Synthetic Metals, *12* (1985) 97- 102

CHARGE-TRANSFER-INDUCED CHANGES IN THE ELECTRONIC AND LATTICE VIBRATIONAL PROPERTIES OF ACCEPTOR-TYPE GICS

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ABSTRACT

We report on several charge-transfer-induced changes in the electronic and phonon properties of stage 1 and 2 graphite-H_2SO_4: c-axis LO and LA phonon dispersion, E_{2g} ($q = 0$) intralayer graphitic phonon frequency, and resonant Raman scattering from the E_{2g} modes. The data are discussed in terms of microscopic models.

INTRODUCTION

Graphite-H_2SO_4 compounds were discovered in 1841 by Schaufhautl [1]. They have been rather extensively studied in the past ten years [2]. These compounds are prepared in an electrochemical cell by the anodic oxidation of graphite in H_2SO_4. Using low cell current the graphitic anode will evolve through a sequence of decreasing stage index compounds with a chemical formula given by $C_p^+HSO_4^-(H_2SO_4)_x$, where p is monitored by the total electrochemical charge Q passed during the reaction. Recent simultaneous studies of coulometry, (00ℓ) x-ray diffraction, and dilatometry by Bessenhard et al. [2] have refined somewhat the previously reported ranges for p which correspond to the respective stage 1-4 compounds. The graphite-H_2SO_4 compounds are of particular interest to the field of graphite intercalation compounds (GICs), because stage 1 and 2 compounds can be prepared with unusually wide ranges of charge transfer $f = 1/p$: $\sim 1/60 < f < 1/48$ (stage 2) and $\sim 1/28 < f < 1/21$ (stage 1). Graphite-H_2SO_4 therefore provides an excellent opportunity to study the role of charge transfer on a variety of physical properties of acceptor-type GICs.

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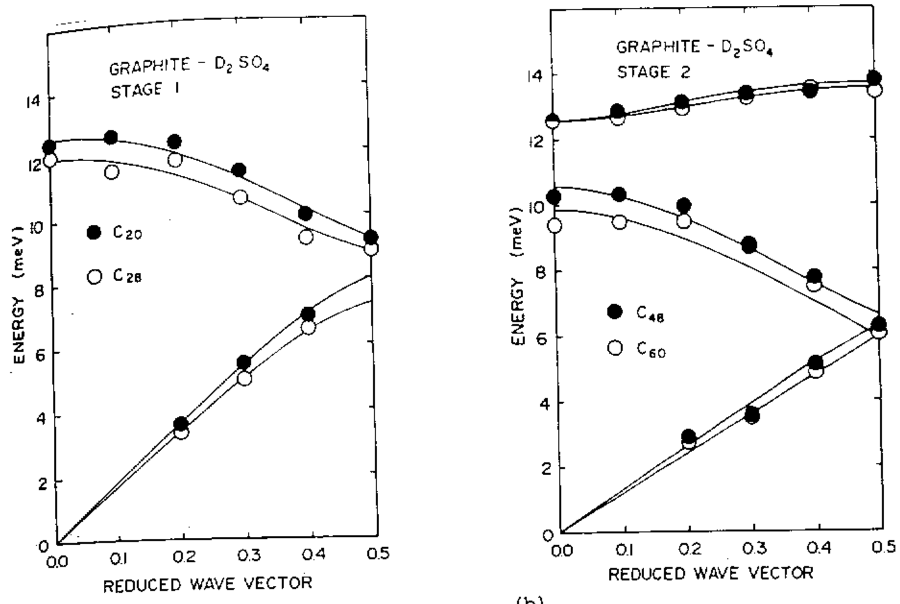
0379-6779/85/$3.30

We have carried out several studies in graphite-H_2SO_4 to explore the role of charge transfer on the lattice constants and the electronic and the phonon properties: (1) the c-axis separation between successive intercalate layers, (2) the in-plane carbon-carbon bondlength, (3) the c-axis LA and LO phonon dispersion, (4) the frequency of the zone-center, Raman-active (E_{2g}) intralayer graphitic modes, and (5) the laser frequency dependence of the Raman scattering cross section of these modes. Items (1) and (2) are reported in a separate paper in these proceedings [3]. The results of items (3)-(5) are presented herein.

C-AXIS LA AND LO PHONON DISPERSION

Inelastic neutron scattering experiments were carried out at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). The samples were prepared *in situ* on a triple axis instrument using a constant cell current which produced a stage 1 (p = 21) sample in ∿3.5 days. The electrochemical cell was constructed from quartz. D_2SO_4, rather than H_2SO_4, was used for the electrolyte, because hydrogen strongly absorbs thermal neutrons. The evolution of the sample was monitored using the (00ℓ) reflections. As the stage 1 or 2 compounds evolved with time (or charge Q) from the low to the high charge-transfer state, the c-axis was observed to undergo a continuous contraction and the c-axis phonon branches were observed to upshift in frequency. The (00q) LA and LO data presented here are representative of the end point stage 1 or 2 compounds exhibiting the lower or upper limit for the respective c-axis repeat distance. The cell current was reduced by a factor of ∿100, while the phonon data were being acquired.

The stage 1 and 2 c-axis phonon dispersion is shown in Figs. 1a and 1b. The high and low charge-transfer data are represented by the solid and open circles, respectively. The solid lines are calculated using a rigid ion model with interactions including first and second nearest neighbors. The model also treats the intercalate layer as a rigid sheet. Initial calculations modeled the intercalate layer as a nonrigid, three-layer sandwich (O_2-S-O_2) with force constants assigned to yield high frequency c-axis molecular branches consistent with available Raman and infrared data on H_2SO_4. The calculated phonon branches at lower frequency, corresponding to those shown in Figs. 1a,1b, were found to shift insignificantly in energy as the SO_4 internal force constants were raised to the rigid layer limit. Subsequent calculations were therefore carried out in this limit. The calculated dispersion curves shown in the figures are based on a set of force constants determined from a least squares fit to the data and are listed in Table I. Examination of the nearest neighbor force constants in Table I shows that (1) the C-C force constant in stage 2 is nearly equal to that of HOPG; (2) the C-SO_4 force constant in stage 2 is nearly equal to that of



(a) (b)

Fig. 1 (a, b). LA and LO c-axis phonons in graphite-D_2SO_4.

Table I. Interplanar Force Constants (10^3 dyn/cm) for $C_p^+HSO_4^-(H_2SO_4)_x$ per C-Atom.

Stage	P	Nearest Neighbor		Next Nearest Neighbor		
		C - C	C - SO_4	C - C	C - SO_4	SO_4 - SO_4
1	∿20		1.97	-0.010		-0.12
1	∿28		1.78	0.002		-0.18
2	∿48	2.65	2.01	0.064	-0.13	
2	∿60	2.81	1.82	-0.016	-0.18	
HOPG	∞	2.81		-0.041		

stage 1, indicating that the primary contribution is from elastic forces rather than electrostatic forces; and (3) the charge-transfer-dependent change in the force constants is as expected, considering the sign of the net charge on the respective layers. Modeling of a c-axis potential function, which can explain the charge transfer effect on the c-axis phonons as well as on the c-axis repeat distance, is currently under way.

RESONANT RAMAN SCATTERING FROM THE E_{2g} HIGH FREQUENCY GRAPHITIC PHONONS

Resonant Raman scattering is a common phenomenon in semiconductors and insulators. In these solids the resonance in the scattering cross section occurs when the incident photon energy E matches either an exciton band or an optical band gap. We find that the cross section for light scattering from the high frequency (∿1600 cm^{-1}) E_{2g} graphitic phonon peaks at an energy equal to the threshold for interband absorption. We suggest that this is a general phenomenon observable in other Raman-active metals. In Figs. 2a and 2b we display the superposition of the normalized cross section σ/E^2 and ε_2 in the vicinity of the valence-to-conduction interband threshold for the $C_{28}{}^{+}$ (stage 1) and the $C_{48}{}^{+}$ (stage 2) compounds. The data were collected using techniques described elsewhere [4]. We define the normalized cross section to be $N/P{\cdot}T{\cdot}E$, where N is the net peak count under the ∿1600 cm^{-1} phonon line, P is the incident laser power, T is the spectrometer transmission, and E is the incident photon energy. The peak in the normalized cross section is seen to be in close proximity to the center of the respective interband threshold. Similar data are observed for the $C_{60}{}^{+}$ and $C_{21}{}^{+}$ compounds. The dashed lines in the figures (Lorentzians) are seen to fit the data (+) reasonably well. However, calculations to be described briefly below result in a much more complex functional representation for the normalized cross section which is slightly asymmetric. The scattering model invokes the usual three-step process utilizing the $\vec{A}\cdot\vec{p}$ interaction: (1) absorption of the incident photon causing an interband transition, (2) the scattering of the excited electron or hole, (3) the emission of the scattered photon while recombining the electron and hole. The calculation was carried out in the framework developed by Camley and Mills [5] for backscattering in opaque materials and takes explicit account of the interband and electron(hole)-phonon matrix elements and the lifetime of the excited electron. In Fig. 3 we display the data and the theoretical fit for the $C_{28}{}^{+}$ compound. The near Lorentzian character of the calculated normalized cross section and the good agreement between theory and experiment are evident.

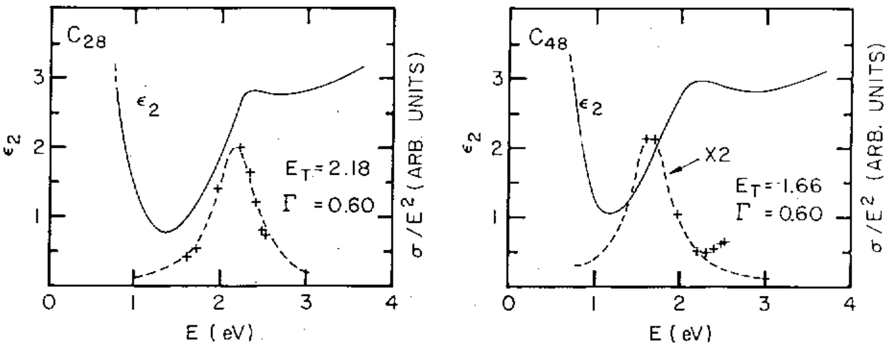


Fig. 2. Imaginary part of the dielectric function $\varepsilon(0,\omega)$ and normalized cross section σ/E^2 vs photon energy E. The dashed curve is a Lorentzian fit to σ/E^2.

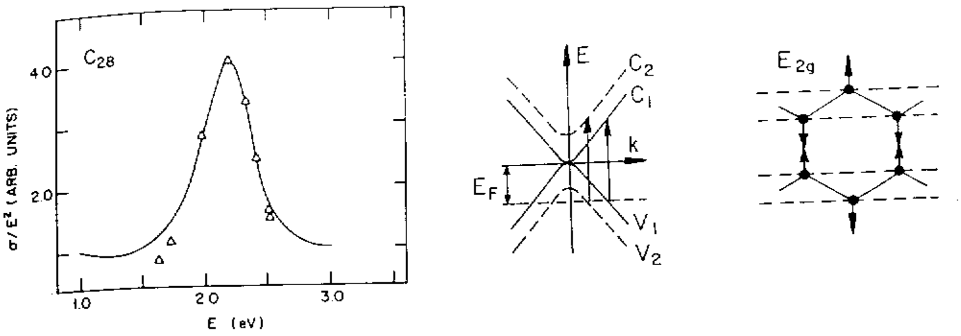


Fig. 3. Calculated (solid line) and experimental cross section vs photon energy. Band structure shown is for stage 1 (solid bands) and stage 2 (solid and dashed bands).

CHARGE-TRANSFER-INDUCED SHIFTS IN THE E_{2g} GRAPHITIC PHONON FREQUENCY

Increasing charge transfer for fixed stage index has an effect on the intralayer graphitic phonons similar to that which we observe in the c-direction. With increasing charge transfer f, a continuous contraction in the in-plane C-C distance d_{C-C} [3] is observed, which is expected to stiffen the intralayer bonds and thereby up-shift the E_{2g} high frequency graphitic phonons. This in-plane phenomenon has been studied theoretically by Pietronero and co-workers in the limit of high stage index [6,7]. In the graphite-H_2SO_4 system, we are provided an unusual opportunity to observe this effect in the stage 1 and 2 compounds, as a continuous function of charge transfer. As in the case of the interlayer c-axis phonons, this GIC system allows the observation of the direct effect of charge transfer on the intralayer phonon frequencies, because during the "overcharge" periods there occurs a minimal change in the character of the intercalate layer (hydrogen is exchanged with the electrolyte, and the concentration of SO_4 tetrahedra remains constant). In Fig. 4 we display the results of an *in situ* study of the zone center intralayer phonon frequency as a function of charge transfer. The (+) and (x) indicate data collected above and below the acid level, respectively. The data superimpose during the periods where hydrogen is exchanged (and the stage index is fixed) and differ when the bulk is in the mixed stage condition. During the "overcharge" intervals ($C_{60}^+ \rightarrow C_{48}^+$ and $C_{28}^+ \rightarrow C_{20}^+$), the intralayer frequency is observed to exhibit a linear dependence on Q/M, where Q is the electrochemical charge and M is the initial HOPG mass. From the slopes of the lines L1 and L2, we calculate the derivative of the intralayer frequency with respect to charge transfer $f = 1/p$: $d\omega/df = 460 \pm 30\ cm^{-1}$ (stage 1) and $d\omega/df = 1050 \pm 120\ cm^{-1}$ (stage 2). We may then calculate the derivative $d\omega/da = (d\omega/df)(df/da)$, where $a = d_{C-C}$. Using the

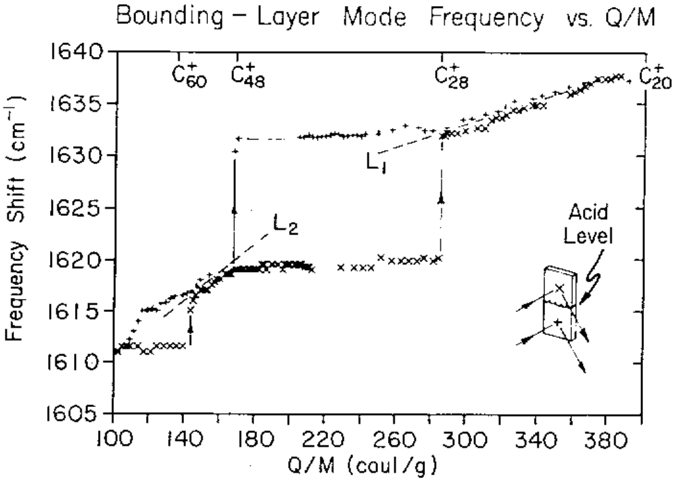


Fig. 4. E_{2g} graphitic intralayer phonon frequency vs Q/M.

results of Ref. 3 for df/da, we arrive at values for $d\omega/da$: $1.1\pm0.2\text{x}10^{4}\ \text{cm}^{-1}/\text{Å}$ (stage 1) and $1.3\pm0.2\text{x}10^{4}\ \text{cm}^{-1}/\text{Å}$ (stage 2). These values are quite similar. This suggests that the interplanar coupling of the next-neighbor carbon layers in stage 2 plays a small role, and therefore a theory of a single carbon layer should explain the dominant contribution to the charge transfer dependence of the frequency shift in both the stage 1 and 2 compounds.

ACKNOWLEDGMENTS

We thank R. M. Nicklow of ORNL for making available to us the neutron scattering facilities at the HFIR. The Ames Laboratory and ORNL are operated, respectively, for the United States Department of Energy (USDOE) by Iowa State University under contract no. W-7405-Eng-82 and by Martin Marietta Energy Systems, Inc., under contract no. DE-AC05-84OR21400. Research at the University of Kentucky was supported by the USDOE under grant no. DE-FG05-84ER45151.

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