

Charge-Transfer-Induced Shifts in the C-Axis Longitudinal Phonons of Graphite-H₂SO₄

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Introduction

The stage 1 and 2 graphite intercalation compounds (GIC's) formed by the electrochemical reaction of graphite with sulfuric acid (H₂SO₄) can be prepared with a wide range of charge transfer values. For a given stage compound, the charge transferred between carbon and intercalate layers is changed by the electrochemical conversion of H₂SO₄ to negatively charged HSO₄⁻ in the intercalated layers [1]. This relatively small change in the chemical character of the intercalate layer makes graphite-H₂SO₄ an ideal system to study the effect of charge transfer on the electronic and lattice dynamical properties of acceptor-type GIC's. In another paper at this conference [2], we present results of neutron diffraction studies carried out on graphite-H₂SO₄ which show that, as the stage 1 and 2 compounds undergo increases in charge transfer, both the c-axis and a-axis lattice constants contract. These contractions would be expected to lead to an upshifting in frequency of both the in-plane and out-of-plane graphitic modes. Recent Raman scattering studies [3] report that the ~1600 cm⁻¹ intralayer graphitic phonons upshift linearly with increasing charge transfer in both the stage 1 and 2 compounds. In this paper we report the results of inelastic neutron scattering studies of the c-axis longitudinal phonons of stage 1 and 2 graphite-H₂SO₄. The c-axis phonons are also observed to upshift with increasing charge transfer. The data are analyzed in terms of a phenomenological force constant model in which the H₂SO₄/HSO₄⁻ layer is treated as a rigid molecular sheet.

Experimental Details

Plates of highly-oriented-pyrolytic-graphite (HOPG) obtained from Union Carbide were electrochemically reacted with 98% D₂SO₄ (Ventron-Alpha) using a constant current source (~100 microamps). Deuterated H₂SO₄ is used in these studies because hydrogen has a high absorption coefficient for neutrons. At these currents, with the initial graphite masses

used, a time of ~70 hours was needed to reach the stage 1 C₂₁⁺(HSO₄⁻)(H₂SO₄)_{2.5} compound. The cell current was reduced to ~1 microamp while the phonon data was being recorded, which essentially fixed the sample stoichiometry during the data collection period. The samples were suspended in the acid by a platinum clip, and a Pt-foil counter electrode was used to complete the electrochemical circuit. Throughout the paper we abbreviate the sample stoichiometry by the form C^{+p}. The charge transfer is then f=1/p holes per C-atom. The neutron data were taken using a triple axis spectrometer in the High Flux Isotope Reactor (HFIR) facility at the Oak Ridge National Laboratory.

Results and Discussion

In Fig's 1a and 1b we display, respectively, the results for the low- and high-charge-transfer forms of the stage 1 and 2 compounds. The experimental data are indicated by the symbols and the results of our model calculations are indicated by the solid lines. The data were taken on pure stage compounds as determined by (001) elastic scattering scans. A phenomenological force constant model was used to analyze the data. In the calculations the intercalate layers were treated as rigid units. This reduces the size of the dynamical matrix to a 2x2 for stage 1, and a 3x3 for stage 2. The justification for this approximation is that the S-O bond stretching frequency is a factor of ~10 larger than the observed (q=0) stage 1 LO phonon frequency. As can be seen in Fig's. 1a and 1b, treating the molecular layer as rigid is evidently a good approximation, as the data are reasonably well described by nearest neighbor force constants only. These force constants are shown schematically above the data in Fig's. 1a and 1b. In the case of the stage 1 compound, the fit was improved slightly by adding the second neighbor force constant (C). The values for the respective force constants are listed in the figures in the units eV²-amu. To put these units into perspective, a good fit

to the c-axis LA and LO phonon data [4] for pristine graphite (HOPG) was obtained using only nearest-neighbor forces, with the force constant value $D = 0.0176 \text{ eV}^2\text{-amu}$. The effect on the LO branch due to the maximum charge transfer increase during the stage 1, 2 "overcharging" periods, as the electrochemical conversion of H_2SO_4 in the intercalate layers is called in the literature, is about 0.5-0.7 meV. The corresponding change in the force constants, as determined by the data analysis, is indicated in the figures. For the case of the stage 1 compound, the LO branch upshifts by 0.7 meV as the charge transfer increases from $f=1/28$ to $f=1/21$. In the stage 2 case, the lower LO phonon branch upshifts by 0.5 meV, whereas the upper LO branch remains essentially unchanged as the charge transfer f increases from $1/60$ to $1/48$. These observations will be discussed in terms of the nature of the long and short range elastic and electrostatic forces between the layers.

Acknowledgements

This work was supported in part by

grants from the USDOE #DE-AC05-84OR21400 and #DE-FG05-84ER4515. It is a pleasure to acknowledge helpful discussions with Prof.s K.R. Subbaswamy and G.W. Lehman.

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*The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This work supported by the Director for Energy Research, Office of Basic Energy Sciences.

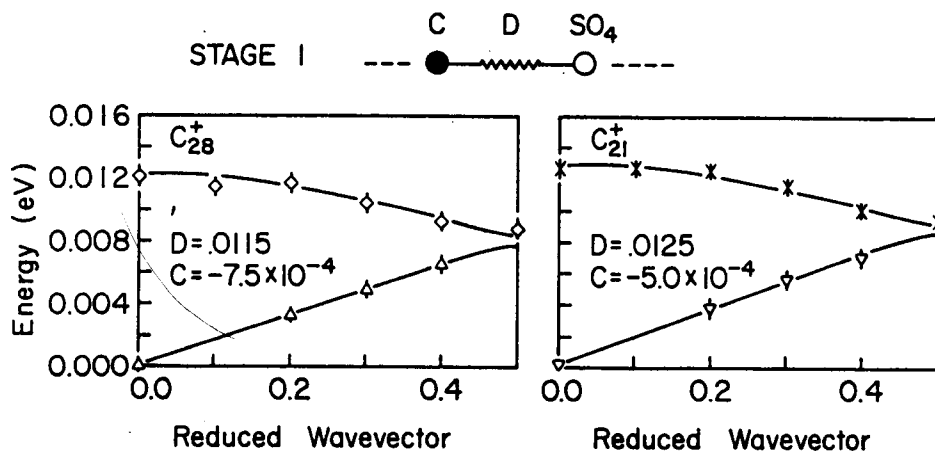


Fig. 1A

C-axis LA, LO phonon frequency vs reduced wave vector for stage 1 C_{28}^+ & C_{21}^+ graphite- H_2SO_4 . The solid line represents the calculated dispersion.

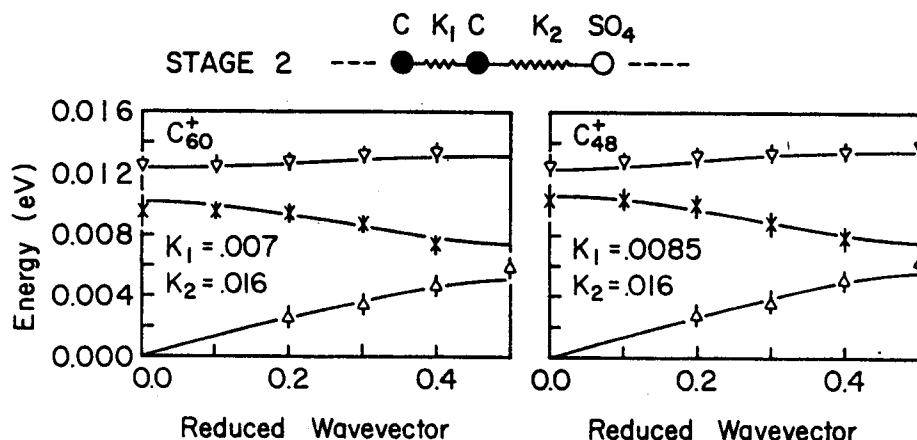


Fig. 1B

C-axis LA, LO phonon frequency vs reduced wave vector for stage 2 C_{60}^+ & C_{48}^+ graphite- H_2SO_4 . The solid line represents the calculated dispersion.