Charge-Transfer Effects in Graphite Intercalates: *Ab Initio* Calculations and Neutron-Diffraction Experiment

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First-principles, total-energy electronic-structure calculations have been used to study the effects of charge transfer in graphite intercalation compounds. Together with an *in situ* diffraction study on graphite undergoing intercalation with sulfuric acid, the results strongly support the idea of a universal relationship between charge transfer and the C—C bond length.

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When a graphite intercalation compound (GIC) is formed, an exchange of electrons takes place between the intercalant layers and those of the host, generating ionic binding between the layers, and creating highly mobile charge carriers in the graphite layers. This charge transfer thus serves as both the driving force for intercalation and the source of high electrical conductivity in GIC's, and its extent and nature are important issues in research on these materials. In the present article, we describe the results of a self-consistent calculation from first principles, directed towards understanding the essential physics of the changes induced in the graphitic layers by charge transfer. In addition, we present experimental neutron-diffraction data on a system (sulfuric acid–graphite) for which there is an independent electrochemical measure of charge transfer, thus enabling us to check the results of our calculation for a specific property; in this case the effect of charge transfer on bond lengths in the graphitic layers.

That the C—C in-plane bond distance d_{CC} contains information about charge transfer was recognized many years ago in the careful x-ray work of Nixon and Parry,[1] who showed that d_{CC} is expanded relative to pure graphite in stages-1 to -6 potassium GIC's, with a smooth dependence on intercalant density. Subsequently, Pietronero and Strässler[2] (PS) proposed that there is a universal relationship between d_{CC} and the charge transfer per carbon atom f_{C}, and that charge transfer for any GIC can be determined by means of a straightforward diffraction measurement. While many other methods exist for the estimation of charge transfer, different techniques often give widely conflicting results. Although intriguing, the empirical approach of PS left considerable room for doubt, especially since the then-existing data offered no ability to verify their predictions, and PS merely gave estimates of charge transfer based on available values of d_{CC}. Our calculations, combined with new neutron-diffraction data and a reexamination of older data, support PS's basic idea, but lead to quantitatively different results. In addition, our calculations can clearly be extended to obtain detailed information on the effects of charge transfer on other properties, such as phonon frequencies, elastic constants, and electronic wave functions.

The calculations were carried out by use of *ab initio* pseudopotentials[3] within the local-density-functional formalism,[4] with the Hedin-Lundqvist form of exchange and correlation.[5] This method has provided an accurate description of the structural and cohesive properties of carbon in the diamond and graphite structures.[6,7] In the present work, we consider a system which is computationally tractable and focuses on the changes induced in the graphitic layers solely as a result of charge exchange with the intercalant. It consists of graphitic layers arranged in *AA* stacking sequence, with the intercalant represented by ions of charge Z, with $|Z| < 0.33$, located midway in the interlayer spaces between each pair of facing graphitic hexagon centers. The system thus has a unit cell with two carbon atoms, one "intercalant" ion with charge Z, and $8+Z$ valence electrons. For negative Z, simulating acceptors, $Z/2$ valence electrons are depleted from each C atom. For positive Z, simulating donors, the extra Z electrons per unit cell will be almost entirely donated to the C atoms because the intercalant potential $(\sim Z/r)$ is too weak to compete with the much stronger C potential. Hence, charge transfer is basically complete in the present model, and can be varied at will by choice of Z. The electronic wave functions were expanded in a linear combination of atomic orbitals basis set,[6-8] with sixteen orbitals on each site. The calculation was carried out fully self-consistently,[8] with 32 **k** points in the irreducible portion of the Brillouin zone. For each value of Z, the total energy of the system was minimized to obtain the change in d_{CC} with charge transfer. As the

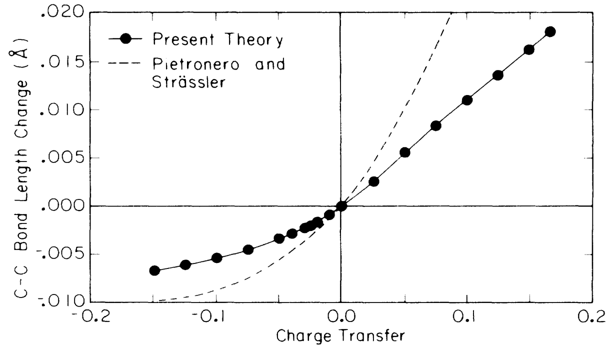

FIG. 1. Dependence of bond-length change on charge transfer, as calculated in the present work, and by PS (Ref. 2).

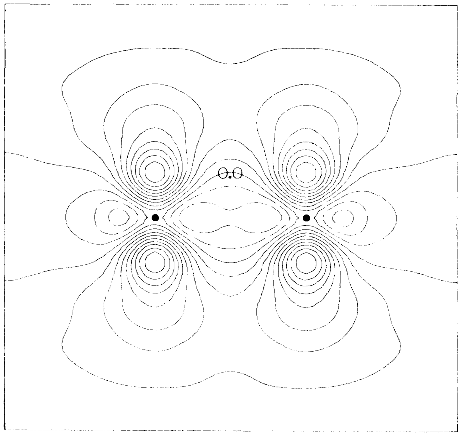

FIG. 2. Plot of the charge-density difference between a donor GIC with $Z=0.2$ and graphite, in a plane through a C—C bond. The solid dots mark the C-atom positions. The intercalant sites are at the four corners. The contour spacing is 10^{-3} electron/(a.u.)^3. The dotted lines indicate charge depletion.

"intercalant" in the calculation is pointlike, and changing the c-axis parameter I_c by as much as 30% had only minor effects on the final results, I_c was kept at the experimental value for graphite.

The application of our stage-1 model to predict bond-length changes for higher stages should be justified. Stage 2 presents no difficulties, as all graphitic layers are equivalent bounding layers (flanked by an intercalate layer). For stages ≥ 3, there are interior graphitic layers as well, possessing a much smaller portion of the transferred charge. We, like PS, assume that interior and bounding layers have the same in-plane lattice parameter a_0, i.e., the charge-transfer–induced strain is shared uniformly. Under this assumption, supported by the fact that a unique a_0 was observed in high-stage GIC's,[1] $d_{\text{CC}}=a_0/\sqrt{3}$ is insensitive to the c-axis distribution of charge, and is independent of it if the d_{CC} vs f_{C} relation is linear, which is very nearly the case for the small f_{C} values applicable to stages ≥ 2. If the interior and bounding layers were to assume different lattice parameters, an incommensurability energy, far larger than the strain energy involved in making all layers assume the same a_0, would be required.

The calculated d_{CC} (1.419 Å) for pure graphite is in excellent agreement with experiment[1] ($d_{\text{CC}}=1.421$ Å). By our computing the total energy as a function of the graphitic-basal-plane area, the sum of the elastic constants $C_{11}+C_{12}$ was found to be 125×10^{11} dyn/cm^2, in very good agreement with a value of 124×10^{11} dyn/cm^2 that can be deduced from sound-velocity measurements.[9] The calculated bond-length change as a function of charge transfer per C atom, $f_{\text{C}}=Z/2$, is shown in Fig. 1. Also shown are the molecular-orbital results of PS. Some of the physical origins of the bond-length changes have been discussed by PS,[2] and by Kertesz, Vonderviszt, and Hoffman[10] who calculated bond-length changes with a rigid-band model. A previously unrecognized mechanism that contributes to the C—C bond-length change can be seen by an examination of Fig. 2, in which the calculated charge-density difference between donor-intercalated graphite ($Z=0.2$) and graphite ($Z=0$) is plotted in a plane containing the c axis, passing through a C—C bond. The donated charge (solid lines) resides in the π orbitals. In addition, charge is *depleted* (dashed lines) from the σ bonds. The external potential must be causing electron transfer from σ to π orbitals, thereby weakening the C—C bond and increasing the bond length. The opposite behavior is observed in charge-difference plots for acceptor intercalants. This σ-π transfer cannot be obtained from rigid-band models.[10] Figure 2 also shows negligible electron density around the intercalant sites, thus explicitly demonstrating the complete charge transfer that we expect in our model. From our calculations, the bond-length change is almost linear for donor GIC's but nonlinear and smaller in magnitude for acceptor GIC's, an asymmetry which is observed experimentally.

We now compare (Fig. 3) our calculations for acceptor GIC's with an experiment[11] on sulfuric-acid–graphite compound, a system which offers the key advantage of an electrochemical method of intercalation, allowing us to place the intercalation compounds on the charge-transfer scale.[12-14] When one electron flows through the external circuit of a sulfuric-acid–graphite electrochemical cell, one electron is transferred from the graphitic layers to intercalated acid molecules, leading to a chemical formula $\text{C}_p{}^+(\text{HSO}_4)^-(\text{H}_2\text{SO}_4)_x$, where x has been determined from weight-uptake measurements[13] to lie between 2.0 and 3.2, depending on p. The oxidation number p and the charge transfer per C atom $f_{\text{C}}=p^{-1}$ are completely determined by the mass of the starting graphite and the total charge $Q=it$ which has flowed in the external circuit. If the constant current i is in microamperes, and the intercalation time t in hours, then one finds p via $p=2230.4m/it$, where m is the start-

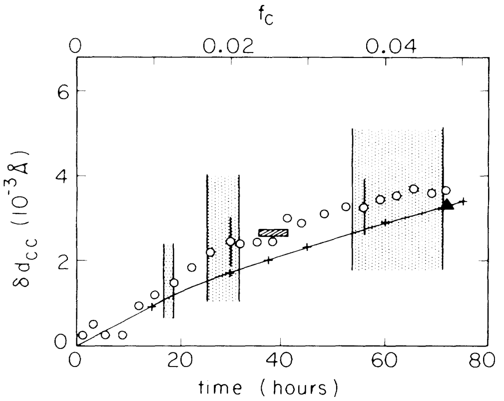

FIG. 3. Decrease of C—C bond length vs charge transfer per C atom, or vs intercalation time, for graphite intercalated with D_2SO_4 (circles), H_2SO_4 (triangle), and $SbCl_5$ (shaded horizontal bar at time ~40 h). The crosses connected by the solid line represent the current calculations.

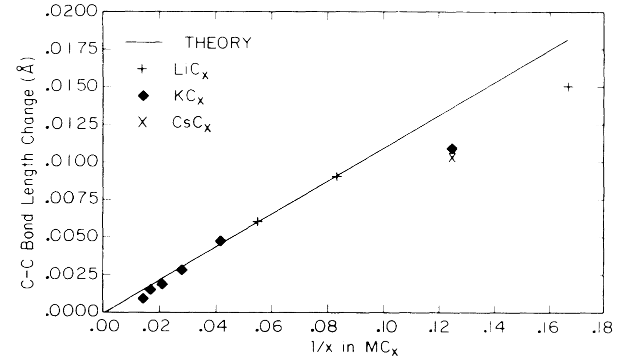

FIG. 4. Increase of C—C bond length in alkali-metal GIC's, as determined experimentally (KC_x and CsC_x, Ref. 1; LiC_x, Ref. 18), and as derived from the current calculations, under the assumption of complete charge transfer.

ing graphite mass in milligrams.

Our cell, filled with D_2SO_4 rather than H_2SO_4 for the sake of greater transparency to neutrons, was mounted on a triple-axis diffractometer for the *in situ* measurements. Changes in d_{CC} were determined by our measuring the shifts in position of the (100) and (110) graphitic Bragg rings from the positions observed for the starting graphite. The diffraction from these basal-plane reflections forms rings because the type of graphite used, highly oriented pyrolytic graphite, is essentially a two-dimensional polycrystal in the basal plane. The contraction in d_{CC} as a function of time, or of charge transfer, is shown in Fig. 3. The shaded areas in Fig. 3 delineate regions of pure stage (stages 3, 2, and 1, from left to right). Between these regions, the points represent an average over a mixture of two phases (stages) whose individual values of d_{CC} are too close to be resolved as separate peaks in our experiment. Within the pure-stage regions, charge transfer is still proceeding continuously, as evidenced by contraction in the interlayer spacing[14,15] and changes in phonon frequencies[16,17] across the limits of pure stage 1 and pure stage 2. Also shown in Fig. 3 are two independent data points on (i) a saturated stage-1 H_2SO_4-graphite compound (rather than D_2SO_4), and (ii) stage-2 $SbCl_5$-graphite compound. In the latter case, charge transfer was estimated by our assuming the completion of the dissociation reaction $3SbCl_5+2e^- \rightarrow 2SbCl_6{}^{-1}+SbCl_3$ within the GIC, and the left- and right-hand limits of the bar arise from an uncertainty in the composition of the C_xSbCl_5 sample, which could have x between 24 and 28.

The agreement between the theoretical and experimental curves is good, in both shape and magnitude. The experimental points lie systematically higher but the differences are within experimental uncertainty. The error bars shown were estimated from other intercalation runs, in which systematically higher or lower values were obtained (our most recent data followed the calculated curve almost exactly), the discrepancies arising from slight shifts in sample position and increasing mosaic spread of the c axis during intercalation. More accurate data are desirable to ascertain how precisely f_C can be determined through the calculated d_{CC} vs f_C relationship. The use of relatively low-resolution neutron diffraction, a choice dictated by the low absorption of neutrons in the cell and liquid, limited the accuracy of our experiment. As shown by Nixon and Parry,[1] more accurate measurements can be achieved by conventional x-ray diffractometry in a straightforward fashion if the sample environs are more transparent, and the samples themselves have smaller mosaic spreads.

Turning to donor compounds, we now compare our theoretical results with data[1,18] on alkali-metal GIC's (Fig. 4), assuming complete charge transfer, and assess the resulting implications. For donor GIC's there is an expansion of d_{CC} which is generally larger in magnitude than the contraction observed for acceptor GIC's. The experimental data for the MC_x compounds are plotted against x^{-1}, which is the same as f_C if the charge transfer is complete. For stage 2 and higher stages, the experimental points fall right on the calculated line. This is strong evidence that the theory applies to donor as well as acceptor GIC's, and that the alkali-metal atoms almost completely donate their valence electrons to the graphite host. For stage-1 compounds, Fig. 4 seems to imply that the degree of charge transfer is high but incomplete (~0.8), although there may be some difficulty with this interpretation because the stage-1 compounds have in-plane structures and densities differing from those of higher-stage compounds.

In summary, the variation of the C—C bond length as a function of charge transfer has been determined from accurate first-principles calculations. Our results agree qualitatively with previous theories[2,10] and quantitatively with experimental data for acceptor GIC's where the charge transfer is known. For alkali-metal GIC's, the good agreement between our theory and experimental data indicates a high degree of charge transfer. The agreement of the present theory with data on a wide range of intercalants gives strong support to the concept of a universal relationship between charge transfer and the C—C bond length in GIC's.

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