_6Li is greater than that for pyrolytic graphite host, nor why the linewidth for the bounding layer graphite mode for the acceptors such as AsF_5 , FeCl_3 , and AlCl_3 is more narrow.^{8,9,13}

The graphite-lithium compounds studied in this work represent the simplest intercalation compounds from a structural point of view. Nevertheless, the lattice modes for these materials show zone-center modes considerably broadened from those of the host graphite material and no evidence for zone-folded K -point modes as would be expected from the $p(\sqrt{3} \times \sqrt{3}) R30^\circ$ superlattice in-plane structure, thereby suggesting the presence of a significant amount of in-plane disorder.

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- ¹M. S. Dresselhaus and G. Dresselhaus, *Physics and Chemistry of Materials with Layered Structures*, edited by F. Lévy (D. Reidel Publishing Co., Dordrecht, Holland, 1979), Vol. 6, p. 423.
- ²J. J. Song, D. D. L. Chung, P. C. Eklund, and M. S. Dresselhaus, *Solid State Commun.* 20, 1111 (1976).
- ³P. C. Eklund, G. Dresselhaus, M. S. Dresselhaus, and J. E. Fischer, *Phys. Rev. B* 15, 3180 (1977).
- ⁴R. J. Nemanich, S. A. Solin, and D. Guérard, *Phys. Rev. B* 16, 2965 (1977).
- ⁵N. Caswell and S. A. Solin, *Phys. Rev. B* 20, 2551 (1979).
- ⁶M. Zanini, L. Ching, and J. E. Fischer, *Phys. Rev. B* 18, 2020 (1978).
- ⁷S. A. Solin, *Mater. Sci. Eng.* 31, 153 (1977).
- ⁸P. C. Eklund, E. R. Falardeau, and J. E. Fischer, *Solid State Commun.* 32, 631 (1979).
- ⁹C. Underhill, S. Y. Leung, G. Dresselhaus, and M. S. Dresselhaus, *Solid State Commun.* 29, 769 (1979).
- ¹⁰C. L. Lau and M. S. Dresselhaus, *Phys. Rev. B* 21, 3635 (1980).
- ¹¹M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, and D. D. L. Chung, *Mater. Sci. Eng.* 31, 141 (1977).
- ¹²P. C. Eklund, N. Kambe, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* 18, 7069 (1978).
- ¹³G. M. Gualberto, C. Underhill, S. Y. Leung, and G. Dresselhaus, *Phys. Rev. B* 21, 862 (1980).
- ¹⁴S. Y. Leung, C. Underhill, G. Dresselhaus, and M. S. Dresselhaus, *Solid State Commun.* 33, 285 (1980).
- ¹⁵M. Zanini, S. Basu, and J. E. Fischer, *Carbon* 16, 211 (1978); S. Basu, C. Zeller, P. J. Flanders, C. D. Fuerst, W. D. Johnson, and J. E. Fischer, *Mater. Sci. Eng.* 38, 275 (1979).
- ¹⁶R. J. Nemanich and S. A. Solin, *Phys. Rev. B* 20, 392 (1979).
- ¹⁷P. C. Eklund and K. R. Subbaswamy, *Phys. Rev. B* 20, 5157 (1979).
- ¹⁸D. Guérard and A. Héroid, *Carbon* 13, 337 (1975).
- ¹⁹N. Kambe, M. S. Dresselhaus, G. Dresselhaus, S. Basu, A. R. McGhie, and J. E. Fischer, *Mater. Sci. Eng.* 40, 1 (1979).
- ²⁰J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London* 57, 477 (1945).
- ²¹B. T. Kelley, W. H. Martin, and P. T. Nettle, *Philos. Trans. R. Soc. London Ser. A* 260, 37 (1966).